tion was cooled to 0° and the precipitated succinimide was collected on a filter and washed with several portions of cold benzene (wt. 1.19 g., m. p. 123–124.5°).

B. **Dehydrobromination.**—The benzene solution from above was concentrated, transferred to a small flask, and the remainder of the benzene was removed. To the residual yellow oil 8 ml. of isoquinoline was added portionwise with agitation. The flask was then set in an oil-bath and the bath was heated to 180° for twenty-five minutes, then to 190° for five minutes, after which the flask was removed and allowed to cool.

An excess of dilute hydrochloric acid was added to the mixture and the acid solution was extracted thoroughly with benzene. The benzene extracts were combined; the dark solution was washed first with dilute hydrochloric acid and then with water and finally concentrated to a small volume. The resulting black oily solution was transferred to a short-path distilling bulb with benzene and the low-boiling material was distilled at atmospheric pressure. Distillation of the residue yielded 1.50 g. (76%) of a pale yellow oil; b. p. 110° (0.2 mm.), $n^{20}\text{D}$ 1.5468. After redistillation the oil was water-white ($n^{20}\text{D}$ 1.5468) and a sample of it solidified on standing to a low-melting solid. Another sample of this colorless redistilled oil was then taken up in absolute ether–petroleum ether (30–60°) and the solution was inoculated with the solid and cooled to yield fluffy white needles which were collected on a filter, washed with petroleum ether and air dried; m. p. 41–42.5°. Subsequent hydrolysis of this compound to III identified it as *o*-cyanohydrocinnamonitrile. The crystalline dinitrile was recrystallized two times from absolute ether–petroleum ether (30–60°) and submitted for microanalysis; m. p. 41–42.5°.

Anal. Calcd. for $C_{10}H_8N_2$: C, 76.90; H, 5.16. Found: C, 76.79; H, 5.29.

Hydrolysis of *o*-Cyanohydrocinnamonitrile (II).—A mixture of 0.50 g. of II, 5 ml. of 20% potassium hydroxide and 5 ml. of 95% ethanol was brought to boiling on a steam cone and was allowed to reflux until ammonia evolution had practically ceased (twenty-four hours). Most of the alcohol was distilled, the aqueous residue was cooled and then was neutralized dropwise with concentrated hydrochloric acid. Before the neutral point was reached, a brown solid separated which was collected on a filter, washed with several ml. of water (washings added to the filtrate) and dried; 0.12 g., m. p. 205–215° (dec.). This basic substance was not identified. Acidification of the basic filtrate from above yielded 0.07 g. of an infusible, neutral solid which was presumed to be the diamide of III. After standing overnight, the acidic filtrate had deposited crystals of acid which were collected, washed and dried; 0.14 g., m. p. (155°) 164–166°. Concentration of the mother liquors yielded an additional 0.14 g. of crude acid. One recrystallization from water (Darco) raised the melting point to 166.5–168°. After two more recrystallizations from water the product melted at 166.5–168° alone or when mixed with authentic III prepared as described below.

Anal. Calcd. for $C_{10}H_{10}O_4$: C, 61.85; H, 5.19. Found: C, 61.99; H, 5.29.

Preparation of *o*-Carboxyhydrocinnamic Acid[4] (III).—The oxidation of 2.00 g. of 1,2-dihydronaphthalene with aqueous potassium permanganate solution at 9–11° yielded 0.34 g. of III, m. p. 163–167° (lit.[4] 162–164°), along with unchanged hydrocarbon. After several recrystallizations from water (Darco) the pure acid melted at 166.5–168° (lit.[4] 166–167°).

Dimerization Experiments with *cis*- and *trans*-1-Cyano-1,3-butadiene.—Into a small distilling flask was placed 3.0 g. of higher-boiling 1-cyano-1,3-butadiene ($n^{20}\text{D}$ 1.4960) and *ca.* 0.1 g. of picric acid. The flask was stoppered and left on a steam cone until the material had thickened to a sirupy consistency (sixteen hours). When the contents of the flask was submitted to high vacuum distillation there was obtained as distillate 2.0 g. (66%) of oily dimer, $n^{20}\text{D}$ 1.5172. From the Dry Ice-trap there was recovered *ca.* 0.5 g. (16%) of monomeric cyanodiene. A small amount of polymeric residue remained in the flask.

