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THE DIAZO ROUTE TO 2-VINYLCYCLOPROPYLIDENES[1]

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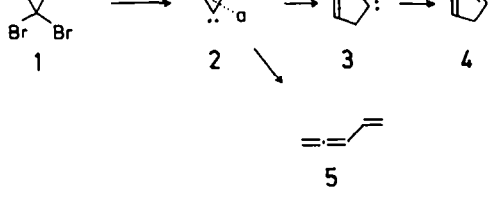
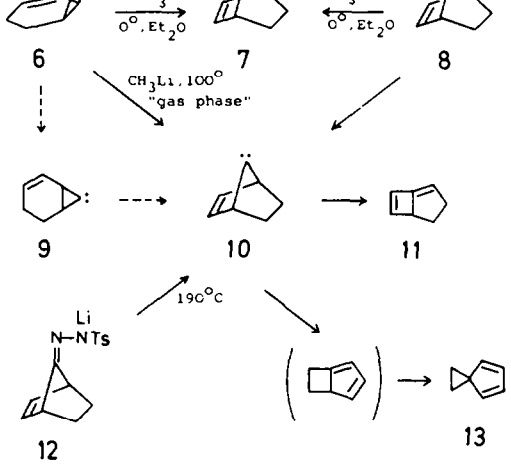
Abstract—2-Vinylcyclopropylidene (**2**), 3-methyl-2-vinylcyclopropylidenes (**79, 81**) and 2-(1-propenyl)cyclopropylidenes (**95, 97**) were generated from the corresponding nitrosoureas in methanol at room temperature. The diazo route is initiated by the formation of 2-vinylcyclopropanediazonium ions (e.g. **43**) which do not undergo 1,3-carbon shifts. No cyclopentenyl products were found in weakly basic methanol where the diazonium ions prevail. Ring opening of the diazonium ions gives pentadienyl cations and products derived therefrom. Delocalisation of the pentadienyl cations was demonstrated by the distribution of deuterium and methyl labels. In the presence of strong base, 1-diazo-2-vinylcyclopropanes (e.g. **48**) arise by deprotonation of the diazonium ions. Rearrangement of **48** was excluded by independent generation of the potential product, 4-diazocyclopentene (**103**). Substantial quantities of 3-methoxycyclopentene (**108**) were obtained from **103**, but not from **48**. The 2-vinylcyclopropylidenes **2**, **79** and **95**, arising by loss of nitrogen from the corresponding diazo compounds, undergo allene formation and Skattebøl rearrangement competitively. *Cis*-oriented methyl groups at either C-2 (**81**) or C-2′ (**97**) prevent the Skattebøl rearrangement. The cyclopentenylidenes **3** and **83** yield 4-methoxycyclopentenes (**52, 86**) in excess over cyclopentadiens (**4, 84**). In the presence of methyl vinyl ether, cycloaddition of **3** and electrophilic addition of 3-cyclopentenyl cation (**51**) occurred in a 1 : 14 ratio. Stereospecific formation of **52** indicates protonation of a 'foiled carbene' (**3a**) to give a bishomocyclopropenyl ion (**51a**). Our studies confirm that the various routes to 2-vinylcyclopropylidenes converge at the carbene stage.

The rearrangement of vinylcyclopropylidenes (**2**) to cyclopentenylidenes (**3**) was discovered by Skattebøl[2] when he observed that the reaction of 1,1-dibromo-2-vinylcyclopropane (**1**) with methyl lithium at −78° gave 86% cyclopentadiene (**4**). Only 14% of the 'normal' allene product, 1,2,4-pentatriene (**5**), was obtained. The **4**:**5** ratio decreases with increasing temperature (**4**:**5** = 1 at *ca* 30°).[3] Labelling experiments and product substitution patterns have unequivocally demonstrated that bond a of **2** breaks and that the integrity of the carbene carbon is retained.[4] Many examples of the Skattebøl rearrangement have been reported.[5–12]



Warner questioned the intermediacy of carbenes in the 'purported vinylcyclopropylidene to cyclopentenylidene rearrangement'.[13] From his results with specific substrates (*vide infra*) he concluded that 'these rearrangements do not involve carbenes but rather species in which bonding to lithium is necessary'. In fact, cyclopropylidene carbenoids[14] are well characterised and fairly stable species. Their ^{13}C-NMR spectra[15] show strong deshielding of the carbenoid carbon, decreased ^{13}C, ^{13}C coupling and large ^{13}C, ^{6}Li coupling constants. These observations suggest lithium-substituted carbocation structures which are also supported by *ab initio* calculations.[16]

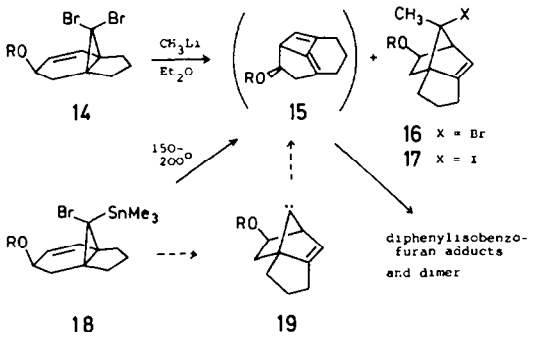
The potential role of cyclopropylidene carbenoids in the 7-norcarenylidene (**9**) → 7-norbornenylidene (**10**) rearrangement has been thoroughly studied. Both 7,7-dibromonocarene (**6**) and 7,7-dibromonorbornene (**8**) afforded *syn*-7-bromo-*anti*-7-methylnorbornene (**7**) on treatment with methyl lithium (ether, 0°).[3,6] 7-Norbornenylidene (**10**), generated by the diazo route from **12** (190°), produced the bicyclo[3.2.0]heptadienes **11** and **13** (*ca* 10 : 1), arising from vinyl and alkyl shifts,



respectively.[3,17] In the reaction of **6** or **8** with methyllithium in ether, **12** and **13** were minor by-products (*ca* 1%).[3] However, when vapours of either **6** or **8** were passed over solid methyllithium deposited on glass turnings, the yields of **11** and **13** increased substantially.[3] Thus **10** may be generated from dihalide precursors under suitable conditions but is either bypassed or rapidly scavenged in ethereal solution.

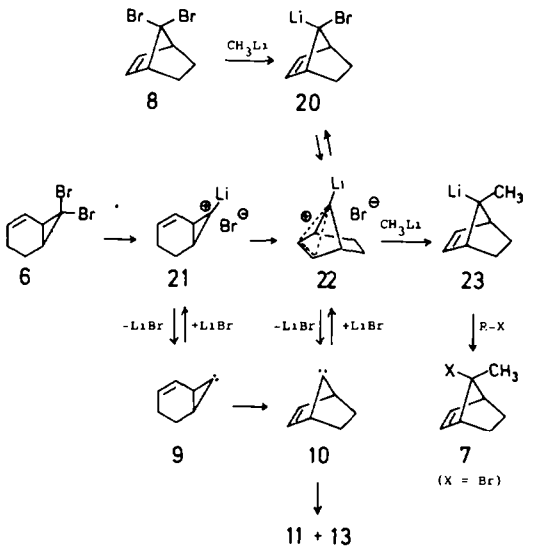
Additional evidence comes from Warner's work. When dibromide **14** was treated with methyllithium in ether, **16** (an analogue of **7**) was obtained, along with a

small quantity of **15** (an analogue of **11**).[13] The highly strained alkene **15** was trapped by diphenylbenzofuran or dimerised. Structures of the adducts and dimers have been established by X-ray analysis.[18] Pyrolysis of the organotin educt **18** afforded products derived from **15**.[19] Moreover, addition of 12-crown-4 to the reaction of **14** with methyllithium prevented the formation of **16**



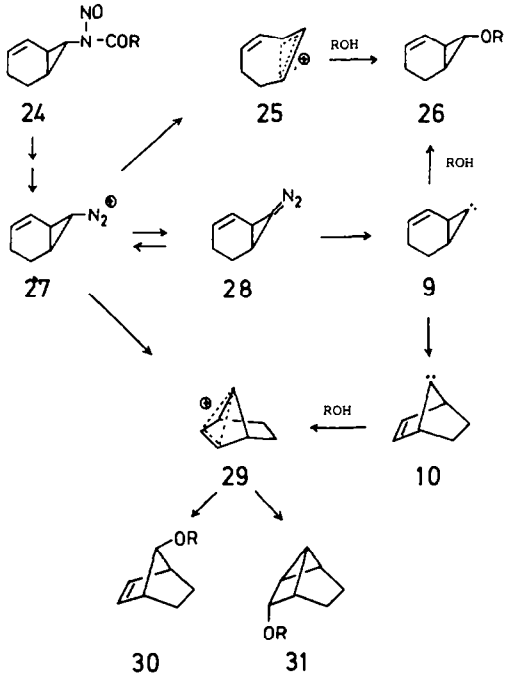
in favour of **15**. In contrast to **15**, product **16** clearly originates from organolithium intermediates. Plausible mechanisms (**22** → **23** → **7**) have been suggested[5c,13] to explain the stereochemistry and account for the fact that CD_3I as solvent led to **17**—no deuterium was incorporated.[13]

A key question is whether the Skattebøl rearrangement proceeds at the carbenoid (**21** → **22**) or carbene stage (**9** → **10**). The results summarised above are compatible with either view. If **22** is the first norbornenyl intermediate, sequestering of Li, elevated temperatures, and 'gas phase' conditions[3] will favour reaction **22** → **10** at the expense of reaction **22** → **23**. On



the other hand, **10** as the first norbornenyl intermediate may be diverted by lithium salts (**10** → **22**) from typical carbene behaviour (**10** → **11** + **13**). We must note that the absence of lithium salts prevents formation of **7** but does not inhibit the Skattebøl rearrangement.

