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Substituent Effects in the Thermal Isomerization of 1,2-Dicarbonyl Derivatives of 3,6-Bridged 1,2,3,6-Tetrahydropyridazines

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Received Agust 12, 1974

JOHN A. CAMPBELL, IAN HARRIS, DONALD MACKAY, and TIMOTHY D. SAUER. Can. J. Chem. **53**, 535 (1975).

The Diels–Alder adducts of cyclopentadiene and azodiacyls or azodiaroyls isomerize to 1,3,4-oxadiazines at rates which show a trend qualitatively related to the rotation rates of the corresponding *N,N*-dimethylamides. The isomerizations probably occur by a cyclic concerted mechanism.

The ring substituents in the adducts of 1,4-dimethyl-2,3-diphenylcyclopentadiene and azodibenzoyl or azodiacetyl accelerate the isomerization; the kinetic evidence supports a cyclic intermediate in the reaction in isooctane as solvent but is more consistent with a dipolar intermediate in aqueous ethanol.

Some generalizations about the effect of substituents on the isomerization are presented on the basis of these and earlier experiments.

JOHN A. CAMPBELL, IAN HARRIS, DONALD MACKAY et TIMOTHY D. SAUER. Can. J. Chem. **53**, 535 (1975).

Les produits d'addition de Diels–Alder entre le cyclopentadiène et les azodiacyles et les azodiaroyles s'isomérisent en oxadiazines-1,3,4 à des vitesses qui indiquent une tendance reliée qualitativement aux vitesses de rotation des *N,N*-diméthylamides correspondantes. Les isomérisations se produisent probablement par un mécanisme cyclique concerté.

Les substituants sur les cycles dans les produits d'addition du diméthyl-1,4 diphényl-2,3 cyclopentadiène avec l'azodibenzoyle ou l'azodiacétyle ont comme effet d'accélérer la vitesse d'isomérisation. Les données cinétiques sont en accord avec un intermédiaire cyclique lorsque la réaction est effectuée dans l'isooctane alors qu'en milieu éthanol aqueux, le mécanisme impliquerait probablement un intermédiaire dipolaire. On présente quelques généralisations sur l'effet des substituants sur de telles isomérisations en se basant sur ces expériences et d'autres rapportées antérieurement. [Traduit par le journal]

Introduction

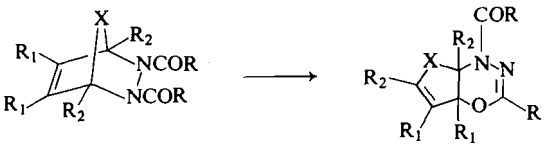
For some time we have been studying the generalized isomerization of the bridged pyridazine **1** to the *cis*-fused 1,3,4-oxadiazine system **2** and have shown that its rate is highly dependent on the nature of X, R, R_1, and R_2. Our experiments have concentrated on the [2.2.1] system with a one-carbon bridge, in particular the azodicarbonyl adducts **3** of cyclopentadiene (1, 2) and those, **5**, of 2,5-dimethyl-3,4-diphenylcyclopentadienone (3).

In the series **3** → **4** the participation of acyl groups in the isomerization showed a marked steric acceleration, with a rate order of R = CMe_3 > Ph > Me, and, in the phenyl case at least (1), appeared to involve a concerted cyclic mechanism (transition state **7**). Ester groups however, *e.g.* in **3** (R = OEt), did not participate.

The cyclone-derived substituents in the adducts **5** had a powerful accelerating effect. Thus the azodibenzoyl adduct **5***a* could only be transiently detected, the isomeric 1,3,4-oxadiazine **6***a* being the isolated product, whereas adducts of azo esters, *e.g.* **5***c*, though stable enough for isolation, could be isomerized readily and reversibly to **6***c* (3).[1] Detailed kinetic studies were not carried out but the mechanism for the isomerization of **5***c* was most reasonably interpreted as involving the doubly ambident dipolar intermediate **8**.

We wish now to discuss in more detail the effect of the group R in **3**, especially in the substituted phenyl series **3***d–h*, and of ring substituents in the presence of a methylene rather than a keto bridge, *viz.* the adducts **9** in contrast with **5**. We also present in summary some

[1]Both **5***c* and **6***c* isomerized irreversibly to the isomeric 1,2-diazetidine which was thus the end product (3). The mode of fusion of the oxadiazine ring in compounds **6** (oxygen to benzylic carbon) and the stereochemistry follow by mechanistic analogy with the formation of **4**, from their spectra (3), and, in the case of **6***c*, by its chemical reactions (4).



