acetic acid at 50° is added to a solution of 10.1 g (0.05 mole) of pyrene in 300 ml of glacial acetic acid contained in a 500-ml erlenmeyer flask and preheated to 50°. The reaction mixture is stirred at 48–51° for 45 min; 30 ml of warm water is then added; and the mixture is stirred for an additional 15 min. The reaction mixture is cooled to about 15–20° and crude bipyrene is collected on a Büchner funnel and washed with two 10-ml portions of warm 90% aqueous acetic acid. The still-wet product is then suspended in a solution of 5 g of sodium bisulfite and 10 g of sodium hydrosulfite dihydrate in 200 ml of 50% aqueous ethanol and stirred at 65° for 30 min. The hot suspension is filtered and the product is washed successively with warm water (50 ml) and warm 95% ethanol (50 ml): yield of crude bipyrene, 6.4–6.8 g. Concentration at 40° of the original filtrate to about 120 ml yields an additional crop, which is collected on a Büchner funnel and stirred with 50 ml of the bisulfite solution previously described: total yield, 7–7.5 g (70–75%); mp 310–315°. A further dilution of the original filtrate with water yields 2.0–2.5 g of brown-red solid containing 1,6- and 1,8-pyrenediones, 1-iodopyrene, and other products; this mixture can be separated by column chromatography.[8]

The crude bipyrene is purified in the following manner. Crude material (2.5 g) is dissolved in 425 ml of hot toluene and the solution is decolorized with carbon (5 g) and rapidly filtered. The product crystallizes out, but is redissolved by heating, giving a deep blue fluorescent solution which is kept overnight at room temperature. Bipyrene crystallizes as light-green, lustrous plates, 1.5–1.6 g, mp 334–336° (uncor). Concentration of the filtrate and extraction of the filter paper and decolorizing carbon yields additional material. Total yield of recrystallized bipyrene is 1.7–1.8 g (68–72%).

A sample of bipyrene purified by sublimation at 275° (0.05 mm), followed by recrystallization from p-xylene, melted at 336–338°. A sample of bipyrene recrystallized three times from 1:1 (v/v) toluene–pyridine and dried at 110° (0.1 mm) for 2 hr melted at 335–337°; this material produced a homogeneous, blue fluorescent spot on a thin layer chromatogram (silica gel and 90:5:5 (v/v) heptane–toluene–acetic acid), R_f 0.41 ± 0.01. The product was found to be identical with an authentic sample of 1,1′-bipyrene[3] by mixture melting point (332–334°) and ultraviolet spectrum.[3] The infrared spectrum of II showed a characteristic triplet at $\nu_{\max}^{\mathrm{KCl}}$ 853, 846, and 835 cm^{-1}, not exhibited by pyrene. The reported melting points for bipyrene are 319–320°,[1] 327–328°,[2,3] and 325–326°.[4] The approximate solubility of pure bipyrene at 22° (in grams per 100 ml of solvent) is p-xylene, 0.1; pyridine, 0.185; and glacial acetic acid, 0.007.

Registry No.—II, 5101-26-8.

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(8) A. J. Fatiadi, *J. Chromatog.*, **20**, 319 (1965).

Formation of 2-Methyl-2,4-pentanediol during a Meerwein–Ponndorf–Verley Reduction

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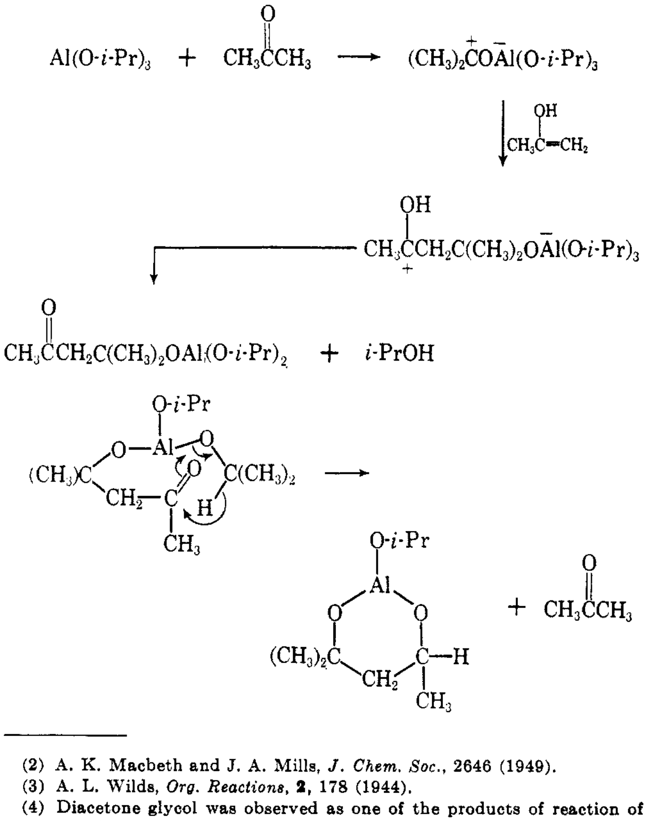
During gas chromatographic analysis of reaction products obtained on Meerwein–Ponndorf–Verley (MPV) reduction of 1,2-cyclohexanedione with aluminum isopropoxide,[1] a large, unexpected peak was observed. With the quantity of reagent dione held constant, the size of this unusual peak varied directly with aluminum isopropoxide stoichiometry. Reductions were carried out normally in toluene and under total reflux; the peak was not observed in chromatograms of either distillate or residue (after normal isolation) of one reduction from which acetone was distilled as it formed. The peak was observed, however, as a product on refluxing acetone and aluminum isopropoxide in toluene. On condensation of its corresponding effluent, the product proved to be 2-methyl-2,4-pentanediol (diacetone glycol).