The diazo route to 7-norcarenylidene (**9**) suffers from a similar ambiguity.[20,21] Norcarene-7-diazonium ions (**27**), generated by deacylation of nitrosoamides **24**, gave products derived from the partially opened 7-norcarenyl cation **25**, among which **26** predominated. Strong base (e.g. lithium methoxide) initiated the Skattebøl rearrangement by deprotonation of **27**. *Anti*-7-Norbornenyl (**30**) and *endo*-6-tricyclo[3.2.0.0^{2,7}]-heptyl products (**31**) were formed in a base-dependent ratio, pointing to the intervention of 7-norbornenyl cations (**29**).[22] One must wonder whether **29** arises by protonation of 7-norbornenylidene (**10**) or by

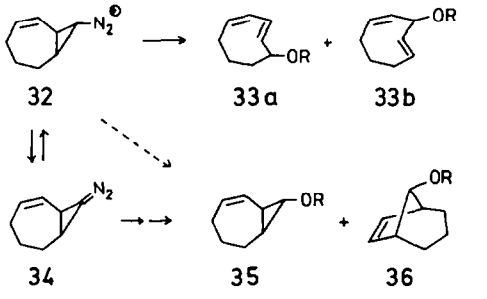


rearrangement of a cationic precursor. Although alkoxide raised the combined yield of **30** and **31** to 90%, a small quantity of **30** was also found in weakly basic solutions.[21] Even worse, experiments with

$$CH_3OD\text{–}HCO_2Na$$

revealed that a significant portion of **30** (*ca* 40%) was formed without incorporation of deuterium.[21] Thus a (minor ?) reaction path from **27** to **29** bypasses **28**, **9** and **10** (π participation in the extrusion of nitrogen from **27** leads directly to **29**). On the other hand, it is difficult to account for the effect of strong base without invoking carbene intermediates.

Such complications were not encountered with the homologous bicyclo[5.1.0]octenyl system.[23] In weakly basic solution, diazonium ions **32** produced cyclooctadienyl ethers (**33**), along with a small quantity of **35**. With 0.4 M $NaOCH_3$, **32** gave **35** (24%) and **36** (76%). Except for the formation of **35**, the diazonium and diazo



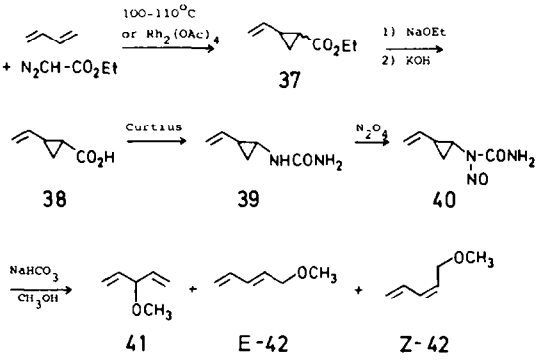
pathways are cleanly separated. However, as no tricyclic products were found, the immediate precursor of **36**—carbene or carbocation—is not readily identified.

Inevitable deficiencies of the previous studies induced us to explore the diazo route to the parent 2-vinylcyclopropylidene (**2**) and to some methyl-substituted analogues. The sterically less confined substrates promised more definitive mechanistic conclusions.

RESULTS AND DISCUSSION

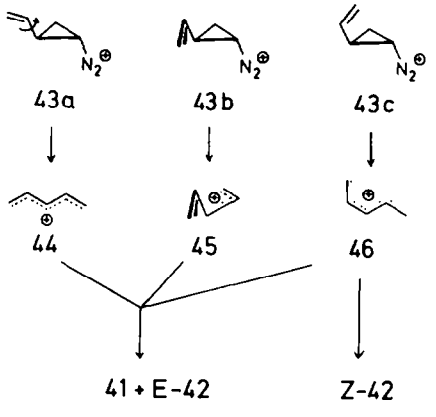
Decomposition of 2-vinylcyclopropanediazonium ions (**43**)

The addition of ethoxycarbonyl carbene (from ethyl diazoacetate) to butadiene[24] is greatly improved by rhodium acetate as the catalyst[25] (refluxing butadiene, 85% yield). The resulting mixture of ethyl 2-vinylcyclopropanecarboxylates (**37**, *trans*:*cis* = 55:45) was equilibrated (2 M NaOEt in EtOH, 9 d reflux, *trans*:*cis* = 92:8) and hydrolysed (KOH aq, 2 hr reflux) to give 2-vinylcyclopropanecarboxylic acid (**38**) (78% yield, *trans*:*cis* = 90:10). Curtius degradation of **38**, following Weinstock's procedure,[26] afforded *trans*-2-vinylcyclopropylurea (**39**; 67%). Nitrosation (N_2O_4, Et_2O, NaOAc, −5 to 0°) completed the synthesis of N-nitroso-N-(*trans*-2-vinylcyclopropyl)urea (**40**; 71%).



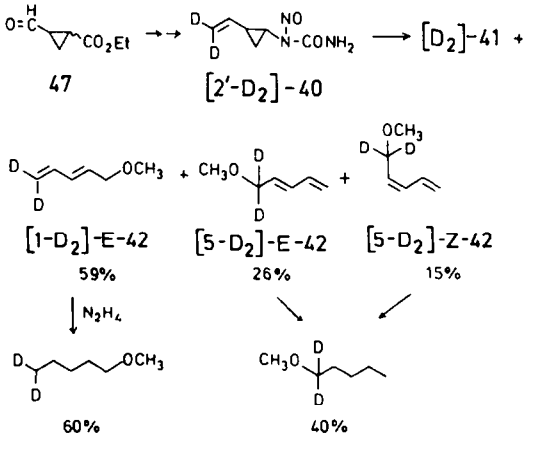
Treatment of **40** with MeOH–$NaHCO_3$ produced 3-methoxy-1,4-pentadiene[27] (**41**; 52%) and 5-methoxy-1,3-pentadiene[27,28] (**42**; 48%). The components of **42** (41:7) were separated only by GC on capillary columns. The NMR spectrum of **42** revealed separate 5-H signals of the two components at δ 3.92 and 4.06 (40:8); all other signals overlapped. Diimide reduction of the mixture yielded 1-methoxypentane. Therefore, the minor component was assigned as *Z*-5-methoxy-1,3-pentadiene (*Z*-**42**).

Deacylation of nitrosoureas in protic solvents generates diazonium ions.[29] Subsequent deprotonation of the diazonium ions may lead to diazoalkanes. In weakly basic media, such as MeOH–$NaHCO_3$, and in the absence of additional electron-withdrawing groups, the intervention of diazo compounds is negligible.[29] Therefore the pentadienyl ethers **41**, **42** are thought to arise from the decomposition of 2-vinylcyclopropanediazonium ions (**43**). As no cyclopentenyl products were observed, the diazonium ions **43** and any intermediates derived therefrom do not undergo Skattebøl rearrangement or π participation. The reaction path from **43** to **41**, **42** is of interest in its own right. The ring opening of cyclopropanediazonium ions obeys the Woodward–Hoffmann rules and is most probably a concerted reaction.[30] Direct formation of



delocalised pentadienyl cations (**44**, **46**) from **43** requires conformers **43a**, **c** with the vinyl group oriented antiparallel and parallel to the C-1—C-2 bond, respectively. Intermediate conformations (**43b**) lead to '1-vinylallyl cations' (**45**) which achieve pentadienyl delocalisation only after rotation about the C—C single bond. If **45** contributes to product formation (i.e. if solvent attack competes with rotational equilibration), a label at C-2′ of **43** should be unevenly distributed among C-1 and C-5 of *E*-**42**.

