

### Experimental

**Preparation of N-Acetyl-3,5-dibromo-L-tyrosine.**—Technical grade L-tyrosine (ca. 96%) was brominated in 1-mole lots in 5 parts of glacial acetic acid with slightly more than 2 moles of bromine by the method of Zeynek.<sup>6</sup> On this scale it was desirable to add the bromine gradually with stirring and complete the reaction by warming to 80–90°. After slow cooling the sparingly soluble hydrobromide was then easily filtered and washed free of color with cold acetic acid. The filtrate, which contains part of the product, was suitably used as solvent for brominating a second and third lot. The hydrobromide was dissolved in water and the amino acid precipitated with the calculated amount of ammonia; yield 75–83%. Without further purification the material was acetylated as usual and obtained initially as tan microcrystals; over-all yield 65–68%. It is easily soluble in organic solvents and was best purified by crystallization (carbon) from water or preferably 15% methanol as colorless glistening plates (hemihydrate), m.p. 118–120° (dec.);  $[\alpha]^{25D} +34.5^\circ$  (c 4, methanol); solubility in water, 0.25 per 100 cc. of solution at 25°. It titrates as a diacid (glass electrode) with inflection points at pH ca. 5.6 and 9.3.

*Anal.* Calcd. for  $(C_{11}H_{11}O_4NBr_2)_2 \cdot H_2O$ : neut. equiv. (diacid), 194.9; N, 3.59. Found; neut. equiv., 195.0; N, 3.55.

**N-Acetyl-3,5-dibromo-DL-tyrosine** was prepared similarly from DL-tyrosine.<sup>7</sup> It is much less soluble than the L-form and was crystallized from methanol; m.p. 213–215° (dec.).

*Anal.* Calcd. for  $C_{11}H_{11}O_4NBr_2$ : neut. equiv. (diacid), 190.5; N, 3.68. Found: neut. equiv., 190.9; N, 3.62.

**Resolution of  $\alpha$ -Phenylethylamine with Acetyl-L-leucine.**—The reagents (1 mole) were combined in 250 cc. of water and the salt dissolved in 850 cc. more hot water. Successive crops were systematically recrystallized from (initially) 6–7 parts of water and after two series gave 130.5 g. (89%) of the (+)-amine salt as narrow prisms, m.p. 185–190° (dec.);  $[\alpha]^{25D} -8.8^\circ$  (c 4, methanol); solubility in water at 25°, 5.57 g./100 cc. The foot fractions gave fine needles of the considerably more soluble (–)-amine salt but this was not completely purified. The (+)-amine salt was decomposed as usual and the amine was extracted with benzene, dried and distilled; yield 80%, based on DL-form. The amine had  $[\alpha]^{25D} +39.2^\circ$  (without solvent,  $d^{25}_4$  0.94) in agreement with reported values.<sup>8</sup> The impure (–)-amine obtained similarly from the more soluble salt had  $[\alpha]^{25D} -33.6^\circ$ . Acetyltyrosine satisfactory for re-use was recovered in 94% yield.

(6) R. Zeynek, *Z. physiol. Chem.*, **114**, 275 (1921); C. T. Mörner, *ibid.*, **88**, 124 (1913).

(7) M. Fling, Thesis, Iowa State College, 1946; *C. A.*, **44**, 4050 (1950).

(8) A. W. Ingersoll, *Org. Syntheses*, **17**, 80 (1937).

**Resolution of  $\alpha$ -p-Tolylethylamine with Acetyl-L-leucine.**—The reagents (0.5 mole) were combined in 500 cc. of water and the salts fractionated as usual. The isomeric salts were not greatly different in appearance and solubility but after four crystallizations the (+)-amine salt was obtained (63%) as narrow prisms,  $[\alpha]^{25D} -12.7^\circ$  (c 4, water). The (–)-amine salt formed fine needles but was not purified. The (+)-amine was obtained as usual and had  $[\alpha]^{25D} -34.0^\circ$  (without solvent,  $d^{25}_4$  0.917).<sup>9</sup> The resolution is rather less convenient than that with (+)-camphoric acid.<sup>9</sup>

