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Anomalous Reactions of Lithium Aluminum Hydride

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The preparation and properties of a number of branched 1,2- and 1,3-diols are described. The lithium aluminum hydride reduction of β -hydroxybutyraldehyde gives ethanol, among other products. The reduction of acetylacetone leads to a mixture consisting of 19% diketone (starting material), 70.5% pent-3-en-2-ol, and 2.5% of corresponding diol.

In connection with the study of the formation of homologous cyclic carbonates in the accompanying paper² it was necessary to prepare the required diols. The present paper describes the methods of preparation and properties of some of the needed compounds.

The methods used for the synthesis of the necessary diols were: (1) lithium aluminum hydride reduction of ketols and esters of dicarboxylic acids; (2) addition of Grignard reagents to β -hydroxyketones; (3) solvolysis of olefin dibromides.

The lithium aluminum hydride reduction of esters of ethylphenyl- and ethylisoamylmalonic acids proceeds smoothly, giving the corresponding 1,3-diols in 75% and 72% yield, respectively. However, the reduction of diethyl succinate resulted in a low yield of the desired 1,4-diol. This result is probably due to incomplete extraction of the diol from the reaction mixture.³

In the reduction of benzoin, we observed temperature-dependence in the stereochemical specificity of the hydride attack. Thus, whereas the reduction at 0° produced mesohydrobenzoin in 90% yield, the reduction similarly in boiling tetrahydrofuran gave a mixture of the isomers, meso- and isohydrobenzoin, in a ratio 3:1. This ratio is changed into 1.5:1, upon performing the reduction in boiling dioxane. The data here produced amplify the observations already recorded regarding the effect of temperature on the stereospecificity of the hydride attack.⁴

Unlike compounds described above, the lithium aluminum reduction of aldol took an anomalous course. This reaction yielded a complex mixture consisting of the required diol, ethanol, crotyl alco-

hol, and some other unidentified polymeric materials. The yield of 1,3-butanediol was 39%, whereas that of ethanol, actually isolated, amounted to 15%.

The observation described here clearly suggest that the reduction of aldol might have taken, at least partially, an anomalous course, involving C—C bond cleavage. Of course, the latter reaction might possibly have occurred either prior to or after the carbonyl group was reduced. In an experiment designed toward this establishment, 1,3-butanediol was similarly treated with a molar equivalent of lithium aluminum hydride. It was found that in comparable working conditions the unchanged diol could be recovered in high yield, but no ethanol could be detected.

From this, one can conclude that in the reduction process of aldol a carbon-carbon bond cleavage occurs prior to the hydride attack at the carbonyl group. This indicates that the final product in this reduction is determined by the order in which the groups are attacked. Initial reduction of the carbonyl group leads to the desired diol while prior reaction of the hydroxyl group can subsequently result in diol, or, by reversal of the aldol formation and further reduction, ethanol. In contrast to the reduction reaction, the addition of methyl magnesium iodide to acetaldo in ordinary conditions resulted in 70% yield of the corresponding diol. This reflects the different capacities of the above organometallic complexes of initiating a retrograde reaction of the aldol formation.

An inspection of the literature revealed that, although certain β -hydroxyketones are not affected by the mixed metal hydride complexes,⁵ yet C—C bond cleavages have actually been observed in the lithium aluminum hydride reductions of certain 1,3-bifunctional systems, of which at least one was of unsaturated character. Thus, similar C—C bond

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fissions have been reported in the reductions of cyanohydrines,⁶ β -nitro alcohols,⁷ β -nitroamines,^{7a} β -ketonitriles,⁸ and in diaryl ketones.⁹

The reduction of acetylacetone with an excess of lithium aluminum hydride produced a mixture consisting of 70.5% pent-3-en-2-ol, 19% of the starting β -diketone, 2.5% of 2,4-pentanediol, and 8% of yellow solid product. This finding was indicated by the infrared and ultraviolet spectra as well as by chemical evidence. Thus, all liquid fractions gave similar infrared spectrum showing bands (cm.^{-1}) at 3450, 1709, 1671, and 1639–1580, in the ultraviolet region of the spectrum, they show the presence of a single absorption band at 272 $\text{m}\mu$, which are typical for enolized β -diketones.¹⁰ Accordingly, they responded positively to both alcoholic ferric chloride solution and 2,4-dinitrophenylhydrazine reagent.¹¹

It is interesting to note that unlike the reduction of 2-hydroxymethylenecyclopentanone and of 2-hydroxymethylenecyclohexanone, which has been reported to produce the respective mixture of isomeric diols and unsaturated alcohols in a ratio of 1:14 and 1:6,^{5a} the ratio between the diol and the unsaturated alcohol in the foregoing reaction is of the order 1:28.