Although catalysis of aldol additions by aluminum isopropoxide in the MPV reduction is well recognized,[2,3] this appears to be the first example of both a *reductive* aldol addition during an MPV reduction[4] and an MPV side reaction which must act to increase yields of desired alcohol by removing acetone from the MPV–Oppenauer equilibrium.

Although the mechanism of formation of this glycol has not been investigated, it presumably includes an aluminum isopropoxide promoted aldol dimerization of acetone to an aluminate of diacetone alcohol and an MPV reduction of this derivative to the aluminate of diacetone glycol. The process probably resembles that suggested for the acid-catalyzed aldol condensation of benzaldehyde and acetophenone.[5] One of several plausible routes may involve coordination of the aluminum with an acetone molecule, addition of the generated cationic moiety to acetone enol, and synchronous or stepwise exchange and MPV reduction. Aluminum isopropoxide, a Lewis acid, should be capable of catalyzing the keto–enol tautomerism of acetone. (See Scheme I.)

SCHEME I



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(1) C. H. Snyder, *J. Org. Chem.*, **31**, 4220 (1966).

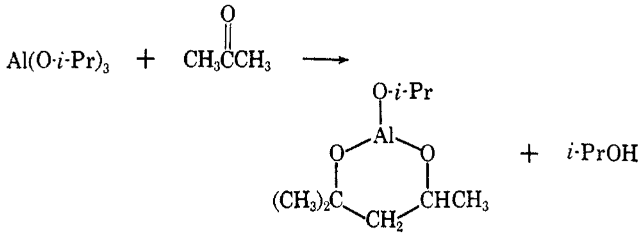
(2) A. K. Macbeth and J. A. Mills, *J. Chem. Soc.*, 2646 (1949).

(3) A. L. Wilds, *Org. Reactions*, **2**, 178 (1944).

(4) Diacetone glycol was observed as one of the products of reaction of acetone and magnesium amalgam by L. Bouveault and R. Locquin (*Ann. Chim. Phys.*, **21**, 407; *Chem. Abstr.*, **5**, 472 (1911)).

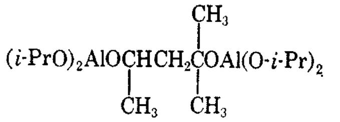
(5) J. Hine, "Physical Organic Chemistry," 2nd ed., McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p 265, and references cited therein.

The net stoichiometry for this mechanism would be



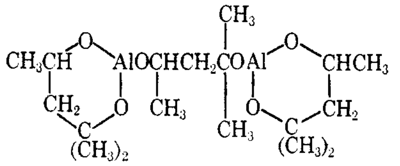
I

However, while 1 mole of glycol should be produced from 1 mole of acetone in any case, the possibility of other routes producing II or III makes the stoichiometric relation between glycol and aluminum isopropoxide uncertain. Accordingly, since in some cases reported here it is uncertain whether acetone or aluminum isopropoxide is the limiting reagent, a discussion of per cent theoretical yields is meaningless at present.



$$(i\text{-PrO})_2AlO\underset{CH_3}{CH}CH_2\underset{CH_3}{\overset{CH_3}{C}}OAl(O\text{-}i\text{-}Pr)_2$$

II



III

Small quantities of the glycol were obtained from reactions of 1,2-cyclohexanedione and of acetone itself with aluminum isopropoxide in toluene. Results obtained with acetone are presented in Table I; results obtained with the dione are similar but more complex since acetone stoichiometry in those reactions was a function of oxidation of aluminum isopropoxide by the dione.

TABLE I

REACTION OF 200 MMOLES OF ACETONE WITH ALUMINUM ISOPROPOXIDE IN 75 ML OF TOLUENE AT 105°

Expt	Time, hr	$Al(O\text{-}i\text{-}Pr)_3$, mmoles	2-Methyl-2,4-pentanediol, mmoles
1, 2[a]	5	40	5.3, 5.5
3	5	134	38
4, 5	5	67	22, 19
6	5	6.7	None obsd
7	17	67	27
8	24	67	29
9[b]	5	67	17

[a] These two runs were part of a previously reported study (ref 1) and were carried out at gentle reflux (*ca.* 105°) with 20 mmoles of acetone in 25 ml of toluene; 10 mmoles of 1,2-cyclohexanediol were present in each run. [b] At 73–77°.