We prepared [2′-D_2]-**37** from ethyl 2-formylcyclopropanecarboxylate (**47**),[31] utilising the CD_2I_2–Zn(Cu) reagent.[32] Conversion to [2′-D_2]-**40** and reaction of the latter with MeOH–$NaHCO_3$ proceeded as above. The pentadienyl ethers **41** and **42** were separated by preparative GC. In the ^{1}H-NMR spectrum of the *E*,*Z*-**42** mixture (15% *Z*-**42** by GC) the 5-H signal of *Z*-**42** (δ 4.06) was virtually absent. Thus *Z*-**42** was labelled exclusively at C-5, in accordance with its origin from **46**. The signal intensities of 5-H of *E*-**42** (1.18) and of all vinyl protons (3.82) indicated the presence of 59% [1-D_2]-*E*-**42** and 26% [5-D_2]-*E*-**42**. The deuterium distribution was confirmed by diimide reduction of [D_2]-**42**, followed by mass spectrometry of the deuterated 1-methoxypentane. The CH_2–OCH_3^+



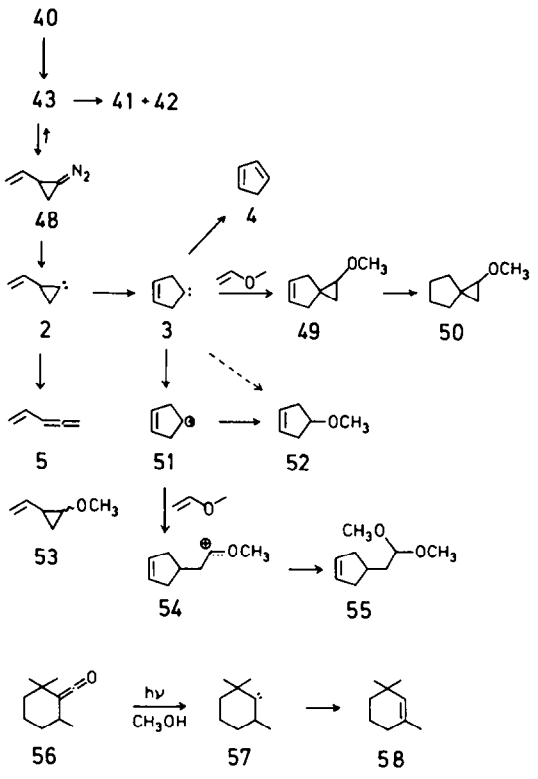
and CD_2–OCH_3^+ fragments were observed in a 60:40 ratio. From these data we arrive at an upper limit of

20% for an eventual contribution of **45**, assuming equal rates of solvent attack at C-1 and C-5 of **46** (and neglecting secondary isotope effects). Any discrimination by **46** in favour of *E*-**42** (the more stable product) lowers the formal contribution of **45**. In the extreme, with **45** completely excluded, **46** has to give *E*-**42** and *Z*-**42** in a 2.2:1 ratio. Within the limits thus defined, the ratio of **44**:**46** varies from 1.7 to 1.1. These figures suggest similar populations of **43a** and **43c**, in accordance with the rotational potential function of vinylcyclopropane derived from NMR,[33] electron diffraction,[34] Raman spectra[35] and *ab initio* investigations.[36]

Decomposition of 2-*vinyl*-1-*diazocyclopropane* (**48**)

In the presence of sodium methoxide, nitrosourea **40** yielded only minor quantities of methoxypentadiens **41**, **42** (Table 1). The major products were 1,2,4-pentadiene (**5**), cyclopentadiene (**4**), and 4-methoxycyclopentene (**52**). The product distributions were independent of methoxide concentration from 0.1 to 2.0 M. Obviously the strong base induced the formation of 2-vinylcyclopropylidene (**2**) *via* deprotonation of diazonium ion **43** and decomposition of 2-vinyl-1-diazocyclopropane (**48**). The ratio of **5**:(**4** + **52**) = 1.14 was close to the **5**:**4** ratio obtained from **1** and methyllithium at 22° (1.04).[3] Similar partitioning supports a common intermediate in the organometallic and diazo routes to **2**. The 1-methoxy-2-vinylcyclopropanes (**53**) are also products most probably derived from **2**. Evidence has been presented previously that cyclopropylidenes react in methanol–methoxide to give cyclopropyl ethers competitively with allene formation.[37] Samples of **53** were synthesised independently to aid the identification and to assure that **53** did not rearrange[38] to **52** on our GC columns.

The efficient trapping of 3-cyclopentenylidene (**3**) by methanol was unexpected. Hydride shifts are very fast reactions of dialkylcarbenes, precluding their addition to alkenes.[39] Photolysis of the ketene **56** in methanol gave exclusively 1,3,3-trimethylcyclohexene (**58**).[40] Although the inertness of carbene **56** toward methanol might be due to steric shielding, the contrasting reactivity of **3** invited further investigation. At least three plausible reaction mechanisms are conceivable for the reaction of carbenes with alcohols to give ethers: (a) one-step insertion into the O—H bond (comparable to the C–H insertion of singlet carbenes, (b) electrophilic attack of the carbene at oxygen, followed by proton transfer and (c) protonation of the carbene to give a carbocation (or ion pair). The electrophilic cyclopentadienylidene follows path (b) whereas the nucleophilic cycloheptatrienylidene is protonated to produce tropylium ions.[41] Protonation by alcohols has also been demonstrated for vinylcarbenes[42–44] and phenylcarbene[44,45] although those carbenes behave as electrophiles in their addition reactions with alkenes.



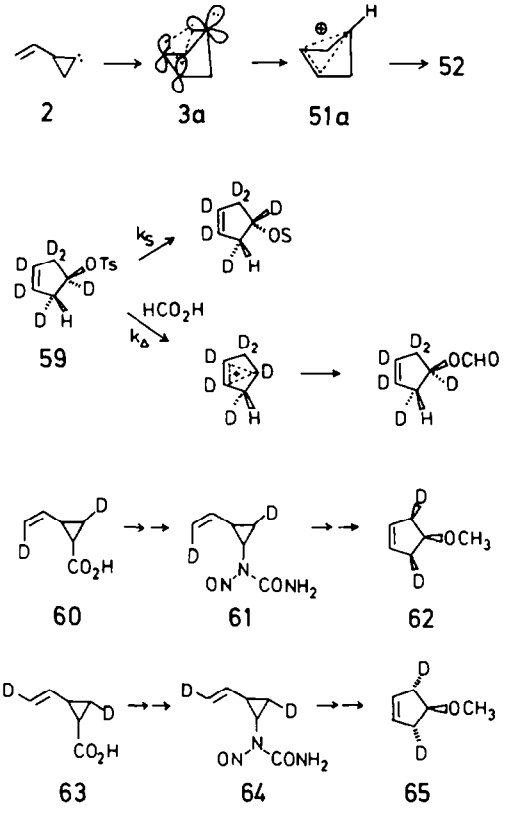
In a first attempt to elucidate the reaction path leading to **52** we treated **40** with CH_3OD–CH_3ONa. The yield of **5** was unaffected while the **52**:**4** ratio dropped from 2.0 to 1.6 (Table 1). The results are suggestive rather than conclusive evidence for the protonation of **3**. There is no precedent for isotope effects of carbene protonation. Cleavage of **40** in a mixture of methanol and methyl vinyl ether produced several new products (in addition to those listed in Table 1). The major component was **55** (6.7%), identified by comparison with an authentic sample.[46] The acetal **55** results from electrophilic addition of 3-cyclopentenyl cation (**51**) to methyl vinyl ether, followed by reaction of the stabilised carbocation **54** with methanol. In contrast, cycloaddition of **3** to methyl vinyl ether accounted for at most 0.5% of 1-methoxyspiro[2.4]hept-4-ene (**49**). The structure of **49** was assigned by comparison of its hydrogenation product with authentic **50**, obtained from methylenecyclopentane and methoxycarbene(oid). We have not been able to identify unequivocally the spiropentanes (4 isomers) which might arise from the addition of **2** to methyl vinyl ether. Our experiment reveals that cation **51** is the major (if not exclusive) species which may be trapped by methyl vinyl ether. We infer that **51** is also the (major) precursor to **52**.

