

Photochemical Rearrangement of Bicyclo[3,3,1]nona-3,7-diene-2,6-diones

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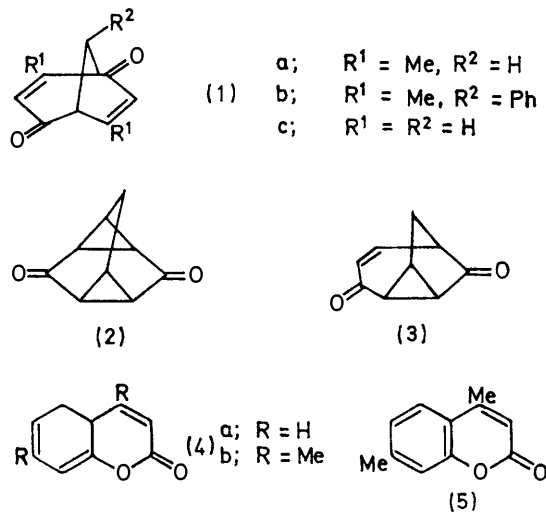
Bicyclo[3,3,1]nona-3,7-diene-2,6-dione (1c) rearranges photochemically to the triasteranedione (2) (tetracyclo[3,3,1,0^{2,8},0^{4,6}]nonane-3,7-dione) by successive 1,2-acyl shifts and to a dihydrocoumarin by a 1,5-acyl shift. The 4,8-dimethyl analogue (1a) similarly gives a substituted triasteranedione (7) and a dimethyldihydrocoumarin, but the 4,8-dimethyl-9-phenyl compound (1b) gives, in addition to a triasteranedione (11), the epimeric diones (14) and (15) (4,8-dimethyl-6-phenylbicyclo[3,3,1]nona-3,7-diene-2,9-diones), products of a 1,3-acyl shift; no product of a 1,5-acyl shift is observed. Mechanistic aspects of these and related rearrangements are discussed.

THE intense yellow colour of the ketones 4,8-dimethylbicyclo[3,3,1]nona-3,7-diene-2,6-dione (1a) and its 9-phenyl analogue (1b) was noted¹ in 1903; recently the structures of these compounds have been rigorously assigned.² We were interested in the unusual combination of structural features in which the chromophores of both an $\alpha\beta$ -unsaturated ketone and a $\beta\gamma$ -unsaturated ketone are present. The colour and the u.v. spectra indicated considerable interaction of the chromophores, and suggested that the ketones might be unusually photosensitive. The photorearrangements of the ketones (1a and b) and the unsubstituted dione (1c) are described here.

Bicyclo[3,3,1]nona-3,7-diene-2,6-dione (1c) was irradiated in benzene through Pyrex. Reaction was rapid and two major photoproducts were formed.³ Chromatography enabled the ready isolation of a solid, m.p. 153–155°, shown by mass spectrometry to be an isomer of the dione (1c). Its n.m.r. spectrum showed only a broad multiplet, at τ 7.58–7.63, indicating the absence of olefinic protons. The i.r. (ν_{\max} 1690 cm^{-1}) and u.v. [λ_{\max} 288 nm (ϵ 105)] spectra were consistent with the absence of unsaturation. The absence of double bonds suggested the presence of a tetracyclic diketone, and in particular of the triasteranedione (2), the product of successive 1,2-shifts which might be formed *via* the tricyclic ketone (3). Comparison of our photoproduct with an authentic sample of the triasteranedione showed their identity.

The second photoproduct could not be obtained by chromatography. G.l.c. indicated that it was rapidly

converted in air into a further product. Chromatography of the crude reaction mixture afforded coumarin. G.l.c. established that the second photoproduct



was the precursor of coumarin and it was concluded that it was a dihydrocoumarin, possibly (4a) which is isomeric with the dione (1c).

