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AN ACID STABLE CYCLOHEXADIENONE

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The susceptibility of cyclohexadienones to change in acidic media has been the subject of numerous studies.[2] Data sufficient to outline a detailed mechanism for the change from dienone to phenol have been presented.[2 c,h] In this note the synthesis of an acid stable cyclohexadienone is reported. The absorption spectrum of a species closely related to the postulated initial intermediate of the dienone-phenol rearrangement is determined.

Protonation of the oxygen atom of a cyclohexadienone with concomitant formation of the delocalized ion (I) will be mirrored by the appearance of a new maximum in the ultraviolet region. To be certain that only the ion (I) is

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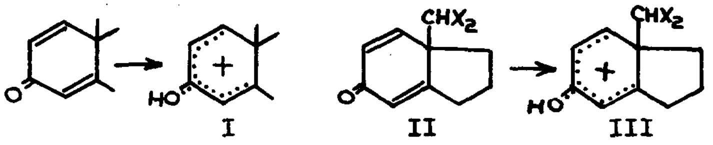
[1] Present Address.

[2] [a] R. T. Arnold and J. S. Buckley, *J. Amer. Chem. Soc.* **71**, 1781 (1949); [b] C. Djerassi, G. Rosenkrantz, J. Romo, J. Pataki and St. Kaufmann, *Ibid.* **72**, 4540 (1950); [c] R. B. Woodward and T. Singh, *Ibid.* **72**, 494 (1950); [d] A. S. Dreiding, W. J. Pummer and A. J. Tomasewski, *Ibid.* **75**, 3159 (1953); [e] C. Djerassi and T. T. Grossnickle, *Ibid.* **76**, 1741 (1954); [f] E. N. Marvell and E. Magoon, *Ibid.* **76**, 5118 (1954); [g] A. M. Gold and E. Schwenk, *Ibid.* **80**, 5683 (1958); [h] S. M. Bloom, *Ibid.* **80**, 6280 (1958); [i] H. Christol, R. Jacquier and M. Mousseron, *Bull. Soc. Chim. Fr.* (1959) 11; [j] J. Elks, J. F. Oughton and L. Stephenson, *Proc. Chem. Soc.* (1959) 6; [k] S. M. Bloom, *J. Amer. Chem. Soc.* **81**, 4728 (1959).



I II III

responsible for the spectral change, a dienone stable to acid should be utilized. The compound, 5-keto-8-dichloromethyl-$\Delta^{4,9;6,7}$dihydroindane (II X = Cl) seemed suited for this purpose and was accordingly synthesized <u>via</u> a Riemer-Tiemann reaction on 5-indanol.[3] On dissolution in sulfuric acid a colorless solution was obtained, possessing maxima at 2675 Å, logϵ 4.02 and 3200 Å, logϵ 3.52, and differing markedly from the spectrum of (II X = Cl) in 95% ethanol. (Fig. 1)

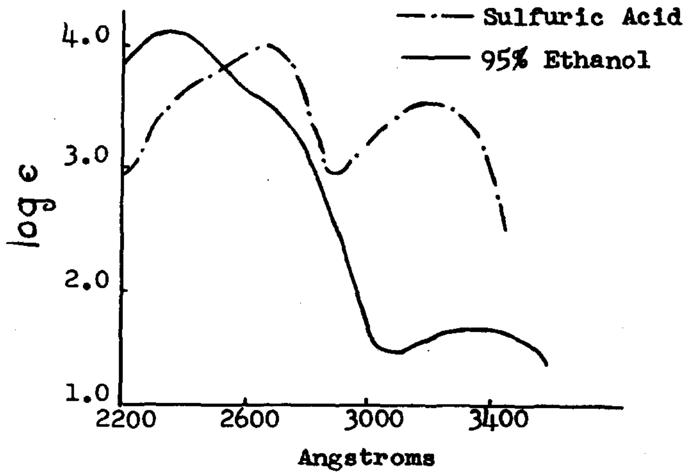


Fig. 1

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[3] See R. B. Woodward, J. Amer. Chem. Soc. 62, 1208 (1940) for an earlier case. In this work 10% potassium hydroxide and a reaction time of 5 hr were used.

The dienone (II X = Cl) was recovered nearly quantitatively by diluting a sulfuric acid solution with water after one hour. The new absorption spectrum provides direct evidence for the existence of the delocalized ion (III X = Cl).

The choice of 5-keto-8-dichloromethyl-$\Delta^{4,9;6,7}$ dihydroindane for this study is of sufficient interest to warrant further comment. Earlier work had shown that the migration of the alkyl chain of 5-keto-8-methyl-$\Delta^{4,9;6,7}$ dihydroindane (II X = H) did not occur in acetic anhydride.[4] It seemed clear that if the migrating methyl group in (II X = H) could be so substituted to make the bond to C-8 more difficult to break, no rearrangement would occur. The choice of 5-keto-8-dichloromethyl-$\Delta^{4,9;6,7}$ dihydroindane followed.

[4] S. M. Bloom, *J. Amer. Chem. Soc.* **81**, 4728 (1959).