Photolysis of 5,5-dibenzyl-Δ^3-1,3,4-oxadiazolines[1]

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Abstract: Photolysis of dibenzyl-Δ^3-1,3,4-oxadiazolines (**3**) in the presence of dimethyl acetylenedicarboxylate (DMAD) gives only modest yields of the expected symmetrical 3,3-dibenzylcyclopropenes (**4**), but these are accompanied by more than six by-products, including unsymmetrical cyclopropenes, methylenecyclopropanes, and various pyrazoles. The origin of this array of products can be explained by a series of steps starting with photolysis of **3** to form a diazoalkane that undergoes 1,3-dipolar cycloaddition to DMAD, generating a 3*H*-pyrazole as initial product. The latter is further photolyzed to a symmetrical cyclopropene in competition with benzyl group migration by thermal 1,5-sigmatropic or ion-pair rearrangement to afford a 4*H*-pyrazole. The 4*H*-pyrazole in turn undergoes photolysis to an unsymmetrical cyclopropene, which rearranges to a methylenecyclopropane. The 4*H*-pyrazole also undergoes autoxidation, in the presence of air, to afford a benzoyl-4*H*-pyrazole. Additionally, in competition with rearrangement, the various pyrazoles lose a benzyl group or a methoxycarbonyl group to afford pyrazoles with one less substituent.

Key words: 5,5-dibenzyl-Δ^3-1,3,4-oxadiazolines, photolysis of; 3,3-dibenzyl-3*H*-pyrazoles, rearrangement of; 3,4-dibenzyl-4*H*-pyrazoles, autoxidation of; 3,4-dibenzyl-4*H*-pyrazoles, photolysis of; cyclopropenes, rearrangement to methylenecyclopropanes.

Résumé : La photolyse des dibenzyl-Δ^3-1,3,4-oxadiazolines (**3**) en présence d'acétylènedicarboxylate de diméthyle (ADCD) ne fournit que de faibles rendements des 3,3-dibenzylcyclopropènes (**4**) symétriques attendus; toutefois, ceux-ci sont accompagnés par plus de six sous-produits incluant des cyclopropènes non symétriques, des méthylènes cyclopropanes et divers pyrazoles. On peut expliquer l'origine de cette série de produits par une série d'étapes commençant par la photolyse du produit **3** conduisant à un diazoalcane qui subit une cycloaddition 1,3-dipolaire sur l'ADCD pour conduire au 3*H*-pyrazole comme produit initial. Ce dernier peut subir une photolyse subséquente en cyclopropène symétrique, en compétition avec une migration sigmatropique-1,5 thermique du groupe benzyle ou une transposition de la paire d'ions qui conduit à un 4*H*-pyrazole. Le 4*H*-pyrazole subit à son tour une photolyse en cyclopropène non symétrique qui se réarrange en un méthylènecyclopropane. Le 4*H*-pyrazole subit aussi une autooxydation, en présence d'air, qui conduit au benzoyl-4*H*-pyrazole. De plus, en compétition avec les réarrangements, les divers pyrazoles perdent un groupe benzyle ou un groupe méthoxycarbonyle pour fournir des pyrazoles important un substituant de moins.

Mots clés : photolyse de 5,5-dibenzyl-Δ^3-1,3,4-oxadiazolines, réarrangement de 3,3-dibenzyl-3*H*-pyrazoles, autooxydation et photolyse de 3,4-dibenzyl-4*H*-pyrazoles, réarrangement de cyclopropènes, à méthylènecyclopropanes.

[Traduit par la rédaction]

Introduction

As part of our ongoing studies of reactive intermediates, we wished to prepare a series of dibenzylcyclopropenes with the general structure **4***a–e*. Earlier experience with three-membered rings indicated that **4** ought to be formed by extended photolysis of a mixture of dimethyl acetylenedicarboxylate (DMAD) and appropriate Δ^3-1,3,4-oxadiazolines (**3**), available in good yield from simple dibenzylketones (**1***a–e*) by oxidation of their acetylhydrazones (**2**) using lead tetraacetate (LTA) (1–3) (Scheme 1).

The crucial photolysis stage giving **4** would consist of a sequence of five steps, for each of which there is ample precedence. First, photolytic cleavage of **3** would form diazoalkane **5**, which would be trapped by DMAD to give 3*H*-pyrazole **6** (2). Further irradiation in situ would convert **6** into vinyl diazo compound **7**. This in turn would readily lose nitrogen on continued photolysis to give a vinyl carbene (**8**), which characteristically can collapse to the desired cyclopropene (**4**) (4–8) (Scheme 2).

Judging from previous reports, the conversion of a 3*H*-pyrazole to a cyclopropene is highly efficient, normally occurring with yields approaching 100% (4, 6, 9), and the method can even be used to generate more highly strained ring systems such as cyclopropabenzenes (10); similarly the

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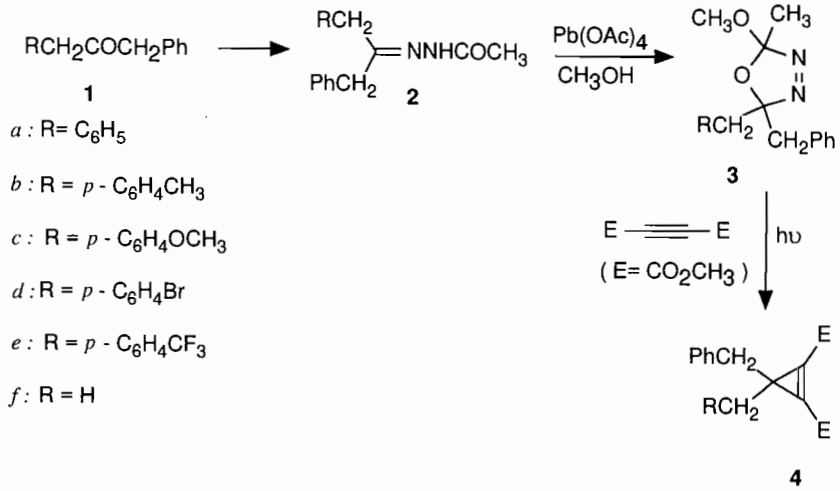
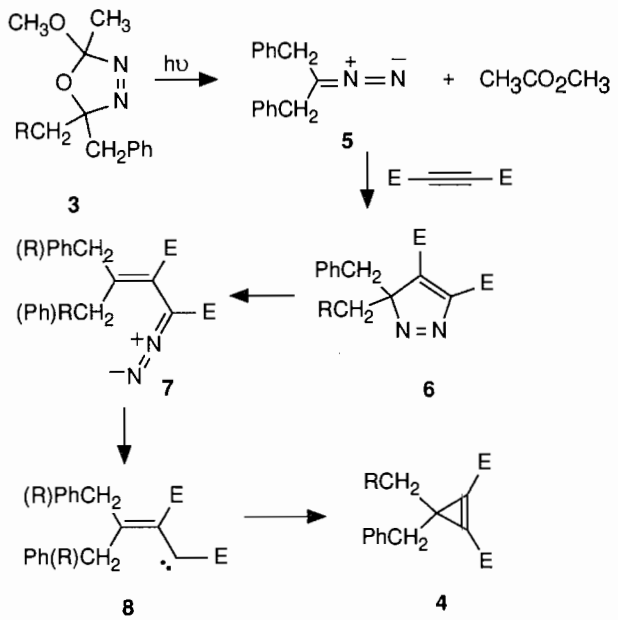
Scheme 1.



Scheme 2.



(R as in Scheme 1, *a* - *e*)

3*H*-pyrazole is obtained from the oxadiazoline typically in yields of about 70% (2). Although the photolytic steps each require somewhat different wavelengths for optimum efficiency, in practice either a Hanovia medium-pressure mercury lamp (4) or a Rayonet apparatus with 300 nm lamps (2) can provide enough spectral width to make a "one-pot" process feasible. We had anticipated, then, that this composite photolysis stage would give something like 60% of the desired three-membered ring and that, overall, we would have an attractive and simple route to our target molecules. It was thus surprising and disappointing to discover that the cyclopropenes (**4**) were produced in only low yields during the photolysis, and that they were accompanied by a wide range of other products in comparable amounts. One of these additional products has already been reported (3), and it is the purpose of this paper to clarify the nature of the other products, to suggest their origins, and to present details of a set of versatile and potentially useful reactions.

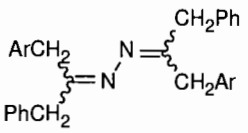
Results and structural assignments

As outlined above, the major products from the photolysis of Δ^3-1,3,4-oxadiazolines in the presence of DMAD were expected to be cyclopropenes (**4**). As for possible by-products, inspection of the literature suggested that these would include azines (**9**) formed by self-reaction of two molecules of the diazoalkanes (2), dienes (**10**) formed from vinyl carbenes (**8**) by a hydrogen shift (4, 7), 1:2 adducts (**11**) formed by cycloaddition of a molecule of a diazoalkane to a 3*H*-pyrazole such as **6** (11), oxiranes (**12**) formed by loss of nitrogen from the oxadiazolines (2), and 4*H*-pyrazoles (**13**) produced by migration of a group from the 3-position of 3*H*-pyrazoles (**6**) (6).

In practice, it was found that not only were the desired cyclopropenes formed in yields of merely 10–30%, but also that the six or more by-products fitted none of the precedents described above. Thus the mixture of by-products nearly always included 1,3-diarylpropenes (**14** and **15**), unsymmetrical cyclopropenes (**16**), methylenecyclopropenes (**17** and **18**), dibenzylpyrazoles (**19**), monobenzylpyrazoles (**20**), and pyrazole N-oxides (**25**), plus frequently one or more of the benzoyl pyrazoles **21**, **22**, and **23**.

Separation and isolation of the various products was achieved using centrifugal chromatography, a particularly sensitive process in this study owing to the presence of strongly absorbing chromophores in all the products. Structures followed from analysis of their spectroscopic properties, and some of the more significant features of those spectra are given below. Assignment of structure to compounds in the series **16** has already been outlined (3) and ^{13}C NMR data are summarized in Table 1.

The compounds **17** and **18** initially presented a challenge, since they co-eluted under every elution condition tried. Moreover when a *para* substituent was present in the starting material, there were generally two isomers of each, giving a total of four isomers in the mixture. Fortunately, the last system examined proved to be an exception; with a *para*-trifluo-



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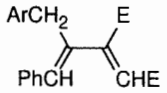

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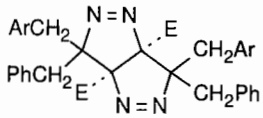

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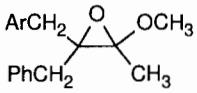

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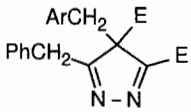

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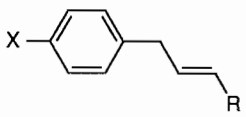

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a : X = H, R = C_6H_5

b : X= CH_3, R= C_6H_5

c : X = H, R = *p* - $C_6H_4CH_3$

d : X = CH_3O, R= C_6H_5

e : X = H, R = *p* - $C_6H_4OCH_3$

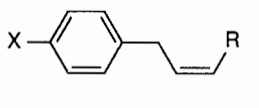
f : X = Br, R = C_6H_5

g : X = H, R = *p* - C_6H_4Br

h : X = CF_3 , R = C_6H_5

i : X = H, R = *p* - $C_6H_4CF_3$

j : X= R= H



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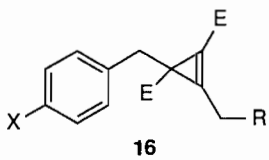

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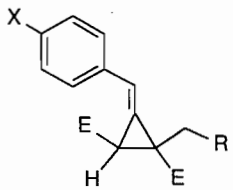

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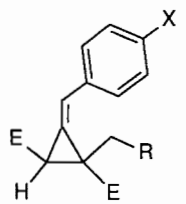

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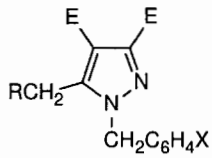

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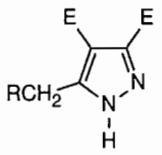
romethyl group present, *only two* isomers were produced, **17***h* and **18***h*, which, with some care, could be cleanly separated, and their formulae established. Furthermore, their spectra permitted disentanglement of the spectra of the mixed isomers from other experiments. In their ^{1}H NMR spectra each compound showed one proton (δ ca. 3.4 ppm) coupled (J = 2 Hz) to a single vinyl proton (δ ca. 6.7 ppm), and both sets of compounds had signals from one methylene group. In the series **17** this was a singlet, by coincidental equivalence of diastereotopic protons, whereas in series **18** the CH_2 signal was an AB quartet, presumably in consequence of the closer proximity of the other aryl group. Long-range C-H correlation spectra for **17***h* confirmed that the *para*-trifluoromethylphenyl group was bonded to the vinyl group, and a similar investigation on a mixture enriched in **18***a* identified a carbonyl carbon (δ = 170.3 ppm in the ^{13}C NMR spectrum; see Table 2) as being close to the methylene group. The geometry indicated for these compounds followed from NOE experiments. Thus in **17***h*, irradiation at the frequency of the methylene hydrogens gave signal enhancement for both the vinyl-H and the *ortho*-H of the phenyl ring, whereas irradiation of the methine-H caused signal enhancement for the *ortho*-H of the trifluoromethylphenyl group but not of the vinyl or the methylene hydrogens, showing that the methine-H was close to the aryl group on the exocyclic double bond, and *trans* to the methylene group. In contrast, irradiation of the methine-H in **18***a* gave no enhancement of the signal from the methylene hydrogens but a small enhancement of the vinyl-H signal.

Although compounds **21**, **22**, and **23** were isolated directly from the photolysis mixtures on different occasions, they were also formed regularly, although in varying amounts, from an unstable compound, described below, and it thus appeared they were closely related. In support of this hypothesis, the three products **21***a*, **22***a*, and **23***a*, apparently derived from **6**, all showed strong peaks in their mass spectra at m/z = 105, suggestive of the benzoyl fragment, whose presence was also indicated by a series of characteristic signals in their ^{1}H NMR spectra. Both **22***a* and **23***a* had prominent IR peaks at ca. 3300 cm^{-1} indicating the presence of an N-H group, and the ^{13}C NMR spectrum of **23***a* made an excellent fit with that for the corresponding acetyl compound **23***d* (12). The ^{1}H NMR spectra of compounds **22** showed that they had one ester group and one benzyl group. The signal from the methylene group of the latter, at ca. 4.5 ppm, indicated a fairly deshielded environ-



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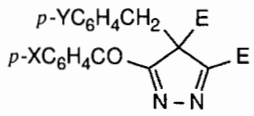
a : R = Ph

b : R = *p* - $C_6H_4CH_3$

c : R = *p* - C_6H_4Br

d : R = H



21

a : X = Y = H

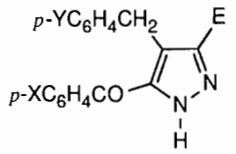
b: X = H, Y = CH_3

c : X = H, Y = OCH_3

d : X = Br, Y = H

e : X = H, Y = Br

f : X = CF_3, Y = H



22

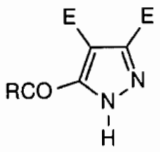
a : X = Y = H

b : X = H, Y = CH_3

c : X = H, Y = OCH_3

d : X = H, Y = Br

e : X = CF_3, Y = H



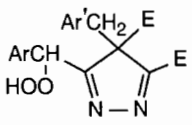
23

a : R = Ph

b : R = *p* - C_6H_4Br

c : R = *p* - $C_6H_4CF_3$

d : R = CH_3



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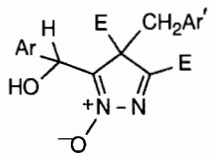

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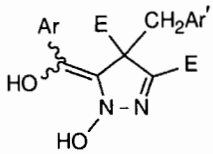

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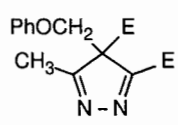
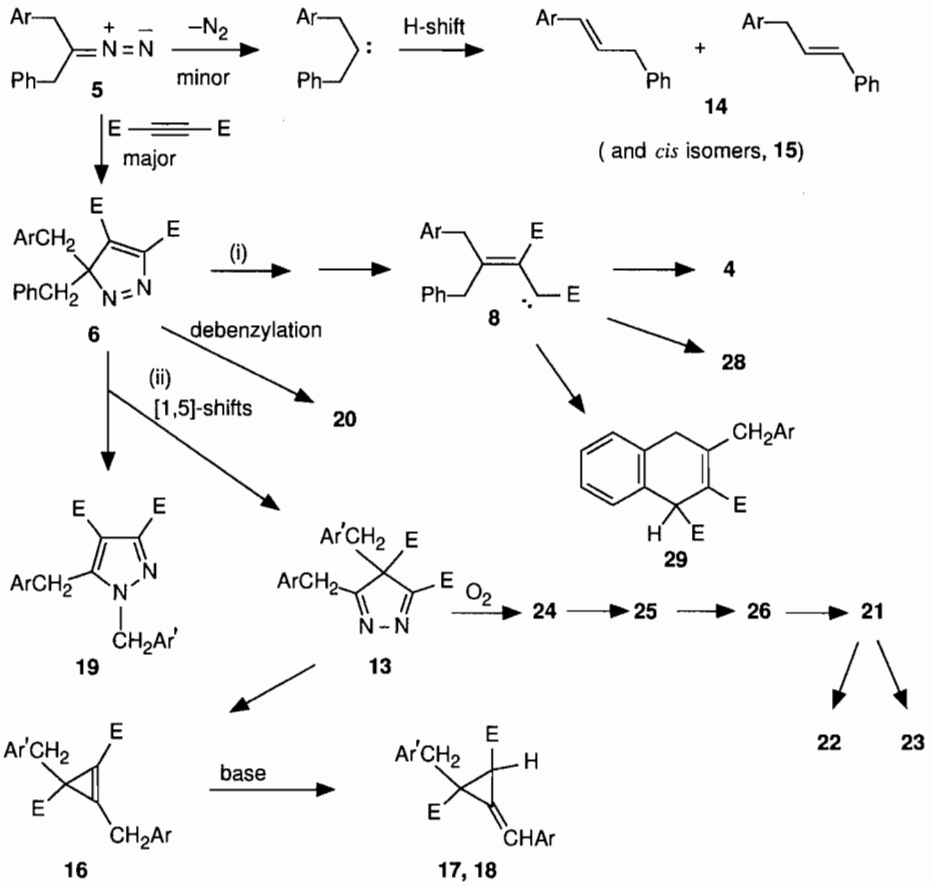


27

ment, consistent with the placement shown. Compounds **21** gave infrared spectra without N-H peaks. In the ^{1}H NMR spectrum of **21***a* the methylene group appeared as an AB quartet at ca. 3.8 ppm suggesting the presence of a benzyl group bonded to a quaternary carbon, and in the ^{13}C NMR spectrum there was one signal at ca. 78 ppm, typical of a quaternary carbon bearing electron-withdrawing groups. Further information was obtained from a long-range C-H correlation investigation. Thus the hydrogens of the methoxyl at 3.7 ppm coupled with the ester carbonyl carbon at 163 ppm, and those at 4.1 ppm coupled with the carbonyl carbon at 160 ppm, thus indicating clearly which low-field carbons were from carbonyl groups, the former presumably being from the sp^3-bound ester group. Consequently, the signals at 173 and 168 ppm have to be assigned to the ring sp^2 carbons, and appropriately both showed coupling with the methylene hydrogens, which in turn also couple with the quaternary carbon at ca. 78 ppm. These relationships, plus mass constraints and the fact that the quaternary carbon of a 4*H*-pyrazole typically absorbs at ca. 63–80 ppm (13, 14), dictate that compounds **21** must have a 4*H*-pyrazole nucleus.