Similarly, 4,8-dimethylbicyclo[3,3,1]nona-3,7-diene-2,6-dione (1a) was irradiated in benzene through Pyrex; again two photoproducts were obtained. Chromatography of the crude reaction mixture afforded 4,7-dimethylcoumarin (5) and an impure oil, which on exposure to air rapidly gave 4,7-dimethylcoumarin. The second

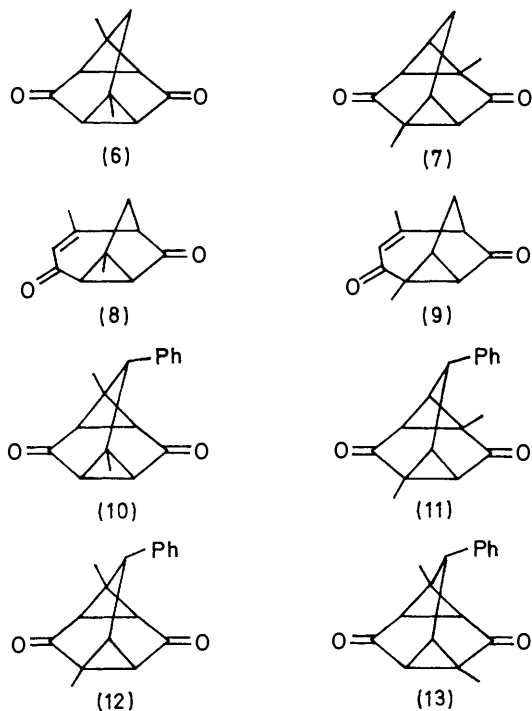
¹ E. Knoevenagel, *Ber.*, 1903, **36**, 2136.

² P. A. Knott and J. M. Mellor, *J. Chem. Soc. (C)*, 1971, 670.

³ P. A. Knott and J. M. Mellor, *Tetrahedron Letters*, 1970, 1829.

photoproduct, an oil, was shown by mass spectrometry to be an isomer of the dione (1a). Again i.r. (ν_{\max} 1690 cm^{-1}) and n.m.r. [τ 7.96, 8.06, and 9.06 (sharp s)] spectra indicated the absence of unsaturation. Consistent with the spectra, and by analogy with the reaction of the dione (1c), the unstable photoproduct is considered to be a dihydrocumarin, possibly (4b), and the saturated dione to be the triasteranedione (6) or (7).

The tetracyclic structures could originate either by two successive 1,2-alkyl shifts, *i.e.* migration of the 1,9-bond followed by migration of the 5,9-bond [to give (6)], or by two successive 1,2-acyl shifts, *i.e.* migration of the 1,2-bond followed by migration of the 5,6-bond [to give (7)]. A discrimination between the two structures is not possible from the observed spectra, but might have been possible if a tricyclic intermediate had been



isolable. A 1,2-alkyl shift leads to structure (8) from the dione (1a) but a 1,2-acyl shift leads to the isomeric tricyclic ketone (9). In the event, even after irradiation for only a short period, we were unable to isolate any tricyclic intermediate.

In order to establish the rearrangement pathway we irradiated the dione (1b). Among the possible tetracyclic products, the dione (10) has a plane of symmetry such that the two methyl groups have an identical environment, but the dione (11) has the two methyl groups in different environments. The diones (12) and (13), products of successive 1,2-alkyl and 1,2-acyl shifts,

⁴ H. F. Zimmerman, R. D. Rieke, and J. R. Scheffer, *J. Amer. Chem. Soc.*, 1967, **89**, 2033.

⁵ R. B. Woodward and R. Hoffman, 'The Conservation of Orbital Symmetry,' Academic Press, New York, 1970.

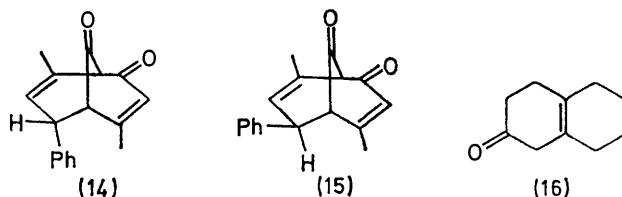
⁶ D. I. Schuster, M. Axelrod, and J. Auerbach, *Tetrahedron Letters*, 1963, 1911.

⁷ J. J. Hurst and G. H. Whitham, *J. Chem. Soc.*, 1963, 710.

were not considered, as such a pathway was not observed on photorearrangement of (1a).

