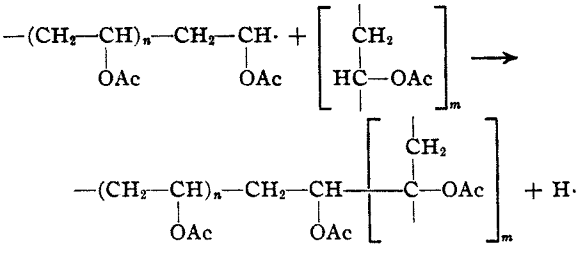
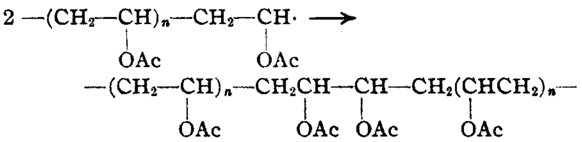
of 1,2-glycol structure present need not arise from "head to head" polymerization; it might also be produced by a chain transfer mechanism whereby a growing free radical of polyvinyl acetate could become attached to a preformed chain



$$-(CH_2-\underset{OAc}{CH})_n-CH_2-\underset{OAc}{CH}\cdot + \left[-CH_2-\underset{OAc}{HC}-\right]_m \longrightarrow -(CH_2-\underset{OAc}{CH})_n-CH_2-\underset{OAc}{CH}-\left[-CH_2-\underset{OAc}{C}-\right]_m + H\cdot$$

or by a chain termination reaction.



$$2\ -(CH_2-\underset{OAc}{CH})_n-CH_2-\underset{OAc}{CH}\cdot \longrightarrow -(CH_2-\underset{OAc}{CH})_n-CH_2\underset{OAc}{CH}-\underset{OAc}{CH}-CH_2(\underset{OAc}{CH}CH_2)_n-$$

Subsequent hydrolysis in either case would liberate a 1,2-glycol group in the molecule.

RAYON DEPARTMENT
E. I. DU PONT DE NEMOURS & CO., INC.
BUFFALO, N. Y.
RECEIVED MARCH 28, 1946

Synthesis of Arylpropylamines. II. From Chloroacetone[1]

BY T. M. PATRICK, JR.,[2] E. T. MCBEE AND H. B. HASS

During some work on the synthesis of pressor amines, the reaction of chloroacetone and benzene to give phenylacetone[3] came to our attention. It seemed worthwhile to study the reaction of chloroacetone with other aromatic compounds as a means of obtaining ketones which could be converted to desired amines.

From chlorobenzene there was obtained *p*-chlorophenylacetone in 11% conversion and 16% yield based on chloroacetone. Bromobenzene, fluorobenzene and anisole, however, failed to give the desired ketones by this method.

1-(*p*-Chlorophenyl)-2-propylamine, a compound of the benzedrine type, was prepared from *p*-chlorophenylacetone both by the modified Leuckart synthesis using formamide, and by sodium amalgam reduction of the ketoxime, in 20 and 35% yields, respectively.

Acknowledgment.—The authors wish to express their appreciation to the Abbott Laboratories for a grant which made this research possible.

Experimental

***p*-Chlorophenylacetone.**—A mixture of 175 g. (1.43 moles) of chlorobenzene and 82 g. (0.62 mole) of aluminum chloride held at 100° was agitated and 27.8 g. (0.30 mole) of chloroacetone was added dropwise over a period of forty-five minutes. Heating and stirring were continued for five hours longer. The cooled reaction mixture was shaken with crushed ice and hydrochloric acid. The organic layer was dried and rectified, giving 7 ml. (8.1 g.) of chloroacetone, 51 ml. (56 g.) of chlorobenzene, 4.7 ml. (5.8 g.) of a fraction boiling at 85–86° at 1 mm., and 2.8 ml. of intermediate fractions. The high boiling fraction had $n^{20}{}_D$ 1.5452, $d^{20}{}_{20}$ 1.1397, m. p. 6–8°. Permanganate oxidation of a small portion yielded *p*-chlorobenzoic acid.