In a like manner, 3.0 g. of the lower-boiling isomer ($n^{20}\text{D}$ 1.4852) was heated for eighteen hours to yield 0.4 g. (13%) of dimer ($n^{20}\text{D}$ 1.5112). Recovered monomer amounted to *ca.* 0.5 g. (16%) while the major portion of the material remained as polymer in the flask. From a second experiment with the same quantity of lower-boiling isomer, 0.4 g. (13%) of dimer ($n^{20}\text{D}$ 1.5155) and 0.9 g. (30%) of monomer were isolated after nine hours at 100°.

Several grams of once-crystallized dimer was heated with picric acid on the steam cone for twenty-five hours and then distilled. The material was unchanged, and left no polymeric residue upon distillation.

Summary

The cyclic dimer of 1-cyano-1,3-butadiene has been isolated and characterized as 1-(β-cyanovinyl)-2-cyano-3-cyclohexene. The structure was proved by aromatization of the dimer to *o*-cyanohydrocinnamonitrile and hydrolysis of this dinitrile to the known *o*-carboxyhydrocinnamic acid. Experiments with the *cis* and *trans* isomers of 1-cyano-1,3-butadiene indicate that the higher-boiling isomer (presumably *trans*) is the chief source of the dimer.

Urbana, Illinois Received October 11, 1948

[Contribution from the Chemical Laboratories of the University of Maryland]

1,3,5,7-Octatetraene

By G. Forrest Woods and Louis H. Schwartzman[1]

The reaction of 2,4-pentadienal[2] with methylmagnesium bromide was shown to yield 1,3-hexadien-5-ol. This latter substance was dehydrated very readily over activated alumina to yield 1,3,5-hexatriene.[3]

$$CH_2{=}CH{-}CH{=}CH{-}CHO + CH_3MgBr \longrightarrow$$
$$CH_2{=}CH{-}CH{=}CH{-}CHOH{-}CH_3 \longrightarrow$$
$$H{-}(CH{=}CH)_3{-}H$$

Pentadienal has now been utilized as a starting material for the synthesis of 1,3,5,7-octatetraene.

Allylmagnesium bromide (I) reacts very smoothly with 2,4-pentadienal (II) to yield 1,3,7-octatrien-5-ol (III). The possibility of a rearrangement in the reactions leading to (III) or rearrangement of (III) itself had to be considered.[3,4] Accordingly, 1,3,7-octatrien-5-ol was catalytically reduced to the saturated alcohol, 4-octanol (IV) and identified as the α-naphthylurethan, and the

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(1) National Institute of Health Predoctorate Fellow.

(2) (a) Woods and Sanders, This Journal, **68**, 2483 (1946); (b) Woods and Sanders, *ibid.*, **69**, 2926 (1947).

(3) Woods and Schwartzman, *ibid.*, **70**, 3394 (1948).

(4) Heilbron, Jones, McCombie and Weedon, *J. Chem. Soc.*, 84, (1945).