Table 1. Product distributions from the deacylation of **40** (averages of 5 runs with [$NaOCH_3$] ranging from 0.1 to 2.0 M)

	4	**5**	**41**	**42**	**52**	*t*-**53**	*c*-**53**
CH_3OH (%)	13.6	46.2	3.4	3.1	26.9	5.6	1.2
CH_3OD (%)	15.4	46.4	3.4	3.5	24.5	5.7	1.1

Stereochemical studies

MINDO/2 calculations on the Skattebøl rearrangement[47] indicate interaction of the empty *p*-orbital of the divalent carbon with the π bond. According to these views the Skattebøl rearrangement generates 3-cyclopentenylidene as a 'foiled carbene'.[48] Structure **3a** reasonably explains the unusual reactivity of 3-cyclopentenylidene toward methanol. The σ-orbital of **3a** with its pair of electrons would accept a proton to give the bishomocyclopropenyl ion **51a**. The π route to **51a** has recently been explored by Lambert *et al.*[49] The reaction of the labelled cyclopent-3-enyl tosylate **59** was found to proceed with inversion (k_s) in acetic acid and in aqueous dioxane. In formic acid, however, the reaction occurred entirely with retention. The low nucleophilicity and high ionising power of formic acid

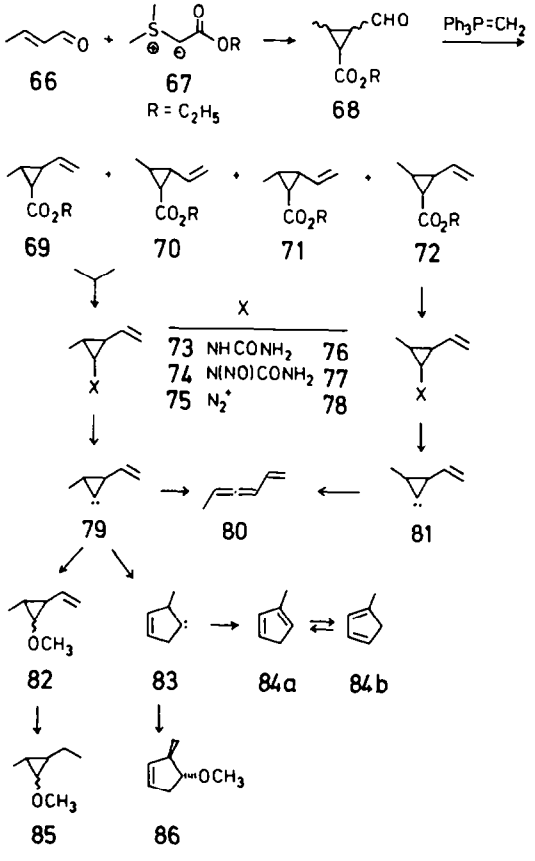


promote double bond participation (k_Δ), previously not thought to occur in five-membered rings. The ion **51a** has also been generated by protonation of cyclopentadiene in the gas phase.[50] The experimental proton affinities for the α- and β-positions of cyclopentadiene differ by only 6.9–8.6 kcal mol^{-1}, much less than expected for the 'classical' structure **51**. According to MINDO/3 calculations, **51a** is 6.2 kcal mol^{-1} lower in energy than **51**.[50]

To elucidate the stereochemistry of the **2** → **52** transformation, we prepared the labelled nitrosoureas **61** and **64** from *Z,Z*- and *E,E*-[1,4-D_2]-butadiene,[51] respectively. The isomeric purities, determined by NMR of the carboxylic acids **60** (> 98%) and **63** (85%), agreed with those reported for the corresponding butadienes.[51] The 4-methoxycyclopentenes **62** and **65** were isolated from the reactions of **61** and **64**, respectively, with 0.1 M $NaOCH_3$, and were analysed by deuterium-decoupled ^{1}H-NMR. Both chemical shifts and coupling constants (Experimental) indicated that the deuterium in **62** was *cis* to OCH_3 (> 98%) while **65** was a mixture of the *trans, trans* (85%) and *trans, cis* (15%) isomers (consistent with the isomeric purity of the starting material). Our stereochemical results exclude any planar intermediate on the reaction path **2** → **52** and confirm the bishomocyclopropenyl formulation **51a** of the 3-cyclopentenyl cation.

3-Methyl-2-vinylcyclopropylidenes

Crotonaldehyde (**66**) and dimethylsulfonium carboethoxymethylide (**67**)[52] produced a mixture of stereoisomeric ethyl 2-formyl-3-methylcyclopropanecarboxylates (**68**) (we observed four isomers whereas Payne[52] reported only two). By Wittig reaction, **68** was converted into the ethyl 3-methyl-2-vinylcyclopropanecarboxylates **69**–**72** (70:13:0.5:16.5). Assignment of the isomers was confirmed by the formation of **69** and **70** from ethyl diazoacetate and *E*-1,3-pentadiene (see below). **71** and **72** were among the products obtained from ethyl diazoacetate and *Z*-1,3-pentadiene. Preparative GC afforded pure **72** and a mixture of **69** and **70**. In the subsequent Curtius degradation, *cis*-2-vinylcyclopropyl isocyanates undergo a 3,3-sigmatropic rearrangement to give dihydro-2-H-azepin-2-ones.[24] Therefore, **73** was the only urea obtained from the **69**–**70** mixture.



Deacylation of the nitrosourea **74** in 2 M $NaOCH_3$ produced 1,3,4-hexatriene (**80**, 36%),[53] methylcyclopentadiene (**84**, 3%), 1-methoxy-3-methyl-2-

vinylcyclopropanes (**82**, 5%), methoxyhexadienes (37%) and *trans*-4-methoxy-3-methylcyclopentene (**86**, 19%). Products **80**, **84** and **86** were assigned by comparison with authentic samples; **86** was obtained by methylation (NaH, CH_3I) of the known[54] alcohol. The methoxyhexadienes, arising from the decomposition of diazonium ion **75**, were identified after hydrogenation to give 1-, 2- and 3-methoxyhexane (6:72:22). Hydrogenation also afforded the 2-ethyl-1-methoxy-3-methylcyclopropanes **85** (two isomers, 1:1.3, configuration of OCH_3 unknown), prepared independently from methoxycarbene(oid) and *E*-2-pentene.

With minor deviations, *trans*-3-methyl-2-vinylcyclopropylidene (**79**) reproduced the product pattern obtained from **2**. Allene formation and Skattebøl rearrangement proceeded at similar rates; the cyclopentenylidene **83** reacted predominantly and stereoselectively with methanol to give **86**. In contrast, the epimeric nitrosourea **77** produced only 1,3,4-hexatriene (**80**, 90%) and methoxyhexadienes (10%). Hydrogenation of the mixture afforded 1-, 2- and 3-methoxyhexane (22:68:10), along with hexane. Products expected from the Skattebøl rearrangement of *cis*-3-methyl-2-vinylcyclopropylidene (**81**) were not observed.

2-(1-Propenyl)cyclopropylidenes

The metal-catalysed additions of ethyl diazoacetate to *E*- and *Z*-1,3-pentadiene have been reported.[55,56] In our hands, *E*-1,3-pentadiene and rhodium acetate as the catalyst yielded 69% of **87** (two epimers, 54:46), along with 7% of **69** and **70** (see above). After equilibration (epimer ratio 93:7), **87** was processed in the usual manner to give *trans*-2-(1-propenyl)cyclopropyl-urea (**89**). Similarly, *Z*-1,3-pentadiene gave 62% of **88** (epimer ratio 56:44) in addition to 28% of **71** and **72**. Conversion of **88** to **92** proceeded smoothly whereas nitrosation of both ureas, **89** and **92**, suffered from poor yields (8–9%), due to the enhanced nucleophilicity of the double bond.

Treatment of **90** with 2 M $NaOCH_3$ afforded *E*-1,2,4-hexatriene (**96**, 43%),[57] methylcyclopentadiene (**84**, 6%), methoxyhexadienes (15%), 2-(*trans*-1-propenyl)-1-methoxycyclopropanes (**99**, 4%) and *trans*-4-methoxy-3-methylcyclopentene (**86**, 32%). Hydrogenation converted the methoxyhexadienes to 1-, 2- and 3-methoxyhexane (13:68:19). The 1-methoxy-2-propylcyclopropanes (**101**, *trans*:*cis* = 1.6) from the hydrogenation of **99** were identified by independent synthesis form 1-pentene and methoxycarbene(oid). The *Z*-configurated nitrosourea **93** and 2.0 M $NaOCH_3$ afforded *Z*-1,2,4-hexatriene (**98**, 75%),[57] methoxyhexadienes (15%) and methoxycyclopropanes (**100**, 10%). After hydrogenation, we observed 1-, 2- and 3-methoxyhexane (14:66:19) and **101** (*trans*:*cis* = 7), along with hexane.