The common source of **21**, **22**, and **23** appeared to be a yellow compound that was formed consistently in all experiments. Although the yellow material could be preserved for months when stored under N_2, exposure to air quickly gave rise to mixtures of **21**, **22**, and smaller amounts of **23**. The assignment of a structure for this yellow precursor proved to be difficult. In the UV spectra there were longer wavelength absorption maxima at 282 and 372 nm and in the IR spectra there were strong peaks at 3300 cm^{-1} pointing to an OH or NH group, a feature confirmed by the effect of added D_2O (exchange) on the ^{1}H NMR spectrum. In the ^{1}H NMR spectra, signals included a one-proton exchangeable singlet at ca. 8.0 ppm, a one-proton singlet at ca. 5.7 ppm, and an AB quartet with signals located at ca. 3.3 and 3.8 ppm, along with two methyl ester groups and an appropriate number of aromatic hydrogens (without any indication of pronounced deshielding). Apparently one benzyl group had been modified in some way at the methylene group, while the other evidently remained intact. In the ^{13}C NMR spectra, salient features included two sp^2 carbon signals very close together at ca. 143 ppm, a methine carbon signal at ca. 100 ppm, a quaternary carbon signal at ca. 64 ppm, and one methylene carbon signal at ca. 43 ppm. A single-bond C-H correlation spectrum of the yellow compound from **3***d* confirmed that there were no other methine groups, and that the proton giving the signal at 8.1 ppm was not attached to a carbon. Long-range C-H correlation experiments on the yellow compounds from both **3***a* and **3***c* showed coupling of the methylene protons to both the carbon at 64 ppm and one (or both?) of the carbons at 143 ppm, but unfortunately did not pick out any coupling between the methine-H and nearby carbons, nor other helpful structural

Scheme 3.



relationships. In NOE experiments on the yellow compound from **3***d*, irradiation of either of the methylene hydrogens caused enhancement of the signal at 8.0 ppm and that at 5.7 ppm, as well as of that of an *ortho*-H of the unsubstituted phenyl group. Irradiation of the proton absorbing at 5.7 ppm caused enhancement of the signal at 8.0 ppm as well as of those *ortho*-H of the bromophenyl group and one of the methylene protons. Lastly, irradiation of the proton at 8.0 ppm caused enhancement of the signal from the *ortho*-H of the bromophenyl group.

Bearing in mind that the yellow materials in question decomposed to benzoyl pyrazoles (**21**–**23**) and absorbed at 3300 cm^{-1} in the infrared, hydroperoxide **24** was first considered as a possible structure. In this, the groups are disposed suitably to fit the observed interactions in the long-range correlation experiments, and the quaternary carbon signal at 64 ppm well suits C4 of a 4*H*-pyrazole (13, 14). Moreover, this structure is mechanistically reasonable, for it is known that 4*H*-pyrazoles are readily formed from 3*H*-pyrazoles (6, 15), and autoxidation of benzylic compounds, such as cumene, to hydroperoxides is well precedented. It had to be noted, however, that in similar 4*H*-pyrazoles the sp^2 carbons of that ring usually give signals at 160–180 ppm rather than at ca. 143 ppm as observed (cf. compounds **21**, **27**, and **34**, and examples in refs. 13 and 14), and it was not clear how a hydroperoxy group could significantly affect the chemical shifts of the sp^2 carbons of the pyrazole ring. Further, the yellow colour was not an obvious consequence of the structure **24**. Nevertheless **24** is a plausible product from **13**, and a solution to the puzzle was sought based on the premise that **24** is indeed formed by radical chain autoxidation of **13**, but it is then converted swiftly to the yellow compound **25**.

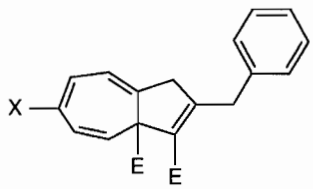
Given that hydrogen peroxide or peracids are effective reagents for converting *N*-heterocycles to corresponding *N*-oxides, we propose that **24** are rapidly converted to corresponding pyrazole *N*-oxides (**25**) by intramolecular reaction. Models for **25** do have absorptions in the UV/visible spectrum (16, 17) and the exchangeable OH, the IR, and the NOE results fit well. Moreover, with an *N*-oxide structure, the chemical shifts of the ring carbons should be significantly affected. Finally, the formation of benzoyl pyrazoles **21**, **22**, and **23** from **25** can be accounted for nicely, as described in the Discussion.

Discussion

The origin of the various products can be ascribed to transformation of the diazoalkane **5** by one minor and two major pathways, each followed by further reaction as in Scheme 3. The minor pathway is loss of nitrogen from **5** to give a carbene, but both major pathways derive from trapping of **5** by the DMAD to produce the 3*H*-pyrazole **6**. This then either rearranges (path ii) or loses nitrogen (path i) to give the vinyl carbene **8** that collapses to some of the products of Scheme 3.

This basic scheme is supported by the results from photolysis of oxadiazoline **3***a* (without DMAD) at −70°C in toluene-d_8. After 4 h it had been converted almost totally to methyl acetate and the diazoalkane **5***a*, in whose carbon spectrum the diazocarbon appeared at 48 ppm. During storage at −20°C for 15 h, approximately 70% of the compound had decomposed to azine **9***a* plus smaller amounts of propenes **14***a* and **15***a*, and after 5 days the decomposition was complete. In no other experiment was any trace of such an azine found, indicating that the rate of reaction of the diazoalkane with DMAD is substantially faster than its self-reaction. On the other hand, since propenes were consistently found in modest amounts in both this and all other photolysis experiments, photolytic loss of nitrogen from **5** was competitive with dipolar cycloaddition to DMAD. Once a carbene was generated by nitrogen loss, a rapid H-shift gave propenes. Moreover, since only hydrogen shifts seem to have occurred, without any evidence for a phenyl shift, the precursor carbene presumably reacted from the singlet state (18). As might be expected, when propenes **14** and **15** were produced, the yields of *trans* isomer tended to exceed those of the *cis* isomer, and when a *para* substituent was present in **3**, both positional isomers of the two propenes were produced in essentially equal amounts.

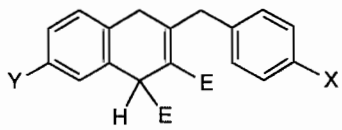
The nitrogen-loss pathway (i) from the 3*H*-pyrazole (Scheme 3) was the route we had expected the bulk of the material to follow. Although the expected cyclopropenes (**4**) were indeed produced, the yields were low and the product mixtures also included, on occasion, small amounts of dihydroazulenes (**28**) and substances believed to be dihydronaphthalenes (**29**). Those compounds are also produced in small amounts by thermolysing the pure cyclopropenes (**4**) in an inert solvent, and presumably arise by attack of the intermediate vinyl carbene **8***a* on one of the aromatic rings (3, 19, 20). Additional evidence for the intermediacy of the carbene **8***a* was provided by photolysis of **3***a* in methanol (in the presence of DMAD), when ether **30** was produced, in an amount comparable to that of symmetric cyclopropene **4***a*, by carbene insertion into the O—H bond of the alcohol (18–20). In principle, carbene insertion can follow several pathways (21–25), including direct insertion into the O—H bond, attack on the carbene by the nucleophilic oxygen to give a zwitterion that then undergoes an H-shift, and protonation of the carbene to give a cation that combines with the counterion. Which pathway occurs is dependent on the structure of the carbene, but the last pathway is known for at least some vinyl carbenes (26). If this last pattern were followed, protonation of vinyl carbene **8***a* would form an allylic cation that ought to give two ethers, **30** and **31**, of which, if anything, **31** should be favoured. However, since **31** could not be detected, it seems unlikely that a cationic pathway is followed in this system.



28

a : X = H

b : X= Br

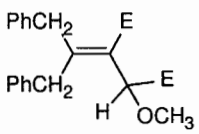


29

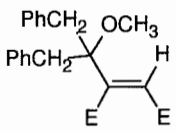
a : X = Y = H

b : X= H, Y= OCH_3

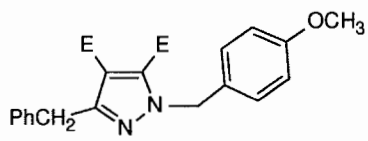
c : X= OCH_3, Y= H



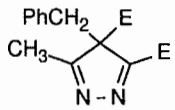
30



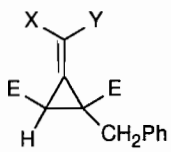
31



32

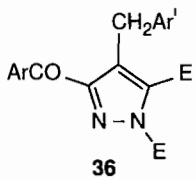


33



34 : X= Ph, Y= H

35 : X= H, Y= Ph



36

That the other major pathway for reaction of the 3*H*-pyrazole was rearrangement is supported by the finding, in every case, of compounds **16**, **19**, and **17** and **18** (Scheme 3). The thermal rearrangement of 3*H*-pyrazoles has been called the VanAlphen–Hüttel rearrangement after its discoverers (27), and in most cases can be considered as taking place by a thermally allowed [1,5]-sigmatropic shift of a group from the 3-position either to the 1-position, or to the 4-position (6, 15,

28–31). Although 1*H*-pyrazoles are more stable than 4*H*-pyrazoles, the latter frequently constitute the predominant rearrangement product, pointing to kinetic control and late development of aromatic character in the transition state (5). Not surprisingly, ease of migration is a function of substituent, and it has been found that ester and acyl groups are much more mobile than alkyl, aryl, or benzyl groups, so that 3*H*-pyrazoles with ester or acyl groups in the 3-position rearrange rapidly at room temperature (29, 30), frequently not even being isolable (31). One explanation for this, based on careful work with the comparable indene system, is that the energy barrier for the process is reduced by secondary interaction between a vacant π^* orbital of the migrating group and an occupied orbital of the five-membered ring (32). Although steric factors also play a part, clearly when there is no π^* orbital, i.e., with alkyl and benzyl groups, no such lowering of the barrier is possible, and the rearrangement should be slow. Thus for our systems we would not have expected a rapid rearrangement.

On the other hand, the conjugate acid of the pyrazole can also undergo concerted rearrangement (33) and in acetic acid solution benzyl groups do migrate much faster than other alkyl groups. This suggests there is substantial charge transfer in the transition state for such reactions, and that migrating tendency then also becomes a function of ability to stabilize a positive charge (33). However, the rearrangement of 3*H*-pyrazoles is not always concerted, and we recently reported strong evidence for a two-step process in which an ion pair is formed when the migrating group can form a particularly stable cation (34). There thus appears to be a mechanistic spread ranging from a one-step (concerted) process to a two-step, ion-pair process.

To check whether the benzyl migration was being catalyzed by adventitious acid, some photolyses were performed in tubes that had been washed with ammonia and others in solvents containing a small amount of triethylamine. However, those precautions made no significant difference to the proportion of products arising from rearrangement. Temperature also seemed to have little effect. Although most experiments were run at ambient temperature, essentially identical results were found in one experiment performed using dichloromethane as solvent with the temperature maintained at or below −15°C until work-up. It was also striking that, in contrast to earlier work, in our reactions there was no evidence for any ester migration from the putative 4*H*-pyrazole intermediate **13**, which might have been expected to behave this way (27, 30, 34).

In light of these findings, we believe that 3, 3-dibenzyl-3*H*-pyrazoles (e.g., **6**) rearrange by the two-step, ion-pair mechanism (cf. ref 34). Calculations have shown that such a process is reasonable for cyclopentadiene systems (35) and, in the present case, five observations support this interpretation. First, although 1-benzyl-1*H*-pyrazoles were produced, there was always formed a small amount of debenzylated compound (**20***a–e*), indicating that the migrating benzyl group could become detached. The result is formally similar to the debenzylation reported by others (36) from reactions at a much higher temperature (205°C). Secondly, when photolysis of **3***a* was performed in the more polar solvent methanol, the yield of debenzylated product **20***a* from unrearranged 3*H*-pyrazole was increased at the expense of the yield of cyclopropene **4***a*. Thirdly, the *para*-substituted systems (**6***b–e*) gave evidence of preferential migration in the sense *p*-$MeOC_6H_4CH_2$ > $C_6H_5CH_2$ > *p*-$CF_3C_6H_4CH_2$, paralleling ability to support a benzylic cation. Fourthly, with *p*-methoxybenzyl, the isomeric 1*H*-pyrazole **32** was also formed, a compound most simply accounted for by assuming that the ion-pair intermediate is loose enough for collapse to occur at either nitrogen. Lastly, in the photolysis of the related oxadiazoline **3***f* in methanol-d_4, the products included not only both cyclopropenes **4***f* and **16***j* and the 1-benzyl-1*H*-pyrazole **19***j*, but also the 4-benzyl-4*H*-pyrazole **33** and the debenzylated 1*H*-pyrazole **20***d*.

Additional evidence for Scheme 3 came from the finding that, if the diazoalkane was first generated (at low temperature) and then DMAD was added, the "missing" 3*H*-pyrazoles (**6***a*, **6***b*, and **6***d*) could be isolated. They are not stable at room temperature, decomposing to give a product mixture similar to that from direct photolysis. Moreover, it was not possible to isolate **6***c* under these conditions, suggesting that the *p*-methoxybenzyl group can migrate rapidly even at room temperature.

Thus the crucial steps proposed in Scheme 3 for the production from **6** of products **16**, **17** and **18**, and **19** are the following. First, there is a shift of a benzyl group, by a pathway involving a tight ion-pair intermediate (loose in the case of *p*-$MeOC_6H_4CH_2$) to give some **19** but mainly the 4*H*-pyrazole **13** (compare findings in ref. 37), as well as small amounts of **20**, by complete loss of the migrating group. Then **13** generates the unsymmetrical cyclopropene **16** by photochemical loss of nitrogen (3). The two isomeric methylenecyclopropenes (**17** and **18**) are then produced from **16** either by a base-catalyzed proton shift or by [1,5]-sigmatropic rearrangement to the more acidic ester enol (not shown), which then undergoes a base-catalyzed allylic rearrangement. There are many precedents in cyclopropene chemistry for base-catalyzed rearrangements (38), and since a benzylic hydrogen vinylogous to an ester is weakly acidic, strong bases do not have to be sought. Either the traces of base introduced deliberately or, in cases where that was omitted, the diazoalkane (39), can be assigned to that role. In the latter case, some of the diarylpropenes (**14** and **15**) would have originated from 1,3-diaryl-2-propyl cations, rather than from carbenes. It is possible that **17** and **18** are also subject to photochemical interconversion, but this was not investigated.

Base-catalyzed isomerization of **16** was confirmed by two observations. First, when the photolysis of **3***a* was conducted in the presence of added base, no **16***a* was present in the product mixture, although both **17***a* and **18***a* were found. Secondly, treatment of pure cyclopropene **16***a* with triethylamine in chloroform caused total isomerization within a few minutes. In the latter case, along with **17***a* and **18***a* in approximately equal amounts, there were found much smaller amounts of **34** and **35**, whose structures followed from their NMR spectra and NOE experiments. Since the isomerization is presumably equilibrium controlled, structures **17** and **18** must be more stable than both cyclopropene **16**, and its isomers **34** and **35**. The fact that **34** and **35** were not observed as co-products of the photolyses could simply mean that the yields of these compounds were too small.

The sequence of reactions leading to benzoyl pyrazoles **21**, **22**, and **23** is probably the following. First **6** rearranges, by preferential migration of that benzyl group with the better cationic stabilization, to afford 4*H*-pyrazole **13**. The doubly acti-

vated methylene group of **13** then undergoes autoxidation, by a radical chain mechanism, to afford hydroperoxide **24**, which is short lived, undergoing intramolecular *N*-oxidation to afford the yellow pyrazole-*N*-oxide **25**. A 1,4-sigmatropic H-shift in **25** affords the enolic hydroxylamine **26**, which leads to acyl pyrazole **21** in one of two ways. One of these is 1,4-elimination of water and the alternative involves ketonization followed by 1,2-elimination of water. The 4*H*-pyrazoles **21** can also generate 5-acylpyrazoles **22** and **23** by loss of one of the groups at C4, the driving force presumably being the fact that the products are aromatic. The route may involve ion pairs or nucleophilic attack on the ester group that is lost.

Conclusion

Dimethyl 3,3-dibenzyl-3*H*-pyrazole-4,5-dicarboxylates, produced by photolysis of oxadiazolines in the presence of DMAD, undergo benzyl shifts at ambient temperatures by an ion-pair mechanism, to give mainly 3,4-dibenzyl-4*H*-pyrazole-4,5-dicarboxylates as initial products. The latter undergo further photolysis to afford cyclopropenes by loss of nitrogen. These 4*H*-pyrazoles are unusually sensitive to air, and are also converted, through unstable hydroperoxide and *N*-oxide intermediates, to benzoyl pyrazoles **21**, **22**, and **23**.