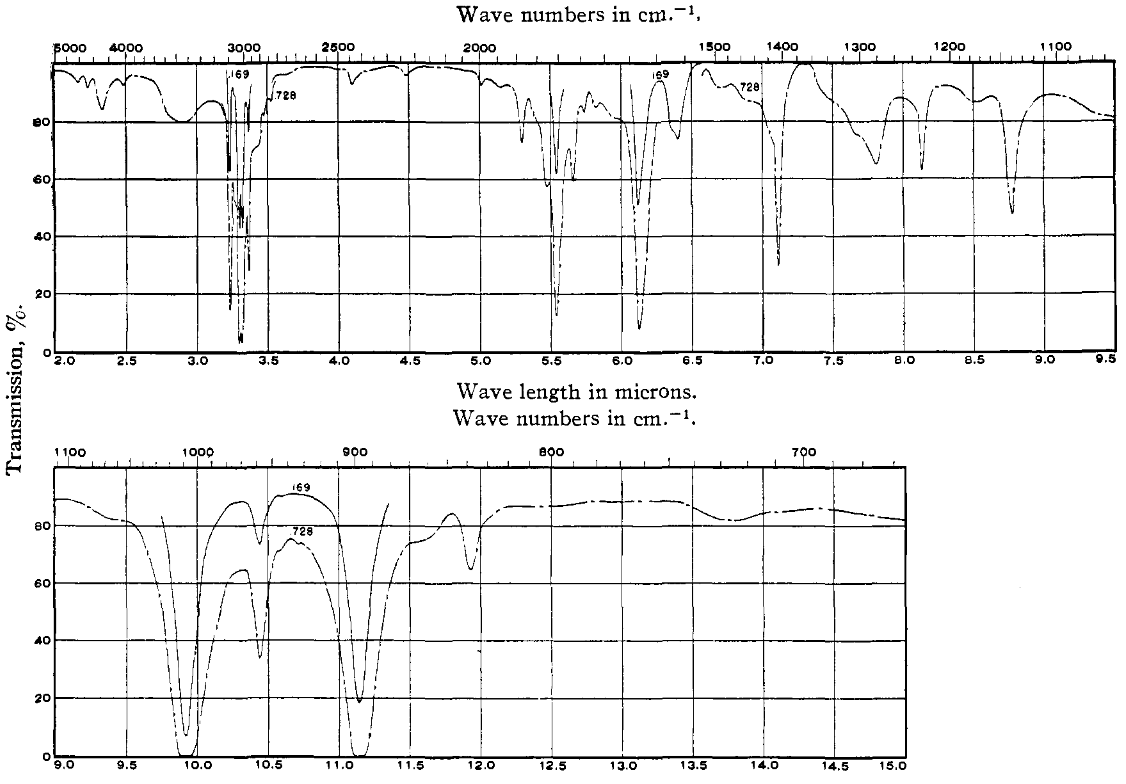
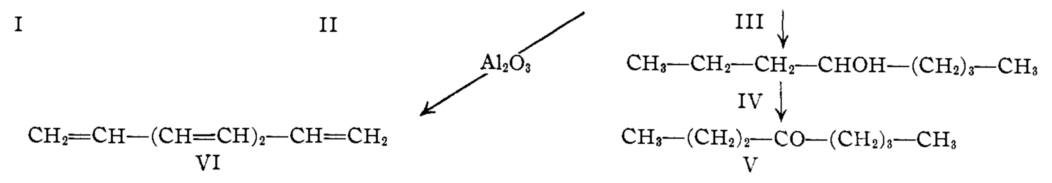


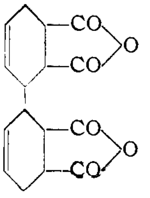
Fig. 1.—Infrared absorption spectrum of 1,3,5,7-octatetraene.

alcohol oxidized to the known 4-octanone (V) and identified as the semicarbazone. In this manner the absence of any rearrangement was established. The catalytic dehydration with activated alumina of the unsaturated alcohol, 1,3,7-octatrien-5-ol, led to the hydrocarbon 1,3,5,7-octatetraene (VI), a white crystalline solid melting at approximately 50° which was recrystallized from petroleum ether. The hydrocarbon sublimes on warming and rapidly polymerizes on standing. The equations for these reactions are given below.



The following facts were used to establish the structure of VI. The hydrocarbon, VI, upon catalytic reduction, absorbed almost four moles of hydrogen and the product of reduction was established as *n*-octane. The infrared spectrum,[5] Fig. 1, which is very similar to that of 1,3,5-hexatriene[4] indicates the absence of allenic, acetylenic, or benzenoid structures. Elemental analyses indicate the formula C_8H_{10}.

It is interesting to note that the ultraviolet absorption spectra, Fig. 2, of octatetraene is considerably different from that reported for cyclooctatetraene.[6] Treatment of octatetraene in petroleum ether with bromine leads to a relatively stable tetrabromide, $C_8H_{10}Br_4$, of unknown structure, while the Diels–Alder reaction yields a molecule into which two maleic anhydride structures have been incorporated. Several structures for this substance, $C_{16}H_{14}O_6$, are possible, one of which is the partially hydrogenated diphenyltetracarboxylic acid dianhydride, VII. It seemed that this substance should readily undergo dehydrogenation to the known 2,2′,3,3′-diphenyltetracarboxylic acid dianhydride. Since our attempts to dehydrogenate this substance were unsuccessful, we believe that the adduct is not VII. However, quantitative hydrogenation of this same adduct led to the absorption



VII

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(5) The infrared spectrum was kindly determined for us by Dr. Don C. Smith of the Naval Research Laboratory.

(6) Cope and Bailey, THIS JOURNAL, **70**, 2305 (1948).