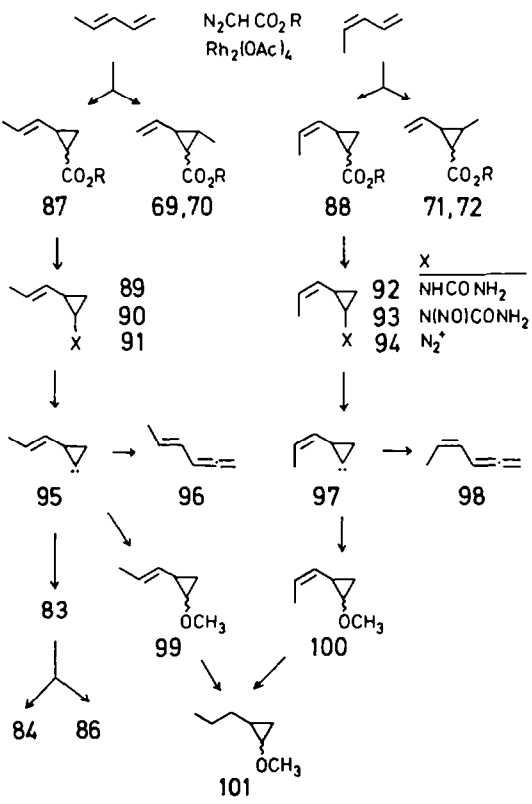
The close similarity of the product distributions obtained from the cyclopropylidenes **2**, **79** and **95** is obvious. On the other hand, cyclopropylidenes **81** and **97** share the inability to undergo Skattebøl rearrangements competitively with allene formation.

CONCLUSIONS

The diazo route to 2-vinylcyclopropylidenes is a multistep process. We summarise the reactivity of the various intermediates and review the arguments that assign the Skattebøl rearrangement to the carbene.

(a) 2-Vinylcyclopropanediazonium ions do not undergo 1,3-carbon shifts. No cyclopentenyl products were found in weakly basic media where the diazonium ions prevail. The only reaction of the diazonium ions (except for deprotonation) is ring opening to give pentadienyl cations and products derived therefrom. Delocalisation of the pentadienyl cations was demonstrated by the distribution of deuterium (see [2'-D_2]-**40**) and methyl labels. Both 3-methyl-2-vinyl- (**75**, **78**) and 2-(1-propenyl)cyclopropanediazonium ions (**91**, **94**) produced similar relative yields of 5-methoxy-1,3-hexadiene (72, 68, 58 and 66%, respectively).

(b) An eventual rearrangement of 2-vinyldiazocyclopropane, **48** → **103**, was excluded by independent generation of 4-diazocyclopentene (**103**) from the corresponding tosylhydrazone (**102**). Sodium methoxide, but not pyridine, effected base-catalysed conversion of **102** to its conjugated isomer, **104**.



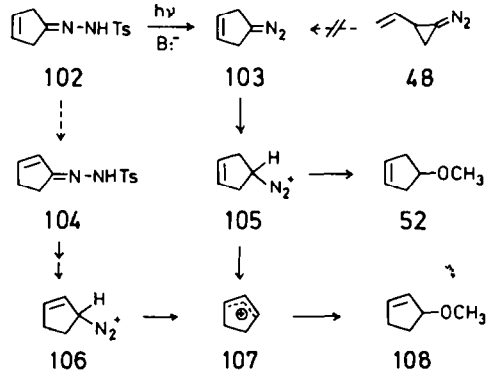
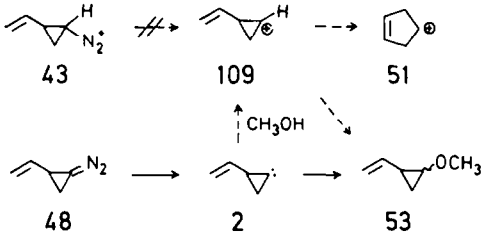


Table 2. Product distributions obtained from 2-vinylcyclopropylidenes

	Methoxycyclopropane (%)	Allene (%)	Cyclopentadiene (%)	4-Methoxycyclopentene (%)
2	7	49	15	29
79	8	57	5	30
95	5	51	7	38

Photolysis of **102** in methanol–pyridine produced 3-methoxycyclopentene (**108**, 37%) along with 4-methoxycyclopentene (**52**, 63%). Obviously, a fraction of the diazonium ions **105** (or the cyclopentenyl cations derived therefrom) undergoes 1,2-hydride shifts to give the allylic ions **107**.† 3-Methoxycyclopentene (**108**) was never obtained from 2-vinylcyclopropyl precursors.

(c) The electronic properties of 2-vinylcyclopropyl cations (**109**) resemble those of 2-vinycyclopropylidenes (**2**). Both intermediates have empty *p* orbitals available for interaction with the π bond. It is entirely plausible that **109** should undergo 1,3-carbon shifts, *if not diverted to other routes*. All efforts to detect cyclopropyl cations in the gas phase[58,59] or in solution[60] have failed so far. The barrier for the cyclopropyl to allyl cation transformation has been calculated at various levels of sophistication and found to be either non-existent or very small.[61–65] (In



contrast, substantial barriers have been calculated for the cyclopropylidene to allene transformation,[66,67] providing a chance for competitive reactions.) Moreover, in our case, **109** cannot arise from the diazonium ion **43** (see (a)), the only remaining route being protonation of **2**. We have not been able to trap **109** in strongly basic media by electrophilic addition to methyl vinyl ether. Although this failure might be due to rapid rearrangement of **109**, analogous attempts aimed at scavenging the parent cyclopropyl cation were also unsuccessful.[68] In the light of both theory and experiment any contribution of **109** to the formation of cyclopropyl ethers (e.g. **53**) and to the Skattebøl rearrangement is considered to be highly improbable.

(d) The arguments summarised above support the rearrangement of 2-vinylcyclopropylidenes by exclusion of alternative mechanisms. The trapping of 3-cyclopentenylidene (**3**) by methyl vinyl ether to give **49**, albeit in low yield, provides more direct evidence. Our data reveal a steric bias to the Skattebøl rearrangement, exerted by *cis*-methyl substituents either at C-2 (cyclopropane ring) or at C-2′ (terminal position of the vinyl group). Severe repulsions disfavour the s-*cis* conformation of **81** and **97**, thus preventing 1,3-carbon shifts. Generation of **81** and **97** from organometallic precursors led to analogous results.[69] In summary, our studies confirm that the various routes to 2-vinylcyclopropylidenes converge at the carbene stage. Different product forming steps, due to different reaction conditions and reactants, tend to obscure the concurrent parts of the mechanism.

† Admittedly, the photolysis of **102** did not reproduce the strongly basic conditions employed for the generation of **48**. We should remember, however, that 4-diazocyclopentene (**103**) is not expected to react *via* **3** at ambient temperature. The rapid decomposition of diazocyclopropanes is a consequence of ring strain. Unstrained diazoalkanes are protonated rather than thermolysed even in strongly basic methanol solutions.[29] Therefore, the behaviour of cyclopentenediazonium ions (**105**) provides a crucial test for the intervention of diazocyclopentene (**103**).

EXPERIMENTAL

M.ps were determined with a Büchi apparatus and are uncorrected. ^{1}H-NMR spectra were recorded on Bruker WP 80 and WM 250 instruments. The chemical shifts are given in δ (ppm) downfield from TMS. Mass spectra (MS) were obtained with a Varian MAT CH 5 spectrometer. Gas chromatographic (GC) analyses were performed with Perkin–Elmer F 22 and Siemens Sichromat 1 instruments. The GC columns used were glass capillaries of 0.23–0.38 mm i.d., coated by the dynamic mercury plug technique. Preparative GC separations were made on Varian 920 instruments, using glass columns of 6–9 mm i.d., packed with Chromosorb W. Stationary phase, length of the column, and temperature are reported below for the individual separations. Microanalyses were performed by the Microanalytical Laboratory I. Beetz, Kronach, Germany.

N-*Nitroso*-N-(trans-2-*vinylcyclopropyl*)*urea* (**40**)

Ethyl diazoacetate (2.0 g, 17 mmol) was added slowly to rhodium acetate (30 mg) in refluxing 1,3-butadiene (20 ml). 15 min after completion the dry-ice condenser was replaced by a cooled trap to recover excess butadiene. Distillation of the residue *in vacuo* afforded 2.0 g (90.5%) of product, b.p. 30° at 0.01 mm, consisting of 52.6% *trans*-**37**, 42.7% *cis*-**37**, 2.6% diethyl fumarate and 2.0% diethyl maleate (GC).

The product mixture (4.5 g, 32 mmol) was dissolved in absolute EtOH (8 ml) and refluxed for 9 days with 16 ml of 2 M NaOEt. The *trans*:*cis* ratio of **37** was now 91.7:8.3 (GC). Aqueous KOH (2.7 g, 16 ml of water) was added, followed by heating at the reflux temp for 2 hr. Most of the EtOH was evaporated *in vacuo*. The dark residue was acidified with 20% HCl and extracted three times with 20 ml portions of ether. The combined ethereal extracts were washed with a sat NaCl aq prior to drying over $MgSO_4$. Distillation of the solvent at ordinary pressure (20 cm Vigreux column), followed by distillation of the residue *in vacuo*, afforded 2.7 g (78.4%) of **38**,[24] b.p. 25–30° (0.01 mm). Esterification of a small sample with diazomethane indicated a *trans*:*cis* ratio of 90.3:9.7.

