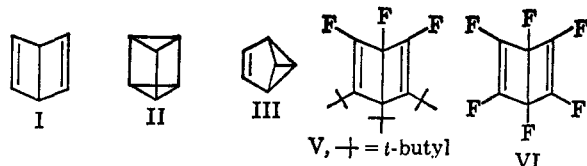


zene (I), prismane (II), and benzvalene (III). Such valence isomerizations have not been reported in benzene itself, although it has been irradiated at 2537 and 1850 Å in the gas phase, in solution, and in solid nitrogen matrix at 4°K.<sup>7</sup> It was of interest to investigate whether a correlation between the rate of photoisomerization of substituted benzenes and their lowered symmetry<sup>8</sup> exists. Results on the irradiation of hexafluorobenzene IV are reported here.



Irradiation of hexafluorobenzene vapor at 35 mm at 25° with an unfiltered medium-pressure mercury arc gave a single volatile product (mp 6.0°). The initial quantum yield for its formation was of the order of 0.003 but the conversion was limited to about 10% by the simultaneous deposition of a yellow polymer on the windows of the cell. Gas chromatography on temperature-programmed (25° until 20 min, 2.9°/min thereafter), 10-ft diisodecyl phthalate column served to separate the product from unreacted hexafluorobenzene. Retention times were 6.1 and 36.5 min, respectively. The product thus isolated gave only a single, sharp peak on a KEL-F Oil No. 3 column. No decomposition was observed on either of these columns. The structure of the product was deduced from the following evidence. The molecular weight (mass spectrum) of 186 and the analysis (C, 39.04; F, 60.40; C<sub>6</sub>F<sub>6</sub> requires C, 38.73; F, 61.27) showed that the product was isomeric to IV. In its ultraviolet spectrum (vapor) the compound showed end absorption ( $\epsilon_{2200}$  950;  $\epsilon_{2100}$  1800) but no maximum above 2000 Å. This excluded a conjugated diene structure such as fulvene. The fluorine nmr spectrum<sup>9</sup> showed only two signals with an intensity ratio 2:1 at 121.2 and 190.1 ppm. The chemical shifts of the fluorine atoms in V have been reported<sup>10</sup> to lie at +103 and +181 ppm, the bridgehead fluorine being at the higher value. These data suggest that the photoisomer of hexafluorobenzene is hexafluorobicyclo[2.2.0]hexa-2,5-diene (VI). The F-F coupling constants are less than 3 cps, which is of the same order as the reported values<sup>10</sup> in V. The infrared spectrum (vapor) of VI showed bands at 1751 (s), 1339 (vs), 1269 (w), 1235 (m), 1074 (vs), 924 (vs), 886 (vs), 817 (w), and 671 (w) cm<sup>-1</sup>; the first of these confirms the presence of fluorine-substituted -C=C- bonds,<sup>11</sup> and the number of allowed

fundamentals is in agreement with a structure of reasonably low symmetry. VI is stable as a solid at -20° and in CCl<sub>4</sub> solution at room temperature. Irradiation at 1850 Å converted it into IV and some solid polymer.

The irradiation of hexafluorobenzene (i) in methylcyclohexane solution at 2537 Å, (ii) in ether solution at 2850-3200 Å, (iii) in cyclohexane solution at >3025 Å in the presence of benzophenone as sensitizer, or (iv) in the gas phase at 2537 Å with mercury as sensitizer resulted in a mixture of as yet unidentified but mostly higher molecular weight products. Under these conditions VI was notably absent from the product mixture as shown by gas chromatography under the same conditions as used in the direct vapor-phase photolysis. Since the products formed in (iii) and (iv) must arise from triplet hexafluorobenzene, these results indicate that in the photoisomerization of hexafluorobenzene to VI the triplet is not the excited state involved.

The formation of hexafluoro(Dewar benzene) from IV indicates that steric effects or the reduction of the benzene symmetry by substituents is not a precondition for valence isomerization. The stabilization of small rings by fluorine substituents is well known.<sup>12</sup>

Kaplan, *et al.*,<sup>5</sup> recently reported that in the photoisomerization of xylenes in the gas phase only 1,2 migration of the methyl groups takes place, while in solution both 1,2 and 1,3 shifts occur. This led them to conclude that it is sufficient to postulate that the intermediate in the gas phase is of a benzvalene structure, whereas in solution either a prismane, or a set of easily interconvertible Dewar structures, or both, may serve as intermediates. If the present results on hexafluorobenzene can be extrapolated to a disubstituted benzene, such as xylene, then it is possible to narrow down the alternatives in the solution photolysis of the xylenes. The isolation of a Dewar benzene in the gas-phase photolysis of IV is compatible with the absence of 1,3 shifts in the xylene system only if the condition of easy interconvertibility of Dewar structures, required for the interchange of the ring carbons, is not met. This, in turn, indicates that the prismane structure is the intermediate in the 1,3 migrations in solution.