Irradiation of the dione (1b) led to three photoproducts and chromatography afforded a tetracyclic dione. The n.m.r. spectrum showed no signals attributable to olefinic protons; a pair of signals corresponding to six protons was observed at τ ca. 8.7. In deuteriochloroform the signals were separated by 3.2 Hz, but in pyridine the separation was 1.4 Hz. The signals are therefore associated with methyl groups in different environments, and the photoproduct of the dione (1b) is assigned the structure (11). By analogy the product from the dione (1a) must be (7), and the triasteranediones are obtained by successive 1,2-acyl shifts.

The two other photoproducts from the dione (1b) have similar spectra. The i.r. spectrum of each (ν_{\max} 1675 and 1725 cm^{-1}) indicates the presence of an unsaturated and a saturated ketone system. The n.m.r. spectrum has signals attributable to two olefinic protons. The mass spectra indicate that the products are isomeric with the dione (1b) and therefore they must be bicyclic. The photoproduct of m.p. 146–148° is assigned the structure (14) and the product of m.p. 170–172° structure (15), on the basis of observed coupling constants and the shielding effects attributable to the phenyl group.



The identification of the photoproducts leads to a number of observations. The diones (1a–c) give products by successive 1,2-acyl shifts; the diones (1a) and (1c) give photoproducts by a 1,5-acyl shift but not by a 1,3-acyl shift, and the dione (1b) gives photoproducts by a 1,3-acyl shift but not by a 1,5-acyl shift.

These results contrast with previous observations concerning the photoreactivity of $\alpha\beta$ -unsaturated ketones and $\beta\gamma$ -unsaturated ketones. The major pathway for the rearrangement of $\alpha\beta$ -unsaturated ketones gives cyclopropyl ketones.⁴ If the dione (1b) is considered as an $\alpha\beta$ -unsaturated ketone, the expected migration in an allowed [$\sigma_{2a} + \pi_{2a}$] process⁵ would be the 1,2-acyl shift not the 1,2-alkyl shift. The former is observed. Two distinct pathways are observed for $\beta\gamma$ -unsaturated ketones. Rearrangement by a 1,3-acyl shift leads to isomeric $\beta\gamma$ -unsaturated ketones^{6–9} and rearrangement by a 1,2-acyl shift leads to cyclopropyl ketones.^{10–12} The 1,3-acyl shift appears to be a reaction of the singlet state and to be found in those $\beta\gamma$ -unsaturated ketones which

⁸ L. A. Paquette and R. F. Eizember, *J. Amer. Chem. Soc.*, 1967, **89**, 6205.

⁹ E. Baggiolini, and K. Schaffner, and O. Jeger, *Chem. Comm.*, 1969, 1103.

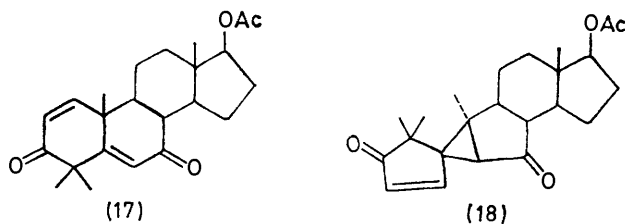
¹⁰ J. R. Williams and H. Ziffer, *Tetrahedron*, 1968, **24**, 6725.

¹¹ J. Ipaktchi, *Tetrahedron Letters*, 1969, 2153.

¹² K. Kojima, K. Sakai, and K. Tanabe, *Tetrahedron Letters*, 1969, 3399.

show an enhanced and red-shifted $n \rightarrow \pi^*$ transition. The 1,2-acyl shift is observed either with ketones, such as the octalone (16), which show neither enhancement nor red shift in the $n \rightarrow \pi^*$ transition, or when irradiation is carried out in the presence of a triplet sensitiser such as acetone.^{9,11} The 1,2-acyl shift is probably a reaction of the triplet state. The photorearrangement of the dione (1b) is unusual, as both 1,3- and 1,2-rearrangements are observed simultaneously. Although most of our reactions were conducted in benzene we have examined the rearrangement of the dione (1b) in acetic acid, methanol, ether, and cyclohexane but find that in all cases both rearrangements are observed. Whether a $\beta\gamma$ -unsaturated ketone gives products of 1,3-rearrangement through the singlet or products of 1,2-rearrangement through the triplet, by direct irradiation, probably depends upon the balance between the rate of photoreaction from the singlet and the rate of intersystem crossing. Our observation of considerable 1,2-rearrangement may indicate that intersystem crossing is particularly facilitated.