The yellow solid product, which has been isolated in the foregoing reaction, was analyzed as $\text{C}_8\text{H}_{12}\text{O}_4$. The chemical and spectroscopic data now at hand suggest that this compound might be a dimethyl-dihydroxy derivative of 1,3-cyclohexadione, but it was not investigated any further.

In common with analogous aliphatic and alicyclic enolizable β -dicarbonyls, it appears that the final product of the reduction of acetylacetone is determined by the order in which the groups, in both forms of the tautomeric mixture, are attacked. Initial reduction of the enol form, followed by elimination of an oxygen atom and further reduction, can subsequently result in pent-3-en-2-ol, while normal reduction of the diketone form leads to the desired diol. Accordingly, these results clearly suggest that, at ordinary reaction conditions, acetylacetone reacts predominantly *via* its enolic form,¹² but, unlike analogous alicyclic systems,^{5a} the

former shows a lesser tendency to lose an oxygen atom to form a C—C double bond. Considering the differences in effectiveness between lithium aluminum hydride and Grignard reagents in promoting an oxygen atom, elimination from the enolic forms of β -dicarbonyls,¹³ Freeman's finding,¹⁴ which observed monoaddition of phenyl magnesium bromide to acetylacetone at ordinary conditions and simple double addition on forcing conditions, is consistent with the data presented here.

The preparation of vic-diols by means of hydrolysis of the corresponding dibromides appears to be of limited practical value, and was found particularly valueless for the production of certain 2-alkyl-1,2-alkanediols. Thus, the solvolysis of 2-methyl-2,3-dibromobutane in aqueous sodium carbonate gave the corresponding diol in 51% yield, whereas similar treatment of isobutylene bromide failed to produce the desired 1,2-diol, but gave in part isobutyraldehyde.¹⁵

EXPERIMENTAL¹⁶

Materials. Diethyl ethylphenylmalonate (Riedel de Haen, Germany), diethyl ethylisoamylmalonate (Bubeir Dolder, Basel), and ethyl lactate (B.D.H.) were used without further purification. Commercial acetylacetone was fractionated and the cut boiling at 136–137° (680 mm.), λ_{max} 272 $\text{m}\mu$, ϵ 8540 (lit., λ_{max} 270 $\text{m}\mu$, $\epsilon = 10,000^{10}$) was used.

β -Hydroxybutyraldehyde (aldol) was prepared in 45% yield by the method of Grignard and Reiff.¹⁷ A fraction boiling at 85° (13 mm.) (lit.,¹⁸ b.p. 72° at 12 mm.) was used.

Benzoin, m.p. 128–129°, was prepared according to Adams and Marvel.¹⁹

Formation of diols by means of LiAlH_4 . The general technique described below is typical for the preparation of compounds listed in Table I. To a slurry of lithium aluminum hydride (5 g., 0.13 mol.) in dry ether (100 ml.) was added dropwise with agitation a solution of diethyl ethylisoamylmalonate (25.8 g., 0.10 mol.) in dry ether (100 ml.). After addition was completed, the reaction mixture was refluxed for two hr. and then allowed to stand overnight at room temperature. The excess of LiAlH_4 was decomposed with water (ice cooling) and the organo-metallic complex was decomposed by means of an equivalent amount of 25% aqueous phosphoric acid. The organic layer was separated and the aqueous layer was first centrifuged and then continuously extracted with ether. The ethereal extracts were combined, carefully dried, and after solvent removal the

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(14) J. P. Freeman, *J. Am. Chem. Soc.*, **80**, 1926 (1958).

(15) C. M. Suter and H. D. Zook, *J. Am. Chem. Soc.*, **66**, 738 (1944).

