Tetrahedron Letters No.21, pp. 1829-1832, 1970. Pergamon Press. Printed in Great Britain.

PHOTOCHEMICAL REARRANGEMENT OF BICYCLO-(3, 3, 1)-NONA-3, 7-DIENE-2, 6-DIONES TO TRIASTERANEDIONES.

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(Received in UK 23 March 1970; accepted for publication 3 April 1970)

The recent synthesis of triasteranes[1] leads us to report our findings concerning the photochemistry of bicyclo-(3, 3, 1)-nona-3, 7-diene-2, 6-diones. Rearrangement affords triasteranediones and this route constitutes a third method of generation of this strained skeleton[2].

Bicyclo-(3, 3, 1)-nona-3, 7-diene-2, 6-dione (1), m.p. 81-84°; M^+ 148; was prepared from the dienol acetate of bicyclo-(3, 3, 1)-nona-2, 6-dione[3] by treatment with N-bromosuccinimide in carbon tetrachloride under carefully controlled conditions to give intermediate dibromoenol acetates, which were not isolated. Hydrolysis with aqueous acid gave in 50% overall yield the required dienedione (1). The attempted preparation of the same dienedione (1) by bromination of bicyclo-(3, 3, 1)-nona-2, 6-dione with bromine in acetic acid[4], followed by dehydrobromination under a variety of conditions was less satisfactory.

Irradiation of the dienedione (1) in benzene through pyrex led to the rapid disappearance of starting material and formation of two major photoproducts. One, a dihydrocoumarin, was rapidly oxidized and in a chromatographic separation was isolated as coumarin. The other, m.p. 153-155°; M^+ 148; ν_{max} 1690 cm.$^{-1}$; λ_{max} 288 nm. (ϵ 105); and τ 7.58-7.63 (broad multiplet), was isolated in 40% yield. The spectral data are consistent with the structure (2). Confirmation that the photoproduct was triasteranedione (2) was obtained by comparison with an authentic sample - no depression of the mixed melting point and identical t.l.c. behaviour[5].

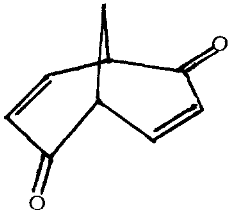
Triasteranedione may be formed by two possible routes: by two successive 1,2 acyl shifts, typical of the photochemistry of β-γ unsaturated ketones[6], via the intermediate (3), or by two successive 1,2 alkyl shifts, typical of the photochemistry of α-β-unsaturated ketones[7], via the same intermediate (3). A discrimination between the two pathways is not possible with the unsubstituted dienedione (1) but is possible by irradiation of the substituted dienedione (4)[8]. Two successive 1,2 acyl shifts would lead to formation of the dione (5) but two successive 1,2 alkyl shifts would lead to formation of the dione (6).

Irradiation of the dienedione (4) gave three major photoproducts, a dione, m.p. 146-148°; M^+ 252; ν_{max} 1635, 1675 and 1725 cm.$^{-1}$; λ_{max} 253 nm. (ε 5200), 260 nm. (ε 4850), 265 nm. (ε 4120) and 328 nm. (ε 256); τ 2.6-3.0 (5H), 3.91 (1H), 4.41 (1H), 5.76 (1H), 6.50 (1H), 6.62 (1H) a quartet J = 6.3 Hz and J = 1.3 Hz, 8.10 (3H) a quartet J = 2.6 Hz and J = 1.5 Hz, and 8.89 (3H) a doublet J = 1.3 Hz, a dione m.p. 170-172°; M^+ 252; ν_{max} 1635, 1675 and 1725 cm.$^{-1}$; λ_{max} 260 nm. (ε 2875), 265 nm. (ε 2635) and 335 nm. (ε 223); τ 2.6-3.0 (5H), 4.00 (1H), 4.50 (1H), 6.06 (1H), 6.46 (1H), 6.96 (1H), 7.81 (3H) a doublet J = 1.4 Hz and 8.15 (3H) a triplet J = 1.65 Hz., and a triasteranedione, m.p. 146-148°; M^+ 252, ν_{max} 1685 cm.$^{-1}$; λ_{max} 252 nm. (ε 600) and 290 nm. (ε 200); τ 2.6-2.9 (5H), 6.17 (1H), 7.68 (4H) a multiplet, 8.69 (3H) a singlet, and 8.72 (3H) a singlet.