Experimental

Melting points were determined on a Thomas Hoover capillary melting point apparatus. NMR spectra were recorded on Varian EM-390, Bruker AM-500, or, when unspecified, Bruker AM-200 spectrometers using $CDCl_3$ as solvent and for internal reference either TMS (proton spectra) or solvent $CDCl_3$ (δ = 77.20 for ^{13}C spectra). Centrifugal chromatography was carried out on silica gel (Merck Kieselgel 60 PF_{254}) plates in a model 7924T Chromatotron apparatus, under nitrogen, using a gradient elution protocol starting with low-boiling petroleum spirit containing 5% diethyl ether plus 0.1% methanol, and finishing with neat acetonitrile. Infrared spectra were recorded as thin films for liquids or Nujol mulls for solids.

General procedure for preparation of dibenzylketones (1)
For those which were not commercially available, an adequate synthesis was available (40) by reaction of dibenzyl cadmium with the appropriate 4-substituted phenylacetyl chloride, obtained from the corresponding acid using thionyl chloride (41). Brief characteristics of compounds, some of them new, follow.

(4-Trifluoromethylphenyl)acetyl chloride, a clear oil, bp 75–80°C/0.5 Torr (1 Torr = 133.3 Pa). ^1H NMR, δ: 7.58 (d, J = 8.0 Hz, H-3, H-5), 7.34 (d, J = 8.0 Hz, H-2, H-6), 4.15 (s, CH_2).

*1-(4-Methylphenyl)-3-phenylpropan-2-one (1*b*)*, clear oil (44%), bp 148–155°C/0.4 Torr (lit (40*a*) bp 143°C/0.3 Torr). IR (cm^{-1}): 3035 w, 2925 w, 1719 s, 1603 w, 1514 m, 1496 m, 1453 m. ^1H NMR (90 MHz) δ: 7.35–7.00 (m, 9H), 3.68 (s, 2H), 3.65 (s, 2H), 2.31 (s, 3H); this fits well the published ^1H NMR data (40*b*).

*1-(4-Methoxyphenyl)-3-phenylpropan-2-one (1*c*)*, a clear oil (29%), bp 175–185°C/0.7 Torr (lit (40*a*) bp 152–154°C/0.4 Torr. ^1H NMR (90 MHz) δ: 7.35-6.80 (m, 9H), 3.77 (s, 3H), 3.68 (s, 2H), 3.62 (s, 2H).

*1-(4-Bromophenyl)-3-phenylpropan-2-one (1*d*)*, yellowish oil (44%), bp 180–200°C/0.02 Torr (lit. (42) mp 54°C). IR (cm^{-1}): 3085 w, 3065 w, 3030 w, 2920 w, 1718 s, 1600 m, 1590 m, 1487 s, 1451 m, 1404 m. ^1H NMR (90 MHz) δ: 7.50–7.05 (m, 9H), 3.68 (s, 2H), 3.62 (s, 2H).

In one preparation of **1***d*, dibenzyl(4-bromobenzyl)carbinol was also produced, as a pasty solid. IR (mull) cm^{-1}: 3570(sharp) m, 3025 m, 1598 w, 1483 s. ^1H NMR, δ: 7.40 (d, J = 8.3 Hz, 2H, H-3, H-5 of Ar), 7.31–7.17 (m, 10H), 7.09(d, J = 8.3 Hz, 2H, H-2, H-6 of Ar), 2.73 (s, 4H), 2.70 (s, 2H).

*1-Phenyl-3-(4-trifluoromethylphenyl)propan-2-one (1*e*)* (38%), bp 130–140°C/0.3 Torr. IR (cm^{-1}): 3065 w, 3035 w, 2915 w, 1722 s, 1618 m, 1605(sh), 1585 m, 1494 m, 1452 w, 1418 m. ^1H NMR, δ: 7.55 (d, J = 8.0 Hz, 2H, H-3, H-5 of Ar), 7.4–7.3 (m, 3H), 7.25–7.15 (m, 4H), 3.78 (s, 2H), 3.74 (s, 2H). ^{13}C NMR, δ: 204.8 (CO), 138.1(br, Ar-C1), 133.7 (Ph-C1), 130.0 (Ar-C2), 129.6 (Ph-C2), 129.0 (Ph-C3), 127.5 (Ph-C4), 125.6 (q, J_{CF} = 3.8 Hz, Ar-C3), 49.9 (C3), 48.5 (C1), signals from Ar-C4 and CF_3 too dispersed for detection.

Also produced with **1***e* was dibenzyl(4-trifluoromethylbenzyl)carbinol (11%), bp 185–190°C/0.5 Torr. IR (cm^{-1}): 3580 m, 3070 w, 3060 w, 3035 m, 1615 m, 1600 m, 1581 w, 1491 m, 1445 s, 1413 s. ^1H NMR, δ: 7.50 (d, 2H, H-3, H-5 of Ar), 7.40–7.15 (m, 12H), 2.81 (s, 2H), 2.77 (s, 2H), 1.49 (s, OH). MS (ci, NH_3) *m/z*: 388 (M + NH_4^+, 100%), 108 (15%), 91 (22%); MS (ei) *m/z*: 279 (M − Bn^+, 30%), 261 (5%), 211 (M − $ArCH_2^+$, 10%), 159 ($ArCH_2^+$, 25%), 119(10%), 91 (100%).

General procedure for preparation of oxadiazolines (3)
A two-step process was used, involving oxidation of the acetylhydrazone (**2**) formed from the corresponding dibenzyl ketone. Virtually quantitative yields of the hydrazone were obtained by overnight refluxing of equimolar amounts of the ketone and acetylhydrazine in methanol, in the presence of a trace of acetic acid.

Acetylhydrazones (2)

*Hydrazone (2*a*)*, mp 118–119°C. IR, cm^{-1}: 3240 m, 3205 m, 3060 m, 3030 m, 2855 m, 1687 m, 1667 m, 1631 m, 1602 w, 1532 m, 1493 m, 1439 m, 1427 m, 1405. ^1H NMR (90 MHz), δ: 9.4 (s, NH), 7.3–7.0 (m, 10H), 3.56 (s, 4H), 2.24 (s, 3H, MeCO). ^{13}C NMR, δ: 173.7 (CO), 151.7 (C—N), 136.8 and 134.3 (2 × Ph-C1), 129.4 and 129.3 and 128.8 and 128.5 (2 × Ph-C2 and 2 × Ph-C3), 127.3 and 127.0 (2 × Ph-C4), 44.1 and 34.3 (2 × CH_2), 20.6 (Me).

*Hydrazone (2*b*)*, mixture of two isomers. IR (cm^{-1}): 3210 m, 3090(sh), 3055(sh), 3035 m, 2925 m, 1710(sh), 1673 s, 1615 m, 1513 m, 1495 m, 1450 m, 1423 m. ^1H NMR (90 MHz), δ: 8.6(br, NH), 7.3–6.9 (m, 9H, aryl-H), 3.57 and 3.53 and 3.48 and 3.45 (all s, 4H, 2 pairs of CH_2), 2.32 (s, 3H, MeCO), 2.30 and 2.29 (both s, 3H, ArMe).

*Hydrazone (2*c*)*, mixture of two isomers, mp 115–117°C. IR (cm^{-1}): 3190 m, 3110 w, 3080 w, 3025 w, 1671 s, 1630 w, 1610 w, 1583 w, 1509 m, 1492 m. ^1H NMR (90 MHz) δ: 8.63 (br, 1H, NH), 7.4–6.8 (m, 9H aryl-H), 3.80 (s, 3H, OMe), 3.57 and 3.50 and 3.47 and 3.42 (all s, 4H, 2 pairs of CH_2), 2.28 (s, 3*H*, MeCO).

*Hydrazone (**2**d)*; initial solid was essentially a single isomer, mp 121-124°C. IR (cm^{-1}): 3180 m, 3085 w, 3065 w, 3030 w, 1717 w, 1687 s, 1635 w, 1483 m. ^1H NMR (90 MHz) δ: 9.25 (s, br, 1H), 7.45–7.00 (m, 7H), 6.89 (d, 2H, H-3, H-5 of Ar), 3.54 (s, 2H), 3.49 (s, 2H), 2.24 (s, 3H, MeCO). Later crops of crystals were mixtures of both isomers.

*Hydrazone (2*e*)*; mixture of two isomers, first batch mp 113–126°C, second batch mp 131–137°C. ^1H NMR, δ: 9.45 and 9.28 (both s, br, 1H, NH), 7.54 (d, J = 7.5 Hz, 2H, 3-H, 5-H of Ar), 7.4–7.0 (m, 7H), 3.60 and 3.56 (both s, 4H, 2 × CH_2), 2.25 and 2.22 (two s, 3H, MeCO).

*Oxadiazolines (**3**)*

The oxidation of the hydrazones was accomplished using lead tetraacetate (1–3), and gave mixtures of by-products similar to those reported (3). Characterizations of new compounds are given below; first the target molecules, then the by-products.

*5-Benzyl-2-methoxy-2-methyl-5-(4-methylbenzyl)-Δ^3-1,3,4-oxadiazoline (**3**b)*; (80%), colourless oil, approximately equal amounts of the two isomers. IR (cm^{-1}): 3030 s, 3005 s, 2940(sh), 2930 s, 1738 m, 1605 w, 1575 w, 1515 s, 1498 s, 1454 s, 1433 s, 1405 m. ^1H NMR, δ: 7.30–6.85 (m, 9H), 3.31 and 3.26 (two d, J = 14.1 Hz, 2H, two halves of two AB quartet from CH_2 groups), 3.24 (d, J = 14 Hz, 2H, two coincident halves of two AB quartets from CH_2 groups), 3.17 and 3.13 (two s, 3H, 2 × OMe), 3.04 and 2.99 and 2.93 and 2.89 (four d, J = 14 Hz, 4H, two AB quartets from CH_2 groups), 2.32 and 2.24 (two s, 3H, 2 × ArMe), 1.00 and 0.93 (two s, 3H, 2 × 2-Me).

*5-Benzyl-2-methoxy-5-(4-methoxybenzyl)-2-methyl-Δ^3-1,3, 4-oxadiazoline (**3**c)* (73%), colourless oil consisting of the two isomers. ^1H NMR, δ: 7.4–6.9 (m, 9H), 3.81 and 3.74 major (two s, 3H, ArOMe); 3.33 and 2.93 (two d, J = 14.2 Hz), and 3.28 and 3.01 (two d, J = 14.4 Hz) (2 × CH_2, minor); 3.29 and 3.06 (two d, J = 14.2 Hz) and 3.24 and 2.90 (two d, J = 14.4 Hz) (2 × CH_2 major); 3.21 and 3.19 major (two s, 3H, 2-OMe); 1.04 major and 0.96 (two s, 2-Me). ^{13}C NMR, δ (major): 158.7 (Ar-C4), 134.3 (Ph-C1), 133.7 (C2), 131.6 (Ar-C2), 131.0 (Ph-C2), 127.9 (Ph-C3), 126.9 (Ph-C4), 126.8 (Ar-C1), 124.0 (C5), 113.7 (Ar-C3), 55.1 (ArOMe), 51.0 (2-OMe), 43.3 and 42.6 (2 × CH_2), 20.6 (Me); (minor): 158.8 (Ar-C4), 134.9 (Ph-C1), 133.7 (C2), 132.0 (Ar-C2), 130.6 (Ph-C2), 128.3 (Ph-C3), 127.0 (Ph-C4), 126.1 (Ar-C1), 124.2 (C5), 113.3 (Ar-C3), 55.0 (ArOMe), 50.9 (2-OMe), 41.47 and 40.7 (2 × CH_2), 20.4 (Me).

*5-Benzyl-5-(4-bromobenzyl)-2-methoxy-2-methyl-Δ^3-1,3,4-oxadiazoline (**3**d)* (62%), colourless oil consisting of the two isomers. IR (cm^{-1}): 3065 m, 3035 m, 3000 m, 2940 m, 2915(sh), 2840 w, 1740 m, 1605 w, 1595 w, 1575 w, 1490 s, 1455 m. ^1H NMR, δ (major): 7.45 (d, J = 8.3 Hz, H-3, H-5 of Ar), 7.30–7.15 (m, 3H of Ph), 7.04 (m, 2H of Ph), 6.89 (d, J = 8.2 Hz, H-2, H-6 of Ar); 3.25 and 2.89 (two d, J = 14.2 Hz, CH_2), 3.22 and 3.03 (two d, J = 14.0 Hz, CH_2); 3.21 (s, OMe), 1.07 (s, 2-Me); (minor): 7.30–7.15 (m, aryl-H); 3.31 and 2.92 (two d, J = 14.2 Hz, CH_2); 3.25 and 3.01 (two d, J = 14.2 Hz, CH_2); 3.19 (s, OMe), 0.98 (s, 2-Me). ^{13}C NMR, δ (major): 134.8 (Ph-C1), 134.1 (C-2), 133.4 (Ar-C1), 132.8 (Ar-C2), 131.6 (Ar-C3), 131.2 (Ph-C2), 128.6 (Ph-C3), 127.3 (Ph-C4), 123.7 (C5), 121.3 (Ar-C4), 51.3 (OMe), 43.7 and 41.1 (2 × CH_2), 20.6 (Me); (minor): 134.1 (Ph-C1), 134.0 (C2), 133.9 (Ar-C1), 132.5 (Ar-C2), 131.1 (Ar-C3), 130.7 (Ph-C2), 128.1 (Ph-C3), 127.2 (Ph-C4), 123.7 (C5), 121.2 (Ar-C4), 51.3 (OMe), 43.1 and 41.8 (2 × CH_2), 20.3 (2-Me).

*5-Benzyl-2-methoxy-2-methyl-5-(4-trifluoromethylbenzyl)-Δ^3-1,3,4-oxadiazoline (**3**e)* (31%), a mixture of the two isomers one of which formed crystals preferentially. IR (cm^{-1}): 3070 w, 3035 w, 3000 w, 2945 w, 2840 w, 1740 w, 1620 m, 1575 w, 1492 w, 1435 m, 1429 m, 1418 m. ^1H NMR, δ: 7.59 (d, J = 8.2 Hz, 2H, H-3, H-5 of Ar), 7.43 (d, J = 8.0 Hz, 2H, H-2, H-6 of Ar), 7.25–7.19 and 7.0 (m, 5H of Ph); 3.35 and 2.95 and 3.34 and 3.15 (two AB quartets, J = 14.2 Hz, 2 × CH_2); 3.20 (s, OMe), 0.98 (s, 2-Me). ^{13}C NMR, δ: 139.1 (Ar-C1), 134.2 (Ph-C1), 133.9 (C2), 131.14 (Ar-C2), 131.11 (Ph-C2), 128.1 (Ph-C3), 127.3 (Ph-C4), 125.3 (q, J_{CF} = 3.7 Hz, Ar-C3), 123.7 (C5), 51.4 (OMe), 43.5 and 41.9 (2 × CH_2), 20.1 (2-Me). Other isomer (from spectra of mixture): ^1H NMR, δ: 7.6–7.4 (m, H-3, H-5 of Ar), 7.4–7.0 (m, H-2, H-6 of Ar and 5H of Ph); 3.38 and 3.05 and 3.29 and 3.04 (two AB quartets, J = 14.2 Hz, 2 × CH_2); 3.23 (s, OMe), 1.03 (s, 2-Me). ^{13}C NMR, δ: 138.6 (Ar-C1), 134.7 (Ph-C1), 133.9 (C2), 131.5 (Ar-C2), 130.7 (Ph-C2), 128.6 (Ph-C3), 127.4 (Ph-C4), 124.9 (q, J_{CF} = 3.9 Hz, Ar-C3), 123.7 (C5), 51.3 (OMe), 43.7 and 41.3 (2 × CH_2), 20.3 (Me).

By-products from LTA oxidation

2-Methoxy-1-(4-methoxyphenyl)-3-phenylpropane: ^{13}C NMR, δ: 158.1 (Ar-C4), 139.2 (Ph-C1), 131.1 (Ar-C1), 130.5 (Ar-C2), 129.6 (Ph-C2), 128.4 (Ph-C3), 126.2 (Ph-C4), 113.8 (Ar-C3), 83.9 (C2), 57.6 (2-OMe), 55.3 (Ar-OMe), 40.3 and 39.4 (2 × CH_2).

2-Methoxy-1-phenyl-3-(4-trifluoromethylphenyl)propane: IR (cm^{-1}): 3065 w, 3030 w, 2930 m, 2825 w, 1615 w, 1490 w, 1450 w, 1432 w, 1412 w. ^1H NMR, δ: 7.52 (d, J = 8.0 Hz, 2H, H-3, H-5 of Ar), 7.35–7.20 (m, 7H, H-2, H-6 of Ar and Ph-H_5), 3.60 (quintet, J = 6.2 Hz, 1H, H-2), 3.24 (s, 3H, OMe), 2.7–2.9 (m, 4H, 2 × CH_2); ^{13}C NMR, δ: 143.4 (br, Ar-C1), 138.7 (Ph-C1), 129.9 (Ar-C2), 129.6 (Ph-C2), 128.5 (Ph-C3), 126.4 (Ph-C4), 125.2 (q, J_{CF} = 4 Hz, Ar-C3), 83.3 (C2), 57.7 (OMe), 40.3 and 40.1 (C1 and C3).

Co-eluting with **3***d* was a small amount of 2-acetoxy-1-(4-bromophenyl)-3-phenylpropane (7%), its presence being deduced from characteristic NMR signals in the mixture. ^1H NMR (partial), δ: 5.26 (quintet, J = 6.6 Hz, H-2), 2.79 (d, J = 6.6 Hz, 2 × CH_2), 1.91 (s, MeCO). ^{13}C NMR (partial), δ: 170.5 (CO), 137.5 (Ph-C1), 136.5 (Ar-C1), 131.3 (Ar-C2), 129.5 (Ph-C2), 128.5 (Ph-C3), 126.8 (Ph-C4), 75.0 (C2), 39.8 (CH_2).

Co-eluting with **3***e* was a small amount of 2-acetoxy-1-phenyl-3-(4-trifluoromethylphenyl)propane (8%). IR (cm^{-1}): 3065 w, 3030 w, 2950 w, 2925 w, 2850 w, 1740 s, 1616 w, 1605(sh), 1581 w, 1490 w, 1450 w, 1432 w, 1413 w. ^1H NMR, δ: 7.53 (d, J = 8.0 Hz, H-3, H-5 of Ar), 7.34–7.16 (m, H-2, H-6 of Ar and Ph-H_5), 5.31(quintet, H-2), 2.9–2.8 (m, 2 × CH_2), 1.93 (s, MeCO). ^{13}C NMR, δ: 170.4 (CO), 141.8 (Ar-C1), 137.2 (Ph-C1), 129.9 (Ar-C2), 129.6 (Ph-C2), 128.7

(Ph-C3), 126.9 (Ph-C4), 125.4 (q, J_{CF} = 3.7 Hz, Ar-C3), 74.9 (C2), 40.3 and 39.9 (C1 and C3), 21.2 (COMe).