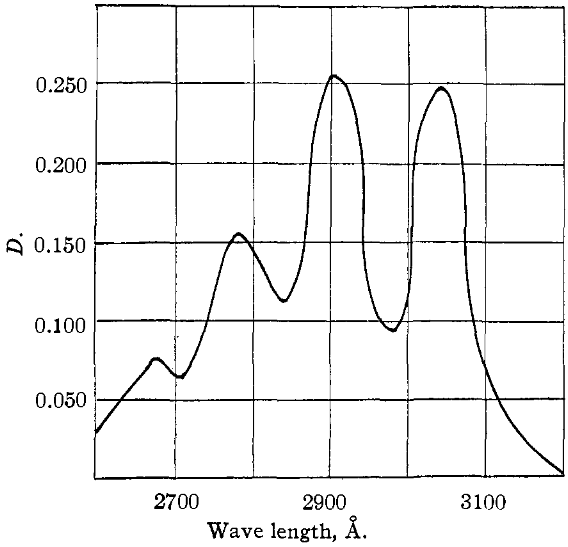

Fig. 2.—Ultraviolet absorption spectrum of 1,3,5,7-octatetraene.

of two moles of hydrogen showing that the molecule still had two ethylenic links, again substantiating the proof of four ethylenic links in the original hydrocarbon. Since 1,3,5,7-octatetraene can exist in either of three geometrical isomerides, we believe that we have one of these isomers pure in view of our method of purification. The difficulties of assigning configuration to this substance would be greater than for 1,3,5-hexatriene[4] in which instance we were unsuccessful.

To illustrate a property of octatetraene we report an incident which occurred in handling the material. A freshly recrystallized sample of octatetraene of about 1 g. was standing in a Büchner funnel covered with a beaker. This material underwent a decomposition somewhat less violent than an explosion. Marked white fumes were given off and a pungent aldehyde odor was present. We assume that a combustion takes place as a consequence of the heat liberated in the polymerization of octatetraene. It was because of the rate of polymerization that we are unable to report a melting point or give an evaluation to the extinction coefficients of the ultraviolet or infrared absorption curves of octatetraene.

Experimental

1,3,7-Octatrien-5-ol (III).—An ethereal solution (600 ml.) of allylmagnesium bromide was prepared from 80 g. of allyl bromide and 45 g. of powdered magnesium using Gilman's procedure.[7] The ether solution of allylmagnesium bromide was then pumped with nitrogen away from the excess magnesium powder. To this chilled solution, was added 41 g. of pentadienal[2] dissolved in 100 ml. of anhydrous ether. The mixture was stirred for an additional fifteen minutes at room temperature. The Grignard addition complex was decomposed with a saturated aqueous solution of ammonium chloride and the ether layer separated, washed with water and sodium bicarbonate solution, and dried over magnesium sulfate. After removal of the ether under reduced pressure the octatrienol was distilled in a nitrogen atmosphere: b. p. 70–71° (6 mm.), $n^{22}\mathrm{D}$ 1.4931; yield 55 g. (90%). *Anal.* Calcd. for $C_8H_{12}O$: C, 77.37; H, 9.74. Found: C, 77.35; H, 9.84.

Reduction of 1,3,7-Octatrien-5-ol.—This material (4 g.), dissolved in 70 ml. of ethyl alcohol, was hydrogenated with Raney nickel at room temperature and atmospheric pressure. The hydrogen uptake was 91% of the calculated value for three ethylenic links, and the time required for this uptake was approximately thirty minutes. The alcoholic solution was filtered and distilled under reduced pressure. The 4-octanol (3.8 g.) distilled at 79° (20 mm.), $n^{24}\mathrm{D}$ 1.3890.[8]

The α-naphthylurethan of 4-octanol, prepared in the usual way and recrystallized from petroleum ether (30–60°), melted at 60–61° and gave no depression in a mixed melting point determination with an authentic sample of this compound. *Anal.* Calcd. for $C_9H_{25}NO_2$: C, 76.22; H, 8.42. Found: C, 76.21; H, 8.22.

4-Octanol (6.9 g.) was oxidized with potassium dichromate (31.4 g.) dissolved in 200 ml. of water containing 42 g. of sulfuric acid. The temperature of the oxidation medium was not allowed to rise above 50°. The product, 4-octanone, was isolated by steam-distillation and extraction with ether. The ether extract was dried over magnesium sulfate and the ether removed under reduced pressure. 4-Octanone (3 g.) boiled at 164–168°.