**Resolution of  $\alpha$ -Phenylethylamine with Acetyldibromo-L-tyrosine.**—The reagents (0.1 mole) were combined in 150 cc. of water (carbon) and the initial crop (27 g.) was recrystallized twice from 10 parts of water. The less soluble (–)-amine salt (17.8 g.) forms small flat prisms,  $[\alpha]^{25D} +43.8^\circ$  (c 4, methanol), unchanged after recrystallization. Additional amounts (total 20.6 g., 87.5%) were obtained from intermediate fractions. The amine from this salt was recovered as usual and had  $[\alpha]^{25D} -39.2^\circ$ .<sup>8</sup> Evaporation of the mother liquors gave fine needles of (+)-amine salt of which one fraction had  $[\alpha]^{25D} +48.0^\circ$  (c 4, methanol) but no attempt was made to purify this salt. Acetyldibromo-L-tyrosine was readily recovered.

**Resolution of  $\alpha$ -Phenyl-n-propylamine with Acetyldibromo-L-tyrosine.**—The reagents (0.1 mole) were combined in 900 cc. of water and the resolution conducted substantially as in the preceding example. The less soluble (–)-amine salt forms fine needles,  $[\alpha]^{25D} +52.2 \pm 0.3^\circ$ ; yield 83%. The remaining salt was much more soluble and was not purified. The (–)-amine from the less soluble salt had b.p. 202–206° (752 mm.),  $[\alpha]^{25D} -12.2^\circ$  (c 4, ethanol). No previous resolution of this amine has been found.

**Resolution of Acetyldibromo-DL-tyrosine.**—The acid and (–)- $\alpha$ -phenylethylamine (0.05 mole) were combined in 100 cc. of water and the less soluble salt was twice recrystallized (carbon) as previously described. For decomposition the pure salt (9.2 g.) in 150 cc. of boiling water was treated with a slight excess of concentrated hydrochloric acid. Pure acetyldibromo-L-tyrosine hemihydrate (5.5 g., 58% of the DL-form taken) crystallized on cooling. It had m.p. 119–120° and  $[\alpha]^{25D} +34.7^\circ$  (c 4, methanol) in close agreement with the product from natural L-tyrosine. The crude D-form (9.5 g.),  $[\alpha]^{25D} -22.5^\circ$ , was similarly recovered from the resolution liquors and converted to the (+)-amine salt. The twice recrystallized salt (7.5 g.) on decomposition gave pure acetyldibromo-D-tyrosine hemihydrate (5.0 g., 52%) with m.p. 119–120° and  $[\alpha]^{25D} -34.3^\circ$ , in close agreement with values for the antipode. These resolutions are satisfactory but do not proceed quite as readily as the reciprocal resolution of the amine.

(9) A. W. Ingersoll and F. B. Burns, *This Journal*, **54**, 4712 (1932).

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## The Resolution of Amino Acids. IV. Lysine<sup>1</sup>

BY F. J. KEARLEY AND A. W. INGERSOLL

DL-Lysine has been resolved into both forms by means of dibenzoyltartaric acid, with recovery of the active forms as hydrochlorides in about 65% yields. Resolution by means of the new agent, N-acetyl-3,5-dibromo-L-tyrosine, even more easily gave L-lysine monohydrochloride in good yield. Attempted resolutions of lysine with numerous other active acids and of diacetyllysine with various active bases were unsuccessful.

The first resolution of lysine was effected by Berg,<sup>2</sup> the L- and D-forms being obtained alternately through the normal (+)- and (–)-camphorates. More recently the asymmetric anilide synthesis induced by papain has been successfully applied to the carbobenzoxy derivative of lysine by Borsook, *et al.*,<sup>3</sup> and to the isobutyryl and

n-caproyl derivatives by Doherty and Popenoe.<sup>4</sup> Also, by using a repurified preparation of hog kidney enzyme, Greenstein and associates<sup>5</sup> have adapted their general method of selective hydrolysis to the resolution of lysine through the chloroacetyl derivatives.

The method of Berg, with minor modifications,<sup>6,7</sup>

(1) Taken from the Ph.D. thesis of Francis J. Kearley, September, 1950.

(2) C. P. Berg, *J. Biol. Chem.*, **115**, 9 (1936).

(3) H. Borsook, C. L. Deasy, A. J. Haagen-Smit, G. Keighley and P. H. Lowy, *ibid.*, **176**, 1383 (1948); **184**, 529 (1950).

(4) D. G. Doherty and E. A. Popenoe, *ibid.*, **189**, 447 (1951).