The triasteranedione, m.p. 146-148°, is characterised by the n.m.r. spectrum. In $CDCl_3$ the methyl signals are separated by 3.2 Hz but in pyridine the same methyl signals are separated by 1.6 Hz. Hence the signals arise from two methyl groups in different environments and as the triasteranedione (6) is characterised by a plane of symmetry this structure may be rejected. Further in pyridine the signal of the benzylic proton appears as a triplet J ~ 1.5 Hz. The photoproduct must be the triasteranedione (5) and hence the rearrangement must have proceeded by two successive 1,2-acyl shifts rather than by 1,2-alkyl shifts, and this shift corresponds to a photochemically allowed ($\sigma^2 + \pi^2$) addition as a concerted process.

The two other photoproducts from the dienedione (4) have similar spectral characteristics showing an α-β-unsaturated ketone ν_{max} 1675 cm.$^{-1}$ and a second ketone ν_{max} 1725 cm.$^{-1}$, and in the n.m.r. spectrum two signals of vinyl protons are observed. Hence the ketones must be bicyclic and the structures (7) and (8) are indicated. A distinction between the structures may be made by considering two features of the n.m.r. spectra . In the dione m.p. 146-148° the coupling constant between the benzylic proton at 5.76 τ and the adjacent bridgehead proton at 6.62 τ is 6.3 Hz, whereas in the dione m.p. 170-172° no coupling between the benzylic proton at 6.06 τ and the bridgehead proton at 6.96 τ is observed. The dione m.p. 170-172° is therefore (7) and the dione m.p. 146-148° is (8). Coupling constants in a similar system are respectively 6.4 Hz and 0 Hz[9]. Further confirmation of the structure is given by the shielding by the endo phenyl group of the methyl group substituted at the β position of the α-β unsaturated ketone. The signal of this methyl group with the phenyl group exo-dione (7) is situated at 7.81 τ but with the phenyl group endo it is shifted to 8.89 τ.

The unsaturated ketones (7) and (8) are formed by 1,3 acyl shifts. Thus three rearrangements of bicyclo-(3,3,1)-nona-3,7-diene-2,6-diones have been found: 1,2 acyl shifts leading to triasteranediones, 1,3 acyl shifts leading to the bridgehead ketones (7) and (8), and 1,5 acyl shifts leading to dihydrocoumarins. The mechanism of these rearrangements is the subject of further investigations.



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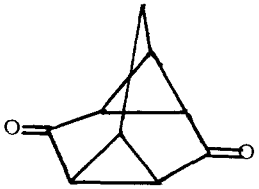

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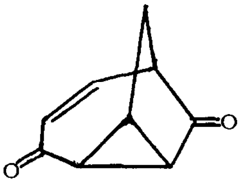

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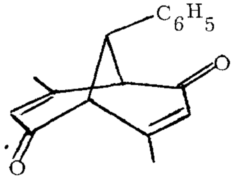

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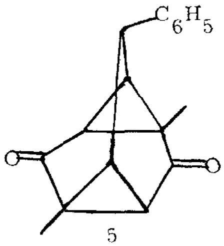

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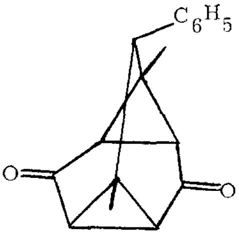

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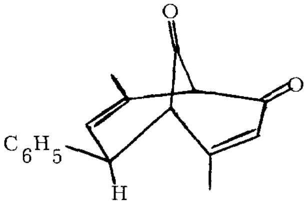

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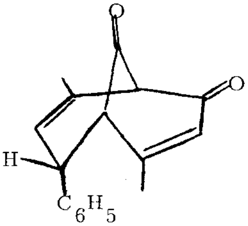

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