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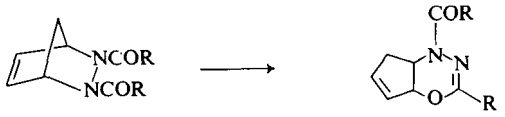
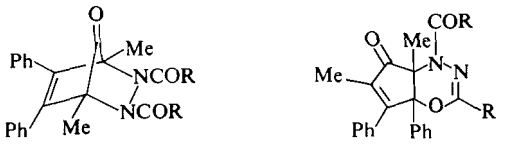


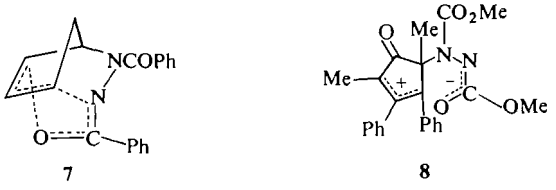
3 4

a R = Ph; *b* R = Me; *c* R = CMe_3; *d* R = *p*-BrC_6H_4; *e* R = *p*-$NO_2C_6H_4$; *f* R = *p*-$MeOC_6H_4$; *g* R = *m*-$NO_2C_6H_4$; *h* R = *o*-$MeOC_6H_4$

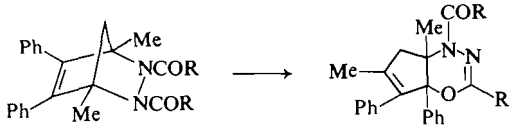


5 6

a R = Ph
b R = Me
c R = OMe

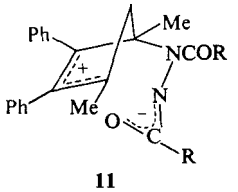


7 8



9 10

a = Ph; *b* = Me



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generalizations about the influence of X, R, R_1, and R_2 on the isomerization **1** → **2**.

Results and Discussion

All the substituted benzoyl derivatives in the series **3** → **4** have been described earlier (1, 2) except **3***g* and *h* and **4***g* and *h*. Compounds **9***a* and *b* and **10***a* and *b* have been used before in unrelated work (5) but their synthesis and properties are described here for the first time.

Azodi-*m*-nitrobenzoyl, m.p. 159–161°, rapidly gave labile crystalline **3***g* with cyclopentadiene. The hindered azodi-*o*-methoxybenzoyl was too unstable for isolation; it reacted slowly with cyclopentadiene to give the stable but amorphous **3***h*, purified by silica gel chromatography. The very labile (1) **9***a* was prepared in benzene at room temperature and purified by precipitation with pentane. The adduct **9***b*, obtained similarly, was more stable except in hydroxylic solvents. The melting points of **9***a* and *b* depended on the rate and time of exposure to heating. The oxadiazines related to these adducts were obtained by heating the latter in inert solvents at suitable temperatures. Their identities followed unequivocally from their spectra.

Kinetic analyses of the isomerizations were carried out by u.v. spectrophotometry as described before (1, 2, 6).

The first-order rate constants for the isomerization of **3***a–f* at 77° in 71% aqueous ethanol have been given earlier but, except for **3***b*, have now been determined for all of them over a range of temperatures. The Arrhenius activation energy and the entropy of activation are given in Table 1, along with the rate constants at 77°. The rate constants for **3***g* and *h* were determined only at 77° and are also given in Table 1.

From the similarity of the activation parameters to those of **3***a* it seems reasonable that all the isomerizations **3***b–f* go through a concerted cyclic transition state.

The isomerizations of the *p*-substituted benzoyl adducts, **3***d–f*, are clearly not subject to any simple linear free energy correlation (unlike the mechanistically related *ortho*-Claisen rearrangement where the rate data correlated well with σ_p^* constants (7, 8)) since all substituents are rate enhancing, though the effect is small except for the nitro group.

