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]

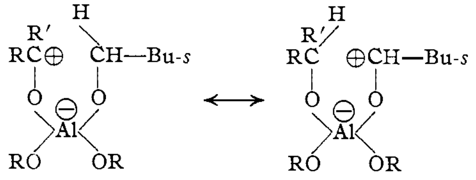
Catalysis with (−)Aluminum 2-Methylbutoxide[1]

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).

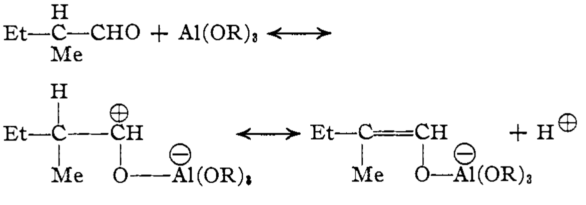
[8] Wilds in "Organic Reactions," Roger Adams, Editor, John Wiley and Sons, Inc., New York, N. Y., 1944, p. 185.

because of its oxidation potential relative to aldehydes[9] and its ease of condensation[10] but since it is reported to have been reduced to an active carbinol in a similar but non-reversible reaction,[11] attempts were made to reduce it. No phenylmethylcarbinol was obtained and it is of interest only to record that successive fractions of (−)2-methylbutanol which distilled from the mixture were progressively more racemized.[12]

p-Chlorobenzophenone was reduced only partially in order to favor the possible asymmetric synthesis but the carbinol was inactive.

The availability of the active alcoholate made it possible to study the Tischtschenko reaction with (+)2-methylbutanal. The kinetics of this reaction are first order in aldehyde and consistent with the possibility of a rapid formation of a complex of one molecule of aldehyde and catalyst.[13] No model for this complex has been proposed but Dr. B. Abramovitch in this Laboratory has been able to relate the role of the catalyst in the Meerwein–Ponndorf–Oppenauer reaction to that of the Tischtschenko[13] by showing a similar promoting effect of electronegative additives like zinc or aluminum halides in the Oppenauer[14] isomerization of dehydroisoandrosterone.

(+)2-Methylbutanal, 94% optically pure, and (−)aluminum 2-methylbutoxide, 96% optically pure, gave an ester which on hydrolysis was shown to be composed of an acid and an alcohol which were of comparable optical purity, 60%. The slightly higher value of the alcohol portion is accountable for on the basis of alkoxyl exchange with the catalyst.[4] The ester was shown not to be racemized by prolonged heating with the catalyst hence the molecules of aldehyde which suffer reduction and oxidation have probably a common intermediate with the racemization step as a side reaction following perhaps the mechanism of the usual acid catalyzed type of enolization.



$$\mathrm{Et{-}\overset{H}{\underset{Me}{C}}{-}CHO} + \mathrm{Al(OR)_3} \longleftrightarrow$$

$$\mathrm{Et{-}\overset{H}{\underset{Me}{C}}{-}\overset{\oplus}{\underset{\underset{O{-}\overset{\ominus}{Al}(OR)_3}{|}}{CH}}} \longleftrightarrow \mathrm{Et{-}\underset{Me}{C}{=}\underset{\underset{O{-}\overset{\ominus}{Al}(OR)_3}{|}}{CH}} + \mathrm{H}^{\oplus}$$

The present information does not allow the assignment of a reasonable role of the complex in the final formation of ester.

Experimental

(−)Aluminum 2-Methylbutoxide.—A solution of 6.5 g. (0.032 mole) of aluminum isopropoxide in 10 g. (0.11 mole) of 2-methylbutanol, α^{26}_{D} −9.26°, 2 dm., homogeneous; n^{20}_{D} 1.4100,[15] was distilled under a 16-plate column until 5 g. of isopropyl alcohol had been collected. The residue was then heated *in vacuo* at 200° to give 8.8 g., 88%, of the solid alkoxide, $[\alpha]^{25}_{\text{D}}$ −1.0° in toluene. Hydrolysis of the product with water produced the unracemized alcohol.

Attempted Reduction of Acetophenone.—A solution of 27 g. (0.094 mole) of (−)aluminum 2-methylbutoxide in 50 ml. of (−)2-methylbutanol was treated with 20 g. (0.16 mole) of acetophenone and the solution subjected to 16-plate distillation. The distillate, collected in four fractions, was 2-methylbutanol, n^{20}_{D} 1.4108–1.4100. The weights and α, 2 dm., were as follows: 5 g., −5.6°; 11 g., −5.5°; 16 g., −3.1°; 13 g., −1.9°. An additional 50 g. of alcohol was put in and the fractionation continued to give 5 g., −7.3°; 30 g., −7.4°; 4 g., −6.8°. The residue was hydrolyzed and the organic layer distilled at 10 mm. into five fractions, 22 g., b. p. 90–150°. These fractions were impure and had homogeneous rotations of *ca.* +1°, 2-dm. No phenylmethylcarbinol was isolated.