The semicarbazone of this material prepared in the usual way melted at 95–97° after several recrystallizations from methyl alcohol–water and gave no depression with an authentic sample of the semicarbazone of 4-octanone. *Anal.* Calcd. for $C_9H_9N_3O$: C, 58.35; H, 10.34. Found: C, 58.42; H, 10.09.

1,3,5,7-Octatetraene (VI).—1,3,7-Octatrien-5-ol was distilled under reduced pressure (25 mm.) in a nitrogen atmosphere through a column, 35 cm. long of 16-mm. Pyrex tubing, filled with activated alumina (8–12 mesh) and heated by means of two electrical heating elements to a temperature of 250–280°. Two connected receivers were used, one cooled with an ice–calcium chloride-bath, and the other with an acetone–Dry Ice-bath. The products solidified in the receiver but, upon warming, the material melted, and most of the water layer was withdrawn by means of a medicine dropper. The residual material was dried over calcium oxide and crystallized from petroleum ether (20–40°) in a nitrogen atmosphere. From such a run 22 g. of 1,3,7-octatrien-5-ol yielded 11 g. (58%) of octatetraene.

The analysis of this substance required a special procedure. A combustion tube was mounted so that two gas entry lines were present into one of which the sample was to be introduced. The two gas lines were connected by a stopcock. The sample of octatetraene was introduced into the system in one line through which a slow stream of nitrogen was passing. The other line was introducing the oxygen. Warming of the sample sublimed the material into the combustion chamber. Finally oxygen was introduced through the sample line and the region of the sample strongly heated to burn the residual polymeric material which had formed from the octatetraene. *Anal.* Calcd. for C_8H_{10}: C, 90.51; H, 9.49. Found: C, 89.75; H, 9.77.

Octatetraene Tetrabromide.—A dilute solution of bromine in petroleum ether was added dropwise to a solution of octatetraene dissolved in petroleum ether. The bromine color was quickly discharged and a white crystalline material precipitated which, after several recrystallizations from acetone-water, melted at 123–125°. This substance is not very stable and evolves hydrogen bromide and darkens on standing. *Anal.* Calcd. for $C_8H_{10}Br_4$: C, 22.56; H, 2.35. Found: C, 23.75; H, 2.78.

Reduction of Octatetraene.—Reduction of octatetraene (4.5 g.) dissolved in 60 ml. of glacial acetic acid with 5% palladinized charcoal catalyst required approximately an

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[7] Gilman and McGlumphy, *Bull. soc. chim.*, **43**, 1322 (1928).

[8] Levene and Marker (*J. Biol. Chem.*, **91**, 405 (1931)) report a boiling point of 79° (16 mm.) and $n^{24}\mathrm{D}$ 1.3898.

hour at the end of which time slightly less than the theoretical amount of hydrogen had been consumed. The solution was filtered, poured into water and the acetic acid neutralized with sodium hydroxide. The product was extracted with ether, and the ether solution dried with magnesium sulfate and finally with metallic sodium. After removal of the ether, the residue was distilled (from sodium). *n*-Octane distilled at 126–128°; n^{30}_D 1.4001; d^{25}_4 0.714.

Diels-Alder Reaction of Octatetraene.—A solution of maleic anhydride (5 g.), octatetraene (2.5 g.), and benzene (50 ml.) was heated under reflux in a nitrogen atmosphere on a steam-bath for six hours. Almost immediately a white solid precipitated which became more copious as the reaction proceeded. Chilling and filtering the benzene solution yielded 4.5 g. of white solid which melted at 238–242° after several recrystallizations from glacial acetic acid. *Anal.* Calcd. for $C_{16}H_{14}O_6$: C, 63.57; H, 4.67; neut. equiv. (four carboxylic groups), 75. Found: C, 63.44; H, 4.78; neut. equiv., 73.

Refluxing of this material in moist xylene yielded another white crystalline solid which after recrystallization from acetone–xylene melted at 247–250°. This is the free tetracarboxylic acid. *Anal.* Calcd. for $C_{16}H_{18}O_8$: C, 56.80; H, 5.36. Found: C, 56.45; H, 5.41.

Reduction of the dianhydride $C_{16}H_{14}O_6$ (0.92 g.) dissolved in 25 ml. of glacial acetic acid with 5% palladinized charcoal at room temperature and atmospheric pressure required approximately one-half hour at the end of which time the reduction had stopped and the hydrogen absorption was the theoretical amount calculated for two ethylenic links. The solution, filtered, was poured into water and the solid isolated by filtration. After several recrystallizations from acetone–water a white solid melting at 260–261° was obtained. *Anal.* Calcd. for $C_{16}H_{22}O_8$: C, 56.13; H, 6.47. Found: C, 56.24; H, 6.58.