2-Acetoxy-5-benzyl-2-methyl-5-(4-methylbenzyl)-Δ^3-1,3,4-oxadiazoline (9%), a mixture of the two isomers. IR (cm^{-1}): 3060 w, 3030 w, 2940(sh), 2925 w, 1760 s, 1724 m, 1606 w, 1515 w, 1498 w, 1453 m, 1436 m. ^{1}H NMR (90 MHz), δ: 7.3–7.0 (m, 9H), 3.7–2.9 (m, 4H, two pairs of CH_2); 2.32 and 2.26 (two s, 3H, ArMe), 1.79 (s, 3H, MeCO), 1.20 and 1.16 (two s, 3H, two 2-Me).

2-Acetoxy-5-benzyl-5-(4-methoxybenzyl)-2-methyl-Δ^3-1,3,4-oxadiazoline (12%), a mixture of the two isomers. IR (cm^{-1}): 3065 w, 3035 w, 3003 w, 2950(sh), 2930 w, 2838 w, 1755(br) s, 1611 s, 1583 m, 1510 s, 1498 s, 1455 m, 1440 m. ^{1}H NMR (90 MHz) δ: 7.3–6.7 (m, 9H); 3.78 and 3.76 (two s, 3H, 2 × ArOMe); 3.6–2.9 (m, 4H, 2 × CH_2); 1.82 and 1.79 (two s, 3H, 2 × MeCO); 1.27 and 1.25 (two s, 3H, 2 × 2-Me). ^{13}C NMR, δ (major): 168.0 (CO), 159.0 (Ar-C4), 134.4 (Ph-C1), 132.3 (Ar-C2), 131.2 (C2), 130.9 (Ph-C2), 128.5 (Ph-C3), 128.38 (C5), 127.3 (Ph-C4), 125.7 (Ar-C1), 113.6 (Ar-C3), 55.4 (Ar-OMe), 43.7 and 41.8 (2 × CH_2), 21.9 (MeCO), 21.0 (Me); (minor): 168.0 (CO), 159.0 (Ar-C4), 133.8 (Ph-C1), 131.9 (Ar-C2), 131.3 (Ph-C2), 128.4 (C5), 128.2 (Ph-C3), 127.3 (Ph-C4), 126.3 (Ar-C1), 114.0 (Ar-C3), 55.4 (Ar-OMe), 43.0 and 42.4 (2 × CH_2), 21.2 (MeCO), 20.9 (Me), C2 not observed.

2-Acetoxy-5-(4-bromobenzyl)-5-benzyl-2-methyl-Δ^3-1,3,4-oxadiazoline (12%), as a 7:3 mixture of the two isomers, mp 78–95°C. ^{1}H NMR, δ (major): 7.4–6.9 (m, aryl-H); 3.53 and 3.33 and 3.17 and 3.08 (two AB quartets, J = 14.2 Hz, 2 × CH_2); 1.79 (s, MeCO), 1.15 (s, Me); (minor): 7.4–6.9 (m, aryl-H); 3.47 and 3.00 (AB quartet, J = 14.2 Hz, one CH_2; signals from other CH_2 obscured); 1.82 (s, MeCO), 1.29 (s, Me). ^{13}C NMR, δ (major): 167.8 (CO), 133.4 (Ph-C1), 133.2 (Ar-C1), 132.6 (Ar-C2), 131.6 (Ar-C3), 131.5 (C2), 131.2 (Ph-C2), 128.2 (Ph-C3), 127.8 (C5), 127.5 (Ph-C4), 121.5 (Ar-C4), 43.0 and 42.8 (2 × CH_2), 21.8 (MeCO), 20.9 (Me); (minor): 167.8 (CO), 134.1 (Ph-C1), 132.9 (Ar-C2), 131.4 (Ar-C3), 131.2 (C2), 130.8 (Ph-C2), 128.6 (Ph-C3), 127.7 (C5), 127.5 (Ph-C4), 121.5 (Ar-C4), 43.8 and 41.7 (2 × CH_2), 21.8 (COMe), 21.1 (Me), Ar-C1 not observed.

General procedure for photolysis of oxadiazolines (3)

In the general method adopted (3) the oxadiazoline (typically 1.5 mmol) and dimethyl acetylenedicarboxylate (in 10% excess) were mixed in benzene (typically 6.0 mL, giving a concentration of ca. 0.25 M) in a quartz tube, and photolyzed with 300 nm light in a Rayonnet apparatus. The reaction mixture became yellow almost at once, and a gentle stream of gas (presumably nitrogen) was evolved. For the initial runs, progress of the reaction was monitored by running ^{1}H NMR spectra at hourly intervals, and typically after 5 h the amount of starting oxadiazoline had dropped to about 5%. In later experiments, therefore, photolysis was halted at this time. The solvent was removed on a rotary evaporator, and the residue was separated by centrifugal chromatography on 4 mm silica gel plates. Between 10 and 17 distinct bands were usually present, although not all fractions could be satisfactorily identified. As a general picture, the first fraction from the plate would be mixed 1, 3-diarylpropenes (**14** and **15**), followed by unchanged starting materials, followed by methylenecyclopropene isomers (**17** and **18**), closely followed by symmetrical cyclopropene **4** and unsymmetrical cyclopropene **16**, followed by the unstable yellow compound **25**, just in front of 1, 5-dibenzyl-1*H*-pyrazole (**19**) and, lastly, 5-benzyl-1*H*-pyrazole (**20**). A variety of other compounds were formed on one or two occasions only. Usually several fractions needed further purification on thinner plates; sometimes equivalent fractions from different runs were combined for this. Yields are of isolated material and are corrected for recovered starting material.

*Photolysis of dibenzyl oxadiazoline (**3**a) (12 runs)*

Typical results from one run are as follows. Similar results were found in other runs, but percentages varied with run and conditions, as did the presence of occasional minor products, which are detailed later.

The known (3) *1,3-diphenylpropenes **14**a and **15**a* (2%).

*Dimethyl 3,3-dibenzylcyclopropene-1,2-dicarboxylate (**4**a)* (35%), was obtained as a pale yellow oil, together with dimethyl (*E*)-1-benzyl-3-(phenylmethylene)cyclopropane-*trans*-1,2-dicarboxylate (**17***a*) and dimethyl (*Z*)-1-benzyl-3-(phenylmethylene)cyclopropane-*trans*-1,2-dicarboxylate (**18***a*) (3%) in approximately 1:1 ratio. It proved impossible to separate these cleanly using the Chromatotron, but partial enrichment of each allowed assignment of signals in NMR spectra. For **17***a*, ^{1}H NMR, δ: 7.5–7.2 (m, Ph-H), 6.79 (d, J = 2.4 Hz, vinyl-H); 3.69 and 3.66 (two s, 2 × OMe); 3.47 (d, J = 2.3 Hz, methine-H), 3.38 (s, CH_2). In an NOE experiment, irradiation of the doublet at 6.79 δ gave enhancement of a phenyl-H signal at 7.4 δ, irradiation of doublet at δ = 3.47 gave enhancement of a phenyl-H signal at 7.3 δ, and irradiation of singlet at δ = 3.38 gave enhancement of vinyl-H at 6.79 δ and of phenyl-H at 7.3 δ. For ^{13}C NMR data see Table 2. MS (ei) on mixture, *m/z*: 336 (M^+, 5%), 304 (15%), 276 (M − EH^+, 15%), 245 (M − Bn^+, 25%), 217 (276 − E^+, 65%), 214 (5%), 202 (35%), 189 (10%), 115 (65%), 91 (100%), 77 (35%). MS (ci, NH_3) *m/z*: 354 (M + NH_4^+, 100%), 337 (M + H^+, 12%), 305 (M − OMe^+, 10%), 252 (12%), 228 (10%), 202 (5%), 121 (7%).

For **18***a*, ^{1}H NMR, δ: 7.5–7.2 (m, Ph-H), 6.88 (d, J = 2 Hz, vinyl-H); 3.91 and 3.11 (AB quartet, J = 16 Hz, CH_2); 3.70 and 3.55 (two s, 2 × OMe); 3.44 (d, J = 2 Hz, methine-H). In an NOE experiment, irradiation of the doublet at δ = 6.88 gave enhancement at phenyl-H signal at 7.38 δ, and slight enhancement of doublet at 3.44 δ. Irradiation of doublet at δ = 3.44 gave possible enhancement at 6.88 δ, but not of methylene signals.

*Dimethyl 2,3-dibenzylcyclopropene-1,3-dicarboxylate (**16**a)* (14%), pale yellow oil. ^{1}H NMR (500 MHz) δ: 7.27 (t, br, J = 7 Hz, 3*H* of Ph), 7.24–7.16 (m, 3*H* of Ph), 7.10 (d, J = 7 Hz, 2H, H-2, H-6 of Ph), 7.04 (d, J = 7 Hz, 2H, H-2, H-6 of Ph); 3.77 and 3.67 (AB quartet, J = 17.8 Hz, 2H, 2-CH_2); 3.71 and 3.55 (two s, 6H, 2 × OMe); 3.32 and 3.24 (AB quartet, J = 14.2 Hz, 2H, 3-CH_2); for ^{13}C NMR see Table 1.

The known (3) *dihydroazulene **28**a*, (2%).

Pyrazole-N-*oxide (**25**a)*, bright yellow oil. UV (1.66 mg/mL MeOH) λ_{max}, nm: 282 (ε = 550), 372 (ε = 420). ^{1}H NMR, δ:

Table 1. Comparative ^{13}C NMR data for unsymmetrical dibenzylcyclopropenes (**16**).

	16*a*	**16***b*	**16***c*	**16***d*	**16***e*	**16***f*	**16***g*	**16***h*	**16***i*
1-COO*C*H$_3$	52.4	52.3	52.4	52.4	52.5	52.3	52.3	52.4	52.5
1-*C*OOMe	159.6	159.6	159.6	159.6	159.6	159.5	159.4	159.4	159.4
3-COO*C*H$_3$	52.2	52.1	52.0	52.2	52.0	52.5	52.5	52.6	52.3
3-*C*OOMe	174.2	174.2	174.2	174.2	174.2	173.8	174.0	172.2	174.0
C1	104.0	104.0	104.0	104.0	103.9	103.8	104.4	104.3	105.0
C2	129.2	129.3	129.2	129.3	obsc	129.1	129.0	obsc	129.28
C3	35.4	35.4	35.4	35.6	35.6	35.2	35.5	35	35.6
2-*C*H$_2$	32.2	32.2	31.2	32.2	31.4	32.1	31.7	32.1	32.0
3-*C*H$_2$	37.6	37.1	37.6	36.7	37.7	37.3	37.6	37.9	37.6
2-CH$_2$-Ar									
C1	134.7	134.8	131.6	134.8	126.4	134.5	133.8	134.4	139.0
C2	129.0	129.0	128.9	129.0	129.9	129.0	130.7	129.0	129.34
C3	128.7	128.6	129.3	128.7	114.5	128.8	131.8	128.9	125.6 (q, J_{CF} =3.8 Hz)
C4	127.2	127.2	136.7	127.2	159.1	127.4	121.1	127.4	obsc
3-CH$_2$-Ar									
C1	138.6	135.4	138.6	130.6	138.7	137.7	138.5	142.9	138.5
C2	129.8	129.7	129.8	130.8	129.6	131.49	129.9	130.0	129.9
C3	128.4	129.1	128.4	113.9	128.4	131.54	128.5	125.3 (q, J_{CF} = 3.5 Hz)	128.6
C4	126.4	135.8	126.4	158.2	126.4	120.4	126.5	obsc	126.6
Aryl-subst.		21.2 (CH$_3$)	21.2 (CH$_3$)	55.4 (OCH$_3$)	55.5 (CH$_3$O)	—	—	obsc(CF$_3$)	obsc(CF$_3$)

8.05 (s, 1H, OH), 7.05–7.4 (m, 10H), 5.76 (s, 1H, >CH-), 3.90 and 3.78 (two s, 6H, 2 × OMe), 3.41 and 3.23 (AB quartet, J = 12 Hz, 2H, CH$_2$); for ^{13}C NMR see Table 3.

*Methyl 5-benzoyl-4-benzyl-1*H*-pyrazole-3-carboxylate (**22**a)* (1%). IR (cm^{-1}): 3270(br) m, 3090 w, 3065 w, 3035 w, 2955 w, 2930(sh), 1724 s, 1654 s, 1598 m, 1575 w, 1563 w, 1489 m, 1449 s, 1442(sh). ^1H NMR, δ: 8.02 (d, br, J = 7.8 Hz, 2H, H-2, H-6 of Bz), 7.58 (t, br, J = 7.6 Hz, 1H, H-4 of Bz), 7.46 (t, br, J = 7.8 Hz, 2H, H-3, H-5 of Bz), 7.3–7.1 (m, 5H), 4.51 (s, 2H, CH$_2$), 3.95 (s, 3*H*, OMe). ^{13}C NMR, δ: 189.1 (PhCO), 160.2 (*C*OOMe), 148.4 (C3 and C5), 140.4 (Bn-C1), 137.8 (Bz-C1), 133.2 (C4), 133.0 (Bz-C4), 130.4 (Bz-C2), 128.7 (Bn-C2), 128.4 (Bn-C3 and Bz-C3), 126.2 (Bn-C4), 52.5 (OMe), 29.1 (CH$_2$). MS (ei) *m/z*: 321 (10%), 320 (M$^+$, 55%), 288 (M − 32$^+$, 35%), 183 (288-PhCO$^+$, 15%), 155 (30%), 127 (15%), 105 (PhCO$^+$, 100%).

The known (3) *dimethyl 1,5-dibenzyl-1*H*-pyrazole-3,4-dicarboxylate (**19**a)* (3.3%), yellow oil. HRMS, Exact Mass calcd. for $C_{21}H_{20}N_2O_4$: 364.1423; found: 364.1420.

*Dimethyl 5-benzyl-1*H*-pyrazole-3,4-dicarboxylate (**20**a)*, trace of a yellow oil. IR (cm^{-1}): 3480 m, 3280(br) s, 3060, 3030, 2955 s, 1730(br) s, 1603 m, 1569 m, 1496 s, 1453 s, 1436 s. ^1H NMR, δ: 7.33–7.15 (m, 5H), 4.25 (s, 2H, CH$_2$), 3.87 and 3.81 (two s, 6H, 2 × OMe). ^{13}C NMR, δ: 163.3 and 162.4 (2 × CO), 148.4 (C3), 143.2 (C4), 136.7 (Ph-C1), 129.0 and 128.9 (Ph-C2 and Ph-C3), 127.2 (Ph-C4), 111.7 (C5), 52.7 and 52.0 (2 × OMe), 31.8 (5-CH$_2$). MS (ei) *m/z*: 274 (M$^+$, 20%), 242 (M − 30$^+$, 100%), 210 (85%), 182 (M − 92$^+$, 25%), 155 (45%), 154 (40%), 91 (35%). MS (ci, NH$_3$) *m/z*: 275 (M + H$^+$, 80%), 192 (55%), 175 (100%), 160 (10%). HRMS, Exact Mass calcd. for $C_{14}H_{14}N_2O_4$: 274.0954; found: 274.0960.

On keeping in solution for some weeks, **25***a* decomposed to a mixture of **21***a*, **22***a*, and **23***a*.

*Dimethyl 5-benzoyl-4-benzyl-4*H*-pyrazole-3,4-dicarboxylate (**21**a)*: IR (cm^{-1}): 3065 w, 3035 w, 2960 m, 1765 s, 1731 s, 1656 s, 1596 m, 1578 w, 1546 w, 1528 w, 1492 w, 1441 s. ^1H NMR, δ: 8.06 (d, J = 8 Hz, 2H, H-2, H-6 of Bz), 7.66 (t, J = 7.3 Hz, 1H, H-4 of Bz), 7.47 (t, J = 7.6 Hz, 2H, H-3, H-5 of Bz), 7.17–7.03 (m, 3*H*, H-3, H-4, H-5 of Bn), 6.79 (d, J = 7.4 Hz, 2H, H-2, H-6 of Bn); 4.07 and 3.73 (two s, 6H, 2 × OMe); 3.92 and 3.82 (AB quartet, J = 14 Hz, 2H, CH$_2$). ^{13}C NMR, δ: 186.4 (Ph-CO), 163.4 and 160.3 (2 × *C*OOMe), 173.1 and 168.1 (C3 and C5), 134.9 (Bz-C4), 134.6 (Bz-C1), 133.0 (Bn-C1), 131.3 (Bz-C2), 128.8 (Bn-C2 and Bn-C3 and Bz-C3), 128.2 (Bn-C4), 77.7 (C4), 54.1 and 53.8 (2 × OMe), 37.5 (CH$_2$). MS (ei) *m/z*: 378 (M$^+$, 5%), 346 (5%), 287 (M − Bn$^+$, 10%), 213 (15%), 105 (Bz$^+$, 100%), 91 (85%), 77 (55%). MS (ci, NH$_3$) *m/z*: 379 (M + H$^+$, 30%), 289 (100%). HRMS, Exact Mass calcd. for $C_{21}H_{18}N_2O_5$: 378.1216; found: 378.1210.

*Dimethyl 5-benzoyl-1*H*-pyrazole-3,4-dicarboxylate (**23**a)*: IR (cm^{-1}): 3450 m, 3240(br) m, 3060 w, 2955 m, 2927 w, 2850 w, 1738 s, 1658 m, 1598 w, 1576 w, 1492 w, 1450 m. ^1H NMR, δ: 8.10 (d, br, J = 8 Hz, 2H, H-2, H-6 of Bz), 7.63 (t, br, J = 7.2 Hz, 1H, H-4 of Bz), 7.49 (t, br, J = 7.5 Hz, 2H, H-3,

Table 2. Comparative ^{13}C NMR data for (*E*)- and (*Z*)-methylenecyclopropanes (**17** and **18**).

