TABLE II

CHARACTERISTIC INFRARED SPECTRAL DATA OF ACETIC ACID, ACETIC ANHYDRIDE, ACETIC DIPHENYLPHOSPHINIC ANHYDRIDE, DIPHENYLPHOSPHINIC ANHYDRIDE, AND DIPHENYLPHOSPHINIC ACID

| Infrared, cm$^{-1}$ | | | | | |
|---|---|---|---|---|---|
| $CH_3C(O)OH$ | $[CH_3C(O)]_2O$ | $CH_3C(O)OP(O)(C_6H_5)_2$ | $[(C_6H_5)_2P(O)]_2O$ | $(C_6H_5)_2P(O)OH$ | Assignments |
| 1718 (s) | 1842<br>1783 (s) | 1773 (s) | ... | ... | COOH, C(O)OC(O), or C(O)OP(O): C=O stretching |
| ... | 1134 (s) | 1183 (s) | ... | ... | COC or COP: CO stretching |
| ... | ... | 1442 (s) | 1441 (s) | 1440 (s) | PC (aromatic) |
| 1295 (s) | ... | ... | | | |
| ... | ... | 1238 (s) | 1238 (s) | 1189 (sh)<br>1181 (s) | P(O)OC(O), P(O)OP(O), or P(O)OH: P=O stretching |
| ... | ... | 916 (s) | 966 (s) | 962 (s) | POC, POP, or POH: PO stretching |

the acetic anhydride was removed by flash evaporation, a crystalline material was isolated. After twice dissolving the solid in small amounts of benzene and removing the solvent by flash evaporation, the product was finally dried on a freeze drier under pressures of less than 1 μ. The dried product (0.41 g, 70% yield) melted between 93.0 and 97.3° in a sealed capillary tube; the melt heated above 100° produced a new solid (mp 144–148°) and a liquid on the cooler regions of the tube.

*Anal.* Calcd for $C_{14}H_{13}O_3P$: C, 64.62; H, 5.00; P, 11.92. Found: C, 64.81; H, 5.38; P, 11.51.

B.—Diphenylphosphinic acid (0.50 g, 2.3 mmoles) was dissolved in acetic anhydride (25 ml) by warming to 60°. The reaction solution was brought to reflux and approximately 2.5 ml of distillate was collected between 110 and 125°. Although the reaction solution was maintained at approximately 140°, the distillation head was warmed with a heat gun to facilitate removal of the distillate. Using the method of Fernandez, *et al.*,[20] we found approximately 2.5 mmoles of acetic acid (theoretical, 2.3 mmoles) in the acetic anhydride–acetic acid distillate. After removing the acetic anhydride by flash evaporation, the white, hygroscopic residue was washed several times with dry carbon tetrachloride and twice dissolved in dry benzene and flash evaporated to dryness, and the residue was finally dried on the freeze drier. The solid (0.17 g, 29% yield based on the acid) melted between 99.0 and 100.0°.

*Anal.* Found: C, 64.44; H, 5.07; P, 12.00.

Carbon tetrachloride, which was used to wash the acetic diphenylphosphinic anhydride, was flash evaporated to dryness. The solid isolated (0.20 g, 42% yield) was found by spectral data to be diphenylphosphinic anhydride containing a trace of acetate group impurity.

C.—A mixture of diphenylphosphinic acid (0.50 g, 2.3 mmoles) and acetic anhydride (25 ml) containing approximately 15 mole % acetic acid (determined by proton nmr) was refluxed for several hours. An approximately 90% yield (0.53 g) of acetic diphenylphosphinic anhydride was obtained when the acetic anhydride–acetic acid mixture was removed by flash evaporation at low temperatures. The anhydride was identified by its infrared spectrum and its melting point.

D.—When diphenylphosphinic acid (0.50 g, 2.3 mmoles) was refluxed either with glacial acetic acid (25 ml) or with dry benzene (25 ml), only unreacted acid (infrared spectral data) was isolated after the solvents were removed by flash evaporation.