A rationalization of the substituent trends

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TABLE 1. Rate constants at 77 °C and activation parameters for isomerization of adducts 3 in 71% aqueous ethanol

Compound	R	$10^4 k$ (s^{-1})	E_a (kcal mol^{-1})	No. of runs (range, °C)	$\Delta S^{\ddagger}$ at 77 °C (cal deg^{-1})	$\Delta G^{\ddagger}$, $RCONMe_2$ rotation[d] (kcal mol^{-1}) (temperature, °C)
3*a*	Ph	2.42	23.3±1.2	6 (69–84)	−5.5±1.8	15.3 (3–17)[e]; 15.0 (77)[f]
3*b*	Me	0.21[a]				18.1 (70–83)[e]; 17.5 (77)[f]
3*c*	CMe_3	74.5	21.3±0.8[b]	7 (61–79)	−5.0±1.2	11–13[g]
3*d*	*p*-BrC_6H_4	6.77	20.1±1.7	5 (69–80)	−9.0±2.5	
3*e*	*p*-$NO_2C_6H_4$	17.5	20.5±0.6	4 (66–78)	−7.6±0.9	
3*f*	*p*-$MeOC_6H_4$	2.64	23.1±0.6	7 (67–79)	−5.6±0.9	
3*g*	*m*-$NO_2C_6H_4$	30.2	[c]			16 (16)[h]
3*h*	*o*-$MeOC_6H_4$	0.21	[c]			19 (87)[h]

[a]From the value at 79.5 °C and an assumed E_a of 22 kcal mol^{-1}.
[b]Only one run in aqueous ethanol; activation data refer to runs in isooctane.
[c]Only one run.
[d]Data from refs. 9*a* and *b*.
[e]Average of values listed in ref. 9*a*, in the temperature range shown.
[f]Highly reliable values calculated from data of ref. 9*b*.
[g]Estimate at unspecified temperature by authors of ref. 9*a*.
[h]Notable inhibitory *ortho* effect (9*a*): $\Delta G^{\ddagger}$ for *o*-nitro compound, 20 kcal mol^{-1} (102°); for *m*-methoxy compound 15 kcal mol^{-1} (1°).

must explain both the most notable trend, the sensitivity to steric assistance shown in the sequence CMe_3 > aryl > Me, and, within the aryl series, the retarding effect of an *ortho* group (surprising in view of the steric effect of CMe_3) and the slight accelerating effect of a *meta* one.

The transition state for isomerization (*e.g.* 7), in which oxygen to carbon bond formation occurs, requires a well developed pyramidal geometry at nitrogen. A large portion of the free energy of activation must involve the energy difference between the planar amide (with sp^2 nitrogen) in the ground state adduct and the nonplanar amide (with sp^3 nitrogen) in the transition state.[2] This difference is simply the conformational energy barrier for amide rotation. A correlation might thus be expected between the latter and the activation energies for isomerization. The barrier heights ($\Delta G_{rot}^{\ddagger}$) for some of the related *N*,*N*-dimethylamides are also given in Table 1. They correspond to rotation rate constants which show, qualitatively at least, the trend found for the isomerization rates.[3]

The interpretation of the effect of R on the isomerization is thus probably the one applicable to amide rotation (9*a*). Bulky alkyl groups (*e.g.* R = CMe_3) are rate enhancing since they destabilize the ground state more than the transition state and aryl groups (phenyl, *m*- or *p*-substituted phenyl) are more effective than simple alkyl groups (*e.g.* R = Me) since ring resonance competes against amide ground state resonance. *o*-Substituted groups, however, create a retardation, ring twisting inhibiting this competing resonance and steric interaction being less severe in the ground state than in the transition state (9*a*). Thus the *o*-methoxy compound 3*h* reacts more slowly than the *p*-isomer 3*f*.

[2]The other contributions to the activation energy of the isomerization, involving changes in bonding type over the six centers, may be much less sensitive to the nature of R. Changes in bonding type, however, must be the dominant factor when R is an alkoxy group, since the cyclopentadiene adducts of azo esters are extremely stable, even though the rotational energy barriers in urethanes are 2–3 kcal mol^{-1} *lower* than in the corresponding amides (9*a*).

[3]Only the value for 3*g* is seriously out of line. Many early data on rotation barriers, however, are of limited reliability (*cf.* ref. 9*b*).

In each of the adducts 3 the group R has an identical neighbor at the adjacent amide link. A more accurate correlation might be observed if there was a common but nonparticipating neighbor throughout the series, as, for example, in the adducts of $RCON{=}NCO_2Et$.

The substituent effect is electronic to some extent as shown by the rate constants for 3*d*–*f*, in which steric effects are presumably negligible. Not enough reliable data are available on the rotational energy barriers of *p*-substituted benzamides to say whether they too are subject to the same electronic effects.