(5) J. P. Greenstein, J. B. Gilbert and P. J. Podor, *ibid.*, **182**, 451 (1950).

(6) N. Weissman and R. Schoenheimer, *ibid.*, **140**, 779 (1941).

(7) A. Neuberger and F. Sanger, *Biochem. J.*, **38**, 125 (1944).

is quite reliable. Its comparative directness is attractive in principle but the fractionations involved may be regarded as rather tedious. Accordingly, it seemed desirable to seek more convenient procedures through the salts of other active acids. The salts of some sixteen acids were tested, including the normal and acid salts of diacids. The acids included all of the better known resolving agents and certain others recently introduced in this Laboratory.<sup>8</sup> In general, the unusual combination of polar groups in lysine salts seems to promote excessive solubility and poor crystallizing power in water and low solubilities in non-polar solvents. Aside from the camphorates, which were re-examined for comparison, only salts of dibenzoyltartaric acid and of N-acetyl-3,5-dibromo-L-tyrosine<sup>9</sup> gave satisfactory resolutions.

Crystallization of the lysine hydrogen dibenzoyltartrates from aqueous 2-propanol gave physically distinct salts of D-lysine and L-lysine. Partially mechanical separation of the salts, followed by recrystallization with selective seeding, gave both salts substantially pure in 76–82% yields. Decomposition with hydrochloric acid permitted recovery of the resolving agent and active lysine hydrochlorides.

Resolution through N-acetyl-3,5-dibromo-L-tyrosine salts was rapid and conventional. The substantially pure L-lysine salt (84%) separated from water in well-defined needles and was easily purified by one or two recrystallizations. Decomposition gave pure L-lysine mono- or dihydrochloride in good yields. An even more convenient and economical modification employing the readily accessible DL-lysine monohydrochloride instead of free lysine was also developed. Recovery of the resolving agent is nearly quantitative.

Attempts to resolve diacetyl-DL-lysine with  $\alpha$ -fenchylamine,  $\alpha$ -phenylethylamine, brucine, cinchonine, quinine, ephedrine and desoxyephedrine were not successful.

### Experimental

**Materials.**—DL-Lysine (17% water solution) and DL-lysine monohydrochloride were generously supplied by the du Pont Company through the courtesy of Dr. A. O. Rogers. Diacetyl-DL-lysine was prepared as usual<sup>9</sup> but was conveniently crystallized from 4:1 methanol-acetone mixture. N-Acetyl-3,5-dibromo-L- and -D-tyrosine were prepared as recently described.<sup>8</sup> Dibenzoyltartaric acid was prepared from (+)-tartaric acid as by Butler and Cretcher<sup>10</sup>; after digestion with benzene to remove benzoic acid, it readily crystallizes from moist ethylene chloride as the monohydrate,  $[\alpha]_D^{25} -118^\circ$  (*c* 4, ethanol). The other acids tested were (+)-tartaric, (-)-malic, (-)-mandelic, (+)-camphoric, (+)-camphor-10-sulfonic, (+)- $\alpha$ -bromocamphor- $\pi$ -sulfonic, (-)- $\beta,\beta'$ -dinitrodiphenic, *p*-nitrobenzoyl-L-glutamic and phthalimido-L-glutamic acids and the N-acetyl derivatives of L-valine, L-leucine, L-phenylalanine, L-phenylglycine and 3,5-dinitro-L-tyrosine.

**Resolution of Lysine with Dibenzoyltartaric Acid.**—Numerous trials with solutions of the acid salt in various concentrations of aqueous lower alcohols showed that the isomeric salts are not greatly different in solubility. However, upon undisturbed cooling of warm solutions the first deposit is usually nearly pure D-lysine salt; this crystallizes

slowly as a hard crust of hexagonal plates. The somewhat more soluble L-lysine salt may later appear spontaneously or by seeding or disturbance, and then crystallizes rapidly as fine, fragile needles. When both salts crystallize together the deposit is best redissolved and another trial undertaken. Purification of each salt is effected by suitable mechanical separation and one or more recrystallizations.

The D-lysine salt crystallizes as a fairly stable dihydrate. When air-dry it has m.p. 136–140° (dec.),  $[\alpha]_D^{25} -86 \pm 2^\circ$  (*c* 4, water).

