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PHOTOCHEMISTRY OF BICYCLO[3.3.1] NONANE-2,9-DIONE AND RELATED COMPOUNDS

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Abstract—A difficulty enolizable β-diketone, bicyclo[3.3.1]-nonane-2,9-dione (I), undergoes facile α-cleavage to isomerize into two enol lactones II (major) and III. The reaction is accompanied by loss of the carbonyl at C_9 position leading to bicyclo[3.3.0] octan-2-one (IV) and 3-(l-cyclopentenyl) propanal (V) as byproducts. The ketone IV is photolabile and is converted slowly into the aldehyde V. Bicyclo[3.3.1.]nonan-2-one (VIII) also undergoes α-cleavage giving 3-(3-cyclohexenyl)propanal (IX), whereas the 9-keto isomer (X) is photostable under the same conditions. The photoreaction of bicyclo[3.2.1.]octane-2,8-dione (XI) proceeds sluggishly to afford the lactone of 3-(2-hydroxy-2-cyclopentenyl)propionic acid (XII).

WHEREAS the thermal reactions of bicyclo[3.3.1]nonane derivatives are well known, few reports have been published on its photochemical behaviour.[1] This paper describes the photochemical reactions of bicyclo[3.3.1]nonane-2,9-dione (I) and related compounds.

When a 1% benzene or n-hexane soln of bicyclo[3.3.1]nonane-2,9-dione (I)[2] was irradiated for 12 hr (74% conversion) with a high pressure mercury arc through a Pyrex filter, two isomeric enol lactones (II, 43%) and (III, 1·5%) were obtained together with a bicyclic ketone[3] (IV, 5·6%) and an unsaturated aldehyde (V, 8·0%).

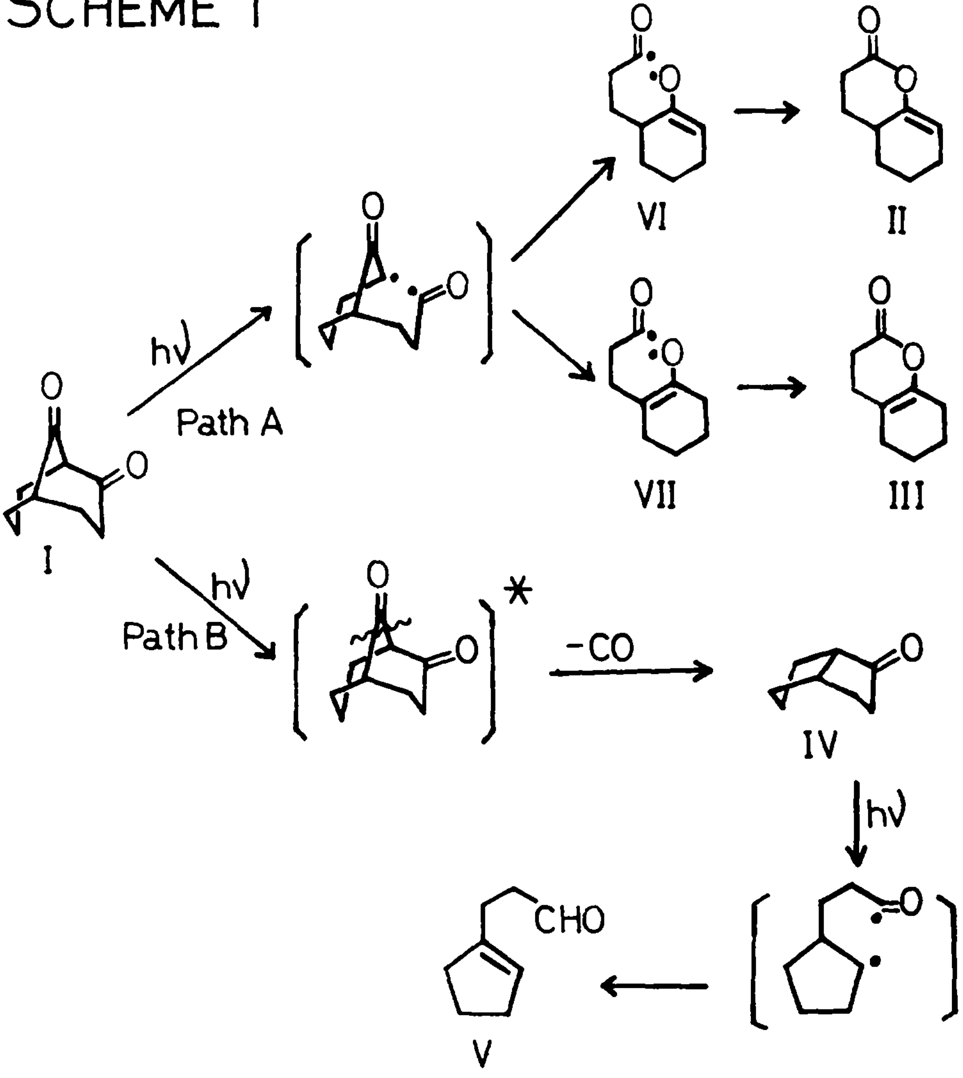
The lactones II and III are both identical with the authentic samples.[4] Although recent reports[5,6] indicate that bicyclo[3.3.1]non-l-ene exists contrary to Bredt's rule, IR and NMR of I failed to indicate the presence of the corresponding enol in any detectable quantity. The fact that the predominant product is the thermodynamically less favourable II rather than III is reminiscent of the photochemical behaviour of other non-enolizable β-diketones.[7] The structure of the unsaturated aldehyde (V) was supported by elemental analysis, IR and NMR. An unsaturated alcohol obtained by LAH reduction of V was identical to an authentic sample prepared from 2-(l-cyclopentenyl)ethyl bromide[8] by means of Grignard reaction with formaldehyde.