**Acknowledgment.** Valuable discussions with Dr. R. Srinivasan are gratefully acknowledged.

(12) A. M. Lovelace, D. A. Rausch, and W. Postelnek, "Aliphatic Fluorine Compounds," Reinhold Publishing Corp., New York, N. Y., 1958.

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Received February 25, 1966

(3) A. W. Burgstahler, P. L. Chien, and M. O. Abdel-Rahman, *J. Am. Chem. Soc.*, **86**, 5281 (1964).

(4) E. M. Arnett and J. M. Bollinger, *Tetrahedron Letters*, 3803 (1964).

(5) L. Kaplan, K. E. Wilzbach, W. G. Brown, and S. S. Yang, *J. Am. Chem. Soc.*, **87**, 676 (1965).

(6) K. E. Wilzbach and L. Kaplan, *ibid.*, **87**, 4004 (1965).

(7) I. Haller and R. Srinivasan, unpublished results. The limits of detection corresponded to a quantum yield of 10<sup>-4</sup>.

(8) It is felt that, since Dewar benzene is known<sup>2</sup> to have a reasonable stability, the valence isomers are not formed at all in the irradiation of benzene.

(9) The nmr spectra were recorded by Dr. E. R. Malinovski of Stevens Institute of Technology. Chemical shifts are referred to CCl<sub>3</sub>F internal standard; calibrations were effected by the sideband technique.

(10) H. G. Viehe, R. Merenyi, J. F. M. Oth, J. R. Senders, and P. Valange, *Angew. Chem. Intern. Ed. Engl.*, **3**, 755 (1964).

(11) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," 2nd ed., John Wiley and Sons, Inc., New York, N. Y., 1960, p 42.

## Photochemical Reactions of Camphorquinone<sup>1</sup>

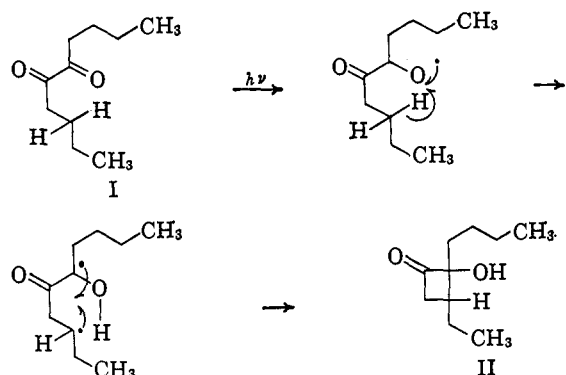
Sir:

Whereas the photochemistry of monoketones has received a great deal of attention, the photochemistry of  $\alpha$ -diketones has been explored to a much smaller extent. One of the most interesting discoveries in this area was that of Urry, *et al.*, who found that simple aliphatic  $\alpha$ -diketones (such as 5,6-decanedione (I)) undergo facile photocyclization in benzene solution to form 2-hydroxy-

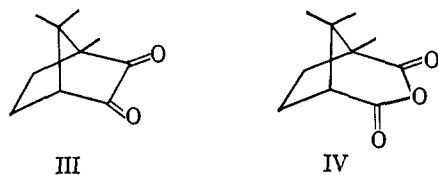
(1) The partial support of this research by the National Science Foundation (Grant No. GP-4128) is acknowledged with pleasure.

cyclobutanones (such as II).<sup>2</sup> This transformation is readily rationalized by assuming that the excited diketone (probably as the  $n-\pi^*$  triplet) suffers an intramolecular hydrogen atom transfer *via* a six-membered cyclic transition state, followed by ring closure as shown in Chart I.<sup>2</sup> This type of mechanism had been put for-

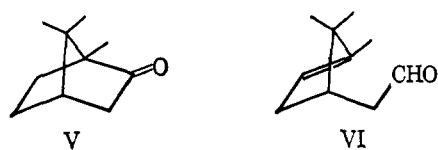
Chart I



ward earlier by Yang and Yang to account for the structurally analogous formation of cyclobutanols from simple aliphatic monoketones.<sup>3</sup> We now wish to report some new photochemical reactions of camphorquinone (III), an  $\alpha$ -diketone whose molecular geometry makes the Urry cyclization reaction improbable.