A soln of **38** (2.7 g, 24 mmol), in acetone (16 ml)–water (4 ml) was treated at 0° successively with Et_3N (2.7 g, 34 mmol) in acetone (44 ml), ethyl chloroformate (3.4 g, 31 mmol) in acetone (12 ml), and sodium azide (2.3 g, 35 mmol) in water (8.4 ml). After 1 hr at 0°, the mixture was poured onto ice and extracted with toluene. The toluene extracts (*ca* 200 ml) were washed with water, dried over $MgSO_4$ and concentrated *in vacuo* to *ca* 50 ml. The carefully dried soln was added dropwise to a distillation flask heated to 110–120°. After the evolution of H_2 had stopped and the azide absorption at 2140 cm^{-1} had disappeared, a stream of dry ammonia was passed into the cooled (0°) soln. The ppt was filtered with suction, washed with cold toluene, and recrystallised from EtOAc to give 2.0 g (67%)

of **39**, m.p. 113°. (Calc for $C_6H_{10}N_2O$: C, 57.11; H, 7.99; N, 22.21. Found: C, 57.17; H, 8.02; N, 21.17%.)

To a suspension of **39** (1.5 g, 12 mmol) and of anhyd NaOAc (1.1 g, 13 mmol) in anhyd ether (50 ml) was added dropwise at −5 to 0° a soln of freshly distilled N_2O_4 (1.21 g, 0.83 ml, 13 mmol) in ether (17 ml). After stirring for 1 hr the mixture was filtered. The residue was washed thoroughly with ether, and the soln was extracted several times with ice-water prior to drying over $MgSO_4$. Evaporation *in vacuo* and recrystallisation from ether–hexane yielded 1.3 g (71%) of **40**, m.p. (dec) 103°. (Calc for $C_6H_9N_3O_2$: C, 46.44; H, 5.85. Found: C, 46.94; H, 5.65%.)

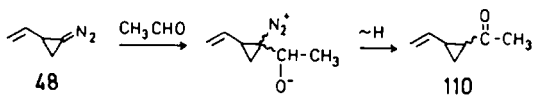
Reactions of **40**

A. Weakly basic conditions. Solns of **40** (0.155 g, 1 mmol) in MeOH (8 ml) were stirred with 3 mmol of sodium formate (0.20 g), $NaHCO_3$ (0.252 g), or Na_2CO_3 (0.318 g). Complete conversion took 3–6 hr at room temp, as indicated by the evolution of N_2. The mixture was diluted with water (16 ml) and extracted with n-pentane (2.5 ml). The extracts were dried over K_2CO_3 and analysed by GC (capillary column coated with polyphenyl ether, 109 m, 40°): **41**,[27] 52%, 975 s, *E*-**42**,[27,28] 41%, 2037 s, and *Z*-**42**, 7%, 2077 s. The product composition was independent of the base (±1%). Yields ranged from 90 to 100%, as determined with 1-methoxycyclopentene as internal standard. Prep. GC (6 m Carbowax, 70°) separated **41** [^{1}H-NMR (CCl_4) δ 3.20 (s, 3H), 3.85 (t, 1H, J = 5.5 Hz), 4.8–6.0 (m, 6H)] and **42** [^{1}H-NMR (CCl_4) δ 3.26 (s, 3H), 3.92 (d, 1.66H, J = 5 Hz), 4.06 (dd, 0.34H, J = 6.6, 1.4 Hz), 4.8–6.2 (m, 5H)]. Because of its downfield chemical shift and enhanced allylic coupling the δ 4.06 signal was assigned to 5-H of *Z*-**42**. Diimide reduction of **42**, following a general procedure,[70] gave a single product, identified by comparison as 1-methoxypentane.

B. Strongly basic conditions. Solns of **40** (20 mg, 0.13 mmol) in MeOH (0.2 ml) were added dropwise to 3 equiv. of NaOMe in MeOH (0.1, 0.5, 1.0, 1.5 and 2.0 M). After being stirred for 5 min, all volatiles were distilled *in vacuo* into a cold trap. GC analysis (capillary column coated with Carbowax, 140 m, 50°) indicated **4**, 999 s, **5**,[6] 1021 s, **41**,[27] 1201 s, *trans*-**53**,[38] 1496 s, *cis*-**53**,[38] 1703 s, **52**,[38] 1821 s and **42**,[27,28] 2110 s, no *Z*/*E* separation. The product distribution obtained with various concentrations of methoxide deviated within experimental error from the average (Table 1). Yields ranged from 60 to 70%, as determined with 3-methoxycyclopentene as internal standard.

Since the physical data of **52** had not been reported, **52** was isolated by GC (4.5 m Carbowax, 70°) from a preparative run (1 g of **40**, 190 ml of 0.1 M $NaOCH_3$). An authentic sample was obtained by NaH–CH_3I-methylation of 3-cyclopent-1-ol[71] (95%). ^{1}H-NMR ($CDCl_3$): δ 2.4 (dd, J = 15.5, 3.3 Hz, *cis*-3,5-H), 2.57 (dd, J = 15.5, 6.6 Hz, *trans*-3,5-H), 3.3 (s, OCH_3), 4,1 (septet, 4-H), 5.7 (s, 1,2-H). The coupling constants $J_{3,4}$ are similar to those reported for 3-cyclopenten-3-ol and its acetate ($J_{cis} \simeq 2\ J_{trans}$).[72]

C. In the presence of methyl vinyl ether. Methyl vinyl ether (50 ml) was condensed into a pressure bottle. 2 M NaOMe (4 ml) and a vial containing a soln of **40** (0.4 g = 2.6 mmol) in MeOH (4 ml) were added. The bottle was closed, removed from the cooling bath, and shaken to start the reaction. After being stirred for 1 hr, the methyl vinyl ether was allowed to evaporate. The residue was diluted with ice-water (20 ml) and extracted with n-pentane (3 × 5 ml). The extracts were dried over $MgSO_4$, and analysed by GC. In addition to the products observed above (*B*), **55**[46] and **110** (*cis*:*trans* = 4) were identified by comparison with authentic samples. The isomers of **110** were obtained from the corresponding carboxylic acids



48 110

(**38**) and methyllithium. **110** became the major product when **40** reacted with base in the presence of acetaldehyde. The formation of **110** is therefore attributed to contamination of our methyl vinyl ether by traces of acetaldehyde. Four additional GC peaks (0.5–2% each) may represent cycloadducts of 2-vinylcyclopropylidene (**2**) to methyl vinyl ether. However, separation and unequivocal identification of these products has not been achieved.

Following catalytic hydrogenation (PtO_2) of the pentane extracts, **50**, 0.5% was detected along with the hydrogenation products of **52**, **53**, **55** (6.7%), and **110**. A sample of **50** was prepared from methylenecyclopentane,[73] dichloromethyl methyl ether and MeLi by the method of Schöllkopf and Paust.[74] ^{1}H-NMR (CCl_4): δ 0.3–0.7 m (2H), 1.2–2.0 m (8H), 2.9 (dd, J = 6 and 2 Hz, 1H), 3.3 (s, 3H). (Calc for $C_8H_{14}O$: C, 76.14; H, 11.18. Found: C, 76.16; H, 11.20%.)

[2′-D_2]-N-*Nitroso*-N-(trans-2-*vinylcyclopropyl*)*urea*, [2′-D_2]-**40**

Zn dust (482 g, 7.4 mol) was added to a soln of copper (II) acetate (29.2 g, 0.15 mol) in warm AcOH (600 ml). After cooling to room temp, the liquid was decanted and the solid washed thoroughly with ether to remove residual acid. To the refluxing suspension of the Zn–Cu couple in ether (600 ml) was added a soln of **47**,[31] 120 g, 0.845 mol and CD_2I_2[32] (145 g, 0.537 mol) in ether (430 ml). The mixture was refluxed for 5 hr. A sat NH_4Cl aq (500 ml) was added slowly with cooling. After 20 min the organic layer was separated and the aqueous layer extracted twice with ether. The combined ethereal solns were washed with 3% HCl, sat. NH_4Cl, and water, dried over $MgSO_4$ and evaporated. Distillation *in vacuo* yielded 31.6 g (41.5%) of [2′-D_2]-**37** (MS: 95% d_2, 5% d_1) which was converted into [2′-D_2]-**40** by the same steps used to prepare **40** (see above).