**Diphenylphosphinic Anhydride.** A.—A flask having an adaptor with a stopcock and containing approximately 0.1 g of acetic diphenylphosphinic anhydride was attached to the freeze drier. Moisture was excluded from the flask by sealing the products under reduced pressure or under dry nitrogen. After evacuating the system and cooling the traps with liquid nitrogen, the flask containing the mixed anhydride was heated in boiling water until the acetic diphenylphosphinic anhydride melted and resolidified. The resulting solid was heated at 100° for an additional 3 hr to ensure complete reaction, cooled to room temperature under reduced pressure, and transferred to the drybox for analysis. In a sealed capillary tube, the product melted at 148.0 to 148.5°.

*Anal.* Calcd for $C_{24}H_{20}O_3P_2$: C, 68.99; H, 4.78; P, 14.03. Found: C, 68.91; H, 5.25; P, 14.48.

B.—Reaction C for the preparation of acetic diphenylphosphinic anhydride was repeated. After removal of the acetic anhydride–acetic acid mixture from the reaction solution, the residual oil was heated above 100° until a crystalline product was obtained. This *in situ* decomposition of the mixed anhydride yielded 0.15 g (31%, based on the acid) of diphenylphosphinic anhydride (infrared spectrum).

**Registry No.**—Diphenylphosphinic acid, 1707-03-5; acetic anhydride, 108-24-7; acetic diphenylphosphinic anhydride, 7594-78-7; diphenylphosphinic anhydride, 5849-36-5.

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[20] J. E. Fernandez, R. T. McPherson, G. K. Finch, and C. D. Bockman, *Anal. Chem.*, **32**, 158 (1960).

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## Reductions in Potassium Hydroxide–Ethylene Glycol Solution[1]

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The two 3-phenyl-2-norbornanols with *endo*-phenyl substituents (I and II) are readily available in quite respectable yields by hydroboration of 2-phenylnorbornene[2] and hydride reduction of 3-*endo*-phenyl-2-norbornanone.[3,4] In contrast, the two 3-phenyl-2-norbornanols with *exo*-phenyl substituents (III and IV) are obtained in comparatively low yields as a mixture, with some of II, from hydride reduction of the ketone mixture obtained *via* the Nef reaction on 3-*exo*-phenyl-2-*endo*-nitronorbornane.[5] The over-all yield of III and IV obtainable as a 4:1 mixture from 3-*exo*-phenyl-2-*endo*-nitronorbornane is *ca.* 8–10%.[6]

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[1] This research was supported in part by a grant from the National Science Foundation.

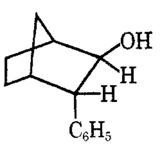
[2] C. J. Collins, Z. K. Cheema, R. G. Werth, and B. M. Benjamin, *J. Am. Chem. Soc.*, **86**, 4913 (1964).

[3] B. M. Benjamin and C. J. Collins, *ibid.*, **88**, 1556 (1966).

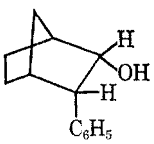
[4] D. C. Kleinfelter and T. E. Dye, *ibid.*, **88**, 3174 (1966).

[5] W. C. Wildman and C. H. Hemminger, *J. Org. Chem.*, **17**, 1641 (1952).

[6] J. E. Mallory, M.S. Thesis, University of Tennessee, 1966; D. C. Kleinfelter, unpublished results.



I



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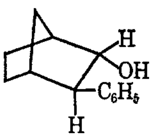
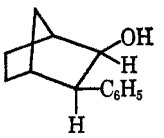


III



IV

During our attempts to isomerize 3-*endo*-phenyl-2-norbornanone to 3-*exo*-phenyl-2-norbornanone the former ketone was heated in a refluxing solution of potassium hydroxide and ethylene glycol. The product obtained showed only weak ketone carbonyl absorption in its infrared spectrum, but strong absorption in the 2.8–3.0-$\mu$ region of infrared absorption frequency. Other features of the spectrum indicated the presence of the alcohols II, III, and IV. Chromatography on alumina gave practically complete separation of II and IV from III. Crystallization of II from the mixture of II and IV was partially successful; integration of signals assigned from comparison with authentic samples (see the Experimental Section) in the nmr spectrum of the filtrate afforded total yield data for II and IV. The percentage yields of II, III, and IV were 21.9, 43.2, and 4.6%, respectively.