Drastic decrease in the yields of II and III was observed in the presence of piperylene as a triplet quencher.[9] The photochemical reaction of I may be summarized as in Scheme 1.

Cleavage at the C_1—C_2 bond in the excited n,π*-triplet state of I would produce the delocalized diradical as an intermediate (Path A). Recombination of the oxygen radical (VI) would give rise to *exo*-enol lactone II, while initial 1,3-hydrogen shift giving VII must be involved in the formation of the minor isomer III. Under the present irradiation conditions, II was converted slowly into III, but III was sufficiently photostable on prolonged irradiation (48 hr).

In Path B, cleavage of the C_1—C_9 or C_5—C_9 bond could produce diradicals whose

SCHEME 1



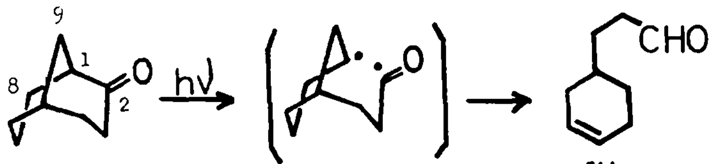
decarbonylation occurring possibly *via* a ketene intermediate[†] should lead to bicyclo[3.3.0]octan-2-one (IV).

When a 1% n-hexane soln of IV was irradiated separately under similar conditions for 6 hr, IV was readily converted to V as the only isolable product in 60% yield.[‡] This result implies that V arises from IV. The photochemical conversion was quenched effectively by the addition of piperylene to indicate that the n,π^*-triplet excited state is responsible for the reaction.

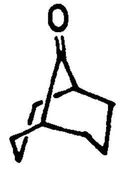
[†] Irradiation of I in ethanol under similar conditions proceeded in an exceedingly complicated way. Among the photoproducts, however, at least two ethyl esters were detected to indicate the ketene intermediate. The structure determination was impossible due to the lack of material.

[‡] Under the present condition, V was photostable. Cf. Ref 10.

Irradiation of bicyclo[3.3.1]nonan-2-one (VIII) also resulted in rearrangement which was initiated by α-cleavage. When a 1% n-hexane soln of VIII was irradiated for 12 hr (66% conversion), 3-(3-cyclohexenyl)propanal (IX)[11] was obtained exclusively in 66% yield, whereas the 9-keto isomer or bicyclo[3.3.1]nonan-9-one (X) was photostable even after 50 hr irradiation.† The formation of IX indicates that hydrogen abstraction by carbonyl carbon of the diradical occurs at C_8 rather than at C_9.