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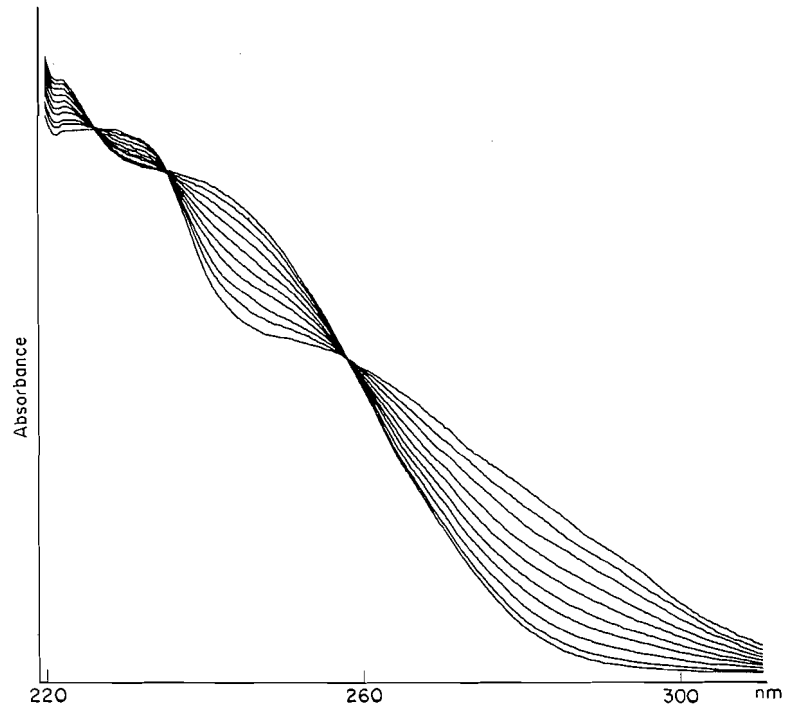

FIG. 1. Isomerization of **9***b* in isooctane at 79.5°. The absorbance decreases with time above 260 nm.

The slightly greater reactivity of **3***g* than **3***e* suggests that the nitro group sterically assists the reaction without causing significant ring twisting. An alternative explanation is that the rate enhancing ring resonance which must put positive charge at *ortho* and *para* carbon atoms would be more effective with the electronegative nitro group in the *meta* rather than the *para* position.

Known values of other amide rotation barriers (**9***a*) permit the prediction that, for example, **3** (R = trichloromethyl) would isomerize very rapidly but **3** (R = 2,4,6-trimethylphenyl) would be very stable.

Isomerization studies on the adducts **9***a* and *b*, in which the degree of ring substitution is intermediate between that in the series **3** and **5**, were done in both isooctane and 71% aqueous ethanol. Clean first-order kinetics (see *e.g.* Fig. 1) were obtained in every case. The rates at 69.5° and the activation parameters are given in Table 2, together with the related data for the unsubstituted counterparts **3***a* and *b*. A remarkable solvent effect is observed.

The ring substituents in **9***a* and *b* are strongly rate enhancing in isooctane though the effect (compared with **3***a* and *b*[4]) is less pronounced for the benzoyl (37-fold) than the acetyl (220-fold) case. The rate ratio of $k_{9a}/k_{9b} = 35$ is again indicative of the greater conformational stability of the *N*-acetyl linkage.

In aqueous ethanol both **9***a* and *b* isomerize extremely rapidly at 69.5° (half lives < 30 s) and *at almost the same rate* in contrast with the 35-fold rate factor in isooctane. The high rates[5] and the levelling effect of the solvent suggest a mechanistic difference in the two solvent systems with the intervention of an intermediate whose formation is not dependent on activation to pyramidal

[4]The rate constant for **3***b* was obtained by extrapolation from the value in refluxing isooctane (99°) using an assumed Arrhenius activation energy of 24 kcal mol^{-1} (*cf.* other E_a values in isooctane from Table 2). It is probably a reasonable estimate.

[5]The ring substituent effect in aqueous ethanol is especially striking for the azodiacetyl adducts with $k_{9b}/k_{3b} = 2500$. Large rate factors with solvent change are not in themselves proof of a change in mechanism. Thus the linear plot of $\Delta H^{\ddagger}$ *vs.* $\Delta S^{\ddagger}$ (isokinetic relationship) in the *ortho*-Claisen reaction of allyl *p*-tolyl ether in a wide range of solvents is indicative of a common mechanism in all of them despite a very large rate spread (10).

