Thus

$$\lambda_m = C_0\epsilon_m = \epsilon'_m (C_0 - \Delta C_0)$$
$$\lambda_d = C_0\epsilon_d = \epsilon'_d (C_0 - \Delta C_0)$$

Therefore

$$\epsilon_m/\epsilon_d = \epsilon'_m/\epsilon'_d \qquad (1)$$

where ϵ'_m and ϵ'_d are the molecular extinction coefficients in the simple aqueous solutions.

By virtue of the relation (1), one can determine $(C_0 - \Delta C_0)$, and the value of $\epsilon'_m((C_0 - \Delta C_0)/C_0)$ calculated therefrom must coincide with the experimental value of ϵ_m, if our model is correct.

The result of the comparison is very much satisfactory as seen in Table I.

Thus the above model may be said to be quantitatively confirmed.

INSTITUTE OF POLYTECHNICS, OSAKA CITY UNIVERSITY
OSAKA, JAPAN

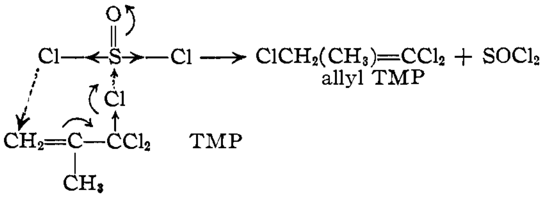
Catalyzed Allylic Rearrangement of a 1,1,1-Trichloro-2-alkene to a 1,1,3-Trichloro-1-alkene

BY DONALD G. KUNDIGER AND HAROLD N. HANEY

RECEIVED AUGUST 31, 1953

1,1,1-Trichloro-2-methyl-2-propene (TMP) is rearranged to 1,1,3-trichloro-2-methyl-1-propene (allyl TMP) by the catalytic action of thionyl chloride. When a mixture of thionyl chloride and chloretone in 5 to 1 mole ratio was heated under reflux for 30 hours,[1] a ratio of 88% TMP to 12% allyl TMP was obtained; but when the thionyl chloride–chloretone mixture was heated for 48 hours, a ratio of approximately 50% TMP to 50% allyl TMP was found. By comparison, when pure TMP is heated at 100° for 48 hours, practically no rearrangement to allyl TMP occurs.[2]

The catalyzed allylic rearrangement of TMP is rationally explained by the following reaction path



We have also found that TMP was rearranged to allyl TMP by powdered soft glass. The TMP (90%) underwent rearrangement in 12 hours at reflux. The electron donor character of the roughened and exposed inner surfaces of the alkaline glass powder may have been responsible for catalyzing this allylic rearrangement. The electron-donor character of the present catalyst is analogous in principle to that reported for ketene acetal where this acetal also catalyzed the present type of rearrangement.[2]

TMP was best separated from allyl TMP by flash distillation. In this manner an over-all accounting of 92% of the products of chloretone was obtained (81% TMP and 11% allyl TMP) with a reaction period of 30 hours.

Experimental Part

I. Reaction of Chloretone with Thionyl Chloride.—Purified chloretone (1.25 moles, 222 g.) and purified thionyl chloride (5.5 moles, 654.5 g.) were heated under anhydrous conditions and under reflux (about 79°) for 48 hours, while dry nitrogen gas was passed through to remove evolved hydrogen chloride and sulfur dioxide. *Anhydrous chloretone must be handled with special care and as rapidly as possible because of its extreme hygroscopicity.* The unreacted thionyl chloride was distilled off through a packed column under 140 mm. pressure. The residual liquid was transferred to a Claisen flask and distilled to give 150.9 g. (75.7%) of a 50–50 mixture of TMP and allyl TMP, b.p. 130–158° (the b.p. of TMP is 130–137°; the b.p. of allyl TMP is 152–158°). This mixture was preceded by a forerun of 7.5 g. which boiled largely at 125–130°. Note: Porcelain boiling chips prevented quite well the troublesome bumping and frothing always experienced with the distillation of the TMP–allyl TMP mixture. Use of a fairly large capillary ebulliator tube through which a slight stream of dry air is drawn with slight suction on the system is preferred. This product ratio was not changed by refluxing the 50–50 mixture for 3 hours or by refluxing in the presence of hydrogen chloride for 30 minutes.

Conversion of Chloretone to TMP.—The following experiment was designed to yield the maximum TMP isolable. The procedure was the same as the preceding experiment except that (a) the reaction mixture was held under reflux 30 hours (steam-bath), (b) half the amounts of the reactants were used, and (c) the crude product, after removal of thionyl chloride, was flash distilled (bath 197–202°). There were thus obtained (a) 80.8 g. (81%) of TMP, n^{25}D 1.4831 (lit. 1.4853), b.p. 135–137°, and (b) residue, which when simply distilled gave 11.2 g. (11%) of allyl TMP, b.p. 153.5–157.2°, and undistilled residue, 3.7%.

Powdered Soft Glass as Catalyst in Allylic Rearrangement of TMP to Allyl TMP.—A teaspoonful of powdered soft glass was mixed into 193.5 g. of TMP in a 3-necked flask fitted with a reflux condenser, a sealed stirrer, and a thermometer in the liquid and protected from atmospheric moisture. Rapid mechanical stirring was necessary to prevent severe troublesome bumping during reflux. Effective stirring also kept the powdered glass suspended. With refluxing and external heating, the temperature in the liquid gradually rose to 157° at the end of 12 hours. Simple distillation of the liquid (crude allyl TMP) resulted in 3.1 g. of forerun, and 174.3 g. (90%) allyl TMP, b.p. 152–157°.

DEPARTMENT OF CHEMISTRY
KANSAS STATE COLLEGE
MANHATTAN, KANSAS

---

[1] We found it necessary to employ about 30 hours reaction of chloretone with purified thionyl chloride in order to obtain complete conversion of chloretone to TMP. Small amounts of allyl TMP are formed. Our experience thus differs from the work of S. M. McElvain and C. L. Stevens (THIS JOURNAL, **69**, 2669 (1947)) in which eight hours was mentioned as sufficient for 93% yield of TMP from chloretone.

[2] D. G. Kundiger and K. H. Froman, *ibid.*, **75**, 1744 (1953).

Chemistry of Aliphatic Phosphonic Acids. II. Dielectric Constants and Viscosity of Some Higher Alkylphosphonates

BY GENNADY M. KOSOLAPOFF

RECEIVED AUGUST 25, 1953

Several determinations of dipole moments of various trialkyl phosphates can be found in the chemical literature. However, only one set of such determinations in the class of alkylphosphonates exists; this set of values was obtained for a very restricted number of such esters.[1] As a part of a comprehensive study of these compounds we determined the dielectric constants of several diethyl alkylphosphonates, containing an even

---

[1] A. E. Arbuzov and P. I. Rakov, *Izvest. Akad. Nauk S.S.S.R., Otdel. khim., nauk*, 237 (1950).