Two epimeric products (14) and (15) are obtained by 1,3-rearrangement of the dione (1b). They may arise as primary photoproducts by the two possible stereospecific rearrangements, or by a non-stereospecific rearrangement, or one may be a secondary photoproduct. There is no decisive evidence but we favour the first explanation. However the photoproducts (14) and (15) and the dione (1b) are in photoequilibrium.



The dionedione (17), in which the two enone chromophores are held in a different structural relationship undergoes photorearrangement *via* the excited triplet state to give the cyclopropyl ketone (18) as the primary photoproduct.¹³ Such a process, requiring bonding between the β -positions of the enone chromophores, is less likely with the bicyclic dionediones for structural reasons.

EXPERIMENTAL

I.r. spectra were measured for chloroform solutions with a Unicam SP 200 spectrophotometer. N.m.r. spectra were measured for deuteriochloroform solutions with a Varian HA 100 spectrometer. U.v. spectra were measured for solutions in ethanol with a Unicam SP 800 spectrophotometer. Mass spectra were measured with an A.E.I. MS12 spectrometer. Photochemical reactions were conducted, unless otherwise stated, by irradiation through Pyrex under nitrogen with a 120 W medium-pressure lamp. Light petroleum refers to the fraction b.p. 40–60°.

Irradiation of 4,8-Dimethylbicyclo[3,3,1]nona-3,7-diene-2,6-dione (1a).—The dione (1a) (1.06 g) in benzene (300 ml) was irradiated for 66 h. Removal of the solvent under reduced pressure gave a yellow oil, which on chromatography

on silica gel afforded five fractions. Elution with ether-light petroleum (15 : 85) afforded 4,7-dimethylcoumarin (131 mg) which gave white needles (80 mg), m.p. 133–134° (from ether-light petroleum) (lit.,¹⁴ 132°), ν_{\max} 1720, 1700, and 1620 cm^{-1} , τ 2.5–3.0 (3H, m), 3.80 (1H), and 7.58 (6H), identical (mixed m.p., i.r. and n.m.r. spectra) with an authentic sample prepared from *m*-cresol.¹⁴ Elution with ether-light petroleum (25 : 75) gave an oil (127 mg) which rapidly decomposed on exposure to air to give 4,7-dimethylcoumarin (5). By chromatography under nitrogen it was possible to isolate a sample shown by g.l.c. to be about 50% pure. In solution in ether this sample was converted in 30 min on exposure to air into 4,7-dimethylcoumarin (5). Elution with ether-light petroleum (50 : 50) afforded unchanged starting material (285 mg). Elution with ether-light petroleum (75 : 25) afforded the triasteranedione (7) (206 mg) as an oil, ν_{\max} 1690 cm^{-1} , m/e 176 (M^+), τ 7.96 (2H, m), 8.06 (4H, m), and 9.06 (6H, s). Elution with methanol gave a yellow oil, assumed to be polymeric.