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TABLE 2. Solvent effect on rate constants at 69.5 °C and activation parameters for isomerization of *3a* and *b* and **9***a* and *b*

Compound	Solvent	$10^4 k$ (s^{-1})	E_a (kcal mol^{-1})	No. of runs (range, °C)	$\Delta S^{\ddagger}$ at 69.5 °C (cal deg^{-1})
3*a*	Isooctane	0.75	26.7±1.0	4 (69–84)	−0.8±1.5
	Aqueous ethanol	1.17	23.3±1.2	6 (69–84)	−5.6±1.8
3*b*	Isooctane	0.0036[a]			
	Aqueous ethanol	0.10[b]			
9*a*	Isooctane	27.4	23.3±0.4	7 (55–69)	−4.5±1.3
	Aqueous ethanol	267	19.1±0.5	9 (40–70)	−12.2±1.6
9*b*	Isooctane	0.79	25.5±0.8	6 (72–86)	−5.2±2.2
	Aqueous ethanol	253	17.9±0.3	7 (40–67)	−16.0±0.8

[a]Estimated from the value at the b.p. (99 °C) and an assumed E_a of 24 kcal mol^{-1}.
[b]See Table 1, footnote [a].

nitrogen. A plausible species is the dipole **11**, with a rigid (tight ion pair) rather than a freely rotating (about C—N) structure, a requirement implied by the negative entropy of activation[6] and the exclusive formation of a diasteromerically pure oxadiazine in the reaction. Stabilization of **11** would be provided by the substituents in the allylic cation portion, especially the electron releasing methyl group, and by the solvent polarity.

In our earlier work with the keto bridged compounds **5** we failed to isolate **5***a* from the reaction of azodibenzoyl and the cyclone, though its intermediacy in the formation of **6***a* in benzene solution could be detected by n.m.r. spectroscopy. We repeated the reaction with azodiacetyl in the hope that we might isolate **5***b*, provided the stabilizing effect of the acetyl group in nonpolar solvents still persisted in the presence of the keto bridge. However our efforts were vitiated by our inability to obtain a sufficiently concentrated solution of the azo compound (2) and the rather high temperature necessary to generate the cyclone from its dimer, factors which prevented the bimolecular formation of the adduct from being competitive with its unimolecular isomerization. Though there was evidence (n.m.r. spectroscopy) for the presence of **5***b* in small amounts during the reaction only the oxadiazine **10***b* (5) could be finally isolated.

[6]A negative contribution to $\Delta S^{\ddagger}$ could also come from a highly ordered solvation of the dipole. Other interpretations of the value of $\Delta S^{\ddagger}$ cannot be discounted. The transition state may be cyclic and have highly polarized bonding (positive in diene, negative in azodicarbonyl portion) without C—N rupture.

To conclude, the results in this and previous papers have established that the effectiveness of X, R, R_1, and R_2 in promoting the isomerization **1** → **2** decreases according to the following rules, other substituent variables being kept constant in each case:

(*i*) for R = alkyl or aryl rates appear to decrease roughly in the order of the rotation rates of the NCOR groups;

(*ii*) R = alkyl or aryl > R = alkoxy or aryloxy;

(*iii*) for $X = (CH_2)_n$, $n = 1 > n = 2 > n = 3 > n = 4$ (11);

(*iv*) X = CO, R_1 = Ph, R_2 = Me > X = CH_2, R_1 = Ph, R_2 = Me > X = CH_2, $R_1 = R_2$ = H.

Experimental

The following spectrometers were used: for i.r. a Beckman IR 10; for n.m.r. a Varian T60; for mass spectrometry an AE 1 MS 30; for u.v. a Coleman EPS-3T Hitachi. Details for the use of the latter in the variable temperature kinetic analyses have been given earlier (2, 6).

The isomerization of **3***h* was followed by the repeated scan technique as was that of **9***b* in isooctane at 79.5° (Fig. 1); others were followed by continuous external recording (Beckman Ten-Inch Linear Recorder) of the increase or decrease in absorbance at a suitable fixed wavelength: **3***g* at 305 nm (increase); **9***a* at 295 nm (increase); and **9***b* at 285 nm (decrease). The isomerization of **3***b* → **4***b* provides no suitable chromophore for u.v. analysis and was followed by refluxing solutions of **3***b* in isooctane (99°) or in 71% aqueous ethanol (79.5°) and by evaporating aliquots at intervals for analysis by n.m.r. spectrometry.

In the variable temperature experiments rate constants were determined at several temperatures over a convenient range (see Tables 1 and 2) and the Arrhenius activation energy calculated from a least-squares plot. The temperature range was limited at the lower end by the impracticality of very long reaction times, during which recorder drift or other instrumental variation might become significant. An upper limit was imposed by the risk of

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damage to the u.v. cells by maintaining them at temperatures too close to the solvent boiling point.