(16) All melting points were determined using a Dr. Tottoli melting point apparatus, and are uncorrected. Ultraviolet absorption spectra were determined with the aid of a Beckman quartz spectrophotometer, model DU, and were taken in 95% ethanol solution. Infrared spectra were taken with a Baird double beam recording spectrophotometer, model B. Analyses were performed by Mrs. Marika Goldstein at the microanalytical laboratory of the Department of Organic Chemistry, the Hebrew University.

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TABLE I
PREPARATION OF 1,2-, 1,3-, AND 1,4-DIOLS BY LITHIUM ALUMINUM HYDRIDE REDUCTION

Diol	Reaction Temp.	B.P.	Mm.	M.P.	n_D^{20}	Yield, %
Mesohydrobenzoin ^a	0			134-136		90
1,3-Butanediol ^b	34	69-70	0.6		1.4445	39
2-Ethyl-2-phenyl-1,3-propanediol ^c	34			79		75
2-Ethyl-2-isoamyl-1,3-propanediol ^d	63	133-135	10		1.4672	72
1,4-Butanediol ^e	34	140-143	27		1.4450	35-40

^a Recrystallized from benzene. J. S. Buck and S. S. Jenkins, *J. Am. Chem. Soc.*, **51**, 2163 (1929) give m.p. 134° for meso-hydrobenzoin. ^b O. J. Schierholtz and M. L. Staples, *J. Am. Chem. Soc.*, **57**, 2710 (1935) give b.p. 207.5° at 760 mm., n_D^{19} 1.4425 for pure 1,3-butanediol. ^c Recrystallized from carbon tetrachloride; H. L. Yale, E. J. Pribyl, W. Braker, J. Bernstein, and W. A. Lott, *J. Am. Chem. Soc.*, **72**, 3716 (1950) give m.p. 78-79°. ^d *Anal. Calcd.* for C₁₀H₂₂O₂: C, 68.9; H, 12.7. Found: C, 69.0; H, 12.4. ^e W. R. Kirner and G. H. Richter, *J. Am. Chem. Soc.*, **51**, 2505 (1929), give b.p. 108° at 4 mm., n_D^{20} 1.4467 for 1,4-butanediol.

residue was distilled fractionally through an efficient column. The m.p., b.p., and yields of the diols prepared are given in Table I.

The reduction of aldehyde. Freshly distilled β -hydroxybutyraldehyde (0.6 mol.) was brought to reaction with lithium aluminum hydride (0.37 mol.) in the manner here reported. The organo-metallic complex was decomposed by adding 55 g. of phosphoric acid (85%) and the crystalline insoluble phosphates formed were removed by filtration. The inorganic precipitate was thoroughly washed with ether, the ethereal extracts were combined, dried (Na₂SO₄), and the solvent was removed. The residue, upon fractional distillation through Widmer column gave three cuts: (1) 8.2 g. (15%) of ethanol, boiling at 78-80° (680 mm.), n_D^{20} 1.3700; (2) 1.5 g. of an impure crotyl alcohol, boiling at 30-32° (30 mm.), n_D^{20} 1.3440; (3) 21 g. (39%) of 1,3-butanediol. In the distilling flask a residue (11 g.) remained. It was transferred into a Claisen flask and was distilled at reduced pressure, yielding 5.5 g. of viscous oil boiling at 108-120° (0.5 mm.), leaving behind 4.5 g. of a polymeric material.

Identification of reaction products. The first cut, ethanol, was identified by preparing its 3,5-dinitrobenzoate, colorless needles melting at 94-95° (from ethanol water). Mixed melting point with an authentic specimen of ethyl 3,5-dinitrobenzoate gave no depression. The second cut gave a positive color test with tetranitromethane.

The action of LiAlH₄ on 1,3-butanediol. When 0.3 mol. of 1,3-butanediol was treated with 0.17 mol. of lithium aluminum hydride in a fashion described above, only unchanged starting material was recovered from the reaction mixture. The recovery amounted to 80-85%.

The reaction of acetylacetone with lithium aluminum hydride. Acetylacetone (1.0 mol.) was brought to reaction with an excess of lithium aluminum hydride (0.65 mol.) at boiling tetrahydrofuran, in a manner reported here. After the usual work-up, the crude reaction product was subjected to fractional distillation giving two fractions: (1) 36 g. of colorless liquid boiling at 119-121° (690 mm.), n_D^{20} 1.4325, λ_{max} 272 m μ (ϵ 1830); (2) 10 g. of a liquid of b.p. 122-127° (690 mm.), n_D^{20} 1.4355, λ_{max} 272 m μ (ϵ 2600).