	17*a*	**17***f*[a]	**17***g*[a]	**17***h*	**18***a*	**18***f*[a]	**18***g*[a]	**18***h*
$COOCH_3$	52.6	52.6	52.6	52.7	52.4	52.4	52.5	52.7
	52.9	52.9	52.9	53.0	53.1	53.1	53.1	53.0
2-*C*OOMe	168.9	168.6	168.6	168.5	169.7	169.5	169.7	169.3
1-*C*OOMe	171.0	170.9	171.0	170.7	170.3	170.2	170.3	170.0
CH_2	32.8	32.8	32.2	32.8	32.4	32.4	31.8	32.8
>C<	33.8	34.0	33.6	34.0	37.3	37.4	37.0	34.0
>CHE	30.7	30.6	30.7	30.7	27.3	(27.6)[c]	27.6	30.7
=C<	125.2	126.1	124.8	128.0	125.8	126.6	125.3	129.7
=CH-	121.2	120.3	121.5	120.1	121.9	121.1	122.3	120.9
Benzyl Ar								
C1	138.8	138.6	137.9	138.5	138.0	(137.7)	137.2	137.7
C2	129.1[b]	129.03[b]	131.0	129.1	129.0	(129.0)	130.6	128.8
C3	128.41	128.45	131.5	128.5	128.42[b]	128.49	131.4	128.5
C4	126.5	126.6	(120.3)[c]	126.7	126.5	(126.5)	120.5	126.7
Vinyl Ar								
C1	135.5	134.5	135.4	139.0	135.2	134.2	135.1	138.6
C2	127.6	129.05[b]	127.6	127.7	127.8	129.2	127.7	127.8
C3	128.9[b]	132.0	128.93	125.8 (q, J_{CF} = 3.9 Hz)	128.6[b]	132.1	128.94	125.9 (q, J_{CF} = 3.5 Hz)
C4	128.40	122.5	128.6	obsc	128.38	122.4	128.40	obsc
Aryl subst.	—	—	—	obsc(CF_3)	—	—	—	obsc(CF_3)

[a]Spectrum obtained at 125 MHz from a mixture with its three isomers.
[b]These assignments may be interchanged.
[c]Parentheses indicate presumed position of signal, obscured by others in sample.

H-5 of Bz); 3.97 and 3.83 (two s, 6H, 2 × OMe). ^{13}C NMR, δ: 186.2 (PhCO), 163.4 (COOMe), 159.1 (COOMe), 147.9 (C3, C5), 136.2 (Ph-C1), 135.2 (C4), 133.8 (Ph-C4), 130.3 (Ph-C2), 128.7 (Ph-C3), 119.4 (C4), 53.2, 53.1. MS (ei) *m/z*: 288 (M^+, 5%), 257 (M − OMe^+, 10%), 225 (10%), 105 (Bz^+, 63%), 91 (60%), 77 (100%). MS (ci, NH_3) *m/z*: 289 (M + H^+, 100%), 275 (15%), 257 (8%). HRMS, Exact Mass calcd. for $C_{14}H_{12}N_2O_5$: 288.0746; found: 288.0755.

Other products from photolysis of ***3****a in the presence of DMAD*

On several occasions dimethyl 1,3,5,7-cyclooctatetraene-1,8-dicarboxylate was isolated (ca. 8%). IR (cm^{-1}): 3060 w, 3020 m, 2955 m, 2910 w, 2850 w, 1722 s, 1656 m, 1640 m, 1605 w, 1495 w, 1435 m. ^1H NMR, δ: 7.19 (d, *J* = 3.3 Hz, 2H, H-2, H-7), 6.07 (dd, *J* = 11.5, 3.3 Hz, 2H, H-3, H-6), 5.95 (d, *J* = 11.1 Hz, 2H, H-4, H-5), 3.88 (s, 6H, OMe). ^{13}C NMR, δ: 166.1 (CO), 143.2 (C-2), 132.8 and 130.2 (C-3 and C-4), 132.2 (C-1), 52.3 (OMe). MS (ei) *m/z*: 220 (M^+, 35%), 188 (35%), 161 (M − E^+, 75%), 160 (100%), 133 (90%), 102 (85%), 91 (75%), 76 (35%). MS (ci, NH_3) *m/z*: 238 (M + NH_4^+, 30%), 221 ($M+H^+$, 100%), 189 (M − OMe^+, 10%), 160 (5%). The NMR data fit well with those in the literature (43), and the IR data fit moderately well with published mull data (44).

On one occasion, a small amount of an unidentified compound was obtained with ^1H NMR, δ: 9.3 (s, br, 1H), 7.20 (dd, *J* = 6.6 Hz, 2.1 Hz, ca. 2H), 6.85 (dd, *J* = 6.6 Hz, 2.1 Hz, ca. 2H), 3.79 (s, 3H, OMe), 3.59 (s, 2H, CH_2), 2.01(s, 3H, Me). ^{13}C NMR (spin sort mode) δ: 176.8 (CO), 167.9 (CO), 158.9 (=C<), 130.5 (intense, =CH-), 125.8 (=C<), 114.2 (intense, =CH-), 102.6 (quat-C), 55.4 (OMe), 40.3 (CH_2), 20.7 (Me).

On a few occasions, and contaminated with other components, small amounts of what is probably the dihydronaphthalene **29***a* (ca. 1.5%), were isolated. Partial spectrum: ^1H NMR, δ: 4.91(s, br, 1H), 4.16 and 4.10 (AB quartet, *J* = 14.2 Hz, 2H, CH_2), 3.80 and 3.66 (two s, 2 × OMe), 3.34 (d, *J* = 20 Hz, 1H, upfield half of an AB quartet).

*Photolysis of oxadiazoline (****3****a) in methanol (1 run)*

Oxadiazoline (**3***a*) was photolyzed as described above, but using methanol as solvent. The majority of the products were the same as with benzene as solvent, but one new component was methyl 4-benzyl-3-methoxycarbonyl-2-methoxy-5-phenylpent-3-enoate (**30**) (4%). IR (cm^{-1}): 3080 w, 3065 w, 3030 w, 3000 w, 2955 m, 2830 w, 1760 s, 1729 s, 1652 w, 1600 w, 1490 m, 1450 m, 1433 m. ^1H NMR (500 MHz) δ: 7.30–7.25(m, 4H of Ph), 7.22(t, *J* = 7 Hz, 2H of Ph), 7.17 (d, *J* = 7 Hz, 2H, H-2, H-6 of Ph), 7.14 (d, *J* = 7 Hz, 2H, H-2, H-6 of Ph), 4.86 (s, 1H, methine-H), 3.81 (s, 3H, 1-OMe), 3.77 (s, 3H, 3-COOMe); 3.63 and 3.59 (AB quartet, *J* = 14.5 Hz, 2H, CH_2 *cis* to 3-E); 3.53 (s, 2H, CH_2 *cis* to CHEOMe), 3.41 (s, 3H, 2-OMe). ^{13}C NMR, δ: 170.6 (C1, i.e., *C*OOMe), 167.9 (3-*C*OOMe), 150.0 (C4), 138.4 and 137.9 (2 × Ph-C1), 131.3 (C3), 129.3 and 129.1 and 128.8 and 128.7 (C2

Table 3. Comparative ^{13}C NMR data for 4*H*-pyrazole *N*-oxides (**25**).

	25*a*	**25***b*	**25***c*	**25***d*	**25***e*
3-COO*C*H$_3$	52.5	52.5	52.5	52.6	52.7
3-*C*OOMe	161.7	161.7	161.7	161.6	161.5
4-COO*C*H$_3$	53.4	53.4	53.3	53.5	53.6
4-*C*OOMe	169.7	169.8	169.7	169.5	169.3
4-CH$_2$	42.7	42.5	42.0	42.7	42.7
5-CH(OH)	100.2	100.1	100.1	99.0	98.5
C3	143.5	143.6	143.5	144.13	144.6
C4	63.7	63.8	63.9	64.0	64.3
C5	143.6	145.4	143.8	144.09	145.3
4-CH$_2$-Ar					
C1	135.1	131.9	127.0	134.9	134.7
C2	130.2	130.1	131.1	130.1	130.1
C3	128.4	129.1[a]	113.8	128.4	128.5
C4	127.31	138.2	158.9	127.4	127.4
5-CH(OH)Ar					
C1	135.7	135.7	135.7	134.6	139.3
C2	127.34	127.3	127.3	128.9	127.5
C3	129.3	129.3[a]	129.3	132.4	126.2 (q, J_{CF} = 3.5 Hz)
C4	126.8	126.7	126.8	120.3	obsc
Aryl subst	—	22.8(CH$_3$)	53.4(OCH$_3$)	—	obsc(CF$_3$)

[a]Assignments may be interchanged.

and C3 of Ph's), 126.9 and 126.7 (2 × C4 of Ph), 77.9 (C2), 57.9 (2-OMe), 52.5 (1-OMe), 52.2 (3-COO*Me*), 39.5 (CH$_2$ *cis* to 3-E), 37.4 (CH$_2$ *cis* to CHEOMe). MS (ci, NH$_3$) *m/z*: 386 (M + NH$_4^+$, 35%), 369 (M + H$^+$, 35%), 354 (65%), 337 (M − OMe$^+$, 100%), 309 (M − E$^+$, 20%), 245 (30%), 91 (27%).

Low-temperature photolysis of **3**a *(2 runs)*
Compound **3***a* was photolyzed in the presence of DMAD in toluene at −40°C, using a thin-walled NMR tube. After 5 h the mixture contained the unstable 3*H*-pyrazole **6***a*, but only about half the oxadiazoline had reacted. Also present was a small amount of symmetric cyclopropene (**4***a*), but apparently no unsymmetrical cyclopropene (**16***a*). After 4 days in solution, compound **6***a* had disappeared, and some of the new signals could be assigned to the 1, 5-dibenzyl 1*H*-pyrazole **19***a*.

In a repeat run, most of the oxadiazoline had been consumed after 10 h. Separation gave propenes **14***a* and **15***a* (2%), unchanged starting material, cyclopropene **4***a* (22%), as well as an unidentified compound with ^1H NMR, δ: 7.35–7.15 (m, ca. 8H), 7.02 (d, *J* = 7 Hz, 2H), 3.89 (s, 2H, CH$_2$), 3.80 and 3.76 (two s, 2 × OMe), 3.49 (s, 2H, CH$_2$). ^{13}C NMR, δ: 166.8 and 158.1 (2 × CO), 138.1 and 137.3 (2 × C1 of Ph), 129.2 and 128.9 and 128.8 (CH of Ph), 126.9 and 126.7 (2 × C4 of Ph), 52.5 (2 × OMe), 40.4 and 38.8 (2 × CH$_2$). Final components were unsymmetric cyclopropene **16***a* (11%), benzoyl 4*H*-pyrazole **21***a* (5%), and monobenzyl 1*H*-pyrazole **20***a* (2%).

*Photolysis of oxadiazoline (***3**b*) (1 run)*
Separation gave a mixture of 1, 3-diarylpropenes (**14***b*, **14***c*, **15***b*, and **15***c*) in ratio approximately 3:3:1:1 (3%), and the following additional compounds in this order. Methylenecyclopropanes **17***c* and **18***c* in approximately equal amounts, but each occurring with about 25% of the positional isomers **17***b* and **18***b* (combined total yield: 10%). This mixture of four components could not be separated on the Chromatotron. IR (mixture) (cm^{-1}): 3030 w, 3005 w, 2950 w, 2925 w, 1728 s, 1510 w, 1494 w, 1448(sh), 1431 m. ^1H NMR (**18***c*), δ: 7.45–7.00 (m, aryl-H), 6.87 (d, *J* = 2.0 Hz, vinyl-H); 3.85 and 3.08 (AB quartet, *J* = 15.7 Hz, 2H, CH$_2$), 3.70 and 3.58 (two s, 2 × OMe), 3.40 (d, *J* = 2.2 Hz, 1H, methine-H), 2.28 (s, 3H, ArMe); **18***b* includes 6.85 (d, *J* = 2.0 Hz, vinyl-H); 3.92 and 3.09 (AB quartet, *J* = 15.9 Hz, CH$_2$); 3.54 (s, OMe), 2.36 (s, ArMe); **17***c* includes 6.75 (d, *J* = 2.3 Hz, vinyl-H); 3.69 and 3.65 (two s, 2 × OMe); 3.45 (d, *J* = 2.3 Hz, methine-H), 3.33 (s, CH$_2$), 2.32 (s, ArMe); (**17***b*) includes 6.79 (d, *J* = 2.3 Hz, vinyl-H), 3.37 (s, CH$_2$), 2.34 (s, ArMe).

*Dimethyl 3-benzyl-3-(4-methylbenzyl)cyclopropene-1,2-dicarboxylate (***4**b*) (16%). IR (cm^{-1}): 3030 w, 2955 w, 2915 w, 2850 w, 1833 m, 1713 s, 1605 w, 1510 w, 1491 w, 1445(sh), 1430 m. ^1H NMR, δ: 7.4–6.9 (m, 9H), 3.74 (s, 6H, 2 × OMe); 3.11 and 3.08 (two s, 2 × CH$_2$), 2.28 (s, 3*H*, ArMe). ^{13}C NMR, δ:160.0 (CO), 138.3 (Ph-C1), 135.9 (Ar-C4), 135.1 (Ar-C1), 129.8 (Ph-C2), 129.7 (Ar-C2), 129.2 (Ar-C3), 128.5 (Ph-C3), 126.8 (C1 and C2), 126.5 (Ph-C4), 52.7 (OMe), 43.0 and 42.6 (2 × CH$_2$), 41.3 (C3), 21.2 (Ar-Me).

*Dimethyl 2-benzyl-3-(4-methylbenzyl)cyclopropene-1,3-dicarboxylate (***16**b*) and dimethyl 3-benzyl-2-(4-methylbenzyl)-cyclopropene-1,3-dicarboxylate (***16**c*)* as a 2:1 mixture (25%). The isomers could not be separated. IR (of mixture) cm^{-1}: 3030 w, 3005 w, 2950 w, 2920 w, 1867 m, 1720 s, 1605 w, 1510 m, 1492 w, 1445 (sh), 1430 m. ^1H NMR of **16***b* (from the

mixture), δ: 7.3–6.9 (m, aryl-H), 3.72 and 3.54 (two s, 2 × OMe); 3.8–3.5 (m, 2-CH_2; partly obscured), 3.29 and 3.18 (AB quartet, J = 14.4 Hz, 3-CH_2); 2.28 (s, ArMe). Partial ^{1}H NMR of **16***c* (remaining signals obscured by those of **16***b*), δ: 3.71 and 3.56 (two s, 2 × OMe); 3.31 and 3.22 (AB quartet, J = 14 Hz, 3-CH_2) 2.31 (s, ArMe).

Pyrazole-N-*oxide* (**25**b), bright yellow oil (3%). ^{1}H NMR, δ: 8.06 (s, br, 1H, OH), 7.4–6.9 (m, 9H), 5.75 (s, 1H, >CH-), 3.90 and 3.77 (two s, 2 × OMe), 3.72 and 3.28 (AB quartet, J = 13.5 Hz, CH_2) 2.25 (s, ArMe). This compound was unstable, and after 2 weeks' exposure to air at room temperature had changed to a complex mixture. Based on the major signals in the ^{1}H NMR spectrum of the mixture the principal component was methyl 5-benzoyl-4-(4-methylbenzyl)-1*H*-pyrazole-3-carboxylate (**22***b*). ^{1}H NMR, δ: 8.02 (d, J = 7 Hz, 2H, H-2, H-6 of Bz), 7.56 (t, J = 7 Hz, 1H, H-4 of Bz), 7.44 (t, J = 7 Hz, 2H, H-3, H-5 of Bz), 7.16 (d, J = 8.0 Hz, 2H, H-2, H-6 of Ar), 7.02 (d, J = 8.0 Hz, 2H, H-3, H-5 of Ar), 4.46 (s, 2H, 4-CH_2), 3.94 (s, 3*H*, OMe), 2.26 (s, 3H, Ar-Me).

*Dimethyl 5-benzyl-1-(4-methylbenzyl)-1*H*-pyrazole-3,4-dicarboxylate (19*b) (6%). IR (cm^{-1}): 3035 w, 3005 m, 2955 m, 2930 (sh), 2860 w, 1730 s, 1602 w, 1531 w, 1511 w, 1491 m, 1477 m, 1445(sh), 1432 s. ^{1}H NMR, δ: 7.3–6.9 (m, 9H), 5.13 (s, 2H, N-CH_2), 4.16 (s, 2H, 5-CH_2), 3.96 and 3.81 (two s, 2 × OMe); 2.31 (s, 3H, ArMe). ^{13}C NMR, δ: 163.6 and 162.8 (2 × CO), 145.3 (C3), 138.1 (Ar-C4), 136.1 (Ph-C1), 132.0 (Ar-C1), 129.7 (Ar-C3), 129.0 (Ph-C3), 128.3 (Ph-C2), 127.1 (Ph-C4), 127.0 (Ar-C2), 114.2 (C4), 54.3 (*N*-CH_2), 52.7 and 52.1 (2 × OMe), 30.3 (5-CH_2), 21.3 (Ar-Me), signal from C5 not clearly visible. MS(ei) *m/z*: 378 (M^+, 10%), 346 (M − $MeOH^+$, 10%), 314 (5%), 273 (M − $ArCH_2^+$, 25%), 241 (20%), 105 ($ArCH_2^+$, 100%), 91 (25%), 77 (20%). HRMS, Exact Mass calcd. for $C_{22}H_{22}N_2O_4$: 378.1580; found: 378.1583.

Compound **20**a *and dimethyl 5-(4-methylbenzyl)-1*H*-pyrazole-3,4-dicarboxylate (**20**b)* as a 3:2 mixture (ca. 4%). Because of overlap by signals from **20***a*, only partial spectra are available for **20***b*. ^{1}H NMR, δ: 4.23 (s, CH_2); 3.92 and 3.84 (two s, 2 × OMe); 2.33 (s, ArMe). ^{13}C NMR, δ: 163.3 and 162.3 (2 × CO), 137.2 (Ar-C4), 133.3 (Ar-C1), 129.9 (Ar-C3), 129.0 (Ar-C2), 52.8 and 52.0 (2 × OMe), 21.2 (Ar-Me).

Photolysis of para-*methoxybenzyl oxadiazoline (***3**c*) (1 run)* Separation gave first a mixture of the 1,3-diarylpropenes **14***d*, **14***e*, **15***d*, and **15***e* in approximate ratio 2:2:1:1 (2%), then the following additional products.