The isooctane used was of spectrophotometric grade and was dried over sodium. The 71% aqueous ethanol was made by diluting 95% ethanol with one third of its volume of water. Anhydrous magnesium sulfate was used for drying organic solutions. Melting points are uncorrected.

*2,3-Di-m-nitrobenzoyl-2,3-diazabicyclo[2.2.1]hept-5-ene (**3g**)*

1,2-Di-*m*-nitrobenzoylhydrazine, m.p. 246–247° (lit. (12) m.p. 240–242°), was converted into its mercury(II) salt and reacted with bromine in methylene chloride as described for previous azo compounds. Concentration of the filtered solution and addition of carbon tetrachloride gave crude product (60%) which was recrystallized from methylene chloride – carbon tetrachloride (1:2) as orange crystals, m.p. 159–161°; ν (Nujol) 1743 cm^{-1} (C=O); λ_{max} ($CHCl_3$) 485 nm (ε 14).

Addition of cyclopentadiene (20 ml) to a solution of the azo compound (1.0 g, 3.05 mmol) in benzene (120 ml) caused the amber color to fade to pale yellow in 5 min. Evaporation and addition of pentane to the yellow residue gave a colorless precipitate which crystallized as prisms (50%), m.p. 196–198°, from benzene–cyclohexane; ν (Nujol) 1695, 1638 cm^{-1} (C=O); λ_{max} (EtOH) 268 nm; τ ($CDCl_3$) 1.1–2.7 (8 phenyl H, complex multiplet), 3.28 (2 vinyl H, closely spaced triplet), 4.56 (2 tertiary H, closely spaced triplet) 7.78, 8.02 p.p.m. (2 methylene H, AB quartet, J = 9.5 Hz).

Anal. Calcd. for $C_{19}H_{14}N_4O_6$: C, 57.87; H, 3.58; N, 14.21. Found: C, 57.74; H, 3.86; N, 14.26.

*cis-4-m-Nitrobenzoyl-4,4a,5,7a-tetrahydro-2-m-nitrophenylcyclopenta-1,3,4-oxadiazine (**4g**)*

Refluxing a solution of **3g** in chloroform for 6 h gave the oxadiazine quantitatively; it was crystallized from methanol as needles, m.p. 206–208°; ν (Nujol) 1650, 1620 cm^{-1} (C=O, C=N); λ_{max} (EtOH) 265 (ε 22 000), sh 295 nm (ε 16 000); τ ($CDCl_3$) 0.7–2.7 (8 phenyl H, complex multiplet), 3.54 (2 vinyl H), 4.5–5.0 (2 tertiary H), 6.72, 7.48 p.p.m. (2 methylene H, AB quartet with further splittings, J_{AB} = 18 Hz).

Anal. Calcd. for $C_{19}H_{14}N_4O_6$: C, 57.87; H, 3.58; N, 14.21. Found: C, 57.64; H, 3.67; N, 13.98.

*2,3-Di-o-methoxybenzoyl-2,3-diazabicyclo[2.2.1]hept-5-ene (**3h**)*

Lead tetraacetate oxidation of 1,2-di-*o*-methoxybenzoyl hydrazine, m.p. 197–199° (lit. (13) m.p. 202–203°), gave more consistent results than reaction of the mercury(II) salt with bromine.

To a stirred suspension of the hydrazide (1.5 g, 5.0 mmol) in methylene chloride (50 ml) at 0° was added, in portions, lead tetraacetate (2.5 g, 5.6 mmol) followed by cyclopentadiene (20 ml). The initial orange-red color faded over 1 h and the mixture was then kept at 5° for 12 h and filtered. The solution was washed in turn with water and aqueous sodium bicarbonate, and then dried and evaporated to a residue (2.4 g) whose n.m.r. spectrum showed the presence of the expected adduct as well as many methoxy containing impurities. The crude material was treated with cold benzene (10 ml), a small amount of insoluble hydrazide was filtered off, and the solution was chromatographed on silica gel. The use of increasing amounts of ether caused the elution of some of the impurities and then with 20% ether the adduct **3h** (1.35 g, 75%) as a glassy solid. It was purified from chloroform solution (5 ml) by adding hexane (75 ml) with stirring and chilling. The colorless adduct had ν (film) 1660–1700 cm^{-1}, broad (C=O); λ_{max} (EtOH) 284 nm (ε 6100); τ (CCl_4) 2.5–3.4 (8 phenyl H), 3.61 (2 vinyl H), 5.00 (2 tertiary H), 6.22 (6 methoxy methyl, sharp singlet), 7.98, 8.40 p.p.m. (2 methylene H, AB quartet, J_{AB} = 8 Hz); *m/e* 364 (P^+, 17%), 135 (o-$CH_3OC_6H_4CO^+$, 100%).

