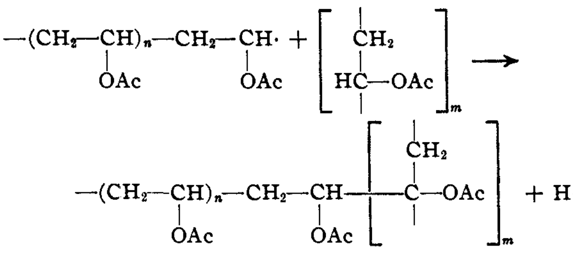
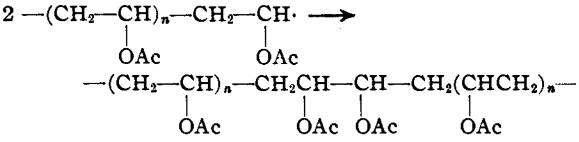
of 1,2-glycol structure present need not arise from "head to head" polymerization; it might also be produced by a chain transfer mechanism whereby a growing free radical of polyvinyl acetate could become attached to a preformed chain



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

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.

---

[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] 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).

[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.

activities of the hydrogen obtained from two fractions and the residue were determined in a Geiger counter.[2]

TABLE I

PROPERTIES OF THE ALKYLATE AND ACTIVITY OF HYDROGEN SAMPLES

Fraction of alkylate			Activity of hydrogen	
B. p., °C.	% Alkylate	n^{20}_D	Counts/min.	Sp. act.
99–100	*ca.* 10	1.389	332 ± 10	8.4×10^6
114–116	*ca.* 10	1.402	300 ± 10	7.6×10^6
Residue	*ca.* 60	...	300 ± 10	7.6×10^6

The activity of the hydrogen from the different fractions was practically the same, and the specific activity corresponds closely to the assumption of a random distribution of all of the hydrogen and tritium atoms in the 2-butene and catalyst, prior to alkylation.

Experimental

A solution composed of 0.48 mole of isobutane and 0.109 mole of 2-butene was added under pressure over a period of fifteen minutes to 0.131 mole of 100% tritium sulfuric acid (sp. act. 5.43×10^7) with vigorous stirring. The reaction chamber was a lead-lined, cylindrical iron vessel held at 10°. A few minutes was allowed for completion of the reaction, after which the excess of isobutane was allowed to evaporate from the reactor. The oil and acid layers in the residue were separated and the former washed with water and dried. The volume of alkylate was 20 ml.; fractionation was carried out in a 20-plate column. Samples of each fraction were burned over copper oxide, the water formed collected and the hydrogen obtained from it by reaction with magnesium at 600°.

If, as suggested above, all of the hydrogen and tritium atoms of the 2-butene and the sulfuric acid were randomly distributed between the alkene and catalyst, before alkylation, specific activity of the hydrogen from the alkene would be

$$5.43 \times 10^7 \times \frac{2 \times 0.131}{8 \times 0.109 + 2 \times 0.131} = 1.25 \times 10^7 \text{ counts/min./mole}$$

As a result of alkylation, the activity of hydrogen derivable from the hydrocarbon would be further reduced. Assuming as a first approximation that alkylation involves only addition of inactive alkane to the alkene of the above tritium content, in the ratio of 1:1, the specific activity of hydrogen obtainable from the alkylate would be $1.24 \times 10^7 \times 8/18$ or 5.5×10^6. This value is of the same order of magnitude as that observed and indicates an extensive exchange either prior to or during alkylation. The agreement of the observed and calculated activities on the above assumption is even better when applied to the residue. Assuming that polymerization of butene precedes alkylation and using a ratio of alkene to alkane in the alkylate of 2:1, one obtains a calculated activity for the hydrogen thus diluted of $1.25 \times 10^7 \times 16/26$ or 7.7×10^6. The observed value was 7.6×10^6. It is to be noted that most of the alkylation resulted in these higher fractions. There is a suggestion here that polymerization of the alkene involved intermediates of longer life than did octane formation, permitting a closer approach to random distribution of the tritium.

The Reactivity toward Exchange of the Individual Reactants.—Forty ml. of isobutane and 6 ml. of 100% tritium sulfuric acid (sp. act. 5.43×10^7) were vigorously stirred for twenty minutes at 10°, in the lead-lined reactor. The specific activity of the hydrogen obtained from a sample of the isobutane was 1.36×10^5. This corresponds to 7.1% of random distribution of the hydrogen atoms of the catalyst and the tertiary hydrogen atoms of the alkane. It also shows that little if any of the exchange noted above involved the alkylate.

Since 2-butene is absorbed rapidly by sulfuric acid, the following procedure was carried out to test the rapidity of exchange. The gaseous alkene was passed through a sintered glass bubbler and into 6 ml. of tritium sulfuric acid of the same composition as previously used. The rate of passage was such that little absorption occurred; all of the effluent gas was collected in a liquid air trap, and amounted to about 2 ml. of liquid. The specific activity of the hydrogen obtained from this material was 6.1×10^5, higher than that obtained from the isobutane upon a twenty-minute contact with the acid, and demonstrates not only a rapid exchange but also a reversible absorption of the alkene in sulfuric acid.

Acknowledgment.—The Shell Development Company generously made available the hydrocarbons used in this investigation.

CHEMISTRY DEPARTMENT
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIFORNIA

RECEIVED FEBRUARY 11, 1946

---

[2] See Harman, Stewart and Ruben, THIS JOURNAL, **64**, 2294 (1942), for details of operation.

NEW COMPOUNDS

Benzyl Heptaacetyl-β-lactoside[1]

A solution of 100 g. of acetobromolactose[2] in a mixture of 300 ml. each of anhydrous ether, benzene, and benzyl alcohol was shaken overnight with 40 g. of dry silver oxide. The filtered solution was halogen-free. Ether, benzene, and excess benzyl alcohol were removed by distillation with steam, the final portion of the aqueous distillate furnishing the first few crystals of the desired product. The residue in the flask crystallized when inoculated, and was recrystallized from warm ethyl acetate by the addition of ether in a yield of 58 g. Benzyl heptaacetyl-β-lactoside separated in clusters of small prisms melting at 145–146°. The rotation $[\alpha]^{20}\text{D}$ −34.4° in chloroform (*c*, 2) was unchanged by four additional recrystallizations.

Anal. Calcd. for $C_{33}H_{42}O_{18}$: C, 54.52; H, 5.83; acetyl, 9.63 ml. of 0.1 *N* NaOH per 100 mg. Found: C, 54.23; H, 6.12; acetyl, 9.75 ml.

CHEMISTRY LABORATORY
NATIONAL INSTITUTE OF HEALTH
BETHESDA, MARYLAND NELSON K. RICHTMYER

RECEIVED APRIL 1, 1946

---

[1] *Cf.* Richtmyer, THIS JOURNAL, **56**, 1637 (1934).

[2] E. Fischer and H. Fischer, *Ber.*, **43**, 2530 (1910).