

## Photochemical Transformations of Dichloromethyl- and Trichloromethyl-cyclohexadienones

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A RECENT report<sup>1</sup> that photolysis of the dienone (I), in ether or hydrocarbon solvents, gives *p*-cresol and chloroform by radical fragmentation is in marked contrast to an earlier report<sup>2</sup> that irradiation of the dienone (II), in aqueous acetic acid, gives 3-(2-chloro-1-methylvinyl)-5-oxohexanoic acid. We now report that these and related cyclohexa-2,5-dienones (4-CHCl<sub>2</sub> or 4-CCl<sub>3</sub>) undergo yet another type of transformation on being irradiated in aqueous dioxan or in methanol. Ultraviolet irradiation (Pyrex filter) of the dienone (I), for example, in aqueous dioxan containing powdered calcium carbonate, gave (after 24 hr.) a 60% yield of a crystalline photo-product (C<sub>8</sub>H<sub>8</sub>Cl<sub>2</sub>O<sub>2</sub>) to which we assign the structure (III) on the basis of the following evidence.

(a) The compound formed a 2,4-dinitrophenylhydrazone and rapidly reduced Tollens' and Fehling's solutions ( $\alpha$ -ketol). (b) Its ultraviolet spectrum (in ethanol) showed a maximum at 211 m $\mu$  ( $\epsilon$ , 15,400) attributable<sup>3</sup> to a cyclopent-2-enone. (c) Its infrared spectrum (dilute solution in CCl<sub>4</sub>) showed sharp bands at 3560 (OH with weak intramolecular hydrogen bonding), 1720

(C=O of cyclopent-2-enone), 1620, and 1585 cm.<sup>-1</sup> (C=C). (d) The n.m.r. spectrum (in CDCl<sub>3</sub>) of the photo-product showed two one-proton quartets in the olefinic region, centred at  $\tau$  2.54 and 3.62 (AB part of ABX system;  $J_{AB} = 6$  c./sec.). The methyl group gave a sharp singlet at  $\tau$  8.18 and the remaining two CH protons (positions 4 and 5) gave a singlet ( $\tau$  5.8) which was not resolvable into separate peaks but showed evidence of complexity under high resolution. A broad one-proton band at  $\tau$  6.2–6.6 was attributable to the OH group. (e) Treatment of the photo-product with dilute aqueous sodium hydroxide caused rearrangement to the isomeric dienone (IV). (f) The formation of compound (III) may be rationalised, in the manner shown, as a transformation of the zwitterion (V) which, on the basis of Zimmerman's<sup>4</sup> mechanistic approach to photochemistry, would be formed from an  $n-\pi^*$  excited state of the dienone.

The enolic nature of compound (IV) was shown by its solubility in dilute sodium hydroxide and by the greyish-purple colour produced on treatment with ferric chloride. Its ultraviolet spectrum

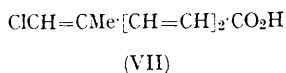
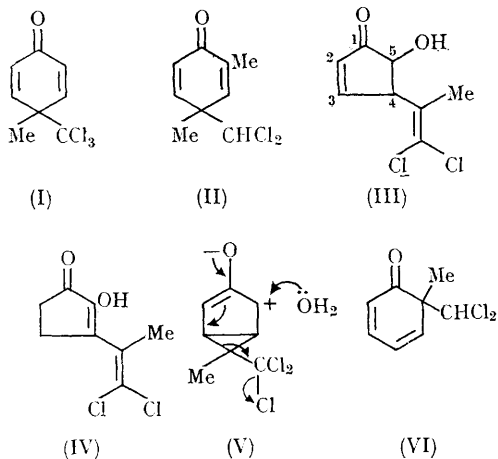
<sup>1</sup> D. I. Schuster and D. J. Patel, *J. Amer. Chem. Soc.*, 1965, **87**, 2515.

<sup>2</sup> E. E. van Tamelen, K. Kirk, and G. Brieger, *Tetrahedron Letters*, 1962, 939.

<sup>3</sup> R. L. Frank, R. Armstrong, J. Kwiatek, and H. A. Price, *J. Amer. Chem. Soc.*, 1948, **70**, 1379.

<sup>4</sup> H. E. Zimmerman and D. I. Schuster, *J. Amer. Chem. Soc.*, 1962, **84**, 4527.

(in EtOH) showed a maximum at  $275\text{ m}\mu$  ( $\epsilon$ , 8,800), shifted to  $336\text{ m}\mu$  ( $\epsilon$ , 36,200) in alkali, and its



infrared spectrum (dilute solution in  $\text{CCl}_4$ ) showed sharp bands at  $3490$  (OH with intramolecular hydrogen bonding),  $1703$  ( $\text{C}=\text{O}$  of cyclopent-2-enone lowered by hydrogen bonding),  $1664$ , and  $1600\text{ cm}^{-1}$  ( $\text{C}=\text{C}$ ). The n.m.r. spectrum (in  $\text{CCl}_4$ ) of compound (IV) consisted of a sharp methyl signal at  $\tau$  7.89, an  $\text{A}_2\text{B}_2$  multiplet at  $\tau$  7.15–7.65, and a broad OH signal at  $\tau$  2.7–3.1.

Irradiation of cyclohexa-2,4-dienones in presence of water, alcohols, or amines is reported<sup>5</sup> to give dienoic acids, esters, or amides, respectively. We find that 6-dichloromethylcyclohexa-2,4-dienones react similarly but with expulsion of hydrogen chloride, to give 7-chlorohepta-2,4,6-trienoic acids (or their derivatives) of undetermined stereochemistry. The gross structure of the acid (VII), from the dienone (VI), was apparent from its ultraviolet and infrared spectra [ $\lambda_{\text{max}}$  (in EtOH)  $294\text{ m}\mu$ ;  $\epsilon$ , 40,100;  $\nu_{\text{max}}$  (in  $\text{CCl}_4$ )  $2950$  (very broad),  $1690$ ,  $1625$ ,  $1610$  (sh), and  $1590$  (sh)  $\text{cm}^{-1}$ ] and from the observation that catalytic hydrogenation of its amide afforded 6-methylheptanoamide (4 moles  $\text{H}_2$  absorbed), identical with an authentic specimen.

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<sup>5</sup> D. H. R. Barton and G. Quinkert, *J. Chem. Soc.*, 1960, 1.