*Anal.* Calcd. for  $C_{24}H_{28}O_{10}N_2 \cdot 2H_2O$ : H<sub>2</sub>O, 6.67; C, 53.30; H, 5.97. Found: H<sub>2</sub>O, 6.60; C, 52.86; H, 5.87.

The L-lysine salt crystallizes as a dihydrate which rather rapidly loses water in air, forming a hemihydrate with m.p. 168–170°,  $[\alpha]_D^{25} -78 \pm 2^\circ$  (*c* 4, water).

*Anal.* Calcd. for  $(C_{24}H_{28}O_{10}N_2)_2 \cdot H_2O$ : H<sub>2</sub>O, 1.75. Found: H<sub>2</sub>O, 1.80.

The constants of the salts assist in guiding the selection of fractions but are not precisely characteristic. Estimation of purity is based mainly on experienced observation of crystalline appearance, with final confirmation through rotation values of regenerated lysine hydrochlorides.

In a typical experiment 29.2 g. (0.2 mole) of DL-lysine in 170 g. of water solution was mixed with 75.2 g. (0.2 mole) of dibenzoyltartaric acid monohydrate in 280 cc. of warm 2-propanol and the mixture was heated in a covered flask to dissolve all traces of salts. Undisturbed cooling overnight gave 40 g. of crude D-lysine salt. The mother liquor on decantation promptly gave 53 g. of crude L-lysine salt, which was collected by suction after an hour. Chilling the filtrate overnight at 5° gave a third crop (6 g.) rich in D-lysine salt. The first crop was dissolved in 2 parts of hot water and the solution diluted with twice its volume of 2-propanol. Substantially pure D-lysine salt then slowly crystallized at room temperature. The decanted liquor was used to recrystallize the third crop. In this manner 41.5 g. (82%) of D-lysine salt was obtained. The crude L-lysine salt was recrystallized similarly but more rapidly; a second crystallization from fresh solvent was required to attain substantial purity; the yield was 36.7 g. (76%). Minor crops from chilling filtrates were retained for crystallization with later runs. In early experiments combined liquors were evaporated to dryness *in vacuo* and the waxy residues, after washing with 2-propanol, were retained for reworking. Because of decomposition losses on evaporation, however, liquors are best re-used as solvent in later runs.

**Active Lysine Hydrochlorides.**—D-Lysine dibenzoyltartrate (10 g.) in 100 cc. of water was decomposed with 7 cc. of 6 N hydrochloric acid and the dibenzoyltartaric acid was extracted with 50 cc. of ether. The aqueous layer was evaporated to a sirup; this was dissolved in 10 cc. of warm 95% ethanol and D-lysine dihydrochloride was precipitated by 40 cc. of acetone. The salt was recovered by decantation, washed with acetone and dried *in vacuo*; yield 3.75 g. (87%),  $[\alpha]_D^{25} -15.3 \pm 0.2^\circ$  (*c* 4, water). The slightly hygroscopic material was triturated with a little absolute ethanol, washed with ether and redried. It then had  $[\alpha]_D^{25} -15.8^\circ$  (*c* 4, water). Berg<sup>2</sup> reported  $[\alpha]_D^{25} -15.63^\circ$  (*c* 3, water). The sample was converted to D-lysine monohydrochloride with the precautions indicated by Rice.<sup>11</sup> The carefully dried product had  $[\alpha]_D^{25} -10.0 \pm 0.2^\circ$  (*c* 4, water).

L-Lysine dihydrochloride and L-lysine monohydrochloride were prepared similarly from L-lysine dibenzoyltartrate and had, respectively,  $[\alpha]_D^{25} +16.0^\circ$  and  $+10.1^\circ$  (*c* 4, water).

**Resolutions with Acetyl-3,5-dibromo-L-tyrosine (A) Direct Procedure.**—The salts (0.2 mole) were formed by dissolving the acid (78.0 g.) in the calculated amount (170 g.) of hot 17% DL-lysine solution. The L-lysine salt separated as a thick mass of fine needles and was filtered off and washed with a little cold methanol in which it is sparingly soluble. Two further small crops were obtained by concentration; filtration was aided by dilution of the sirupy liquors with a little methanol. The much more soluble D-lysine salt remained in the liquors. The successive crystalline crops were recrystallized systematically from 1.5 parts of water and an equal volume of methanol. Further recrystallization in this way or from water alone caused no change in properties.