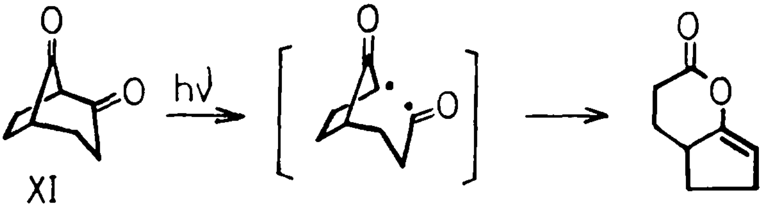
VIII IX



X

Additionally IX was shown to be photostable and the attempt to obtain an oxetane through the intramolecular photocyclo addition of IX was unsuccessful.[10]

Finally, the lower homologue of I or bicyclo[3.2.1]octane-2,8-dione (XI) was subjected to an analogous photoreaction, which proceeded more slowly than I probably due to the absence of the transannular interaction between C_3 and C_7 in the bicyclo[3.3.1]-nonane system. When a 1% n-hexane soln of XI was irradiated for 12 hr, *exo*-enol lactone (XII, 18%) was obtained as the sole product. An unsaturated aldehyde analogous to V was not detected.



XI XII

EXPERIMENTAL

All m.ps and b.ps were uncorrected. NMR spectra were obtained in CCl_4 soln (TMS as an internal standard) using JEOL-60-H spectrometer. GLC was performed on HVSG(30%)-Celite column (2 m). Compounds I,[2] II and III,[4] and VIII[12] were prepared by the published procedures.

2-(1-*Cyclopentenyl)ethanol* (XIII).[13] To a soln of LAH (0·41 g; 10·8 mmoles) in THF (5 ml) was added with stirring to a soln of 1-cyclo-pentenylacetic acid[8] (1·50 g; 11·9 mmoles) in THF (10 ml) in the course of 10 min. After the exothermic reaction had subsided, the mixture was heated under reflux for an additional 2 hr. Workup gave III, b.p. 83–86°/18 mm (lit. [13] b.p. 80–85°/2 mm), (0·84 g; 69%); IR(neat): 3450, 3050, 1645, 1030 and 800 cm^{-1}. (Found: C, 74·7; H, 10·7. Calc for $C_7H_{12}O$: C, 74·9; H, 10·8%).

2-(1-*Cyclopentenyl)ethyl bromide* (XIV). To a cooled (−5°) soln of XIII (0·84 g; 7·5 mmoles) in a mixture of pyridine (2 ml) and benzene (5 ml), a soln of PBr_3 (0·81 g; 3·0 mmoles) in benzene (3) ml) was added gradually below 0°. After the addition was complete the mixture was allowed to warm to room temp and finally was heated under reflux on a steam bath for 1 hr. The mixture was cooled, treated with water, and the supernatant layer was washed with a 5% NaOH aq and water. Evaporation of the solvent followed by

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† An unfiltered high pressure mercury arc did not induce appreciable photoreaction of X within 48 hr. The difference in photoreactivity between VIII and X suggests a certain interaction between C_2 and C_9 carbonyl groups particularly in their excited state. UV absorption of I was observed as follows: λ_{max}(EtOH), 290 nm (log ε 1·81); λ_{max}(n-hexane), 296 nm log ε 1·81).

silica gel column chromatography (eluted with n-hexane) gave XIV (0·95 g; 73%) which was subjected to the following reaction without further purification; IR(neat): 3050 and 1645 cm^{-1}.

3-(1-*Cyclopentenyl*)*propanol* (XV). Gaseous formaldehyde was introduced in the course of 1 hr to a Grignard reagent prepared from XIV (0·95 g; 5·4 mmoles), Mg (0·150 g; 6·2 mg-atoms) and a small amount of I_2 in ether (8 ml). The resulting mixture was extracted with ether and the ethereal layer was washed (water) and dried (Na_2SO_4). Evaporation of the solvent followed by Al_2O_3 column chromatography gave 3-(1-*cyclopentenyl*)*propanol* (XV, 0·20 g; 29%), b.p. 80–85°/20 mm; IR(neat): 3350, 3050, 1650, 1050 and 800 cm^{-1}; NMR δ 5·35 (narrow t, 1H, vinylic), 3·6 (t, 2H, C$\underline{H}$-OH), 2·3–1·5 (m, 10H) and 1·3 ppm (s, 1H, OH). (Found: C, 76·3; H, 11·0. $C_8H_{14}O$ requires: C, 76·1; H, 11·2%).

