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EVIDENCE FOR THE EXPULSION OF bis-CO FROM BRIDGED α-DIKETONES

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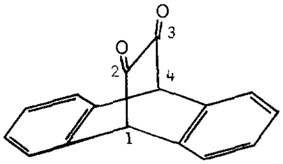
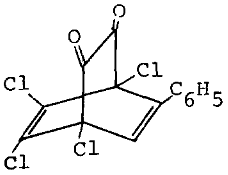
Thermal expulsion of the carbonyl bridge from norbornene-7-ones and norbornadiene-7-ones is a well documented process (1). Especially facile is the thermal decarbonylation (1) of the latter systems. Since a similar double bond arrangement is present in bicyclo[2,2,2]octadiene-2,3-diones thermal bridge expulsion might be expected for these compounds. However, bridged α-diketones of this nature are reported to melt without noticeable decomposition. Presumably, for this reason only the pyrolytic reaction of one bicyclo[2,2,2]octadiene-2,3-dione was described (2).

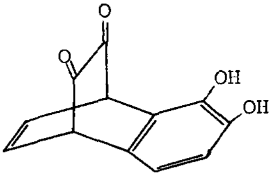
We prepared four bicyclo[2,2,2]octadienediones, I-IV, with the intention to examine the pyrolytic and photolytic bridge expulsion and particularly to establish the nature of the expelled fragment.



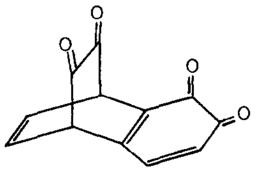
I



II



III



IV

Dibenzobicyclo[2,2,2]octadiene-2,3-dione (I), m.p. (3) 200°, only charred upon heating at 350°, 80% of unchanged diketone was recovered. Pyrolysis of II, m.p. (4) 120°, at 180° gave evolution of CO and a black pyrolyzate from which 32% of 2,3,4,5-tetrachlorobiphenyl was isolated. Compound III (2) decomposed at 220° with evolution of CO and formation of 1,2-dihydroxynaphthalene; heating of IV (2) at 230° gave evolution of CO and a black tar.

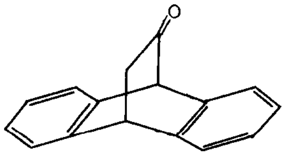
These results prove that pyrolysis of bicyclo[2,2,2]octadienediones leads to bridge expulsion but under more rigorous conditions than norbornadiene-7-ones.

Surprisingly, photolysis of the bridged α-diketones I-IV in benzene solution gave a smooth evolution (5) of CO. Besides carbon monoxide the irradiation (6) of I gave a quantitative yield of anthracene, II produced 97% of tetrachlorobiphenyl, III yielded 1,2-dihydroxynaphthalene (95% crude, 53% pure product) and IV gave 1,2-α-naphthoquinone isolated as benzo[α]phenazine (43%). This photo-induced bridge expulsion sharply contrasts to the behaviour of other bridged α-diketones as for instance camphorquinone which shows no detectable transformation (7) under photolytic conditions mentioned for I-IV.

The mass spectrum of I provides valuable information about the nature of the expelled species. The predominant fragmentation of the parent ion (m/e 234) is the loss of 2 CO, the intensity of the fragment at m/e 206 (M-CO) is negligible. The metastable peak at 135.40 which accompanies the transition $234^+ \rightarrow 178^+ + 56$ suggests the simultaneous loss of two CO units. Furthermore, a small but pertinent peak was present at m/e 56 corresponding with the ion $C_2O_2^+$ as was established with exact mass measurement. These mass spectral data provide evidence for the fact that the α-diketo bridge is expelled, at least in part, as one fragment C_2O_2. Camphorquinone shows in the mass spectrum a successive loss of CO molecules.

Accepting a close parallel between the behaviour of compounds under electron impact and photolytic conditions (8), it seems likely that the photo-induced bridge expulsion of I-IV occurs through extrusion of C_2O_2, or bis-CO as we prefer to name it.

Support for the fact that the bridge connecting 1,2- and 3,4-bond are cleaved (concerted or stepwise) prior to the bridge forming 2,3-bond was found by irradiation of a bridged monoketone, i.c. V (9). Photolysis of V in benzene solution (6) (10%) for one hour gave 44% of anthracene, 19% of dianthracene and 15% of starting material.

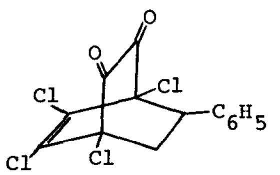


V

The expelled species, ketene, was carried with a nitrogen stream into water and analyzed as acetic acid by titration with base. A 60% yield of ketene was found. In the mass spectrum of V the main fragmentation of the parent ion (m/e 220) was the loss of ketene.

Murray and Hart (10) very recently observed photolytic loss of dimethylketene from some bicyclo[2,2,2]octadienones. The ease with which this ketene is formed by this photochemical reverse Diels-Alder reaction is in strong contrast to the high temperature required for the thermal reaction.

Aromatization may be considered as the important driving force for the reactions described above. However, irradiation (6) of a bicyclo[2,2,2]octene-2,3-dione, i.c. VI (4), in benzene solution for 0.5 hr also gave a smooth decarbonylation yielding 1,2,3,4-tetrachloro-5-phenyl-1,3-cyclohexadiene (11) in 60%. Application of the Woodward-Hoffmann orbital symmetry considerations (12) to these α-diketones shows that concerted fragmentation should be allowed to occur thermally in a disrotatory manner. It is likely that photo-excitation of these bridged α-diketones is introduced primarily through the carbonyl group. Then (13), on basis of molecular orbital correlation diagrams a concerted reverse 2 + 4 cycloaddition is permitted in the stereochemically favourable disrotatory fashion.



VI

Attempts to trap bis-CO during the irradiation of II by chlorine or dienes as cyclopentadiene and 2,3-dimethylbutadiene, failed. Staudinger and Anthes (14) reported as early as 1913 an approach to bis-CO in which oxalylbromide was treated with mercury. The initial formation of bis-CO was assumed, but only CO could be detected. However, Hoffmann type calculations of energy on a complex formed by combination of two molecules of CO suggests that bis-CO could be stable relative to CO even in the ground state.

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6. During all photolysis experiments a Hanau S-81 UV lamp with a Pyrex filter was used.
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