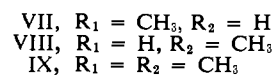
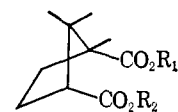


In a series of exploratory experiments, solutions of III were irradiated under a wide variety of conditions. In a nitrogen or argon atmosphere, *no detectable transformations occurred* in solvents such as benzene, carbon tetrachloride, *t*-butyl alcohol, methyl alcohol, or aqueous acetone, using either a bank of Sylvania blacklites (F-15T8-BL, 375 m $\mu$ , 15 w) or a Hanovia high-pressure mercury arc through Pyrex, Corex, or Vycor filters. This result contrasts sharply not only with those just discussed for flexible  $\alpha$ -diketones,<sup>2</sup> but also with the well-known photolytic reaction of camphor (V) in solution to give  $\alpha$ -campholenic aldehyde VI and other products.<sup>4</sup>

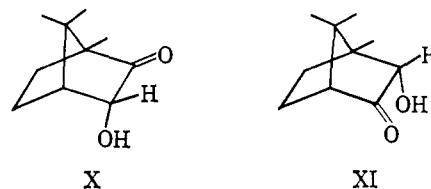


When oxygen was admitted to irradiated solutions of III, however, photochemical reactions did begin to occur, giving a variety of products whose nature depended on the exact experimental conditions. Thus, in carbon tetrachloride or *t*-butyl alcohol (using a 200-w Hanovia lamp and Pyrex filter), III gave chiefly cam-

phoric anhydride (IV), mp 220–222°,<sup>5</sup> and indistinguishable from an authentic sample by glpc and infrared spectral comparison. Several minor products were not characterized. In methyl alcohol, a mixture of acidic (*ca.* 20%) and neutral (*ca.* 80%) products was formed. The acidic fraction was shown to consist of a mixture of the two isomeric camphoric acid monomethyl esters, VII and VIII, since ethereal diazomethane converted the mixture into dimethyl camphorate (IX), identified by direct comparison (glpc and infrared) with an authentic sample.<sup>6</sup>



The neutral fraction from the methanol reaction was identified as a mixture of comparable amounts of the acyloins *endo*-3-hydroxycamphor (X) and *endo*-2-hydroxycamphor (XI) by direct glpc and infrared comparisons with authentic samples prepared by the zinc dust reduction of III.<sup>7</sup> Reduction to this mixture



of acyloins was also the chief result of irradiating III in isopropyl alcohol.<sup>8</sup>

While the requirement for oxygen for the success of these photoreductions is of interest, the most novel findings from a structural point of view were made when III was irradiated in benzene solution; it is to this reaction that we gave most attention. Under blacklite irradiation carbon dioxide was evolved, and three products with glpc retention times less than that of III (on a 5% SE-30 column at 172°) were detected, along with several of longer retention times. The first of these, formed in trace amounts (*ca.* 6 mg from 1.0 g of III in 180 ml of benzene), proved to be biphenyl (mp and mmp 68.5–69.5°,<sup>9</sup> identical glpc retention time and infrared spectrum with that of authentic material).

The second product was obtained as a crystalline solid, mp 161–161.5°, by preparative glpc followed by sublimation. Its elemental analysis was consistent with the molecular formula C<sub>9</sub>H<sub>14</sub>O<sub>2</sub>, corresponding to the loss of a single carbon atom from III (C<sub>10</sub>H<sub>14</sub>O<sub>2</sub>). In the infrared spectrum a strong carbonyl band at 5.61  $\mu$  was evident, and in the nmr spectrum three three-proton singlets ( $\tau$  9.08, 9.00, and 8.98) along with a downfield one-proton peak ( $\tau$  5.68) were observed. These data suggested that the unknown might be camphonolactone

(2) W. H. Urry and D. J. Trecker, *J. Am. Chem. Soc.*, **84**, 118 (1962); W. H. Urry, D. J. Trecker, and D. A. Winey, *Tetrahedron Letters*, 609 (1962).