(8) H. D. DeWitt and A. W. Ingersoll, *THIS JOURNAL*, **73**, 5782 (1951).

(9) A. H. Gordon, A. J. P. Martin and R. L. M. Syngé, *Biochem. J.*, **37**, 79 (1943).

(10) C. L. Butler and L. H. Cretcher, *THIS JOURNAL*, **55**, 2605 (1933).

(11) E. E. Rice, *Biochem. Preparations*, **1**, 63 (1940).

The pure L-lysine salt (monohydrate) had m.p. 166–168° (dec.),  $[\alpha]^{25}_D +36.8 \pm 0.3^\circ$  (*c* 4, water); yield 45.5 g. (84%).

Anal. Calcd. for  $C_{17}H_{25}O_6N_3Br_2 \cdot H_2O$ : C, 37.43; H, 4.99. Found: C, 37.49; H, 4.98.

**L-Lysine Monohydrochloride.**—A sample of the pure L-lysine salt (31.5 g.) was dissolved in 10 parts of hot water and 12 cc. of concentrated hydrochloric acid was added. The resolving agent (hemihydrate) then crystallized on cooling (97%) in condition suitable for re-use. The filtrate was evaporated to dryness *in vacuo*, the residue was taken up in 80 cc. of 95% ethanol and L-lysine monohydrochloride was precipitated by adding 5.9 g. of pyridine and keeping overnight at 5°. The salt was taken up in 10 cc. of water and reprecipitated with 40 cc. of ethanol.<sup>11</sup> After washing with absolute ethanol and ether and drying it weighed 8.75 g. (80%) and had  $[\alpha]^{25}_D +10.1^\circ$  (*c* 4, water);  $+18.7^\circ$  (*c* 4, 0.6 N HCl);  $+19.9^\circ$  (*c* 4, 6 N HCl). Doherty and Popoe<sup>4</sup> report  $[\alpha]^{24}_D +20.5^\circ$  (*c* 3, 6 N HCl). The combined rotation samples were recovered as the dihydrochloride which had  $[\alpha]^{25}_D +16.0^\circ$  (*c* 4, water).

The resolving agent and crude D-lysine hydrochlorides were recovered from the combined resolution liquors as for the L-form. The di- and monohydrochlorides had, respectively,  $[\alpha]^{25}_D -12.9^\circ$  and  $-8.1^\circ$  (*c* 4, water) and accordingly contained about 90% of the D-form.

(B) **Half-equivalent Salt Procedure.**—Acetyldibromo-L-tyrosine (0.10 mole) was dissolved in 100 cc. of hot water containing 0.12 mole of ammonia. DL-Lysine monohydrochloride (0.20 mole) was added and the L-lysine salt (monohydrate) obtained as before (three crops). After systematic

recrystallization from aqueous methanol it weighed 42.5 g. (78%) and was identical with the salt previously described. In a further simplification L-lysine monohydrochloride was obtained directly from this salt by decomposition with exactly one equivalent of hot dilute hydrochloric acid; the resolving agent was filtered off after cooling, the filtrate was evaporated to small volume and the hydrochloride precipitated with ethanol. The salt (13.2 g.) had  $[\alpha]^{25}_D +20.2^\circ$  (*c* 4, 6 N HCl). Crude D-lysine hydrochloride (20.3 g.) isolated similarly from the resolution liquors had  $[\alpha]^{25}_D -7.2^\circ$  (*c* 4, water).

**Supplementary Experiments (a).**—Equivalent amounts (0.01 mole) of N-acetyl-3,5-dibromo-D-tyrosine<sup>8</sup> (ammonium salt) and the *ca.* 90% D-lysine monohydrochloride from (A) above gave the expected pure D-lysine salt. Except for sign of rotation the salt was identical with its antipode; m.p. 166–168° (dec.),  $[\alpha]^{25}_D -37.0^\circ$  (*c* 4, water).

(b).—Attempted resolution of N-acetyl-3,5-dibromo-DL-tyrosine<sup>8</sup> (ammonium salt) with D-lysine (monohydrochloride) failed. The corresponding partially racemic double salt crystallized from water as the dihydrate in transparent thin plates, rapidly converted in air to the anhydrous form, m.p. 265–270° (charring). The salt was not resolved in methanol.