*cis-4-o-Methoxybenzoyl-4,4a,5,7a-tetrahydro-2-o-methoxyphenylcyclopenta-1,3,4-oxadiazine (**4h**)*

A solution of **3h** (1.0 g) was refluxed in tetrachloroethylene (20 ml) for 2 h and evaporated. The slightly brown residue was twice crystallized from benzene–cyclohexane to give dense colorless prisms of **4h**, a metastable polymorph which softened between 90 and 100°, resolidified, and then had m.p. 148–149° (its i.r. spectrum in Nujol showed minor differences from that of the high melting form). Heating at 100° for 3 h gave stable crystals, m.p. 148.5–149.5°; ν (Nujol) 1653, shs 1647, 1636 cm^{-1} (C=O, C=N); λ_{max} (EtOH) sh 278, 284 nm (ε 9900); τ ($CDCl_3$) 2.3–3.3 (8 phenyl H), 3.71 (2 vinyl H), 4.6–5.2 (2 tertiary H), 6.15 (3 methoxy methyl, sharp singlet), 6.33 (3 methoxy methyl, sharp singlet), 6.82, 7.44 p.p.m. (2 methylene H, AB quartet with further splittings, J_{AB} = 16 Hz).

Anal. Calcd. for $C_{21}H_{20}N_2O_4$: C, 69.22; H, 5.53; N, 7.69. Found: C, 68.93; H, 5.37; N, 7.44.

*2,3-Dibenzoyl-1,4-dimethyl-5,6-diphenyl-2,3-diazabicyclo[2.2.1]hept-5-ene (**9a**)*

A solution of azodibenzoyl (238 mg, 1 mmol) and 1,4-dimethyl-2,3-diphenylcyclopentadiene (246 mg, 1 mmol) in benzene (2 ml) at room temperature slowly faded in color and deposited crystals. After 40 min pentane (10 ml) was added slowly and the colorless product (400 mg, 82%) collected and washed with pentane (a longer reaction time led to some isomerization). Crystallization was effected by dissolving it in benzene – methylene chloride, evaporating till crystallization just began (20 ml), and adding pentane–cyclohexane (1:1, 50 ml) with stirring. The crystalline powder had a m.p. dependent on the rate and time of exposure to heating, *e.g.* 109–111° if raised from room temperature in 15 min (if heating was continued slowly above the m.p. the melt solidified and remelted at 162–163°, the m.p. of the pure isomer); ν (Nujol) 1680, 1629 cm^{-1} (C=O); λ_{max} (EtOH) 233, 270 nm; τ ($CDCl_3$) 2.2–3.1 (20 phenyl H), 7.56, 7.83 (2 methylene H, AB quartet, J_{AB} = 9.2 Hz), 8.32 p.p.m. (6 methyl H, sharp singlet).

*cis-4-Benzoyl-4,4a,5,7a-tetrahydryo-4a,6-dimethyl-2,7,7a-triphenylcyclopenta-1,3,4-oxadiazine (**10a**)*

Heating **9a** above its m.p. as described above, or for 10 min in refluxing benzene, gave the oxadiazine quantitatively. It formed fine prisms from 95% ethanol, m.p. 162.5–163.5°; ν (Nujol) 1655, 1640 cm^{-1} (C=O, C=N); λ_{max} (EtOH) 295 nm (12 100); τ ($CDCl_3$) 2.0–3.2 (20 phenyl H) 6.07, 7.40 (2 methylene H, AX quartet, J = 17 Hz), 8.01 (3 vinyl methyl H, sharp singlet), 8.60 p.p.m. (3 tertiary methyl H, sharp singlet).

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Anal. Calcd. for $C_{33}H_{28}N_2O_2$: C, 81.79; H, 5.82; N, 5.78. Found: C, 81.55; H, 6.05; N, 5.75.