Irradiation of 4,8-Dimethyl-9-phenylbicyclo[3,3,1]nona-3,7-diene-2,6-dione (1b).—The dione (1b) (5.0 g) in benzene (300 ml) was irradiated for 5 days. Removal of the solvent under reduced pressure gave partially crystalline material which on chromatography on silica gel afforded four fractions. Elution with ether-light petroleum (15 : 85) afforded 4,8-dimethyl-6-endo-phenylbicyclo[3,3,1]nona-3,7-diene-2,9-dione (14) (426 mg), which gave yellow crystals, m.p. 146–148° (from ether-light petroleum), ν_{\max} 1725 and 1690 cm^{-1} , λ_{\max} 328 nm (ϵ 256), m/e 252 (M^+), τ 2.64–2.96 (5H, m), 3.89 (1H, m), 4.41 (1H, s), 5.7 (1H, m), 6.50 (1H, s), 6.26 (1H, q, J 6.3 and 1.3 Hz), 8.09 (3H, q, J 2.6 and 1.5 Hz), and 8.88 (3H, d, J 1.3 Hz). Further elution with ether-light petroleum (15 : 85) afforded 4,8-dimethyl-6-exo-phenylbicyclo[3,3,1]nona-3,7-diene-2,9-dione (15) (512 mg), which formed pale yellow crystals, m.p. 170–172° (from ether-light petroleum) (Found: C, 80.7; H, 6.4. $\text{C}_{17}\text{H}_{16}\text{O}_2$ requires C, 80.9; H, 6.4%), ν_{\max} 1725 and 1690 cm^{-1} , λ_{\max} 325 nm (ϵ 223); m/e 252 (M^+), τ 2.66–2.92 (5H, m), 3.99 (1H, m), 4.60 (1H, d, J 3.3 Hz), 6.07 (1H, m), 6.46 (1H, s), 6.95 (1H, s), 7.81 (3H, d, J 1.4 Hz), and 8.14 (3H, t, J 1.5 Hz). Elution with ether-light petroleum (25 : 75) afforded starting material (1.85 g). Elution with ether-light petroleum (50 : 50) afforded 2,6-dimethyl-9-phenyltetracyclo[3,3,1,0^{2,3},0^{4,6}]nonane-3,7-dione (11) (1.2 g), m.p. 146–148° (from ether) (Found: C, 80.9; H, 6.2. $\text{C}_{17}\text{H}_{16}\text{O}_2$ requires C, 80.9; H, 6.4%), ν_{\max} 1685 cm^{-1} , λ_{\max} 252 (ϵ 600) and 290 nm (200), m/e 252 (M^+), τ 2.5–2.9 (5H, m), 6.17 (1H, s), 7.68 (4H, m), 8.69 (3H, s), and 8.72 (3H, s).

When the dione (1b) was irradiated for shorter periods in benzene, chromatography afforded no new products. The dione (1b) was also irradiated in acetic acid, methanol, ether, and cyclohexane; in each case chromatography of the crude products afforded the tetracyclic dione (11) and the bicyclic diones (14) and (15). The distribution of products showed no marked solvent dependence.

Irradiation of 4,8-Dimethyl-6-endo-phenylbicyclo[3,3,1]nona-3,7-diene-2,9-dione (14).—The dione (14) (15 mg) in benzene (1 ml) was irradiated for 13 h. G.l.c. analysis showed that after 5 h (in addition to starting material) the bicyclic dione (15) and the tetracyclic dione (11) were present. After 13 h the tetracyclic dione (11) was the major product.

¹³ S. Domb and K. Schaffner, *Helv. Chim. Acta*, 1970, **53**, 1765.

¹⁴ K. Fries and W. Klostermann, *Ber.*, 1906, **39**, 871.

Irradiation of 4,8-Dimethyl-6-exo-phenylbicyclo[3,3,1]nona-3,7-diene-2,9-dione (15).—Similarly the dione (15) (27 mg) in benzene (1 ml) was irradiated for 13 h. G.l.c. analysis showed that after 13 h the tetracyclic dione (11) was the major product.

Irradiation of Bicyclo[3,3,1]nona-3,7-diene-2,6-dione (1c).—The dione (1c) (3 g) in benzene (300 ml) was irradiated for 24 h. Removal of the solvent under reduced pressure gave an oil which on chromatography on silica gel afforded two products. Elution with benzene-chloroform (30:70) afforded coumarin (30 mg), m.p. 67°, identical (mixed m.p.,

i.r. and n.m.r. spectra) with an authentic sample. Elution with chloroform afforded tetracyclo[3,3,1,0,^{2,8},0^{4,6}]nonane-3,7-dione (2) (1.75 g), which formed white crystals, m.p. 154—156° (from ether-chloroform) (lit.,¹⁵ 155°), ν_{\max} 1690 cm^{-1} , λ_{\max} 266 nm (ϵ 105), m/e 148 (M^+), τ 7.58—7.63 (8H), identical (mixed m.p., i.r. spectrum, and t.l.c.) with an authentic sample (comparison by Professor E. Vedejs).

[1/1700 Received, 17th September, 1971]

¹⁵ E. Vedejs, *Tetrahedron Letters*, 1969, 5045.