*Dimethyl 3-benzyl-3-(4-methoxybenzyl)cyclopropene-1,2-dicarboxylate (**4**c)* (6%). IR(cm^{-1}): 3065 w, 3030 w, 3005 w, 2955 m, 2915 m, 1834 m, 1715 s, 1610 m, 1581 w, 1509 m, 1495 m, 1450 m, 1430 s. ^{1}H NMR (90 MHz) δ: 7.17–7.10 (m, 3H of Ph), 7.05–7.01 (m, 2H of Ph), 6.92 (d, J = 8.6 Hz, 2H, H-2, H-6 of Ar), 6.69 (d, J = 8.6 Hz, 2H, H-3, H-5 of Ar), 3.68 (s, 9H, ArOMe and 2 × COOMe), 3.03 and 2.99 (two s, 2 × CH_2). ^{13}C NMR, δ: 160.1 (CO), 158.3 (Ar-C4), 138.4 (Ph-C1), 130.8 (Ar-C2), 130.3 (Ar-C1) 129.8 (Ph-C2), 128.5 (Ph-C3), 126.9 (C1 and C2), 126.5 (Ph-C4), 114.0 (Ar-C3), 55.3 (Ar-OMe), 52.7 (COO*Me*), 43.0 and 42.2 (2 × CH_2), 41.5 (C3).

*Dimethyl (*E*)-1-(4-methoxybenzyl)-3-phenylmethylenecyclopropane*-trans-*1,2-dicarboxylate (**17**e) and dimethyl (*Z*)-1-(4-methoxybenzyl)-3-phenylmethylenecyclopropane*-trans-*1, 2-dicarboxylate (**18**e)* in 1:1 ratio, as a mixture (2.5%). Characteristic ^{1}H NMR signals were discernable as follows; for **17***e*, δ: 6.77 (d, J = 2.2 Hz, vinyl-H), 3.70 and 3.66 (two s, 2 × OMe), 3.44 (d, J = 2.3 Hz, methine-H), 3.30 (s, CH_2); for **18***e*, δ: 6.87 (d, J = 2.0 Hz, vinyl-H), 3.71 and 3.60 (two s, 2 × OMe), 3.38 (d, J = 1.9 Hz, methine-H), 3.06 (d, J = 15.6 Hz, half of CH_2 AB quartet; other half obscured by ester signals).

*The methoxy analogue of **29**a*, as a mixture of two isomers; presumably **29***b* and **29***c*. Distinguishable signals in the ^{1}H NMR spectrum: major isomer, δ: 4.86 (s, br, 1H), 4.19 and 4.06 (AB quartet, J = 14.4 Hz, CH_2), 3.72 and 3.71 and 3.60 (three s, 2 × COOMe and ArOMe); minor isomer, δ: 4.90 (s, br, 1H), 4.10 and 3.99 (AB quartet, J = 13.8 Hz, CH_2), 3.73 and 3.70 and 3.59 (three s, 2 × COOMe and ArOMe).

*Dimethyl 2-benzyl-3-(4-methoxybenzyl)cyclopropene-1,3-dicarboxylate (**16**d)*. ^{1}H NMR, δ: 7.3–7.1 (m, 5H of Ph), 6.92 (d, J = 8.7 Hz, 2H, H-2, H-6 of Ar), 6.74 (d, J = 8.7 Hz, 2H, H-3, H-5 of Ar), 3.79 (m, 2H, 2-CH_2), 3.76 and 3.72 (two s, 9H, 2 × COOMe and ArOMe), 3.22 (m, 2H, 3-CH_2).

*Dimethyl 3-benzyl-1-(4-methoxybenzyl)-1*H*-pyrazole-4,5-dicarboxylate (**32**)* (5%), as a yellow oil. IR (cm^{-1}): 3060 w, 3030 w, 3000 w, 2950 m, 2835 w, 1725 s, 1610 m, 1582 w, 1535 m, 1510 s, 1491 m, 1461 m, 1451 m, 1431 m. ^{1}H NMR, δ: 7.26–7.18 (m, 5H of Ph), 7.16 (d, J = 8.6 Hz, 2H, H-2, H-6 of Ar), 6.88 (d, J = 8.6 Hz, 2H, H-3, H-5 of Ar), 5.40 (s, 2H, N-CH_2), 4.18 (s, 2H, 3-CH_2), 3.82 and 3.78 and 3.74 (three s, 2 × COOMe and ArOMe). In an NOE experiment, irradiation at δ = 5.40 caused enhancement of the doublet at 7.16 δ but had no effect on the singlet at 4.18 δ; equally, irradiation at δ = 4.18 enhanced the multiplet at δ = 7.2, but had no effect on the singlet at δ = 5.4. ^{13}C NMR, δ: 163.3 and 161.1 (2 × CO), 159.4 (Ar-C4), 152.0 (C3), 139.1 (C5), 135.7 (Ph-C1), 129.3 and 128.9 (Ar-C2 and Ph-C3), 128.1 (Ph-C2), 126.3 (Ph-C4 and Ar-C1(?)), 114.3 (C4), 113.6 (Ar-C3), 55.4 (ArOMe), 54.7 (N-CH_2), 53.0 and 51.8 (2 × COO*Me*), 33.4 (3-CH_2). MS(ei) *m/z*: 394 (M^+, 10%), 362 (M − 32$^+$, 10%), 307 (15%), 275 (5%), 121 ($MeOBn^+$, 100%), 91 (Bn^+, 20%).

Pyrazole-N-*oxide* (**25**c) as a bright yellow oil. IR (cm^{-1}): 3350(br) w, 3030 w, 3000 w, 2955 w, 2835 w, 1740 s, 1710 s, 1655 m, 1611 w, 1600 w, 1555 m, 1511 m, 1450 s, 1411 m. ^{1}H NMR, δ: 8.04 (s, br, OH), 7.40–7.35 (m, 2H of Ph), 7.25–7.18 (m, 3H of Ph), 6.98 (d, J = 8.7 Hz, 2H, H-2, H-6 of Ar), 6.70 (d, J = 8.7 Hz, 2H, H-3, H-5 of Ar), 5.74 (s, 1H, >CH-), 3.96 and 3.77 (two s, 2 × COOMe), 3.74 (s, ArOMe), 3.71 and 3.27 (AB quartet, J = 13.7 Hz, CH_2). MS (ei) *m/z*: 394 (M^+, 5%), 121 ($MeOBn^+$, 100%), 105 (10%), 77 (12%). On exposing the solution to the atmosphere for several days, **25***c* was converted primarily to methyl 5-benzoyl-4-(4-methoxybenzyl)-1*H*-pyrazole-3-carboxylate (**22***c*). IR (cm^{-1}): 3270(br) m, 3070 w, 3040 w, 3005 w, 2960 m, 2842 w, 1730 s, 1655 s, 1613 m, 1601 m, 1582 w, 1511 s, 1452 s, 1442 s. ^{1}H NMR, δ: 8.02 (d, J = 7.0 Hz, 2H, H-2, H-6 of Bz), 7.59 (t, J = 7.3 Hz, 1H, H-4 of

Bz), 7.46 (t, J = 7.7 Hz, 2H, H-3, H-5 of Bz), 7.20 (d, J = 8.7 Hz, 2H, H-2, H-6 of Ar), 6.76 (d, J = 8.7 Hz, 2H, H-3, H-5 of Ar), 4.44 (s, 2H, CH_2), 3.97 (s, 3H, COOMe), 3.74 (s, 3H, ArOMe). ^{13}C NMR, δ (partial spectrum): 189.1 (PhCO), 160.1 (*C*OOMe), 158.1 (Ar-C4), 137.9 (Ph-C1), 133.0 (Ph-C4), 132.8 (Ar-C1), 129.8 (Ar-C2), 128.4 (Ph-C3), 113.9 (Ar-C3), 55.4 (Ar-OMe), 52.5 (COO*Me*), 28.2 (CH_2).

*Dimethyl 5-benzyl-1-(4-methoxybenzyl)-1*H*-pyrazole-3,4-dicarboxylate (**19**d)* (25%). IR (cm^{-1}): 3050 w, 3025 w, 2995 w, 2945 m, 2830 w, 1735 s, 1718 s, 1611 m, 1584 w, 1531 m, 1512 s, 1493 s, 1477 s, 1453 s, 1438 s. ^{1}H NMR, δ: 7.2 (m, 3H of Ph), 7.06 (m, 2H of Ph), 6.96 (d, J = 8.8 Hz, 2H, H-2, H-6 of Ar), 6.79 (d, J = 8.6 Hz, 2H, H-3, H-5 of Ar), 5.11 (s, 2H, N-CH_2), 4.19 (s, 2H, 5-CH_2), 3.96 and 3.81 (two s, 2 × COOMe), 3.77 (s, 3H, ArOMe). ^{13}C NMR, δ: 163.4 and 162.7 (2 × CO), 159.6 (Ar-C4), 145.1 (C3), 143.0 (C5), 136.0 (Ph-C1), 129.0 (Ph-C3), 128.6 (Ar-C2), 128.2 (Ph-C2), 127.1 (Ar-C1), 127.0 (Ph-C4), 114.3 (Ar-C3), 114.0 (C4), 55.4 (Ar-OMe), 53.9 (N-CH_2), 52.6 and 52.0 (2 × COO*Me*), 30.2 (5-CH_2).

Finally, dimethyl 5-benzyl-1*H*-pyrazole-3, 4-dicarboxylate (**20***a*) (7%) was isolated.

Photolysis of para*-bromobenzyl oxadiazoline (**3**d) (2 runs)*
Separation after first run gave a mixture of 1,3-diarylpropenes **14***f*, **14***g*, **15***f*, and **15***g* (5%), then the following compounds in this sequence. First a ca. 4:4:3:2 mixture of methylenecyclopropenes **18***g*, **17***f*, **17***g*, and **18***f* (combined yield, 3%). The isomers could not be cleanly separated, and the spectra are those of mixtures, with not all signals being resolved. ^{1}H NMR data, partial spectra: dimethyl 3-(*E*)-(4-bromophenylmethylene)-1-benzylcyclopropane-*trans*-1,2-dicarboxylate (**17***f*), δ: 6.75 (d, J = 2.4 Hz, 1H, vinyl-H), 3.72 and 3.66 (two s, 2 × OMe), 3.46 (d, J = 2.4 Hz, 1H, methine-H), 3.22 (s, 2H, CH_2); dimethyl 1-(4-bromobenzyl)-3-(*E*)-(phenylmethylene)cyclopropane-*trans*-1,2-dicarboxylate (**17***g*), δ: 6.72 (d, J = 2.3 Hz, 1H, vinyl-H), 3.69 and 3.67 (two s, 2 × OMe), 3.45 (d, J = 2.4 Hz, 1H, methine-H), 3.36 (s, 2H, CH_2); dimethyl 1-benzyl-3-(Z)-(4-bromophenylmethylene)cyclopropane-*trans*-1,2-dicarboxylate (**18***f*), δ: 6.83 (d, J = 2.0 Hz, 1H, vinyl-H), 3.82 and 3.13 (AB quartet, J = 15.8 Hz, CH_2), 3.57 (s, OMe); dimethyl 1-(4-bromobenzyl)-3-(*Z*)-(phenylmethylene)cyclopropane-*trans*-1,2-dicarboxylate (**18***g*), δ: 6.89 (d, J = 2.0 Hz, 1H, vinyl-H), 3.77 and 3.11 (AB quartet, J = 15.8 Hz, CH_2), 3.71 and 3.60 (two s, 2 × OMe), 3.39 (d, J = 1.8 Hz, 1H, methine-H).

A minor component, eluting with the methylenecyclopropenes, was not fully purified. Based on comparison with literature data (3), it was probably *2-benzyl-6-bromo-3,3a-bis(methoxycarbonyl)-1,3a-dihydroazulene (**28**b)*. ^{1}H NMR (500 MHz) includes δ: 6.47 and 6.36 (two d, J = 2.6 Hz, 2 × =CH-), 6.09 and 5.75 (two d, J = 5.8 Hz, 2 × =CH-), 4.17 and 3.86 (AB quartet, J = 14.5 Hz, 2-CH_2), 3.77 and 3.64 (two s, 2 × OMe), 2.96 and 2.52 (AB quartet, J = 18.5 Hz, 2 × H-1). ^{13}C NMR (125 MHz), tentative assignments, δ: 173.0 (3a-*C*OOMe), 165.6 (3-*C*OOMe), 157.1 (C2), 143.2 and 139.6 (2 × CH), 138.1 (Ph-C1), 136.0 and 133.4 (2 × CH), 132.1 (C8a), 131.1 (C3 or C6), 129.0 and 128.7 (Ph-C2, Ph-C3), 127.6 (C6 or C3), 126.6 (Ph-C4), 60.8 (C3a), 52.3 and 51.3 (2 × OMe), 47.4 (C1), 36.5 (2-CH_2).

*Dimethyl 3-benzyl-3-(4-bromobenzyl)cyclopropene-1,2-dicarboxylate (**4**d)* (16%). IR (cm^{-1}): 3075 w, 3055 w, 3020 w, 2995 w, 2945 m, 2910 w, 2835 w, 2075 w, 1835 m, 1720 s, 1600 w, 1485 m, 1431 m. ^{1}H NMR, δ: 7.35 (d, J = 8.3 Hz, 2H, H-3, H-5 of Ar), 7.3–7.1 (m, 3H, Ph-H), 7.07 (d, J = 7 Hz, 2H, H-2, H-6 of Ph), 6.97 (d, J = 8.3 Hz, 2H, H-2, H-6 of Ar), 3.76 (s, 6H, 2 × OMe), 3.09 and 3.07 (two s, 2 × CH_2). ^{13}C NMR δ: 159.9 (CO), 138.0 (Ph-C1), 137.2 (Ar-C1), 131.6 (Ar-C2 and Ar-C3), 129.8 (Ph-C2), 128.6 (Ph-C3), 126.7 (C1 and C2), 126.6 (Ph-C4), 120.5 (Ar-C4), 52.8 (OMe), 43.1 and 42.4 (2 × CH_2), 40.8 (C3).

An approximately 10:7 mixture of the asymmetric cyclopropenes, *dimethyl 2-benzyl-3-(4-bromobenzyl)cyclopropene-1,3-dicarboxylate (**16**f) and dimethyl 3-benzyl-2-(4-bromobenzyl)cyclopropene-1,3-dicarboxylate (**16**g)*. ^{1}H NMR assignments from spectrum of mixture: **16***g*, δ: 7.4–6.8 (m, 9H), 3.8-3.6 (m, 2-CH_2), 3.73 and 3.55 (two s, 2 × OMe), 3.23 and 3.13 (AB quartet, J = 14.6 Hz, 3-CH_2); **16***f*, partial spectrum, δ: 3.71 and 3.59 (two s, 2 × OMe), 3.38 and 3.25 (AB quartet, J = 14.6 Hz, 3-CH_2). MS (ei) of mixture *m/z*: 416/414 (M^+, 8%), 384/382 (9%), 357/355 (10%), 325/323 (M − Bn^+, 5%), 297/295 (8%), 245 (20%), 215 (100%), 171/169 (*p*-$BrBn^+$, 60%), 115 (5%), 91 (50%).

Pyrazole-*N*-oxide (**25***d*) eluted in ca. 1:1 ratio with 1*H*-pyrazole (**19***g*) (ca. 3%).
*Compound (**25**d)*. ^{1}H NMR, δ: 7.99 (s, 1H, OH; disappears on shaking with D_2O), 7.47 (d, J = 8.4 Hz, 2H, H-3, H-5 of Ar), 7.4–7.1 (m, 3H, of Ph), 7.07–7.02 (m, 4H, H-2, H-6 of Ar and Ph), 5.66 (s, 1H, >CH-), 3.91 and 3.78 (two s, 2 × OMe), 3.31 (d, J = 13.6 Hz, upfield half of CH_2 AB quartet: other half presumably hidden by ester signals). A one-bond C-H correlation experiment confirmed the assignments as given. In an NOE experiment irradiation of the doublet at δ = 3.31 gave enhancement at 7.99, 5.66, and 3.78 δ whereas irradiation at δ = 3.76 gave enhancement at 7.99, 7.02(d, *ortho*-H of Ph), and 3.31 δ and negative enhancement at 5.67 δ. Irradiation of singlet at δ = 5.67 gave enhancement of signals at 7.99, 7.07(d, *ortho*-H of Ar), and slightly at 3.31 δ. Irradiation of singlet at δ = 7.99 gave enhancement of the signal at δ = 7.07(d, of Ar). There was no change on keeping the mixture with D_2O under nitrogen at −15°C for 4 months.

*Dimethyl 1-benzyl-5-(4-bromobenzyl)-1*H*-pyrazole-3,4-dicarboxylate (**19**g)*. ^{1}H NMR, δ: 7.36 (d, J = 8.4 Hz, 2H, H-3, H-5 of Ar), 7.3–7.0 (m, 5H, of Ph), 6.89 (d, J = 8.5 Hz, 2H, H-2, H-6 of Ar), 5.19 (s, 2H, *N*-CH_2), 4.12 (s, 2H, 5-CH_2), 3.97 and 3.82 (two s, 2 × OMe). ^{13}C NMR, δ: 163.4 and 162.7 (2 × CO), 144.9 (C3), 143.3 (C5), 135.0 (Ph-C1), 134.9 (Ar-C1), 132.1 (Ar-C3), 129.9 (Ar-C2), 129.1 (Ph-C3), 128.4 (Ph-C4), 127.0 (Ph-C2), 121.1 (Ar-C4), 114.2 (C4), 54.5 (*N*-CH_2), 52.8 and 52.1 (2 × OMe), 29.8 (5-CH_2); MS (ei) *m/z*: 444/442 (M^+, 8%), 412 (12%), 380/378 (10%), 353/351 (M − Bn^+, 13%), 331 (5%), 240 (15%), 171/169 (*p*-$BrBn^+$, 10%), 115 (10%), 91 (100%). HRMS, Exact Mass calcd. for $C_{21}H_{19}{}^{79}BrN_2O_4$: 442.0528; found: 442.0522.