*2,3-Diacetyl-1,4-dimethyl-5,6-diphenyl-2,3-diazabicyclo-[2.2.1]hept-5-ene (**9b**)*

Azodiacetyl was prepared in benzene and the solution evaporated, as described earlier (2), to a concentration of 0.27 *M* (determined by n.m.r. spectrometry against the methyl peak in methyl benzoate as standard). To 15 ml of this solution was added 1,4-dimethyl-2,3-diphenylcyclopentadiene (1.00 g, 1.00 equiv.), and after 2 h at room temperature the yellow solution was evaporated to near dryness and pentane (30 ml) added with trituration and chilling. The colorless product (1.2 g, 82%) was recrystallized by dissolving it in cold benzene and adding a 1:1 solution of cyclohexane–pentane with stirring to give colorless prisms, m.p. 115–116°, if inserted at 110° at a heating rate of 2°/min; ν (Nujol) 1693, 1645 cm^{-1} (C=O); λ_{max} (EtOH) 235 (ε 17 600), 252 nm (ε 14 800); τ ($CDCl_3$—CCl_4) 2.5–3.2 (10 phenyl H), 7.6–8.3 (14 H, including slightly broadened 6 acetyl methyl H at 7.94 and 6 sharp tertiary methyl H at 8.04 p.p.m.).

Anal. Calcd. for $C_{23}H_{24}N_2O_2$: C, 76.64; H, 6.71; N, 7.77. Found: C, 76.33; H, 6.75; N, 7.95.

*cis-4-Acetyl-4,4a,5,7a-tetrahydro-2,4a,6-trimethyl-7,7a-diphenylcyclopenta-1,3,4-oxadiazine (**10b**)*

A sample of **9b** (300 mg) was kept at room temperature overnight in methanol (20 ml). Evaporation followed by two crystallizations of the residue from aqueous methanol gave the oxadiazine as large prisms, m.p. 160–161°; ν (Nujol) 1686, 1655 cm^{-1} (C=O, C=N); λ_{max} (EtOH) 243 nm (ε 21 000); τ ($CDCl_3$—CCl_4) 2.3–3.2 (10 phenyl H), 6.27, 7.60 (2 methylene H, AX quartet, J = 17 Hz), 7.70 (3 acetimidoyl methyl H, sharp singlet), 8.03 (3 acetyl methyl H, slightly broadened singlet), 8.48 (3 vinyl methyl H, sharp singlet), 8.80 p.p.m. (3 tertiary methyl H, sharp singlet).

Anal. Calcd. for $C_{23}H_{24}N_2O_2$: C, 76.64; H, 6.71; N, 7.77. Found: C, 76.86, H, 6.68; N, 8.08.

*cis-4-Acetyl-4,4a,5,7a-tetrahydro-2,4a,6-trimethyl-7,7a-diphenylcyclopenta-1,3,4-oxadiazin-5-one (**6b**)*

A solution of the dimer of 2,5-dimethyl-3,4-diphenylcyclopentadienone (1.30 g, 5 mmol cyclone monomer) in tetrachloroethylene (64 ml) containing azodiacetyl (6.7 mmol) failed to react on standing at room temperature for 20 h. When the temperature was raised to 40° n.m.r. spectrometry showed in the methyl region the four peaks of the dimer and the four peaks (two coincident) of the oxadiazine **6b** but also two other singlets at 7.80 and 7.98 τ, attributable to the adduct **5b**. After 3 days the estimated percentage composition was **5b**:**6b**:cyclone = 13:25:62, the proportion of **5b** not being exceeded thereafter.

At 85° reaction was complete in 12 h. Evaporation of the solvent and trituration of the residue with pentane gave the oxadiazine (1.77 g, 94%) which formed prisms from cyclohexane, m.p. 168–169°; ν (Nujol) 1730, 1678, 1664 cm^{-1} (keto and amide C=O, C=N); λ_{max} (EtOH) 242 (ε 15 600), 283 nm (ε 12 600); τ (CCl_4) 2.5–3.1 (10 phenyl H), 7.87 (3 acetimidoyl and 3 acetyl H, coincident, sharp singlet), 8.23 (3 vinyl methyl H, sharp singlet), 9.03 p.p.m. (3 tertiary methyl H, sharp singlet), but all four methyl peaks separated in benzene at 7.76, 7.96, 8.49, and 8.81 p.p.m. (assignments in order as before).

Anal. Calcd. for $C_{23}H_{22}N_2O_3$: C, 73.78; H, 5.92; N, 7.48. Found: C, 73.55; H, 5.90; N, 7.69.

We thank the National Research Council of Canada and the University of Waterloo for financial assistance.

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