Although, as clearly indicated in Table I, glycol yields are a function of aluminum isopropoxide (as well as acetone) stoichiometry, the generation of glycol at 73–77° (experiment 9) suggested the possibility that diacetone glycol may be a by-product of MPV reductions in refluxing isopropyl alcohol. It was expected, moreover, that aluminum isopropoxide might be effective in catalytic amounts in that solvent since the alkoxide should be regenerated by solvolysis of I, II, or III. Truett and Moulton[6] have reported essentially quantitative MPV reductions with aluminum isopropoxide in isopropyl alcohol at total reflux. This suggested that acetone might have been removed from the MPV–Oppenauer equilibrium in their study by an aluminum isopropoxide catalyzed conversion to diacetone glycol. However, reflux of 2.90 g (50 mmoles) of acetone and 10.2 g (50 mmoles) of aluminum isopropoxide in 50 ml of isopropyl alcohol for 1 hr, conditions similar to those used by Truett and Moulton, produced less than 1 mmole of diacetone glycol. Repetition of experiment 9 with toluene replaced by refluxing isopropyl alcohol gave less than 3 mmoles of glycol. The large reduction in yield may be connected with the fact that the reaction mixture is homogeneous in toluene, but heterogeneous in isopropyl alcohol.

Experimental Section

Chemicals.—Acetone was distilled from potassium permanganate, dried with anhydrous potassium carbonate, then fractionally distilled.[7] Isopropyl alcohol was refluxed 0.5 hr with stannous chloride, then 4 hr with calcium oxide.[8] Toluene was distilled at atmospheric pressure and aluminum isopropoxide at 1 mm. The aluminum isopropoxide was handled in a dry nitrogen atmosphere.

Analysis.—Gas chromatographic analyses were performed with an Aerograph A-90-P and a 3-m column of 5% Carbowax 20 M on 60–80 mesh, HMDS-treated Chromosorb W at 200° and with an inlet He pressure of 30 psi. Injector port temperatures proved critical. Below about 105° excessive peak broadening was observed; above about 120° extraneous peaks appeared, presumably owing to pyrolytic dehydration of 2-methyl-2,4-pentanediol.

Reaction of 1,2-Cyclohexanedione with Aluminum Isopropoxide.—These reactions were carried out as described in ref 1.

Reaction of Acetone with Aluminum Isopropoxide.—In a typical reaction 13.6 g (67 mmoles) of aluminum isopropoxide and 11.7 g (200 mmoles) of acetone were heated 5 hr in 75 ml of toluene at 104–105°. The cooled reaction mixture was shaken vigorously with saturated aqueous potassium sodium tartrate and allowed to stand overnight at room temperature. The aqueous phase was separated and continuously extracted with chloroform for 24 hr. Toluene and chloroform solutions were combined, a portion of the solvent was removed by atmospheric distillation, and chloroform was added to give 50.0 ml of solution. Quantitative glpc analysis utilized an external standard solution of distilled 2-methyl-2,4-pentanediol (Aldrich Chemical Co.) in chloroform.

Identification of 2-Methyl-2,4-pentanediol.—Products obtained from refluxing for 5 hr a solution of 1.16 g (20 mmoles) of acetone and 8.2 g (40 mmoles) of aluminum isopropoxide in 25 ml of toluene were subjected to gas chromatography as described. At a column temperature of 160° the retention time of the glycol was approximately four times that of solvent. Effluent corresponding to the glycol peak was condensed to a clear, colorless liquid, $n^{20}D$ 1.4285 (lit.[9,10] $n^{17}D$ 1.4294, $n^{16}D$ 1.4297), whose infrared spectrum was identical with that of authentic 2-methyl-2,4-pentanediol.

Anal. Calcd for $C_6H_{14}O_2$: C, 60.98; H, 11.94. Found: C, 61.27, 61.25; H, 11.88, 11.84.

Registry No.—2-Methyl-2,4-pentanediol, 107-41-5.

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[6] W. L. Truett and W. N. Moulton, *J. Am. Chem. Soc.*, **73**, 5913 (1951).

[7] A. I. Vogel, "Practical Organic Chemistry," 3rd ed, Longmans, Green and Co. Ltd., London, 1964, p 171.

[8] Reference 7, p 886.

[9] M. G. Dupont and M. Darmon, *Bull. Soc. Chim. France*, [5] **6**, 1208 (1939).

[10] D. I. Duveen and J. Kenyon, *J. Chem. Soc.*, 1451 (1936).