We attempted to extend this reduction process to the ketones benzophenone, norbornanone, 1-phenyl-2-norbornanone, and camphor, and the results are listed in Table I.

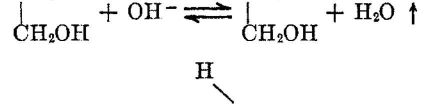
TABLE I

YIELD DATA FOR REDUCTIONS IN POTASSIUM HYDROXIDE–ETHYLENE GLYCOL

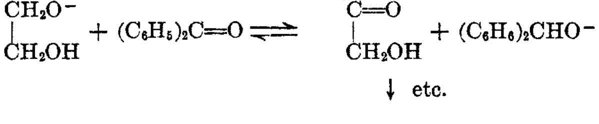
| Ketone | Product | % yield[a] | |
|---|---|---|---|
| 3-*endo*-Phenyl-2-norbornanone | II | 21.9 | 69.7 |
| | III | 43.2 | |
| | IV | 4.6 | |
| Benzophenone | Benzhydrol | 92.7 | |
| 1-Phenyl-2-norbornanone | 1-Phenyl-2-*endo*-norbornanol | 56.7 | 60.4 |
| | 1-Phenyl-2-*exo*-norbornanol | 3.7 | |
| Norbornanone | *endo*-Norbornanol | *Ca.* 43.5 | 48.8 |
| | *exo*-Norbornanol | *Ca.* 5.3 | |
| Camphor | Unidentified alcohol | >0 | |

[a] Reaction time was 24 hr, except for camphor which was 7 days. See the Experimental Section.

The reaction is visualized as proceeding through the following equilibria processes, as illustrated with benzophenone. Step 1 is displaced to the right as the reflux temperature of ethylene glycol allows the water vapor to escape. Step 2 may be displaced to the right by aldol condensation of the hydroxyacetaldehyde formed. Enolization may precede the reduction process as evidenced with 3-*endo*-phenyl-2-norbornanone.



$$\begin{matrix}CH_2OH\\|\\CH_2OH\end{matrix} + OH^- \rightleftharpoons \begin{matrix}CH_2O^-\\|\\CH_2OH\end{matrix} + H_2O\uparrow \qquad (1)$$



$$\begin{matrix}CH_2O^-\\|\\CH_2OH\end{matrix} + (C_6H_5)_2C{=}O \rightleftharpoons \begin{matrix}H\\ \diagdown\\ C{=}O\\|\\CH_2OH\\ \downarrow \text{ etc.}\end{matrix} + (C_6H_6)_2CHO^- \qquad (2)$$

Reports of the reduction of carbonyl groups by primary alkali metal alkoxide–alcohol mixtures are in the literature.[7] While it is certainly not suggested that the reduction reaction reported herein can supplant the Meerwein–Ponndorf–Verley or hydride reductions for most ketones, the simplicity of operation, the relatively low cost of reactants, and the respectable yields thus far obtained in most cases may make the reaction an acceptable one for the reduction of certain ketones. In one case, the preparation of III and IV, the reaction has proven to be far superior to any previously employed.

### Experimental Section[8]

**Reduction of 3-*endo*-Phenyl-2-norbornanone.**—To a mixture of 18.6 g of potassium hydroxide and 500 ml of ethylene glycol was added 18.6 g (0.100 mole) of 3-*endo*-phenyl-2-norbornanone, bp 131–132° (1.4 mm) [lit.[9] bp 166–174° (15–17 mm)]. After initial heating for 10–15 min the potassium hydroxide and ketone dissolved, and the solution was refluxed for 24 hr, during which time an orange color developed. Upon cooling the color changed to dark brown. The brown solution was extracted with three 200-ml portions of ether. Sodium chloride was added for the purpose of salting out. The ether extracts were dried over anhydrous sodium sulfate and decolorized with charcoal, and the ether was evaporated. The residue was distilled under vacuum to give 13.9 g of clear, colorless oil, bp 132–138° (1.3–1.8 mm).