Reduction of 4-Chlorobenzophenone.—A solution of 2 g. (0.009 mole) of the ketone and 6 g. (0.024 mole) of aluminum *t*-butoxide in 36 g. (0.41 mole) of (−)2-methylbutanol was distilled at 16-plates until the head temperature reached 114°, three hours. Hydrolysis of the residue, separation, distillation of the alcohol and crystallization from petroleum ether gave 1.07 g., 53% of 4-chlorobenzhydrol, m. p. 60–61°.[16] A 9.2% solution in benzene gave no rotation.

(+)2-Methylbutyl 2-Methylbutanoate.—(+)2-Methylbutanal, α^{25}_{D} + 45.3°; 2-dm. homogeneous, was prepared by the method of Badin and Pacsu[17] and purified by 16-plate distillation from a batch protected with hydroquinone.

Following the method of Danilov,[18] a mixture of 25 g. (0.29 mole) of the aldehyde and 2 g. (0.007 mole) of (−)-aluminum 2-methylbutoxide was held at 0° for one hour, at room temperature for forty minutes, and at 80° for thirty minutes. Hydrolysis of the alkoxide with water and 16-plate distillation of the organic layer gave 15 g., 60%, of the ester, b. p. 61–61.6° (11 mm.); n^{20}_{D} 1.4135; α^{26}_{D} + 17.7°, 2-dm. homogeneous.

This ester was also isolated as a by-product of the aldehyde preparation, the homogeneous rotation being +26.8°, 2-dm. If this is assumed to be of the same optical purity as the aldehyde, 94%, the pure ester should be α^{25}_{D} + 28.3°, 2-dm. The Tischtschenko ester has 62% of this rotation.

Hydrolysis of the Tischtschenko Ester.—The ester, 5.5 g., was refluxed with 100 ml. of 6 *N* barium hydroxide for thirty-eight hours. The alcohol and acid were isolated by steam distillation and purified by distillation. The acid, α^{22}_{D} + 10.6°, 1-dm. homogeneous; n^{21}_{D} 1.4054, was 59% and the alcohol, α^{21}_{D} −3.01°, 1-dm. homogeneous; n^{21}_{D} 1.4102, was 62% pure.[19]

Summary

1. The preparation of the aluminate of (−)2-methylbutanol is described.

2. This optically active catalyst failed to bring about asymmetric reduction of aceto-

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[9] Baker and Adkins, THIS JOURNAL, **62**, 3305 (1940), and private communication.

[10] Wayne and Adkins, *ibid.*, **62**, 3401 (1940).

[11] Vavon, Riviere and Angelo, *Compt. rend.*, **222**, 959 (1946).

[12] Catalytic reduction of acetophenone in (−)2-methylbutanol over Raney nickel at 2000 p. s. i. and 125° produced inactive phenyl methyl carbinol in 75% yield, with the recovered solvent retaining full activity.

[13] Child and Adkins, THIS JOURNAL, **45**, 3013 (1923); **47**, 798 (1925).

[14] Oppenauer, *Rec. trav. chim.*, **56**, 137 (1937); U. S. Patent 2,229,599, Jan. 21, 1941.

[15] Baker and Linn, THIS JOURNAL, **70**, 3721 (1948).

[16] Montagne, *Rec. trav. chim.*, **26**, 266 (1907), gives m. p. 62°. Various other values are found in the literature.

[17] Badin and Pacsu, THIS JOURNAL, **67**, 1352 (1945).

[18] Danilov, *Trans. State Inst. Applied Chem.* (*Moscow*), No. 5, 66 (1927); *Chem. Abs.*, **22**, 2138 (1928).

[19] These calculations are based on the optical rotations of the purest alcohol (α^{25}_{D} −9.54°, 2 dm.) and acid (α^{25}_{D} +35.38°, 2 dm.) prepared in these laboratories. The purity of the aldehyde was calculated from the optical rotation of the pure alcohol and the data of Badin and Pacsu.[17]

phenone and *p*-chlorobenzophenone.

3. The Tischtschenko reaction with (+)2-methylbutanal leads to ester, the alcohol and acid portion of which have suffered the same extent of racemization.

EVANSTON, ILLINOIS RECEIVED OCTOBER 18, 1948

[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY]

Resonance and Polarity in the Molecules of Three Colored Compounds[1]

BY LAWRENCE M. KUSHNER AND CHARLES P. SMYTH

Dipole moment measurements made in this Laboratory have been used[2,3,4,5] to throw light on the resonance conditions in the molecules of certain un-ionized dyes, the results being satisfactorily correlated with the light absorption of the compounds. Dr. L. G. S. Brooker of the Eastman Kodak Company recently suggested to us measurements on three further colored compounds and furnished samples.