The reaction of [2′-D_2]-**40** with MeOH/$NaHCO_3$ produced **41** (47%), *E*-**42** (45%) and *Z*-**42** (8%). Preparative GC afforded **42** (*E*:*Z* = 85:15). MS: 93.7% d_2, 5.9% d_1, 0.4% d_0; ^{1}H-NMR: δ 3.23 (s, 3.0H), 3.92 (d, 1.11H), 4,06 (dd, 0.07H), 4.8–6.7 (m, 3.82H). Diimide reduction[70] of **42** gave 1-methoxypentane which was purified by GC. The molecular ion region of the mass spectrum indicated complete retention of the deuterium (95.7% d_2, 3.3% d_1, 1.0% d_0) while the parent peak region displayed the fragments $CH_3OCH_2^+$ (*m*/*e* 45) and $CH_3OCD_2^+$ (*m*/*e* 47) in a 60:40 ratio.

[3,2′-D_2]-N-*Nitroso*-N-(trans-2-*vinylcyclopropyl*) *ureas* (**61**, **64**)

Z,*Z*- and *E*,*E*-[1,4-D_2]-1,3-butadienes were obtained from the corresponding 1,4-dichlorobutadienes by Zn(Cu) reduction in D_2O/dioxane.[51] Rhodium-catalysed addition of ethyl diazoacetate followed by equilibration and hydrolysis (see above) afforded the acids **60** and **63**, respectively. ^{1}H-NMR of **60** (CCl_4): δ 1.38 (dd, 3-H, J_{23} = 8.6 Hz, J_{13} = 4.0 Hz), 1.58 (t, 1-H, $J_{12} = J_{13}$ = 4.0 Hz), 2.05 (sept, 2-H, $J_{23} \simeq J_{2'1'}$ = 8.6 Hz, J_{12} = 4 Hz), 4.96 (d, 2′-H, $J_{1'2'}$ = 10.7 Hz), 5.3 (dd, 1′-H, $J_{1'2'}$ = 10.7 Hz, $J_{21'}$ = 8.6 Hz). The coupling constants are in accordance with the configuration assigned to **60**; no significant contamination by other isomers was detected. ^{1}H-NMR of **63** ($CDCl_3$): δ 0.95 (dd, 3-H, J_{13} = 8.1 Hz, J_{23} = 6.3 Hz), 1.55 (dd, 1-H, J_{13} = 8.1 Hz, J_{12} = 4.0 Hz); 2.05 (sept, 2-H, $J_{21'}$ = 8.0 Hz, J_{23} = 6.3 Hz, J_{12} = 4.0 Hz), 5.1 (d, 2′-H, J = 17.6 Hz), 5.3 (dd, 1′-H, $J_{1'2'}$ = 17.6 Hz, $J_{21'}$ = 8.0 Hz). These signals confirm the configuration of **63**, but the spectrum showed additional absorptions at δ 1.3 (dd) and 4.95 (d) indicating the presence of *cis* isomer (15% by integration).

The conversion of **60** and **63** into the nitrosoureas **61** and **64**, respectively, proceeded by the same steps used to prepare **40**. Deacylation of the nitrosoureas (1.0 g, 6.4 mmol) with 0.1 M $NaOCH_3$ (200 ml) gave product distributions very similar to those in Table 1. The deuterated 4-methoxycyclopentenes **62** and **65** were isolated by preparative GC (4.5 m Carbowax + KOH, 70°). **62**: MS: 89.6% d_2, 8.1% d_1, 2.3% d_0; ^{1}H-NMR ($CDCl_3$): δ 2.55 (dt, 3.5-H, $J_{3,4}$ = 6.6 Hz, $J_{3H,3D}$ = 2.3 Hz), 3.3 (s, OCH_3), 4.1 (t, 4-H, $J_{3,4} = J_{4,5}$ = 6.6 Hz), 5.7 (s, 1,2-H). **65**: 86.1% d_2, 10.4% d_1, 3.5% d_0; ^{1}H-NMR ($CDCl_3$, deuterium-decoupled): δ 2.4 (d, 3,5-H, $J_{3,4}$ = 3.5 Hz), 3.3 (s, OCH_3), 4.1 (t,

4-H, $J_{3,4}$ = 3.5 Hz), 5.7 (s, 1,2-H). In the deuterium-coupled spectrum, H–D coupling, superimposed on $J_{3,4}$, prevented satisfactory resolution. Absorptions at δ 2.55 in the ^{1}H-NMR spectra of **65** indicated the presence of 15% of *trans*-3,5-H.

N-*Nitroso*-N-(3-*methyl*-2-*vinylcyclopropyl*)*ureas* (**74**, **70**)

Sodium hydride (4.32 g, 0.18 mol, 60% dispersion in mineral oil) was washed several times with n-pentane and dried *in vacuo*. Dry dimethyl sulfoxide (100 ml) was added and the suspension, maintained under nitrogen atmosphere, was stirred at 80° until the evolution of H_2 ceased. A soln of methyltriphenylphosphonium bromide (46.4 g, 0.13 mol) in dimethyl sulfoxide (200 ml) was then added with cooling. After warming to room temp for 10 min, **68**,[52] a mixture of four isomers 68.5 : 13.0 : 17.7 : 0.8, 0.10 mol was added. The mixture was stirred for 18 hr at room temp and poured onto water (150 ml). Triphenylphosphine oxide was filtered off and the liquid was extracted with n-pentane. The combined extracts were washed with water and dried over Na_2SO_4. Evaporation of the solvent and distillation *in vacuo* (40°, 0.1 mm) provided 10.2 g (66%) of product, containing **69** (70.0%), **70** (12.9%), **71** (0.5%), and **72** (16.4%). Preparative GC (6 m Carbowax, 140°) separated **69** + **70** (83.5 : 16.5) from **72** (97% pure); **71** was not recovered.

Alkaline hydrolysis of the **69** + **70** mixture (55%) and Curtius degradation (60%) followed the procedures reported above to yield **73**, m.p. 127° (from EtOAc). (Calc for $C_7H_{12}N_2O$: C, 59.97; H, 8.63; N, 19.99. Found: C, 60.04; H, 8.73; N, 19.87%.) Nitrosation as described for **40**, afforded the corresponding nitrosourea (**74**) in 41% yield, m.p. (dec.) 70–71°. (Calc for $C_7H_{11}N_3O_2$: C, 49.69; H, 6.55; N, 24.80. Found: C, 49.72; H, 6.58; N, 24.71%.) Treatment of **74** (20 mg, 0.12 mmol) with 2 M $NaOCH_3$ (0.5 ml) gave at least 9 products of which 1,3,4-hexatriene[53] (**80**, 36%), methylcyclopentadiene (**84**, 3%), and *trans*-**86**, 19% were identified by comparison. Methylation (NaH, CH_3I, 2 hr reflux) of the known alcohol[54] and purification by GC (4 m Carbowax + KOH, 60°) provided **86**. ^{1}H-NMR ($CDCl_3$): δ 1.05 (d, J = 7 Hz, 3H), 2.0–2.9 (m, 3H), 3.3 (s, 3H), 3.6 (quintet, J = 4 Hz, 1H), 5.6 (s, 2H). (Calc for $C_7H_{12}O$: C, 74.95; H, 10.78. Found: C, 74.80; H, 10.67%.)

Following catalytic hydrogenation (PtO_2) of the product mixture, 1-, 2- and 3-methoxypentane (6 : 72 : 22) as well as two isomers of **85** (2.1 and 2.7%) were identified by comparison. Samples of **85** were readily available form *E*-2-pentene by the method of Schöllkopf and Paust.[74] Although both isomers were obtained pure by GC, the similarity of their NMR spectra did not permit assignment of configuration. Hexane, methylcyclopentane and *trans*-1-methoxy-2-methylcyclopentane (from the hydrogenation of **86**) were also observed whereas *cis*-1-methoxy-2-methylcyclopentane amounted to less than 1%.

Application of analogous procedures to **72** provided **76**, m.p. 148.5°, in 43% yield and the corresponding nitrosourea (**77**), m.p. 95.5°, in 71% yield. (Calc for $C_7H_{11}N_3O_2$: C, 49.69; H, 6.55; N, 24.80. Found: C, 49.75; H, 6.52; N, 24.75%.) Cleavage of **77** with 2 M NaOMe gave at least four products among which **80** (90%) predominated. Catalytic hydrogenation produced hexane (84%), 1-methoxypentane (1.6%), 2-methoxypentane (11.0%) and 3-methoxypentane (3.4%).

