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ISOMERIZATIONS IN THE DICYCLOPENTADIENE SERIES

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RECENT interest in the thermal rearrangement of dicyclopentadiene alcohols[1] and in the chemistry of related polychloroketones[2] leads us to give a preliminary report on experiments concerned with the isomerization of 4,5,6,7-tetrachloro-3a,4,7,7a-tetrahydro-4,7-methanoinden-8-one (I), m.p. 123-123.5°, $\lambda_{max}^{CCl_4}$ 3.34, 5.48, 6.33 μ (Found: C, 42.32; H, 2.05; Cl, 49.86. $C_{10}H_6Cl_4O$ requires: C, 42.29; H, 2.13; Cl, 49.94), prepared by hydrolysis of the adduct (II)[3] from cyclopentadiene and 1,2,3,4-tetrachloro-5,5-diethoxycyclopentadiene. When I was heated at 135° for 1 hr it was converted in quantitative yield to an isomer, m.p. 82-83°, $\lambda_{max}^{CCl_4}$ 3,23, 3.31, 5.73, 6.30 μ, λ_{max}^{EtOH} 255 mμ (ε 9100) (Found: C, 42.53; H, 2.14, Cl, 49.86). This is formulated as III on the basis of the spectral data and its conversion to IV, m.p. 202-203° (sealed cap.), $\lambda_{max}^{CCl_4}$ 5.28, 5.36, 5.53 μ (Found: C, 46.04; H, 3.67; Cl, 29.89. $C_9H_8Cl_2O_3$ requires C, 45.98; H, 3.43; Cl, 30.17), which was shown to be identical with the product obtained by hydrogenation of the

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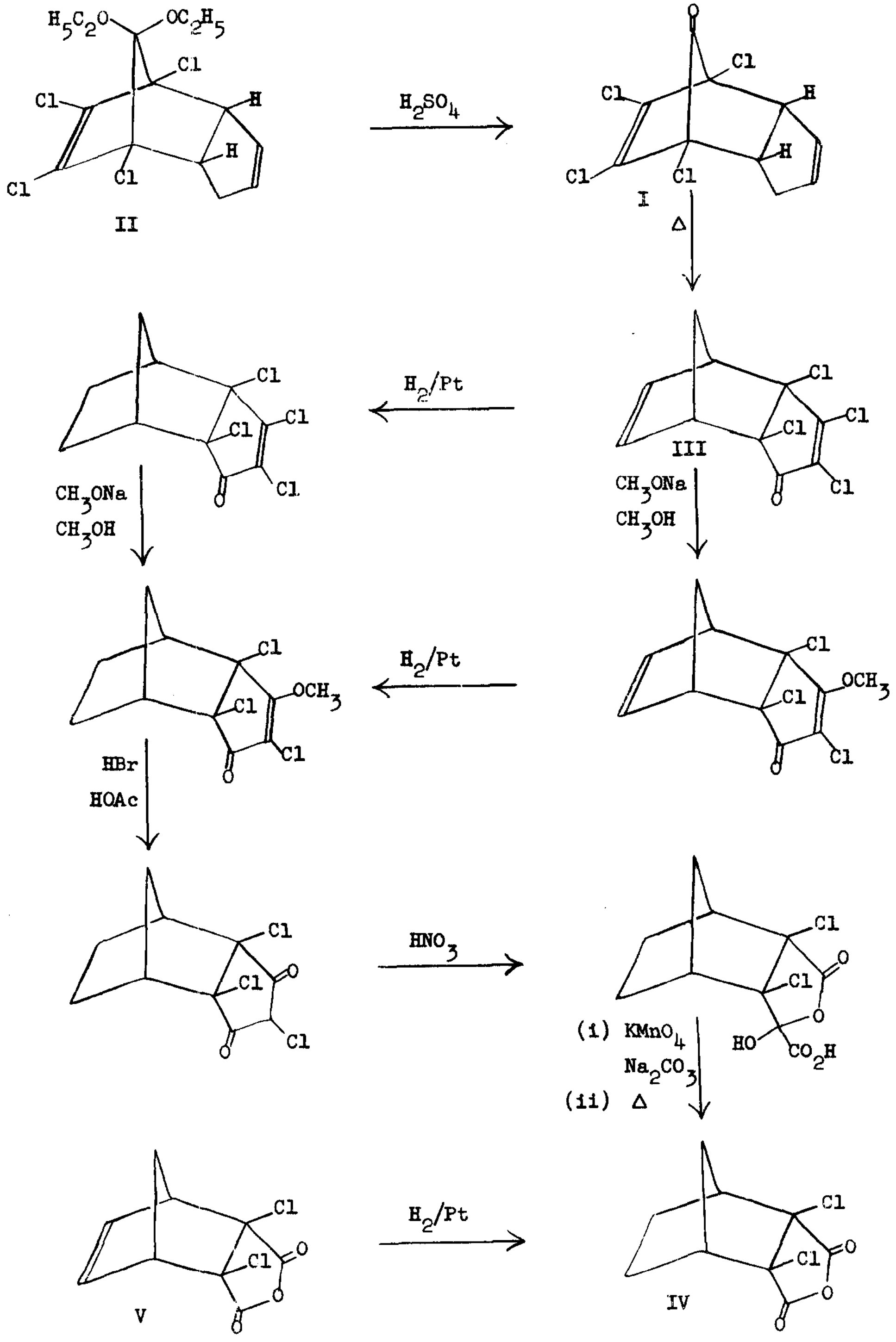
[1] R.B. Woodward and T.J. Katz, Tetrahedron **5**, 70 (1959).