Anal. Calcd. for C_9H_9OCl: C, 64.1; H, 5.4. Found: C, 64.1; H, 4.8.

The semicarbazone, m. p. 188°, was prepared in the conventional manner.

Anal. Calcd. for $C_{10}H_{12}ON_3Cl$: C, 53.2; H, 5.4. Found: C, 53.8; H, 5.4.

1-(*p*-Chlorophenyl)-2-propylamine.—Two methods of synthesizing the amine from the ketone were tried.

(a) Nine grams (0.053 mole) of *p*-chlorophenylacetone and 10 g. (0.22 mole) of 99% formamide were heated under reflux at 160–175° for three hours. The temperature was then raised to 185° for three hours. The liquid had become a clear dark brown. It was cooled and extracted with twice its volume of water to remove excess formamide. Five milliliters of concentrated hydrochloric acid was added, and the mixture was refluxed one hour to hydrolyze the formyl derivative of the amine. The solution was cooled, extracted with ether to remove non-basic components and finally made alkaline with 6 *M* sodium hydroxide. The basic solution was steam distilled. The distillate was extracted with ether and this extract was dried over anhydrous potassium carbonate. After the ether was evaporated, the residue was distilled, yielding 1.8 g. (20%) of 1-(*p*-chlorophenyl)-2-propylamine, b. p. 93–94° at 5 mm., $n^{20}{}_D$ 1.5343, $d^{20}{}_{20}$ 1.0762.[4]

(b) A 3.4-g. portion of *p*-chlorophenylacetone was dissolved in 14 ml. of ethanol and mixed with a solution of 1.4 g. of hydroxylamine hydrochloride and 1.6 g. of anhydrous sodium acetate in 5 ml. of water. The solution was allowed to stand overnight at room temperature. Cooling and diluting the mixture with water caused the oxime to separate as an oil. The crude oxime was dissolved in 35 ml. of glacial acetic acid, and reduced by the slow addition with cooling and shaking of 265 g. of 4% sodium amalgam. The aqueous phase was made basic with sodium hydroxide solution and extracted with ether. Distillation of the ether extract yielded 1.2 g. (35% based on the ketone) of 1-(*p*-chlorophenyl)-2-propylamine.

---

[1] Based upon a thesis submitted by T. M. Patrick, Jr., to the Faculty of Purdue University in partial fulfillment of the requirements for the Degree of Doctor of Philosophy, April, 1943.

[2] Abbott Laboratories Fellow, 1941–1942. Present address: Monsanto Chemical Co., Dayton 7, Ohio.

[3] Mason and Terry, THIS JOURNAL, **62**, 1622 (1940).

[4] Patrick, McBee and Hass, *ibid.*, **68**, 1009 (1946).

DEPARTMENT OF CHEMISTRY
PURDUE UNIVERSITY
LAFAYETTE, INDIANA
RECEIVED DECEMBER 1, 1945

The Exchange of Hydrogen and Tritium Ions During Alkylation, Catalyzed by Tritium Sulfuric Acid

BY T. D. STEWART AND DENHAM HARMAN

A recent paper by Ciapetta[1] stresses the role of hydrogen transfer during alkylation. An indication of very rapid exchange was found by us in a preliminary study of the alkylation of isobutane by 2-butene in the presence of tritium sulfuric acid. The alkylate was fractionated and the

---

[1] F. G. Ciapetta, *Ind. Eng. Chem.*, **37**, 1210 (1945); see also C. K. Ingold, C. G. Raisin and C. L. Wilson, *J. Chem. Soc.*, 1643 (1936), and A. Farkas and L. Farkas, *Ind. Eng. Chem.*, **34**, 716 (1942), for exchange experiments with deuterium; T. M. Powell and E. B. Reid, THIS JOURNAL, **67**, 1020 (1945), for exchange involving tritium. S. F. Birch and A. E. Dunstan, *Trans. Faraday Soc.*, **35**, 1017 (1939), discuss the mechanism of alkylation reactions.