The three compounds are 3-ethyl-5-[4-(1-ethyl-3,3-dimethyl-2(3)-indolylidene)-butenylidene]-rhodanine (I), 1,3-diethyl-5-[4-(1-ethyl-3,3-dimethyl-2(1)-indolylidene)-2-butenylidene]-2-thiobarbituric acid (II) and 1,3-diethyl-5-[(1,3-diethyl-2(3)-benzimidazolylidene)-butenylidene]-barbituric acid (III), all three belonging to a new group of un-ionized dyes known as the merocyanines.[5a] These dyes contain the amide system, the essential grouping of which is

$$>N\left(-\overset{|}{C}=\overset{|}{C}\right)_n-\overset{|}{C}=O \longleftrightarrow \overset{+}{N}\left(=\overset{|}{C}-\overset{|}{C}\right)_n=\overset{|}{C}-O^-.$$

In such dyes one of the two extreme resonance structures is uncharged while the other is a dipole. Some discussion of these dyes from the resonance standpoint has already appeared.[5b] Proof was advanced that in I the polar structure Ib (see Discussion of Results) must be of higher energy and contribute less than the non-polar structure Ia, since replacement of the indolenine ring by one that was more basic (in the restricted sense used by Brooker) reduced the deviation in $\lambda_{\max.}$, whereas replacement by a less basic nucleus increased the deviation. Nevertheless the dipole moment of the compound was expected to be considerable.

Experimental Method

The dipole moments were measured in solution in benzene or dioxane. The benzene used as solvent for the more soluble compounds, I and II, was a thiophene-free product from the Barrett Company, which was purified by drying with sodium wire followed by distillation from the wire (boiling point, 80.55–80.90° at 772.8 mm.; dielectric constant at 30°, 2.2672). The dioxane used as solvent for the almost insoluble compound III was "practical" 1,4-dioxane from the Carbide and Carbon Chemicals Corporation, which was distilled from 101.1 to 101.5° at 762.9 mm., dried over sodium wire and redistilled from the sodium wire, the fraction used boiling at 101.0° at 757.7 mm. Its dielectric constant, measured directly at 30°, was 2.1984 ± 0.0002.

Because of the virtual insolubility in benzene and very low solubility in dioxane of compound III, the preparation of the solutions presented a problem. It was overcome by weighing out the compound in a small glass cup on a high sensitivity analytical balance and transferring both cup and compound to a 100-cc. weighing bottle, to which the dioxane was then added. In the case of the most concentrated solution, it was necessary to warm the mixture to achieve true solution. As there was obviously a risk of evaporating some dioxane, the final weighing to determine the weight of dioxane in the solution was not made until all the solid had been dissolved and the solution had cooled.

The dielectric constants of the dilute solutions were measured with a heterodyne beat apparatus developed from one which has been previously described.[6] The precision of the apparatus was increased by replacing the precision measuring condenser formerly used by a General Radio Company 722-D instrument, on which an 1100 micro-microfarad scale was employed. The dielectric cell was similar to that previously described.[7] The densities of the benzene solutions were measured at 30° with an Ostwald–Sprengel pycnometer, the technique employed being similar to that previously described.[8] The dipole moments were calculated from the experimental data by the method of Halverstadt and Kumler.[9] The dielectric constants, ϵ_{12}, and specific volumes, v_{12}, of the solutions were found to be linear functions of the mole fractions, c_2, of the solutes according to the equations

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[1] This research was carried out with the support of the Office of Naval Research.

[2] Brooker, Sprague, Smyth and Lewis, THIS JOURNAL, **62**, 1116 (1940).

[3] Brooker, White, Keyes, Smyth and Oesper, *ibid.*, **63**, 3192 (1941).

[4] Brooker and Sprague, *ibid.*, **63**, 3203 (1941).

[5] Brooker and Sprague, *ibid.*, **63**, 3214 (1941).

[5a] Papers dealing with these dyes are in course of preparation in Dr. Brooker's Laboratory.

[5b] Brooker, "Frontiers in Chemistry," Vol. III, Interscience Publishers Inc., New York, N. Y., 1945, p. 129.

[6] Lewis and Smyth, *J. Chem. Phys.*, **7**, 1085 (1939).

[7] Smyth and Morgan, THIS JOURNAL, **50**, 1547 (1928).

[8] Lewis and Smyth, *ibid.*, **61**, 3063 (1939).

[9] Halverstadt and Kumler, *ibid.*, **64**, 2988 (1942).