The distillate was dissolved in ligroin (bp 30–60°) and chromatographed on Alcoa F-20 alumina. Eluted with ligroin was 0.35 g of what the infrared spectrum indicated to be a mixture of 3-phenyl-2-norbornanones. Then, with increasing amounts of ether in an ether–ligroin solution there was obtained 4.98 g of a mixture of 3-*endo*-phenyl-2-*endo*-norbornanol (II) and 3-*exo*-phenyl-2-*exo*-norbornanol (IV). From this mixture a total of 3.78 g of II, mp 71.5–72.5° (lit.[10] mp 71–72°), was obtained by repeated crystallization from ligroin. The filtrate (1.20 g) was shown to contain 0.33 g of II and 0.87 g of IV, by integration of the 2-*exo*-hydrogen nmr signal at 4.16 ppm for II and the 2-*endo*-hydrogen signal at 3.80 ppm for IV. Finally, 8.12 g of 3-*exo*-phenyl-2-*endo*-norbornanol, mp 42–43° (lit.[10] mp 42.5–43.5°) was eluted from the column. The percentage yields are recorded in Table I.

**Reduction of Benzophenone.**—The reaction was carried out as described above. The quantities of material employed were 20.0 g (0.110 mole) of benzophenone, 20.0 g of potassium hydroxide, and 500 ml of ethylene glycol. After evaporation of the ether during the work-up, the product was crystallized from ligroin to give 18.8 g of benzhydrol, mp 67–68° (lit.[11] mp 68–69°).

**Reduction of 1-Phenyl-2-norbornanone.**—The reaction was carried out as described above. The quantities of material employed were 10.0 g (0.0538 mole) of 1-phenyl-2-norbornanone, mp 40–41° (lit.[12] mp 40.2–41.0°), 10.0 g of potassium hydroxide, and 300 ml of ethylene glycol. After evaporation of the ether during the work-up, 5.00 g of 1-phenyl-2-*endo*-norbornanol, mp 69–70° (lit.[12] mp 69.2–70.0°), was crystallized from ligroin. By nmr integration of the 2-*exo*-hydrogen signal at 3.86 ppm for 1-phenyl-2-*endo*-norbornanol and the 2-*endo*-hydrogen signal at 3.60 ppm for 1-phenyl-2-*exo*-norbornanol, the 1.10 g of filtrate was shown to be composed of 0.73 g of the *endo* alcohol and 0.37 g of the *exo* alcohol.

**Reduction of Norbornanone.**—The reaction was carried out as described above. The quantities of material employed were 20.0 g (0.182 mole) of Aldrich norbornanone, mp 80–88°, 20.0 g of potassium hydroxide, and 300 ml of ethylene glycol. After evaporation of the ether during the work-up, there was crystallized from ligroin 9.95 g of solid, mp 142–148° (lit.[13] mp 152.0–153.0° for *endo*-norbornanol, lit.[14] mp 127.8–128.5° for

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[7] See, for example, W. Ponndorf, *Z. Angew. Chem.*, **39**, 138 (1926); A. L. Wilds, *Org. Reactions*, **2**, 178 (1944).

[8] Melting points were determined in capillary tubes using a Mel-Temp apparatus (Laboratory Devices, Cambridge, Mass.) and are corrected. Nmr spectral data were obtained with a Varian A-60 nmr spectrometer.

[9] D. C. Kleinfelter and P. R. Schelyer, *J. Am. Chem. Soc.*, **83**, 2329 (1961).

[10] D. C. Kleinfelter, E. S. Trent, J. E. Mallory, and T. E. Dye, *ibid.*, **88**, 5350 (1966).