Fraction 1 was analyzed by its infrared and ultraviolet absorption spectra, showing that it consists of a mixture of 18% acetylacetone and 82% pent-3-en-2-ol.

Anal. Found: C, 67.9; H, 10.3.

In a like manner Fraction 2 was found to consist of a mixture of 30% acetyl acetone, 57% pent-3-en-2-ol, and 13% of 2,4-pentanediol.

Anal. Found: C, 65.45; H, 10.55.

In the distillation flask a residue of a yellow solid product remained (5 g.). It gave upon recrystallization from carbon tetrachloride orange-yellow crystals melting at 192°, λ_{max} 278-282 m μ (ϵ 15,400).

Anal. Calcd. for C₈H₁₂O₄: C, 55.8; H, 6.97; mol. wt., 172. Found: C, 55.3; H, 6.94; mol. wt., 160 (Rast).

It gave an immediate red coloration with an alcoholic ferric chloride solution. This product was not investigated any further.

2,4-Pentanediol. This diol was at last prepared in good yields by employing either the Grignard method or the high pressure catalytic reduction of appropriate β -diketone.

(a) *The Grignard method* furnished this diol in 70% yield by reacting methyl magnesium iodide (2.5 mol.) with freshly distilled acetaldo (1.0 mol.), according to Franke and Kohn.²⁰ (b) *The catalytic reduction* of acetylacetone (1 mol.) was conducted at 70-80 atmospheric pressure and 125° in the presence of Raney nickel (8 g.) during 2 hr., according to Sprague and Adkins,²¹ resulting in a 50-70% yield of the desired diol. The cut boiling at 104-105° (17 mm.), n_D^{20} 1.4358 (reported²¹ b.p. 97-98° at 13 mm., n_D^{20} 1.4349) was collected.

2-Methyl butanediol-2,3. (a) *By Grignard method.* Into a cooled solution of methyl magnesium iodide (3 mol.) in dry ether (500 ml.) was added, dropwise with stirring, a solution of 1 mol. of ethyl lactate in ether (100 ml.), during 1 hr. The reaction mixture, after being refluxed for 1 hr., was poured into cooled 4*N* sulfuric acid, the aqueous layer was separated and then concentrated to one third of its volume by vacuum distillation. Solid sodium chloride was added and the whole was continuously extracted with ether. The crude diol, after solvent removal, was fractionally distilled at reduced pressure, affording the pure diol, of b.p. 93-95° 24 mm., n_D^{25} 1.4380 (reported²² b.p. 80-82° at 13 mm., 178° at 760 mm.), in 55% yield.

Anal. Calcd. for C₅H₁₂O₂: C, 57.7; H, 11.5. Found: C, 57.4; H, 11.5.

(b) *By solvolysis of 2-methyl-2,3-dibromobutane.* A mixture of 2-methyl-2,3-dibromobutane²³ (b.p. 74° at 31 mm., n_D^{20} 1.5118²⁴) (250 gr.) and 2300 ml. of 10% aqueous sodium carbonate solution was heated at 90° under vigorous agitation for 12 hr. The formation of some low boiling liquid is noted during this operation (probably an epoxy derivative). The cooled mixture was then continuously extracted by using ether as solvent. After drying and solvent removal,

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the residue was fractionated at reduced pressure to yield 120 gr. of starting dibromide (b.p. 70° at 30 mm., n_D^{25} 1.4385) and 30 gr. of 2-methyl-2,3-butanediol, b.p. 93–95° at 24 mm., n_D^{25} 1.4375. The yield based upon 2-methyl-2,3-dibromobutane consumed, was 51%. The yield based upon dibromide used amounted to 27% conversion.