(3) N. C. Yang and D. D. H. Yang, *J. Am. Chem. Soc.*, **80**, 2913 (1958).

(4) G. Ciamician and P. Silber, *Ber.*, **43**, 1340 (1910); R. Srinivasan, *J. Am. Chem. Soc.*, **81**, 2604 (1959).

(5) J. W. Brühl, *Ber.*, **24**, 3410 (1891).

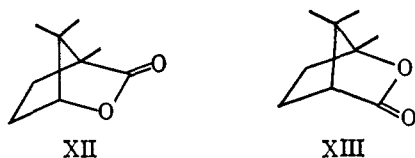
(6) J. W. Brühl and R. Braunschweig, *ibid.*, **25**, 1810 (1892).

(7) For a leading reference see H. Rupe and F. Müller, *Helv. Chim. Acta*, **24**, 265E (1941).

(8) The photoreduction of  $\alpha$ -diketones to acyloins was observed by Urry, *et al.* (ref 2), to occur in aldehydic solvents.

(9) C. D. Hodgman, R. C. Weast, and S. M. Selby, "Handbook of Chemistry and Physics," 41st ed., Chemical Rubber Publishing Co., Cleveland, Ohio, 1960, p 868.

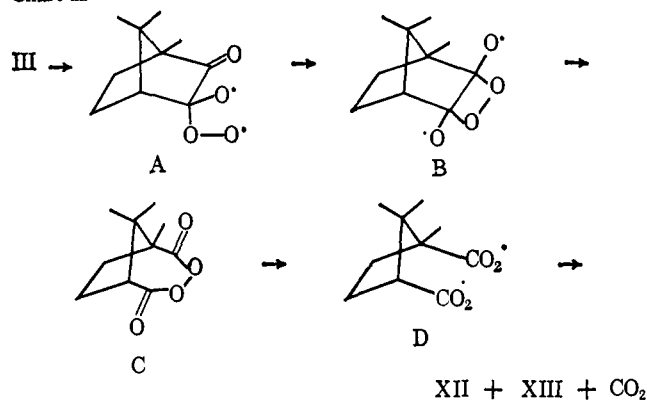
(XII), and this was confirmed by comparison with an independently prepared sample of XII.<sup>10,11</sup>



The third product could not be obtained entirely free of XII and showed a depressed melting range (92.5–105°). Elemental analysis and Rast molecular weight determination again indicated the molecular formula C<sub>9</sub>H<sub>14</sub>O<sub>2</sub>. A strong infrared absorption at 5.62 μ and nmr peaks corresponding to three C-methyl groups (singlets at τ 9.05, 8.95, and 8.72), with no downfield absorption in the τ 6 region, suggested that this was the isomeric campholytolactone (XIII). Once more, this was confirmed by direct glpc, infrared, and nmr comparison with pure XIII, mp 121.5–122°.<sup>12</sup>

Partial loss of these lactones during work-up makes it difficult to estimate their yields with any accuracy. It does appear that they are formed in about equal amounts, probably in the range of 5–10% each. They obviously arise as a result of a complex sequence of steps. One possible mechanism, shown in Chart II,

Chart II



involves addition of oxygen to III to give an intermediate such as A,<sup>13</sup> which can then proceed *via* B to the cyclic diacyl peroxide C, decomposition of which could be expected to yield XII and XIII, perhaps by decarboxylation of the diradical D.<sup>14,15</sup>

(10) W. A. Noyes, *Am. Chem. J.*, **16**, 508 (1894); W. A. Noyes and R. de M. Taveau, *ibid.*, **35**, 385 (1906); J. Bredt, *J. Prakt. Chem.*, **84** (2) 786 (1911).

(11) Although the synthesis of XII according to Noyes could not be repeated, an independently devised synthesis gave a sample of campholactone with very close to the reported melting point (161–162.5°, lit.<sup>10</sup> 160–161°) and with appropriate infrared and nmr spectra.

(12) L. L. McCoy and A. Zagalo, *J. Org. Chem.*, **25**, 824 (1960). In our hands, the lead tetraacetate oxidation of camphoric acid gave campholytolactone (XIII) accompanied by about 13% of campholactone (XII).