Attempts to dehydrogenate the dianhydride, $C_{16}H_{14}O_6$ were unsuccessful. However, when 2 g. of the anhydride was refluxed with 1 g. of palladinized charcoal and 10 ml. of *p*-cymene, a substance which precipitated on cooling was removed along with the catalyst upon filtration. The solid was leached out with hot acetone which upon cooling yielded a white solid. Recrystallization of this material from xylene gave a white solid melting at 267–268°, an isomer of the starting material. *Anal.* Calcd. for $C_{16}H_{14}O_6$: C, 63.57; H, 4.67. Found: C, 63.37; H, 4.76.

Ultraviolet Absorption Spectrum.—The ultraviolet absorption spectra of 1,3,5,7-octatetraene was determined in purified cyclohexane. The instrument was a Beckmann quartz ultraviolet spectrophotometer.

Infrared Absorption Spectra.—The infrared absorption spectra of a sample of octatetraene dissolved in carbon disulfide was determined for us by Dr. Don C. Smith of the Naval Research Laboratory.

Summary

The preparation and properties of an isomer of 1,3,5,7-octatetraene are reported.

COLLEGE PARK, MARYLAND RECEIVED NOVEMBER 1, 1948

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF NORTHWESTERN UNIVERSITY]

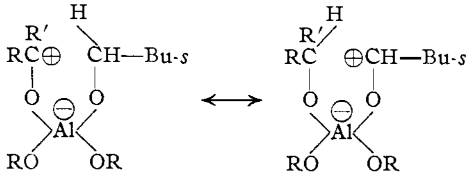
Catalysis with (−)Aluminum 2-Methylbutoxide[1]

BY ROBERT H. BAKER AND LOREN E. LINN[2]

The versatility of aluminum alkoxides in synthetic work prompted the preparation and use of an optically active one with the hope of achieving asymmetric syntheses.

The aluminate of *fermentation* amyl alcohol has been previously described[3] but because of the difficulty of purifying the product we have preferred to prepare the *active* aluminate indirectly from previously purified materials. These indirect preparations have previously been carried out with esters,[4] but in this work the alcohol, (−)2-methylbutanol, was easily exchanged with either aluminum isoproxide, *t*-butoxide, or *d,l*-2-butoxide.[5] With the latter alkoxide there was no activity of the 2-butanol that distilled from the reaction mixture.

In consequence of the high ionic character of the carbonyl group in ketones, 47%,[6] and the electronegativity of aluminum it seems that the principal contributing structure of the activated complex in the Meerwein–Ponndorf reaction would involve a carbonium ion, I or II.[7] The acceptance of the hydride ion would then lead to either of two diastereomers with the thermodynamically most stable being produced in excess.



I II

That this excess would not be expected to be large can be seen from the mass of experience in the reduction of optically active ketones with symmetrical aluminum alkoxides which generally give comparable amounts of the two alcohols.[8] Actually the system is considerably more complex than indicated by formulas I and II due to the fact that as the reaction progresses the nature of the alkoxyl groups changes. This factor would be expected to diminish the yield of asymmetric product.

Acetophenone is not well suited to this reaction

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[1] This work was supported by a grant from the Abbott Fund.

[2] Present address: Hercules Powder Co., Wilmington, Delaware.

[3] Gladstone and Tribe, *J. Chem. Soc.*, **39**, 1 (1881).

[4] Baker, THIS JOURNAL, **60**, 2673 (1938).

[5] This refers to alkoxide made from racemic 2-butanol, and hence may be a mixture of two monomeric racemates.

[6] Pauling, "The Nature of the Chemical Bond," 2nd ed., p. 75, Cornell University Press, Ithaca, N. Y., 1945.

[7] It should be observed that these structures are resonance forms of the structure usually assigned, $R_2C{=}\overset{\oplus}{O}{—}\overset{\ominus}{Al}(OR)_3$, *cf.*, Woodward, Wendler and Brutschy, THIS JOURNAL, **67**, 1425 (1945).

[8] Wilds in "Organic Reactions," Roger Adams, Editor, John Wiley and Sons, Inc., New York, N. Y., 1944, p. 185.