Reduction of V. LAH reduction of V obtained photochemically from I gave XV in 80% yield which was identical in all respects to the authentic sample prepared above.

cis-*Cyclooctene oxide* (XVI). Epoxidation of *cis*-cyclooctene was accomplished according to Payne[14] in far better yield than published.[15]

A mixture of *cis*-cyclooctene (55 g; 0·50 mole), $KHCO_3$ (10 g), benzonitrile (52 g; 0·50 mole) and 30% H_2O_2 (57 g; 0·50 mole) in MeOH (300 ml) was stirred in the course of 40 hr under external cooling with running water. The mixture was diluted with water (500 ml) and extracted with three 200 ml portions of $CHCl_3$. The chloroform layer was concentrated and the residue was diluted with n-hexane (100 ml) to induce the crystallization of benzamide which formed as by-product. Removal of benzamide by filtration followed by distillation of the filtrate gave XVI (52 g; 83%), b.p. 86–88°/30 mm (lit.[15] b.p. 96·5°/40 mm).

cis-*Bicyclo*[3.3.o]*octan-2-one* (IV). The chromic acid soln, prepared from sodium dichromate dihydrate (0·50 g; 1·68 mmoles) and 96% H_2SO_4 (0·38 g; 7·4 mmoles) was diluted with water to 5 ml, and the soln of *cis*-bicyclo[3.3.0]-octan-2-ol[16] (0·67 g; 5·3 mmoles) in ether (1 ml) was added to the above soln under stirring over 10 min while the temp was maintained at 25°. After 2 hr the mixture was extracted with three 10 ml portions of ether and the ethereal layer was washed with saturated Na_2CO_3aq and water. After drying (Na_2SO_4), distillation gave IV (0·55 g; 83%), b.p. 71–73°/15 mm (lit.[17] 58–60°/5 mm), which was shown to be identical with the sample obtained photochemically from I by the comparison of their IR, NMR and GLC (at 100°) retention time.

Bicyclo[3.3.1]*nonan-9-one* (X). A soln of 2-(9-oxobicyclo[3.3.1]nonyl) *p*-toluenesulphonate[18] (5·0 g; 17·1 mmoles) in ether (10 ml) was added dropwise to a well-stirred suspension of LAH (0·61 g; 16·0 mmoles) in ether (5 ml) at room temp during 20 min, and the mixture was heated under reflux for 2 hr. Acidification with dil HCl followed by usual workup gave a crude alcohol which was purified by Al_2O_3 column chromatography. Elution with benzene-ether (1 : 1) gave a bicyclic alcohol (1·1 g; 46%) which was subjected to the next procedure without further purification; IR(neat): 3420 and 1055 cm^{-1}.

To a soln of the alcohol obtained (1·1 g; 7·9 mmoles) in ether (2 ml) a soln (5 ml) of sodium dichromate dihydrate in H_2SO_4 was added dropwise in the course of 10 min and the mixture was heated under reflux. The mixture was extracted (ether), and the extract was washed (water), neutralized ($NaHCO_3$aq) and dried (Na_2SO_4). Purification by passing through silica gel column gave pure X (0·81 g; 74%), m.p. 120–125° (lit.[19] m.p. 126–128°).

Bicyclo[3.2.1]*octane*-2,8-*dione* (XI). To a boiling soln of 1-morpholino-1-cyclopentene[19] (25 g; 0·163 mole) in benzene (250 ml) a soln of acrylyl chloride (14·8 g; 0·163 mole) in benzene (160 ml) was added with stirring. The mixture was stirred and heated under reflux overnight during which precipitates were formed. The solid was collected, washed with small amount of benzene, and stirred with water (300 ml) at room temp in the course of 3 hr. The mixture was extracted with ether and the extract was washed (water) and dried. Evaporation of the solvent followed by distillation (80–100°/4 mm) gave *bicyclo*[3.2.1]*octane*-2,8-*dione* (XI) as a waxy solid (9·3 g; 41%), m.p. 95–96°; IR(nujol): 1745 and 1710 cm^{-1}; UV : λ_{max}(EtOH), 292 nm (log ε 1·70); λ_{max} (cyclo-hexane), 296 nm (log ε 1·72); NMR: δ 2·95 (m, 1H, C_1—$\underline{H}$), 2·6 (t,'H, C_5—$\underline{H}$) and 2·45–1·8 ppm (m, 8H). Found: C, 69·8; H, 7·2. $C_8H_{10}O_2$ requires: C, 69·5; H, 7·3%).

General irradiation procedure. A 1% soln of each carbonyl compound in n-hexane or benzene was placed in a pyrex tube under N_2 atmosphere and irradiated externally by means of 300 W high pressure mercury lamp (Pyrex jacket) at room temp. Yields as well as conversions were calculated on the basis of gas chromatograms.

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