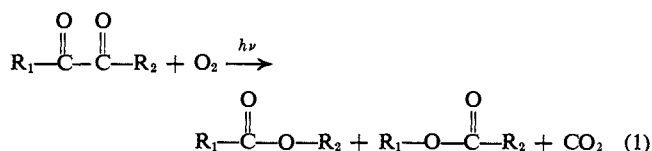
(13) This type of intermediate has been postulated by Professor G. Quinkert to explain some monoketone photooxidation reactions in solution. See G. Quinkert and H. G. Heine, *Tetrahedron Letters*, 1659 (1963); J. Meinwald and R. A. Schneider, *J. Am. Chem. Soc.*, **87**, 5218 (1965).

(14) For recent discussions see J. Hine, "Physical Organic Chemistry," 2nd ed, McGraw-Hill Book Co., Inc., New York, N. Y., 1962, pp 439–450; F. D. Greene, H. P. Stein, C. C. Chu, and F. M. Vane, *J. Am. Chem. Soc.*, **86**, 2080 (1964).

(15) Several other types of mechanism might be invoked to account for lactone formation. Preliminary attempts to prepare the diacyl peroxide C independently, and to examine its thermal and photochemical reactions, have given only ambiguous results so far. We hope to pursue this possibility, along with the possible role of singlet oxygen in this transformation, in future work.

Other products formed in the reaction include a benzene-insoluble polymer (*ca.* 15%), the acyloins X and XI (*ca.* 15%), camphoric anhydride (IV; *ca.* 3%), camphoric acid (*ca.* 7%), and a mixture of other acids (*ca.* 40–50%) containing the hydroxy acids corresponding to the lactones XII and XIII and possibly unstable precursors which decompose to these acids during work-up.

In summary, irradiation of camphorquinone in solution leads to reaction only in the presence of oxygen; a variety of oxidation and reduction products are then formed. In benzene, a novel transformation in which one atom of carbon is extruded as carbon dioxide (eq 1) acquires some importance.



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## New Rearrangements of Hexose 4- and 5-O-Sulfonates

Sir:

In this communication we wish to report the discovery of a ring contraction which occurs during attempted displacements of the 4-O-sulfonate esters Ia–c of pyranoside Id.<sup>1</sup> Further, an additional 1,5 methoxyl migration has been observed with mesylate Ia under conditions less conducive to S<sub>N</sub>2 displacements.

Mesylate Ia, mp 128–129°, was synthesized from the known<sup>2</sup> methyl 2,3-O-isopropylidene-α-D-mannopyranoside following a method previously successful in the glucose series.<sup>3</sup> Treatment of Ia with lithium aluminum hydride afforded the alcohol Id, [α]<sub>D</sub><sup>27</sup> 15.2° (*c* 1.4),<sup>4</sup> *via* O–S cleavage, which in turn could be converted to tosylate Ib, mp 59°, [α]<sub>D</sub><sup>27</sup> –23.9° (*c* 1.1). The physical constants of Ib and d agreed with those of their L enantiomers prepared from L-rhamnose,<sup>5</sup> thus also establishing the structure of Ia.

All attempted displacement reactions on sulfonates Ia and b and on brosylate Ic, mp 44–46°, resulted in ring contraction to give furanoside products. Thus, treatment of Ia with acetate ion in refluxing dimethylformamide (DMF) afforded (after saponification) a 65% yield of a mixture of D-*talo*-IIa and L-*allo*-IIIa, ratio 7:1.<sup>6</sup>

(1) A previous report (C. L. Stevens, P. Blumbergs, and R. P. Glinski, 149th National Meeting of the American Chemical Society, Detroit, Mich., April 1965, Abstracts, p 5C) indicated that displacement of Ia with acetate ion, while difficult, proceeded normally. Later data have shown that the previous structural data, while perhaps consistent with proposed structures, was, in fact, equivocal. Thus, the structures presented in the above reference are corrected herein.

(2) R. G. Ault, W. N. Haworth, and E. L. Hirst, *J. Chem. Soc.*, 517 (1935).

(3) C. L. Stevens, P. Blumbergs, D. H. Otterbach, J. L. Strominger, M. Matsuhashi, and D. N. Dietzler, *J. Am. Chem. Soc.*, **86**, 2937 (1964).

(4) The solvent for rotations was methanol.

(5) (a) P. A. Levine and J. Compton, *J. Am. Chem. Soc.*, **57**, 2306 (1935); (b) I. E. Muskat, *ibid.*, **56**, 2653 (1934).

(6) Determined by vapor phase chromatography (vpc). Compounds IIa and IIIa usually comprised over 80% of the crude reaction mixture.