[11] "Handbook of Chemistry and Physics," 44th ed, Chemical Rubber Publishing Co., Cleveland, Ohio, 1963, p 849.

[12] D. C. Kleinfelter and P. R. Schleyer, *J. Org. Chem.*, **26**, 3740 (1961).

[13] S. Winstein and D. Trifan, *J. Am. Chem. Soc.*, **74**, 1147 (1952).

[14] S. Winstein and D. Trifan, *ibid.*, **74**, 1154 (1952).

*exo*-norbornanol). By nmr integration of the 2-*exo*-hydrogen signal at 4.15 ppm for *endo*-norbornanol and of the 2-*endo*-hydrogen signal at 3.67 ppm for *exo*-norbornanol, the solid was shown to be composed of *ca.* 89% *endo*-norbornanol and *ca.* 11% *exo*-norbornanol.

**Attempted Reduction of Camphor.**—The procedure was that described above except for the following modifications. Since the camphor did not appear to dissolve appreciably and would sublime and clog the reflux condenser, 25 ml of dioxane was added which eliminated the problem. The quantities of material employed were 30.4 g (0.200 mole) of *d*-camphor, 25.0 g of potassium hydroxide, and 500 ml of ethylene glycol. Only a light orange tint developed after 7 days of refluxing. After cooling, the solution was added to ice water, and the white solid that formed was washed repeatedly with water and dried to give 25.6 g of solid, the infrared spectrum of which was not appreciably different from that of pure *d*-camphor except for weak absorption at 2.9 $\mu$. We plan on attempting to reduce camphor under further modified conditions to see whether a successful reduction can be obtained. Perhaps a reaction time longer than 7 days is required.

**Registry No.**—Ethylene glycol, 107-21-1; 3-*endo*-phenyl-2-norbornanone, 7485-53-2; benzophenone, 119-61-9; 1-phenyl-2-norbornanone, 7485-54-3; norbornane, 279-23-2; camphor, 76-22-2.

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# On the Preparation of (3*S*)-2,3-Dimethylpentanal by Reaction of (+)-Tris[(2*S*)-1,2-dimethylbutoxy]methane (I) with Carbon Monoxide and Hydrogen[1]

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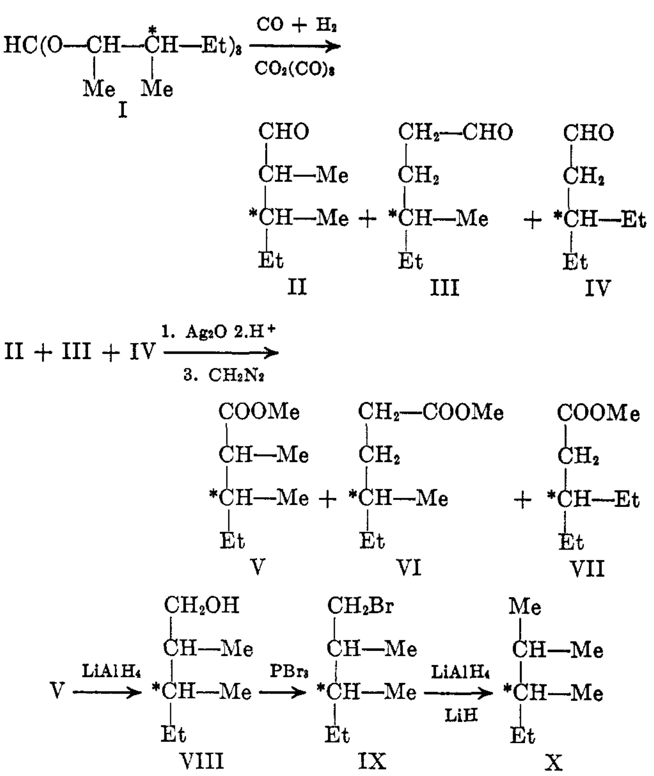
*Received September 12, 1966*