[2] K. MacKenzie, J. Chem. Soc. 473 (1960).

[3] C.A. Peri, Gazz. Chim. Ital. **85**, 1118 (1955).


H5C2O
OC2H5
Cl
H
II
H2SO4
I
Δ
III
H2/Pt
CH3ONa
CH3OH
CH3ONa
CH3OH
OCH3
H2/Pt
HBr
HOAc
HNO3
HO
CO2H
(i) KMnO4
Na2CO3
(ii) Δ
V
H2/Pt
IV

adduct (V) of dichloromaleic anhydride and cyclopentadiene.[4] The route used for the conversion of III to IV is shown in the annexed scheme (all intermediate compounds have been characterized by satisfactory elementary analyses and all show spectra in accord with the structures assigned). The *endo* configuration is assigned to II and V on the basis of analogy;[5] the *endo* configurations of their congeners then follow. This configuration for III is corroborated by the observation that on ultraviolet irradiation it gives a new isomer, m.p. 113.5-114.5°, $\lambda_{max}^{CCl_4}$ 5.52 μ, $\lambda_{max}^{Et_2O}$ 295 mμ (ε 30) (Found: C, 42.09; H, 1.82; Cl, 49.76) which is assigned the cage structure VI.[6]

The rearrangement of I to III is reminiscent of the thermal rearrangement of hydroxydicyclopentadienes recently investigated by Woodward and Katz.[1,7] Although we lack the elegant stereochemical arguments developed by these investigators, we consider that the facility of the reaction and the absence of other products make it very likely that the reaction proceeds by a route analogous to that proposed by them for the hydroxydicyclopentadienes, i.e. *via* VII. The complete conversion of I to III and our failure to observe the reverse reaction must reflect the fact that III is strongly favored in the equilibrium I $\rightleftharpoons$ III. This is consonant with the expected greater

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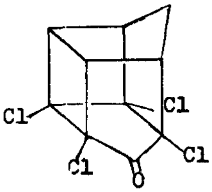
[4] A.M. Clifford and C.E. Gleim, U.S. Pat. 2,391,226 (1945); *cf. Chem. Abstr.* **40**, 3136 (1946).

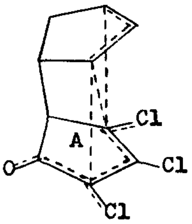
[5] M.C. Kloetzel, *Organic Reactions* Vol. IV, p. 11. John Wiley, New York (1948); K. Alder and M. Schumacher, *Fortschr. Chem. Naturstoffe* **10**, 17 (1953).

[6] *Cf.* R.C. Cookson, E. Crundwell and J. Hudec, *Chem. & Ind.* 1003 (1958); R.C. Cookson and E. Crundwell, *Ibid.* 1004 (1958).

[7] As pointed out by these authors, these reactions are special cases of the Cope rearrangement; cf. E.G. Foster, A.C. Cope and F. Daniels, *J. Amer.Chem.Soc.* **69**, 1893 (1947); and earlier papers.



VI



VII

stability of III, in which the carbonyl group is conjugated and also is relieved in part of the considerable angle strain attendant upon its placement at the single carbon bridge in I.

In the present case, the carbonyl group and chlorine atoms would be expected to lead to an unusually high polarization of the electronic displacements in VII, resulting in a considerable net negative charge on ring A. It was therefore of considerable interest to find that the isomerization of I to III was accelerated by sulfuric acid and by Lewis acids. Indeed, in the presence of a large excess of aluminum chloride at room temperature, I in solution in carbon tetrachloride was converted completely to III within three minutes. The spectacular acceleration of this conversion can be rationalized in terms of the formation of a complex between the aluminum chloride and the carbonyl oxygen atom; this should greatly facilitate the bond-breaking process symbolized in VII. We plan to investigate further the effect of Lewis acids on this and related reactions in the hope of obtaining results of both mechanistic and synthetical import.[8]

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[8] In this connection, it is of interest that several examples of catalysis of the Diels - Alder reaction by acids have been reported.[9]

[9] A. Rodgman and G.F. Wright, J. Org. Chem. 18, 465 (1953); W. Rubin, H. Steiner and A. Wasserman, J. Chem. Soc. 3046 (1949), and earlier papers; L.E. Gast, E.W. Bell and H.M. Teeter, J.Amer.Oil Chem.Soc. 33, 278 (1956).

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