N-*Nitroso*-N-[2-(1-*propenyl*)*cyclopropyl*]*ureas* (**90**, **93**)

Addition of ethyl diazoacetate (10.0 g, 87 mmol) to *E*-1,3-pentadiene (30 ml) and rhodium acetate (20 mg), followed by distillation *in vacuo* (40°, 0.01 mm), afforded 10.5 g (78%) of crude product: **69** (6.8%), **70** (1.6%), *cis*-**87** (40.1%), *trans*-**87** (47.5%), diethyl fumarate (1.5%) and diethyl maleate (2.1%). The mixture was refluxed with 30 ml of 2 M NaOEt for 168 hr to achieve equilibration (**69** : **70** = 53 : 47; *trans* : *cis*-**87** = 94 : 6). A soln of KOH (4.7 g, 84 mmol) in water (30 ml) was then added and reflux continued for 4 hr. The usual isolation procedure yielded 5.5 g (64%) of crude *trans*-2-(*E*-1-propenyl)-cyclopropanecarboxylic acid. ^{1}H-NMR (CCl_4): δ 0.7–2.3 (m, 4H), 1.63 (d, J = 6 Hz, 3H), 5.0 (dd, J = 17 + 8 Hz, 1H), 5.6 (dq, J = 17 + 6 Hz, 1H), 11.8 (s, 1H). Curtius degradation, as described above, gave *trans*-**89**, m.p. 122°, in 76% yield. (Calc for $C_7H_{12}N_2O$: C, 59.97; H, 8.63; N, 19.99. Found: C, 59.83; H, 8.51; N, 19.80%.)

Nitrosation of **89** with N_2O_4 failed. The absence of olefinic protons in the product(s) indicated addition to the double bond. $NaNO_2$ (0.21 mg, 3 mmol) was added to a soln of **89** (0.385 mg, 2.75 mmol) in AcOH (5 ml). After stirring at room temp for 5 min, the AcOH was evaporated *in vacuo* (0.01 mm). The residue was triturated with ether and washed with water. Drying ($MgSO_4$) of the organic layer, evaporation under reduced pressure, and recrystallisation of the residue from ether–pentane yielded 40 mg (8.6%) of **90**, m.p. (dec.) 72°. Immediate treatment of the labile **90** with 2 M NaOMe (1.0 ml) gave at least seven products. *E*-**84**, 6%, and *trans*-**86**, 32%, were identified by comparison. Following catalytic hydrogenation, 1-, 2- and 3-methoxyhexane (13 : 68 : 19) were detected along with hexane, methylcyclopentane, 1-methoxy-2-methylcyclopentane (*trans* : *cis* ≥ 32) and **101**, *trans* 2.2%, *cis* 1.5%. The addition of methoxycarbene(oid)[74] to 1-pentene produced **101** with a *cis* : *trans* ratio of 77 : 23. Although the isomers could not be separated on a preparative scale, ^{1}H-NMR of the mixture (*trans*: δ 2.9 td, $J_{1,2} = J_{1,3c} = 2.6$ Hz, $J_{1,3t} = 6.1$ Hz; *cis*: δ 3.17 dt, $J_{1,3c} = 3.2$ Hz, $J_{1,2} = J_{1,3t} = 6.3$ Hz) assigned the *trans* configuration to the minor, faster eluting component (capillary column coated with OV 101, 144 m, 60°).

Addition of ethyl diazoacetate to *Z*-1,3-pentadiene produced **71** (13.7%), **72** (13.7%), *trans*-**88** (34.5%), *cis*-**88** (27.5%), diethyl fumarate (6.4%) and diethyl maleate (4.1%). Preparative GC (4.5 m Carbowax, 140°) provided the components with > 95% purity. **71**: ^{1}H-NMR ($CDCl_3$): δ 1.27 (t, J = 7 Hz, CH_3), 1.3 (d, J = 5 Hz, CH_3), 1.4–2.2 (m, 1,2,3-H), 4.12 (q, J = 7 Hz, CH_2), 5.2 (m, 2'-H), 6.1 (m, 1'-H); $J_{1',2'} = 17$ and 10 Hz, $J_{2,1'} = 7.8$ Hz, $J_{2',2'} = 2.4$ Hz. (Calc for $C_9H_{14}O_2$: C, 70.09; H, 9.15. Found: C, 70.06; H, 9.18%.) **72**: δ 1.15 (d, J = 6 Hz), 1.27 (t, J = 7 Hz), 1.4–2.1 (m, 3H), 4.12 (q, J = 7 Hz), 5.0–5.2 (m, 1H), 5.3–5.8 (m, 2H). (Found: C, 69.95; H, 9.15%.) *trans*-**88**: δ 0.9 (ddd, *trans*-3-H), 1.28 (t, J = 7 Hz, CH_3), 1.5 (m, 1-H, *cis*-3-H), 1.73 (dd, CH_3), 2.2 (m, 2-H), 4.1 (q, J = 7 Hz, CH_2), 4.82 (qt, 1'-H), 5.5 (dqd, 2'-H), $J_{1,3t} = 9.2$ Hz, $J_{3c,3t} = 3.6$ Hz, $J_{2,3t} = 6.1$ Hz, $J_{2,1'} = 11$ Hz, $J_{1',2} = 10.3$ Hz, $J_{1',3'} = 1.7$ Hz, $J_{2',3'} = 6.6$ Hz, $J_{2,2'} = 1.0$ Hz. *cis*-**88**: δ 1.1 (m, 3-H), 1.25 (t, J = 7 Hz, CH_3), 1.75 (dd, J = 6.1 and 1.7 Hz, CH_3), 1.85–2.25 (m, 1-H, 2-H), 4.15 (q, J = 7 Hz, CH_2), 5.5 (m, 1'-H, 2'-H).

Alkaline hydrolysis of *trans*-**88** afforded 74% of *trans*-2-(*Z*-1-propenyl)cyclopropanecarboxylic acid, m.p. 63°. (Calc for $C_7H_{10}O_2$: C, 66.64; H, 7.99. Found: C, 66.74; H, 7.92%.) Curtius degradation yielded *trans*-2-(*Z*-1-propenyl)cyclopropylureas (**92**), m.p. 92°. (Calc for $C_7H_{12}N_2O$: C, 59.97; H, 8.63; N, 19.99. Found: C, 60.13; H, 8.69; N, 19.94%.) Nitrosation with $NaNO_2$–HOAc, as described for **90**, gave 8.1% of **93**, m.p. (dec.) 80°. The labile nitrosourea was reacted with 2 M NaOMe to give at least four products, among which *Z*-**98**,[57] 75% predominated. Following catalytic hydrogenation (PtO_2), n-hexane, 1-methoxyhexane (2.4%), 2-methoxyhexane (11.3%), 3-methoxyhexane (3.3%), *trans*-**101** (7.0%), and *cis*-**101** (1.0%) were identified by comparison with authentic samples.

3- *and* 2-*Cyclopenten*-1-*on-tosylhydrazones* (**102**, **104**)

Tosylhydrazine (0.93 g, 5 mmol) was dissolved in a sufficient quantity of warm (40°) MeOH. After cooling to 10°, two drops of pyridine and 0.41 g (5 mmol) of 3-cyclopenten-1-one[75,76] were added. Stirring at 10° was continued for *ca* 15 min until a white ppt had formed. The solid was filtered off and recrystallised from EtOH to give 0.74 g (59%) of **102**, m.p. (dec.) 138–140°. ^{1}H-NMR (D_2O–NaOD): δ 2.45 (s, 3H), 3.2 (s, 2H), 3.4 (s, 2H), 6.1 (s, 2H), 7.35 (d, J = 8 Hz, 2H), 8,05 (d, J = 8 Hz, 2H). (Calc for $C_{12}H_{14}N_2O_2S$: C, 57.59; H, 5.64; N, 11.20. Found: C, 57.69; H, 5.72; N, 11.12%.)

When the reaction of 3-cyclopenten-1-one with tosylhydrazine was carried out at 60° overnight, the isomeric tosylhydrazone **104**, m.p. (dec.) 180°, was obtained in 40%

yield. ^{1}H-NMR (D_2O–NaOD): δ 2.45 (s, 3H), 2.85 (m, 4H), 6.65 (m, 2H), 7.4 (d, J = 8 Hz, 2H), 8.1 (d, J = 8 Hz, 2H). This result must be due to isomerisation of the ketone prior to formation of the tosylhydrazone. When **102** was heated to 60° in MeOH–pyridine, no rearrangement was observed. However, **102** isomerised to **104** on standing in MeOH–NaOMe at room temp. The tosylhydrazones **102** and **104** were readily separated by TLC (Al_2O_3, ether).

A soln of **102** (0.125 g, 0.5 mmol) in MeOH (5 ml)–pyridine (0.8 ml, 10 mmol) was photolysed (medium pressure mercury lamp, Pyrex) to give **52** (63%) and **108**[77] (37%). Photolysis of **102** in the presence of NaOMe led to enhanced yields of **108**, owing to partial isomerisation of **102**. When the Na-salt of **104** was irradiated, only **108** was produced. The ethers **52** and **108** were identified by comparison with authentic samples.

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