We wish to report and discuss the results obtained in developing a convenient method to prepare a diastereoisomeric mixture of (3*S*)-2,3-dimethylpentanal (II) and its derivatives with a high optical purity with respect to the 3*S* center of asymmetry by the reaction of I with CO and $H_2$ in the presence of a cobalt catalyst[2,3] (Chart I). Poor results were in fact obtained in the synthesis of II by the usual techniques. By treating I with CO and $H_2$ in the presence of $Co_2(CO)_8$ in benzene solution[3] a mixture of isomeric aldehydes was obtained which was converted into the corresponding methyl esters (Chart I)[4] further separated by rectification, and identified by comparison of their physical properties with those of authentic samples.

The diastereoisomeric methyl 2,3-dimethylpentanoates (V) and methyl 4-methylhexanoate (VI) were thus obtained in pure form while an intermediate fraction was a 68:32 mixture (vpc analysis) of VI and a third isomeric component. To this third product the structure of VII was assigned on the basis of vpc retention time and the infrared spectrum of a 68:32 mixture of authentic samples of VI and VII. No definite evidence of the presence of 2-ethyl-2-methylbutanoic acid methyl ester has been obtained either from vpc or infrared analysis. We conclude therefore that the above component may be present only in very small amounts if any.

Chart I



The isomeric distribution of the aldehydes obtained by reaction of I with CO and $H_2$ thus resulted II:III:IV = 39.5:52.0:8.5.[4]

The optical purity of VI, evaluated by comparison of its optical rotatory power with the one of a sample of VI of known optical purity,[5] was 13.6%.

The minimum optical purity of V, with reference to the 3*S* center of asymmetry, evaluated by conversion into (−)-(*S*)-2,3-dimethylpentane (X) (Chart I),[6] was 80.9%.

Thus by assigning to I, with reference to the 2*S* center of asymmetry, an optical purity of 90.0%,[7] the optical yield, with respect to the 3*S* center of asymmetry in the formation of VI results in 15.2%, while it is 90.0% in the formation of V.

The formation of III and IV may be interpreted as owing to the hydroformylation of intermediate olefin,[2,3] in our case (+)-(*S*)-3-methylpent-1-ene (XII)

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(1) This research was supported in part by Consiglio Nazionale delle Ricerche, Roma.

(2) F. Piacenti, *Gazz. Chim. Ital.*, **92**, 225 (1962).

(3) P. Pino, F. Piacenti, and P. P. Neggiani, *Chim. Ind.* (Milan), **44**, 1367 (1962).

(4) F. Piacenti, P. Pino, R. Lazzaroni, and M. Bianchi, *J. Chem. Soc.*, 488 (1966).

(5) By treating $CH_2N_2$ with a sample of (+)-(*S*)-4-methylhexanoic acid of 86.6% optical purity [L. Lardicci and P. Pino, *Gazz. Chim. Ital.*, **91**, 441 (1962)], methyl (+)-(*S*)-4-methylhexanoate having $[\alpha]^{25}_{D}$ + 8.77 was obtained.

(6) K. Freudenberg and W. Lwowski, *Ann.*, **587**, 223 (1954).

(7) An enolization equilibrium, which only could determine racemization while preparing (−)-(3*S*)-3-methylpentan-2-ol by treating (+)-(*S*)-2-methylbutanal with $CH_3MgBr$, must be considered irrelevant in the conditions adopted, as $CH_4$ evolution was never observed. No racemization was encountered either in the subsequent transesterification between $HC(OEt)_3$ and (−)-(3*S*)-3-methylpentan-2-ol as the same diastereoisomeric composition and optical activity were observed both for the starting alcohol and the recovered one by hydrolysis of I. It is thus reasonable to attribute to I the same optical purity, with respect to the 2*S* center of asymmetry, of (+)-(*S*)-2-methylbutanal (90.0%) [L. Lardicci and R. Rossi, *Atti Soc. Toscana-Sci. Nat. Pisa, Proc. Verbali Mem.*, **68A**, 23 (1961)].