The final compound eluted was **20***a* mixed with about 20%

*dimethyl 5-(4-bromobenzyl)-1*H*-pyrazole-3,4-dicarboxylate (**20***c*). Overlap meant that only partial ^{1}H NMR data could be determined for **20***c*, signals for which included (δ): 7.44 (d, *J* = 8.4 Hz, H-3, H-5 of Ar), 7.10 (d, *J* = 8.4 Hz, H-2, H-6 of Ar), 4.22 (s, CH_2), 3.93 and 3.83 (two s, 2 × OMe). ^{13}C NMR, δ: 132.2 (Ar-C3), 130.7 (Ar-C2), 32.0 (5-CH_2). HRMS (on high molecular mass component of mixture), Exact Mass calcd. for $C_{14}H_{13}{}^{79}BrN_2O_4$: 352.0059; found: 352.0056.

On exposure to the atmosphere for several days, the solution of **25***d* was converted to *dimethyl 4-benzyl-5-(4-bromobenzoyl)-4*H*-pyrazole-3,4-dicarboxylate **21**d* (2% overall). IR (cm^{-1}): 3340(br) w, 3090 w, 3070 w, 3040 w, 2960 m, 2930 m, 2855 w, 1765 s, 1733 s, 1657 m, 1585 m, 1568 w, 1487 m, 1438 m. ^{1}H NMR, δ: 7.93 (d, *J* = 8.6 Hz, 2H, H-2, H-6 of Ar), 7.61 (d, *J* = 8.6 Hz, 2H, H-3, H-5 of Ar), 7.2–7.0 (m, 3*H*, of Ph), 6.76 (d, *J* = 6.6 Hz, 2H, H-2, H-6 of Ph), 4.08 and 3.73 (two s, 2 × OMe), 3.9–3.8 (m, 2H, CH_2). ^{13}C NMR, δ (partial spectrum): 185 (Ar-CO), 173 (C3 or C5), 133.4 (Ph-C1), 132.7 (Ar-C2), 132.2 (Ar-C3), 128.8 (Ph-C2), 128.7 (Ph-C3), 128.3 (Ph-C4), 54.1 and 53.8 (2 × OMe), 37.5 (CH_2).

Performing the photolysis of **3***d* in the presence of triethylamine (1 drop) gave a similar mix of products, but also included dimethyl 1-(diethylamino)maleate. IR (cm^{-1}): 2995 m, 2960 m, 1750 s, 1701 s, 1661 m, 1575 s, 1519 w, 1450 s, 1440 s, 1428 m, *cf.* values in ref 45. ^{1}H NMR, δ: 4.61 (s, 1H), 3.94 and 3.63 (two s, 2 × OMe), 3.18 (q, *J* = 7.1 Hz, 4H, 2 × CH_2), 1.18 (t, *J* = 7.1 Hz, 6H, 2 × CH_3). This spectrum is in good agreement with that published (45, 46). ^{13}C NMR, δ: 168.5 and 166.3 (2 × CO), 129.1 (=C<), 83.1 (=CH-), 54.3 and 50.8 (2 × OMe), 45.1 br (CH_2), 12.8 br (CH_3). This is reasonably concordant with values tabulated for the corresponding dimethyl compound (47).

Photolysis of para*-trifluoromethylbenzyl oxadiazoline (**3**e) (2 runs)*

Separation gave a mixture of 1,3-diarylpropenes **14***h*, **14***i*, **15***h*, and **15***i* as well as the following additional products.

Dimethyl (E)*-1-benzyl-3-(4-trifluoromethylphenylmethylene)-cyclopropane*-trans*-1,2-dicarboxylate (**17**h)* (5%). IR (cm^{-1}): 3080(sh), 3060 w, 3030 w, 3005 w, 2955 m, 2930 w, 2850 w, 1733 s, 1615 m, 1491 w, 1445(sh), 1434 m, 1421(sh), 941 m, 872 m, 822 m, 795 w. ^{1}H NMR, δ: 7.60 (d, *J* = 8.4 Hz, 2H, H-3, H-5 of Ar), 7.51 (d, *J* = 8.3 Hz, 2H, H-2, H-6 of Ar), 7.3–7.2 (m, 5H, of Ph), 6.81 (d, *J* = 2.2 Hz, 1H, vinyl-H), 3.70 and 3.68 (two s, 2 × OMe), 3.50 (d, *J* = 2.2 Hz, 1H, methine-H), 3.37 (s, 2H, CH_2). MS (ei) *m/z*: 404 (M^+, 7%), 385 (M − F^+, 3%), 372 (17%), 344 (M − EH^+, 12%), 313 (M − Bn^+, 15%), 285 (50%), 215 (25%), 183 (10%), 159 (*p*-$CF_3C_6H_4CH^+2$, 22%), 115 (30%), 91 (100%). HRMS, Exact Mass calcd. for $C_{22}H_{19}F_3O_4$: 404.1235; found: 404.1241.

Dimethyl (Z)*-1-benzyl-3-(4-trifluoromethylphenylmethylene)-cyclopropane*-trans*-1,2-dicarboxylate (**18**h)* (3%). IR (cm^{-1}): 3080(sh), 3060 w, 3030 w, 2955 m, 2925 m, 2845 w, 1731 s, 1613 w, 1490 w, 1445(sh), 1432 m, 1420(sh), 964 w, 914 w, 869 m, 839 w, 821 w. ^{1}H NMR, δ: 7.57 (d, *J* = 8.3 Hz, 2H, H-3, H-5 of Ar), 7.43 (d, *J* = 8.3 Hz, 2H, H-2, H-6 of Ar), 7.15 (s, br, 5H, of Ph), 6.93 (d, *J* = 2.0 Hz, 2H, vinyl-H), 3.80 and 3.16 (two d, *J* = 15.7 Hz, CH_2), 3.73 and 3.59 (two s, 2 × OMe), 3.42 (d, *J* = 1.8 Hz, 1H, methine-H). MS(ei) *m/z*: 404 (M^+, 12%), 385 (M − F^+, 7%), 372 (M − 32^+, 55%), 344 (M − EH^+, 35%), 329 (5%), 313 (45%), 285 (100%), 215 (55%), 183 (22%), 159 (25%), 115 (22%), 91 (93%). HRMS, Exact Mass calcd. for $C_{22}H_{19}F_3O_4$: 404.1235; found: 404.1243.

*Dimethyl 2-benzyl-3-(4-trifluoromethylbenzyl)cyclopropene-1,3-dicarboxylate (**16**h)* (ca. 5%). ^{1}H NMR, δ: 7.45 (d, *J* = 8.1 Hz, 2H, H-3, H-5 of Ar), 7.3–7.05 (m, 7H), 3.72 and 3.57 (two s, 2 × OMe), ca. 3.7 (m, 2H, 2-CH_2), 3.35 and 3.19 (two d, *J* = 14.5 Hz, 3-CH_2).

*Dimethyl 3-benzyl-2-(4-trifluoromethylbenzyl)cyclopropene-1,3-dicarboxylate (**16**i)* (5%). IR (cm^{-1}): 3080 w, 3055 w, 3025 w, 2945 m, 2840 w, 1863 w, 1719(br) s, 1611 w, 1578 w, 1488 w, 1442(sh), 1428 m, 1413 m. ^{1}H NMR, δ: 7.52 (d, *J* = 8.0 Hz, 2H, H-3, H-5 of Ar), 7.26–7.15 (m, 5H), 7.05–7.00 (m, 2H), 3.71 and 3.59 (two s, 2 × OMe), 3.7 (m, 2H, 2-CH_2), 3.44 and 3.21 (two d, *J* = 14.3 Hz, 3-CH_2).

*Dimethyl 3-benzyl-3-(4-trifluoromethylbenzyl)cyclopropene-1,2-dicarboxylate (**4**e)* (12%). IR (cm^{-1}): 3065 w, 3035 w, 2955 w, 2925 w, 2845 w, 1837 m, 1722 s, 1617 w, 1602 w, 1491 w, 1448(sh), 1443 s, 1418 m. ^{1}H NMR, δ: 7.5–7.4 (m, 4H, of Ar), 7.30–7.17 (m, 3H, of Ph), 7.10–7.06 (m, 2H, of Ph), 3.76 (s, 6H, 2 × OMe), 3.17 and 3.11 (two s, 2 × CH_2). ^{13}C NMR, δ: 159.9 (CO), 142.4 br (Ar-C1), 137.9 (Ph-C1), 130.2 (Ar-C2), 129.8 (Ph-C2), 128.7 (Ph-C3), 126.8 (C1 and C2), 126.6 (Ph-C4), 125.4 (q, J_{CF} = 3.6 Hz, Ar-C3), 52.9 (OMe), 43.1 and 42.9 (2 × CH_2), 40.7 (C3), signals for Ar-C4 and CF_3 too dispersed for detection. *Pyrazole*-N*-oxide (**25**e)* as a yellow oil. IR (cm^{-1}): 3350 w, 3065 w, 3035 w, 2955 w, 1740 s, 1713 s, 1652 m, 1611 m, 1565 s, 1490 w, 1445 s, 1439(sh). ^{1}H NMR, δ: 8.08 (s, 1H, HO), 7.61 and 7.29 (two d, *J* = 8.2 Hz, 4H of Ar), 7.20–7.15 (m, 3H, Ph-H), 7.07–7.01 (m, 2H, Ph-H), 5.76 (s, 1H, >CH-), 3.92 and 3.79 (two s, 2 × OMe), 3.78 and 3.34 (AB quartet, *J* = 13.5 Hz, CH_2).

*Dimethyl 1-benzyl-5-(4-trifluoromethylbenzyl)-1*H*-pyrazole-3,4-dicarboxylate (**19**i)* (34%). IR (cm^{-1}): 3065 w, 3055 w, 3000 w, 2955 w, 1736 s, 1724 s, 1617 w, 1541 w, 1476 m, 1451 m, 1435 m, 1418 m. ^{1}H NMR, δ: 7.47 (d, *J* = 8.2 Hz, 2H, H-3, H-5 of Ar), 7.26–7.22 (m, 3H, of Ph), 7.11 (d, *J* = 7.9 Hz, 2H, H-2, H-6 of Ar), 6.98–6.94 (m, 2H, of Ph), 5.21 (s, 2H, N-CH_2), 4.25 (s, 2H, 5-CH_2), 3.98 and 3.82 (two s, 2 × OMe). ^{13}C NMR, δ: 163.4 and 162.7 (2 × OMe), 144.5 (C3), 143.4 (C5), 140.1 (Ar-C1), 134.7 (Ph-C1), 129.1 (Ph-C3), 128.6 (Ar-C2), 128.5 (Ph-C4), 126.9 (Ph-C2), 125.9 (q, J_{CF} = 4.0 Hz, Ar-C3), 114.3 (C4), 54.6 (N-CH_2), 52.8 and 52.2 (2 × OMe), 30.2 (5-CH_2), Ar-C4 and CF_3 signals too dispersed for detection.

Compound **25***e* was stable in $CDCl_3$ under nitrogen at −20°C for over 4 weeks, but on exposure to air, gave *methyl 4-benzyl-5-(4-trifluoromethylbenzoyl)-1*H*-pyrazole-3-carboxylate (**22**e)*. ^{1}H NMR, δ: 8.15 (d, *J* = 8.0 Hz, 2H, H-2, H-6 of Ar), 7.71 (d, *J* = 8.2 Hz, 2H, H-3, H-5 of Ar), 7.2–7.1 (m, 5H, of Ph), 4.54 (s, 2H, CH_2), 3.98 (s, 3H, OMe). ^{13}C NMR, δ: 193.2 (ArCO), 159.9 (COOMe), 148.5 (C3 and C5), 140.7 (Ar-C1), 140.2 (Ph-C1), 133.7 (C4), 130.8 (Ar-C2), 128.7 (Ph-C2), 128.5 (Ph-C3), 126.3 (Ph-C4), 125.3 (q, J_{CF} = 3.6 Hz, Ar-C3), 52.6 (OMe), 29.1 (CH_2), signals from Ar-C4

and CF_3 too dispersed for detection. HRMS, Exact Mass calcd. for $C_{20}H_{15}F_3N_2O_3$: 388.1035; found 388.1031.

Photolysis of benzyl methyl oxadiazoline **4***f in methanol (1 run)*

Oxadiazoline **3***f* (0.5 mmol) in methanol-d_4 (1 g) in a thin-walled NMR tube was photolyzed for 5 h. Standard work-up and separation gave the known (ref. 3) symmetrical cyclopropene **4***f* (9%), and unsymmetrical cyclopropene **16***j* (4%), along with the pyrazoles described below.

*Dimethyl 1-benzyl-5-methyl-1*H*-pyrazole-3,4-dicarboxylate (**19***j*)* (13%). IR (cm^{-1}): 3060 w, 3035 w, 3000 w, 2950 m, 2850 w, 1737 s, 1720 s, 1605 w, 1548 m, 1480 m, 1452 m, 1439 s. ^{1}H NMR, δ: 7.30–7.26 (m, 3H of Ph), 7.14–7.09 (m, 2H, H-2, H-6 of Ph), 5.36 (s, 2H, CH_2), 3.95 and 3.84 (two s, 2 × OMe), 2.39 (s, 3H, 5-Me). In an NOE experiment, irradiation of the singlet at δ = 2.39 caused enhancement of signals at both 5.36 and 7.1 δ. ^{13}C NMR, δ: 163.6 and 162.8 (2 × CO), 144.0 and 143.1 (C3 and C5), 135.7 (Ph-C1), 129.1 (Ph-C3), 128.4 (Ph-C4), 127.0 (Ph-C2), 113.2 (C4), 54.2 (*N*-CH_2), 52.7 and 51.9 (2 × OMe), 11.0 (5-Me). HRMS, Exact Mass calcd. for $C_{15}H_{16}N_2O_4$: 288.1110; found 288.1109.

*Dimethyl 4-benzyl-5-methyl-4*H*-pyrazole-3,4-dicarboxylate (**33**)* (18%). ^{1}H NMR, δ: 7.2 (m, 3*H* of Ph), 6.95 (m, 2H of Ph), 3.96 and 3.72 (two s, 2 × OMe), 3.84 and 3.50 (two d, *J* = 14 Hz, 4-CH_2), 2.39 (s, 3H, 5-Me). In an NOE experiment, irradiation of singlet at δ = 2.39 gave enhancement of the methylene-H at 3.50 δ and an *ortho*-H at 6.9 δ. ^{13}C NMR, δ: 176.4 (C3), 166.8 (C5), 165.4 (4-CO), 160.9 (3-CO), 132.8 (Ph-C1), 128.9 and 128.6 (C2 and C3 of Ph), 128.2 (Ph-C4), 76.4 (C4), 53.9 and 53.3 (2 × OMe), 37.6 (CH_2), 14.0 (5-Me).

*Dimethyl 5-methyl-1*H*-pyrazole-3,4-dicarboxylate (**20**d)* (5%). IR (cm^{-1}): 3500(sh) br, 3250(br) s, 2950 s, 2925 s, 2855 s, 1710 s, 1565 m, 1490 m, 1445 s. ^{1}H NMR, δ: 3.94 and 3.86 (two s, 2 × OMe), 2.53 (s, 5-Me). ^{13}C NMR, δ: 163 and 162.4 (2 × CO), 146.2 (C3), 114 (C4), 52.8 and 52.0 (2 × OMe), 11.7 (5-CH_3), C5 not clearly visible. MS (ei) *m/z*: 198 (M^+, 20%), 167 (M − OMe^+, 95%), 166 (100%), 135 (40%), 79 (20%). MS(ci, NH_3) *m/z*: 199 (M + H^+, 40%), 167 (M − OMe^+, 100%), 152 (5%).

Isolation of diazoalkane **5**a

Oxadiazoline (**3***a*) (0.21 mmol) in toluene-d_8 (0.5 mL) in a thin-walled NMR tube was photolyzed at −70°C for 4 h, giving the typical pinkish-yellow solution observed in all of the above procedures. The solution was transferred at the temperature of liquid nitrogen to the precooled probe of the 500 MHz NMR spectrometer, and spectra were recorded as the temperature was gradually raised to ambient. The proton spectrum showed that negligible amounts of starting material remained, while the new signals were consistent with the presence of methyl acetate and 2-diazo-1,3-diphenylpropane (**5***a*). ^{1}H NMR (in C_7D_8) δ: 7.10–7.05 (m, 6H), 6.85 (d, *J* = 6.9 Hz, 4H), 2.81 (s, 4H). ^{13}C NMR, δ: 138.2 (Ph-C1), 128.76 and 128.67 (Ph-C2 and Ph-C3), 126.8 (Ph-C4), 48.1 (), 32.3 (CH_2). There was little change during the 2 h needed to warm up to −20°C, and even after being kept overnight in the freezer (at ca. −15°C), about 30% of diazo-alkane was left intact. After a further 3 days at −15°C, the diazo-alkane had gone completely and the solution was virtually colourless. About 7% of the diazo-alkane had been converted to the 1,3-diphenylpropenes **14***a* and **15***a* in about 2:1 ratio, but the major product was the azine **9***a*. IR (cm^{-1}): 3080 w, 3060 m, 3030 s, 2920 m, 1737 s, 1630 m, 1600 m, 1493 s, 1451 w, 1426 m. ^{1}H NMR, δ: 7.34–7.14 (m, 6H), 7.06–7.01 (m, 4H), 3.70 and 3.58 (two s, 2 × CH_2). ^{13}C NMR, δ: 165.2 (), 138.0 and 137.2 (2 × Ph-C1), 129.6 and 129.5 and 128.7 and 128.6 (2 × Ph-C2 and 2 × Ph-C3), 126.7 and 126.5 (2 × Ph-C4), 42.9 and 36.2 (2 × CH_2). MS (ei) *m/z*: 416 (M^+, 1%), 325 (M − Bn^+, 1%), 194 (22%), 91 (100%). MS (ci, NH_3) *m/z*: 417 (M + H^+, 1%), 314 (3%), 272 (41%), 228 (100%).

Sequential trapping experiments

Oxadiazoline **3** in toluene containing one drop of triethylamine was photolyzed at −65°C for several h, before addition of a solution of dimethyl acetylenedicarboxylate in toluene. Then the solvent and excess volatiles were removed by a stream of nitrogen as the solution warmed up to ambient. Typically this gave a viscous yellow residue.