Treatment of isobutylene dibromide with aqueous potassium carbonate at 55° during 5 days resulted in its 40% conversion into isobutyraldehyde (b.p. 62°, n_D^{20} 1.3725), but no diol could be isolated.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF NORTHWESTERN UNIVERSITY]

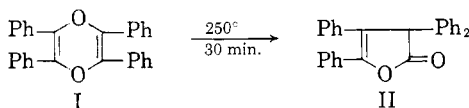
Thermal Rearrangement of Tetraphenyl-*p*-dioxadiene

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Tetraphenyl-*p*-dioxadiene (I) differs markedly from the analogous sulfur compound, 2,5-diphenyl-*p*-dithiadene, in that it rearranges on pyrolysis to give a lactone whereas the sulfur compound decomposes to give a thiophene derivative. Similarities in the chemistry of I and *cis*-dibenzoylstilbene (III), which gives the same lactone on pyrolysis, are discussed.

Parham and Traynelis have recently described the thermal decomposition of 2,5-diphenyl-*p*-dithiadene to give 2,4-diphenylthiophene and free sulfur.² With the thought that a similar reaction might occur in the *p*-dioxane series, the pyrolysis of tetraphenyl-*p*-dioxadiene (I) was carried out; the product, obtained in 90% yield, was not the anticipated tetraphenylfuran but was instead a rearrangement product, 2,2,3,4-tetraphenyl-3-buten-4-ylactone (II).



The product (II) was identified by its elemental analysis, its infrared spectrum [very strong band at 5.58 μ , consistent with a β,γ -unsaturated- γ -lactone,^{3a} weak absorption at 6.02 μ ($-\text{C}=\text{C}-$),^{3b} and medium absorption at 8.06 μ , expected for the system $-\text{O}-\text{C}=\text{C}$],^{3c} and its melting point.

The rearrangement is not acid-catalyzed. A sample of I which had been carefully freed from traces of acid gave a smoother reaction and better yield of II than did a sample of I which had been crystallized from acetic anhydride. Also, the formation of the lactone does not involve formation and subsequent air oxidation of tetraphenylfuran. Pyrolysis of the furan under the same conditions as pyrolysis of I led only to recovered starting material.

The lactone II was first reported by Zinin⁴ in

1872, and some of the chemistry of the compound has been reviewed by Japp and Klingemann.⁵ Zinin oxidized tetraphenylfuran to *cis*-dibenzoylstilbene (III), the pyrolysis of which gave the same lactone (II) as is now obtained upon pyrolysis of tetraphenyl-*p*-dioxadiene (I).

The formation of the same lactone on pyrolysis is not the only point of close resemblance between tetraphenyl-*p*-dioxadiene (I) and *cis*-dibenzoylstilbene (III). Many of the recorded properties are so similar that the actual existence of two compounds might be questioned. In fact, Irvine and McNicoll apparently did confuse the two compounds.⁶ They reduced their "dibenzoylstilbene" and obtained tetraphenylfuran, citing this reduction as proof that their compound was the same as Zinin's III,⁷ but Madelung and Oberwegner have since pointed out⁹ that the compound in question was really I. Both compounds have been prepared in this laboratory, and our work confirms the earlier finding that, although very similar, they are not identical. Both are isomers of $\text{C}_{28}\text{H}_{20}\text{O}_2$. The dioxadiene melts at

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(6) J. C. Irvine and D. McNicoll, *J. Chem. Soc.*, **93**, 950 (1908).

(7) Zinin reduced III to tetraphenylfuran with hydrogen iodide.⁸ Irvine and McNicoll⁶ state that their sample of I is the same as Zinin's III because of its elemental analysis and conversion to the furan; however, the only reduction of a "dibenzoylstilbene" described in the experimental involves hydrogen chloride rather than the iodide, and it is not clear whether the reaction is actually being performed on I or III. We have been unable to verify the formation of tetraphenylfuran upon treating I with hydrogen chloride in refluxing anhydrous methanol according to the procedure of reference (6); the yellow solution became colorless, but no furan precipitated. (After working up the reaction solution, however, there was obtained a small yield of benzoin, which could form tetraphenylfuran.)

(8) N. Zinin, *Chem. Zent.*, **38**, 373 (1867); *J. prakt. chem.*, [1] **101**, 160 (1867); *Jahresber. Fort. Chemie*, **20**, 417 (1867).

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(3) L. J. Bellamy, *The Infra-red Spectra of Complex Molecules*, J. Wiley and Sons, New York, N. Y., 1954. (a) p. 159; (b) p. 31f; (c) p. 102.

(4) N. Zinin, *Ber.*, **5**, 1104 (1872).