(c).—Attempts to obtain pure active lysine derivatives by fractional crystallization of partially active mixtures were not successful with the hydrochlorides, picrates and salicylidene derivatives. In each instance the DL-form was considerably less soluble; the active form was enriched in foot fractions but not completely purified.

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## Unsaturated Sulfonic Acids. I. Diels-Alder Reactions<sup>1</sup>

BY CHRISTIAN S. RONDESTVEDT, JR., AND JAMES C. WYGANT<sup>2</sup>

The methyl esters of 2-phenylethene-1-sulfonic acid and 2-*p*-nitrophenylethene-1-sulfonic acid form adducts with cyclopentadiene. These esters were inert to butadiene. Other derivatives, such as the sodium salts, the sulfonyl chlorides and the N,N-dialkylamides did not react with typical dienes. The adduct from methyl 2-*p*-nitrophenylethene-1-sulfonate and cyclopentadiene consists of stereoisomers, one of which can be converted to a bromosulfone. This observation supplies supporting evidence for the *trans*-configuration of 2-phenylethene-1-sulfonic acid derivatives.

A qualitative similarity between the sulfonyl group in sulfones and sulfonic acids and the carbonyl group was first demonstrated by Kohler.<sup>3,4</sup> The ability of the sulfonyl group to participate in conjugation with a carbon-carbon double bond<sup>5</sup> leads to a prediction that  $\alpha,\beta$ -unsaturated sulfones and sulfonic acids should be able to function as dienophiles. A recent survey<sup>6</sup> uncovered only two unsaturated sulfones—2,3-dihydrothiophene-1,1-dioxide and *p*-tolyl vinyl sulfone—which have undergone the Diels-Alder reaction. More recently, methyl ethylenesulfonate was coupled with cyclopentadiene at 140–150° to form a normal adduct.<sup>7</sup> As part of our investigation of unsaturated sulfonic acids and their derivatives, we have explored the condensation of derivatives of 2-phenyl- and 2-*p*-nitrophenylethene-1-sulfonic acid with typical dienes.

When methyl 2-*p*-nitrophenylethene-1-sulfonate was refluxed with cyclopentadiene in bromobenzene

solvent for one hour, an adduct was formed in 68% yield. Variations in time or temperature reduced the yield, either increasing tar formation or returning more starting material. The product was identified as methyl 6-*p*-nitrophenyl-2,5-endomethano-1,2,5,6-tetrahydrobenzenesulfonate by analysis of the adduct and several derivatives, and by analogy to the host of well-known Diels-Alder adducts.

The adduct is not sterically homogeneous, however. If methyl 2-*p*-nitrophenylethene-1-sulfonate were in the *cis* configuration, the Alder rules<sup>8</sup> predict a single adduct, with an *endo* configuration. Since more than one adduct is formed, the *trans* configuration of the dienophile is more probable. Further evidence for the *trans* assignment can be deduced from the failure of 2-phenylethene-1-sulfonyl chloride (starting material for the nitro derivatives) to be cyclized to benzothiophene-1,1-dioxide,<sup>9</sup> whereas 2,2-diphenylethene-1-sulfonyl chloride is readily cyclized by aluminum chloride in nitrobenzene.<sup>10</sup> Moreover, 2-*o*-nitrophenylethene-1-sulfonyl chloride, a by-product in the nitration of 2-phenyl-

(1) A grant from the University of Michigan Faculty Research Fund supported part of this work.

(2) Abbott Laboratories Fellow, 1950–1951.

(3) E. P. Kohler and H. Potter, *THIS JOURNAL*, **57**, 1316 (1935).

(4) E. P. Kohler, *Am. Chem. J.*, **30**, 680 (1898).

(5) H. P. Koch, *J. Chem. Soc.*, 2892 (1950), and previous papers.

(6) H. L. Holmes in "Organic Reactions," Vol. IV, John Wiley and Sons, Inc., New York, N. Y., 1948, p. 141.

(7) A. Lambert and J. D. Rose, *J. Chem. Soc.*, 46 (1940).

(8) These rules, which predict the steric nature of the adduct, are discussed briefly by M. C. Kloetzel in "Organic Reactions," Vol. IV, John Wiley and Sons, Inc., New York, N. Y., 1948, p. 10.

(9) C. S. Rondestvedt, Jr., Ph.D. Thesis, Northwestern University, 1948.

(10) F. G. Bordwell and Marvin Peterson, private communication.