The product from **3***a* was essentially pure *dimethyl 3,3-dibenzyl-3*H*-pyrazole-4,5-dicarboxylate (**6**a)*. ^{1}H NMR, δ: 7.35–7.10 (m, 6H), 7.05–6.90 (m, 4H), 3.87 and 3.79 (two s, 2 × OMe), 3.86 and 3.46 (two 2H d, *J* = 13.4 Hz, 2 × CH_2). ^{13}C NMR, δ: 162.6 and 160.3 (2 × CO), 148.7 (C5), 148.1 (C4), 133.6 (Ph-C1), 129.6 (Ph-C3), 128.1 (Ph-C2), 127.4 (Ph-C4), 105.1 (C3), 52.8 and 52.7 (2 × OMe), 41.3 (CH_2).

This solution was divided into two: one portion (still in $CDCl_3$) was photolyzed at −65°C for a further 6 h. The ^{1}H NMR spectrum of the product mixture indicated that 1,5-dibenzyl-1*H*-pyrazole **19***a*, yellow pyrazole-*N*-oxide **25***a*, and unsymmetrical cyclopropene **16***a* were major components, in ratio ca. 1:1:2, along with the symmetrical cyclopropene **4***a* as a minor component.

The other portion was stored at room temperature for some days, before separation of decomposition products. The following were isolated: yellow pyrazole-*N*-oxide **25***a* (22%) and 1,5-dibenzyl-1*H*-pyrazole **19***a* (20%). The solution of **25***a* was fairly stable when stored in $CDCl_3$ under nitrogen at −20°C, but after 10 weeks the **25***a* had been converted exclusively to benzoyl 4*H*-pyrazole (**21***a*).

Similarly, oxadiazoline **3***b* gave *dimethyl 3-benzyl-3-(4-methylbenzyl)-3*H*-pyrazole-4,5-dicarboxylate (**6**b)*: IR (cm^{-1}): 3055 w, 3030 w, 2955 w, 2925 w, 1730 s, br, 1655 w, 1635 w, 1600 w, 1545 w, 1513 w, 1495 m, 1450 m, 1438 m. ^{1}H NMR, δ: 7.23–7.10 (m, 3*H* of Ph), 7.00–6.86 (m, 6H), 3.89 and 3.76 (two s, 2 × OMe), 3.86 + 3.83 and 3.45 + 3.41 (four d, *J* = 13.4 Hz, 2 × CH_2 as AB quartets), 2.23 (s, ArMe). The solvent was removed, the residue was taken up in benzene-d_6, and the resulting solution was heated at 65°C in a sealed tube. After 20 min, signals from the dibenzyl 1*H*-pyrazole **19***b* began to be evident, and within 3.5 h those of starting material had virtually disappeared. Based on the ^{1}H NMR spectra, the final mixture contained **19***b* and **25***b* in the ratio 4:3. As judged from satellite peaks in the ^{1}H NMR spectrum, compound **19***b* was also contaminated by approximately 10% of the positional isomer **19***c*.

In the same way, oxadiazoline **3***d* gave **6***d*, as evidenced by

appearance of two overlapping doublets at ca. 3.44 and 3.43 ppm in the crude photolysate. After further photolysis, these signals disappeared, and in the spectrum of the crude product the only signals assignable belonged to isomeric 1,5-dibenzyl-1*H*-pyrazoles **19***f* and **19***g*. Chromatography gave the following compounds: the isomeric 1, 3-diarylpropenes **14***f*, **14***g*, **15***f*, and **15***g* (together ca. 5%); cyclopropene **4***d* (5%); benzoyl 4*H*-pyrazole **21***d* (4%); and its isomer, *dimethyl 5-benzoyl-4-(4-bromobenzyl)-4*H*-pyrazole-3,4-dicarboxylate (**21***e*)* (8%): IR (cm^{-1}): 3300(br) w, 3070 w, 3035 w, 2965 s, 2925(sh), 2855 w, 1765 s, 1732 s, 1656 s, 1585 m, 1488 m, 1443 s, 1405 m. ^{1}H NMR, δ: 8.12 (d, J = 7.4 Hz, 2H, H-2, H-6 of Bz), 7.63 (m, 1H, H-4 of Bz), 7.50 (t, J = 7.2 Hz, 2H, H-3, H-5 of Bz), 7.21 (d, J = 8.3 Hz, 2H, H-3, H-5 of Ar), 6.69 (d, J = 8.3 Hz, 2H, H-2, H-6 of Ar), 4.06 and 3.73 (two s, 2 × OMe), ca. 3.86 and ca. 3.80 (AB quartet, only centre two lines visible, CH_2). An approximately 2:1 mixture of dibenzyl 1*H*-pyrazole **19***g* and its isomer, dimethyl 5-benzyl-1-(4-bromobenzyl)-1*H*-pyrazole-3,4-dicarboxylate **19***f*, with partial ^{1}H NMR, δ: 6.89 (d, J = 8.4 Hz, H-2, H-6 of Ar), 5.12 (s, N-CH_2), 4.18 (s, 5-CH_2), 3.97 and 3.83 (two s, 2 × OMe), and, finally, monobenzyl 1*H*-pyrazoles **20***a* and **20***c* (ca. 6% together), were obtained.

In contrast, the same procedure applied to methoxy oxadiazoline **3***c* did not appear to give any **6***c*. Chromatography gave 1,3-diarylpropenes **14***d*, **14***e* and **15***d*, **15***e* (together 13%), dibenzyl 1*H*-pyrazole (**19***d*) (42%), and pyrazole-*N*-oxide **25***c*. Compound **25***c* was fairly stable when stored in $CDCl_3$ under nitrogen at −20°C for over four weeks, but gradually decomposed to benzoyl monoester **22***c*, plus an unidentified compound with the following partial ^{1}H NMR spectrum, δ: 7.4–7.3 (m, 5H), 7.20 (d, J = 8.6 Hz, 2H, H-2, H-6 of Ar), 6.84 (d, J = 8.6 Hz, 2H, H-3, H-5 of Ar), 6.47 (s, 1H), 5.50 (s, 2H), 3.85 (s, 3H) and 3.78 (s, 3H) (2 × OMe), 3.71 (s, 3H, ArOMe). Irradiation of the singlet at δ = 5.50 gave enhancement at 7.20 δ, while irradiation at δ = 6.47 gave enhancement at 7.34 δ. The implication is that the compound contains the unit *p*-MeO-C_6H_4-CH_2-, in a rather deshielded environment, but that there is no benzoyl group.

*Base-catalyzed isomerization of unsymmetric cyclopropene **16**a*

To unsymmetrical dibenzylcyclopropene **16***a* (0.2 mmol) in $CDCl_3$ (0.4 mL) was added triethylamine (1 drop). The solution changed from yellow to rich gold, and an ^{1}H NMR spectrum run at once showed no sign of starting material. Separation gave a mixture of methylenecyclopropanes **17***a* and **18***a* in approximately equal amounts (42%), followed by a 3:2 mixture (10%) of *dimethyl 1-benzyl-3-(*E*)-(phenylmethylene)cyclopropane-*cis*-1,2-dicarboxylate (**34**) and its (*Z*) isomer (**35**)*. For **34**: ^{1}H NMR (500 MHz) δ: 7.46 (d, J = 8 Hz, 2H, H-2, H-6 of Ph), 7.34–7.15 (m, 8H), 6.95 (d, J = 2.4 Hz, 1H, vinyl-H), 3.69 and 3.63 (two s, 2 × OMe), 3.59 and 2.79 (two d, J = 14.0 Hz, CH_2), 2.75 (d, J = 2.4 Hz, 1H, methine-H). In an NOE experiment, irradiation of doublet at δ = 6.95 enhanced the signal at 7.46 δ (*ortho*-H of vinyl-Ph), but apparently none of the signals at 2.75, 3.59, or 2.79 δ; the remaining signals from the mixture were too close together for unambiguous results. ^{13}C NMR, δ: 169.7 and 168.8 (2 × CO), 137.3 and 135.6 (2 × Ph-C1), 129.2 and 128.83 and 128.6 and 127.7 (2 × Ph-C2 and 2 × Ph-C3), 128.4 and 127.2 (2 × Ph-C4), 123.7 (C3), 122.5 (=CH-), 52.57 and 52.54 (2 × OMe), 41.0 (C1), 31.5 (CH_2), 27.9 (C2). IR (of mixture)(cm^{-1}) 3070 w, 3035 m, 3010 w, 2960 m, 2850 w, 1730(br) s, 1603 w, 1495 m, 1450(sh), 1435 s. MS (ei) on mixture *m/z*: 336 (M^+, 10%), 304 (15%), 276 (10%), 245 (M − Bn^+, 20%), 217 (50%), 202 (20%), 115 (45%), 91 (100%). MS (ci, NH_3) *m/z*: 354 (M + NH_4^+, 100%), 337 (M + H^+, 45%), 322 (10%), 305 (10%), 217 (5%). For **35**; ^{1}H NMR (500 MHz) δ: 7.44 (d, J = 8 Hz, 2H, H-2, H-6 of Ph), 7.34–7.15 (m, 6H), 7.08–7.06 (m, 2H, H-2, H-6 of Bn), 6.87 (d, J = 2.0 Hz, 1H, vinyl-H), 3.69 and 3.68 (two s, 2 × OMe), 3.38 (s, 2H, CH_2), 2.37 (d, J = 2.0 Hz, 1H, methine-H). In an NOE experiment, irradiation of doublet at δ = 6.87 gave enhancement at 7.44 δ (*ortho*-H of vinyl-Ph) and 2.37 δ; whereas irradiation of singlet at δ = 3.38 enhanced the signal at 7.07 δ (*ortho*-H of Bn) and methine doublet at 2.37 δ. ^{13}C NMR (assignments tentative), δ: 170.1 and 169.2 (2 × CO), 136.1 and 135.5 (2 × Ph-C1), 130.0 and 128.78 and 128.5 and 128.0 (2 × Ph-C2 and 2 × Ph-C3), 128.3 (1 × Ph-C4; other C4 obscured), 123.8 (C3), 124.0 (=CH-), 52.7 and 52.45 (2 × OMe), 37.6 (C1), 38.6 (CH_2), 34.3 (C2).

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References

1. (*a*) J. Warkentin. Synthesis, 279 (1970), and refs. therein; (*b*) M. Békhazi and J. Warkentin. J. Am. Chem. Soc. **103**, 2473 (1981); (*c*) J. Am. Chem. Soc. **105**, 1289 (1983); (*d*) M. Békhazi, P.A. Risbood, and J. Warkentin. J. Am. Chem. Soc. **105**, 5675 (1983); (*e*) M. Békhazi and J. Warkentin. Can. J. Chem. **61**, 619 (1983).
2. M.W. Majchrzak, M. BJkhazi, I. Tse-Sheepy, and J. Warkentin. J. Org. Chem. **54**, 1842 (1989).
3. M.W. Majchrzak, J. Warkentin, and J.McK.R. Woollard. Struct. Chem. **2**, 137 (1991).
4. G.L. Closs, W.A. Böll, H. Heyn, and V. Dev. J. Am. Chem. Soc. **90**, 173 (1968).
5. D.R. Arnold, R.W. Humpreys, W.J. Leigh, and G.E. Palmer. J. Am. Chem. Soc. **98**, 6225 (1976).
6. W.J. Leigh and D.R. Arnold. Can. J. Chem. **57**, 1186 (1979).
7. C. Dietrich-Buchecker and M. Franck-Neumann. Tetrahedron, **33**, 751 (1977).
8. (*a*) M. Franck-Neumann. Angew. Chem. Int. Ed. Engl. **6**, 79 (1967); (*b*) M. Franck-Neumann, M. Miesch, and H. Kempf. Tetrahedron, **43**, 853 (1987).
9. M. Franck-Neumann and C. Dietrich-Buchecker. Tetrahedron Lett. **9**, 15 (1969).
10. (*a*) H. Dürr, W. Schmidt, and R. Sergio. Justus Liebigs Ann. Chem. 1132 (1974); (*b*) H. Dürr and H. Schmitz. Angew. Chem. Int. Ed. **14**, 647 (1975).
11. (*a*) M. Franck-Neumann. Angew. Chem. Int. Ed. Engl. **6**, 79 (1967); (*b*) C. Dietrich-Buchecker and M. Franck-Neumann. Tetrahedron, **33**, 745 (1977).
12. O. Tsuge, S. Kanemasa, T. Suzuki, and K. Matsuda. Bull. Chem. Soc. Jpn. **59**, 2851 (1986).
13. (*a*) H. Dürr, H. Kober, R. Sergio, and V. Formacek. Chem. Ber. **107**, 2037 (1974); (*b*) H. Dürr, and W. Schmidt. Justus Liebigs Ann. Chem. 1140 (1974).

14. K.L.M. Stanley, J. Dingwall, J.T. Sharp, and T.W. Naisby. J. Chem. Soc. Perkin Trans. I, 1433 (1979).
15. M.P. Sammes and A.R. Katritzky. Adv. Heterocycl. Chem. **34**, 1 (1983).
16. W.M. Williams and W.R. Dolbier, Jr. J. Am. Chem. Soc. **94**, 3955 (1972).
17. J.F. Hanson, Y.I. Kim, L.J. Griswold, G.H. Hoelle, D.T. Taylor, and O.E. Vietti. J. Org. Chem. **45**, 76 (1980).
18. M. Pomerantz and T.H. Witherup. J. Am. Chem. Soc. **95**, 5977 (1973).
19. (*a*)H.E. Zimmerman and C.J. Samuel. J. Am. Chem. Soc. **97**, 4025 (1975); (*b*) A. Padwa, C.S. Chou, R.J. Rosenthal, and B. Rubin. J. Am. Chem. Soc. **103**, 3057 (1981).
20. D. Bethell, A.R. Newall, and D. Whittaker. J. Chem. Soc. B, 23 (1971).
21. W. Kirmse, K. Loosen, and H.-D. Sluma. J. Am. Chem. Soc. **103**, 5935 (1981).
22. N.C. Mathur, M.S. Snow, K.M. Young, and J.A. Pincock. Tetrahedron, **41**, 1509 (1985).
23. W. Kirmse, J. Kilian, and S. Steenken. J. Am. Chem. Soc. **112**, 6399 (1990).
24. W. Kirmse, T. Meinert, D.A. Modarelli, and M.S. Platz. J. Am. Chem. Soc. **115**, 8918 (1993).
25. W. Kirmse. *In* Advances in carbene chemistry. Vol. 1. *Edited by* U.H. Brinker. JAI Press, Greenwich, Conn. 1994. pp. 1–57.
26. J.A. Pincock, R. Morchat, and D.R. Arnold. J. Am. Chem. Soc. **95**, 7536 (1973).
27. (*a*) J. Van Alphen. Recl. Trav. Chim. Pays-Bas, **62**, 485 (1943); (*b*) R. Hhttel, K. Franke, H. Matin, and J. Riedl. Chem. Ber. **93**, 1433 (1960).
28. M.I. Komendantov, A.P. Zavgorodnyaya, I.N. Domnin, and R.R. Bakmukhametov. J. Org. Chem. USSR (Engl. transl.), **22**, 1389 (1986).
29. (*a*) M. Franck-Neumann and C. Dietrich-Buchecker. Tetrahedron Lett. **17**, 2069 (1976); (*b*) R. Huisgen, H.-U. Reissig, and H. Huber. J. Am. Chem. Soc. **101**, 3647 (1979).
30. (*a*) M. Franck-Neumann and C. Dietrich-Buchecker. Tetrahedron Lett. **13**, 937 (1972); (*b*) Angew. Chem. Int. Ed. Engl. **12**, 240 (1973); (*c*) R. Huisgen, M.P.B. Verderol, A. Gieren, and V. Lamm. Angew. Chem. Int. Ed. Engl. **20**, 694 (1981).
31. T. Yamazaki and H. Shechter. Tetrahedron Lett. **13**, 4533 (1972).
32. (*a*) D.J. Field, D.W. Jones, and G. Kneen. J. Chem. Soc. Perkin Trans. I, 1050 (1978); (*b*) R.J. Bushby and D.W. Jones. J. Chem. Soc. Chem. Commun. 688 (1979).
33. (*a*) G. Wittig and J.J. Hutchinson. Justus Liebigs Ann. Chem. **741**, 89 (1970); (*b*) R. Baumes, J. Elguero, R. Jacquier, and G. Tarrago. Tetrahedron Lett. **14**, 3781 (1973); (*c*) P. Schiess, and H. Stalder. Tetrahedron Lett. **21**, 1413 (1980); (*d*) Tetrahedron Lett. **21**, 1417 (1980).
34. M.W. Majchrzak, E. Jefferson, and J. Warkentin. J. Am. Chem. Soc. **112**, 2449 (1990).
35. S.D. Kahn, W.J. Hehre, N.G. Rondan, and K.N. Houk. J. Am. Chem. Soc. **107**, 8291 (1985).
36. (*a*) R.K. Bramley, R. Grigg, G. Guilford, and P. Milner. Tetrahedron, **29**, 4159 (1973); (*b*) I.I. Grandberg, A.P. Krasnoshchek, A.N. Kost, and G.K. Faizova. J. Gen. Chem. USSR (Engl. transl.), **33**, 2521 (1963).
37. E. Jefferson and J. Warkentin. J. Am. Chem. Soc. **114**, 6318 (1992).
38. M.S. Baird. Top. Curr. Chem. **144**, 147 (1988).
39. R. Huisgen, A. Mitra, and J.R. Moran. Heterocycles, **24**, 2429 (1986).
40. (*a*) R.C. Elderfield and K.L. Burgess. J. Am. Chem. Soc. **82**, 1975 (1960); (*b*) N.J. Turro and G.C. Weed. J. Am. Chem. Soc. **105**, 1861 (1983).
41. L.F. Fieser and M. Fieser. Reagents for organic synthesis. Vol. 1. Wiley, New York. 1967. pp. 1158–1159.
42. S.B. Coan and E.I. Becker. J. Am. Chem. Soc. **76**, 501 (1954).
43. R.C. Kerber, D. Glasser, and B. Luck. Organometallics, **3**, 840 (1984).
44. D. Bryce-Smith and J.E. Lodge. J. Chem. Soc. 695 (1963).
45. F.E. Herkes and H.E. Simmons. J. Org. Chem. **38**, 2845 (1973).
46. A.V. Prosyanik, A.S. Moskalenko, S.V. Bondarenko, and V.I. Markov. J. Org. Chem. USSR (Engl. transl.), **21**, 594 (1985).
47. S. Braun. Org. Magn. Reson. **11**, 197 (1978).