zene afforded 8 g. of a crude oil, which, on standing, deposited 1.83 g. of solid diene ester (ester of XXIV), m.p. 104–108°. Distillation of the residue at 110–185° (0.25–0.6 mm.) produced a second crop of solid ester, weight 1.1 g., bringing the total yield to 2.93 g. (46%). Recrystallization from ether afforded **methyl 3,4,5-trimethoxybenzylidenecrotonate (ester of XXII)** as colorless prisms, m.p. 111.5–112.5°, $\lambda^{\text{alc}}_{\max}$ 249 and 332 mμ (ε 15,320 and 35,100).[14]

*Anal.* Calcd. for $C_{16}H_{18}O_5$: C, 64.73; H, 6.52. Found: C, 64.54; H, 6.30.

Saponification of a portion of the diene ester (ester of XXII) gave a quantitative yield of **3,4,5-trimethoxybenzylidenecrotonic acid** (XXII), m.p. 156–159°, which was recrystallized from benzene as yellow microcrystals, m.p. 162.5–163.0°, $\lambda^{\text{alc}}_{\max}$ 244 and 319 mμ (ε 16,050 and 32,300).[14]

*Anal.* Calcd. for $C_{14}H_{16}O_5$: C, 63.62; H, 6.10. Found: C, 63.52; H, 6.28.

The diene acid (XXII, 36.8 mg.) absorbed two moles of hydrogen with prereduced platinum oxide in methanol to give 25 mg. (71%) of δ-(3,4,5-trimethoxyphenyl)-valeric acid as colorless plates, m.p. 66–68° (reported,[24] m.p. 69–70°).

B. In Ether.—From a Reformatsky reaction with 5 g. (0.0255 mole) of 3,4,5-trimethoxybenzaldehyde, 13 g. (0.073 mole) of methyl γ-bromocrotonate and 13 g. (0.2 mole) of zinc in 80.0 ml. of dry ether was obtained an oil which, upon cooling, gave 3.03 g. (55%) of **methyl β-(3,4,5-trimethoxyphenyl)-β-hydroxy-α-vinylpropionate** (XXIII) as a light yellow solid, m.p. 82–92°. An analytical sample was obtained as silky cream colored needles, m.p. 102.8–103.4°, from ether.

*Anal.* Calcd. for $C_{15}H_{20}O_6$: C, 60.80; H, 6.80. Found: C, 61.00; H, 7.17.

Hydrogenation of 33.6 mg. of XXIII in absolute methanol with platinum oxide afforded 30.0 mg. (86%) of methyl **β-(3,4,5-trimethoxyphenyl)-β-hydroxy-α-ethylpropionate** (XXIV) as colorless needles from ether and methanol, m.p. 107–108.5°. Admixture with an authentic sample (see below) offered no depression in melting point.

**Methyl β-(3,4,5-Trimethoxyphenyl)-β-hydroxy-α-ethylpropionate (XXIV).**—A Reformatsky reaction with 3.5 g. (0.0179 mole) of 3,4,5-trimethoxybenzaldehyde, 4.0 g. (0.061 mole) of zinc and 11.2 g. (0.062 mole) of methyl α-bromobutyrate in 40 cc. of dry ether yielded 2.66 g. (50%) of **methyl β-(3,4,5-trimethoxyphenyl)-β-hydroxy-α-ethylpropionate** (XXIV), m.p. 72–88°. An analytical sample crystallized from ether and methanol, m.p. 109.5–110.5°.

*Anal.* Calcd. for $C_{15}H_{22}O_6$: C, 60.38; H, 7.43. Found: C, 60.07; H, 7.38.

DETROIT, MICHIGAN

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[24] R. D. Haworth, B. P. Moore and P. L. Pauson, *J. Chem. Soc.*, 1050 (1948).

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[CONTRIBUTION FROM THE ROLLIN H. STEVENS MEMORIAL LABORATORY OF THE DETROIT INSTITUTE OF CANCER RESEARCH]

# Reduction of Some Enolizable β-Dicarbonyl Compounds to Unsaturated Alcohols by Lithium Aluminum Hydride. II. β-Diketones[1]

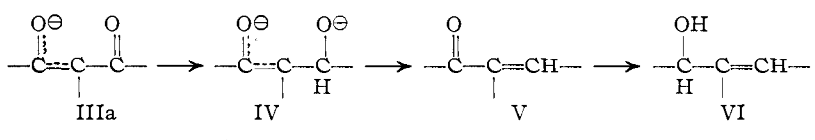
BY ANDRE S. DREIDING AND JOHN A. HARTMAN

RECEIVED MARCH 23, 1953

In confirmation of the previous observation that enolic β-dicarbonyl compounds are reduced to unsaturated alcohols by lithium aluminum hydride it was found that cyclohexane-1,3-dione and two homologs were converted primarily into 2-cyclohexene-1-ol and the corresponding homologs. The reduction of dibenzoylmethane also resulted in the loss of an oxygen, but the simultaneous saturation of the double bond caused 1,3-diphenylpropane-1-ol to be the major product. That the loss of the oxygen during the lithium aluminum hydride treatment is connected with the enolic nature of the β-dicarbonyl compounds was shown by the reduction of the stable enol and keto forms of 1,1-dibenzoylethane, which yielded 2-methyl-1,3-diphenyl-1-propene-3-ol and 2-methyl-1,3-diphenylpropane-1,3-diol, respectively.

It was recently shown that the lithium aluminum hydride reduction of some enolizable β-keto esters and α-hydroxymethylene ketones yielded mixtures of unsaturated alcohols and 1,3-glycols.[2] The study of this reaction has now been extended to enolizable β-diketones and further evidence on its detailed course has been obtained.

In the previous paper,[2] evidence was cited for the postulate that the diketo portions (I) of the β-dicarbonyl compounds were largely responsible for the formation of 1,3-glycols (II), while the enol forms (III) were converted to unsaturated alcohols (VI). The latter reaction was considered to occur *via* the intermediate enolate salts (IIIa and IV) and the unsaturated carbonyl compound (V). This view receives confirmation from the lithium aluminum hydride reduction in boiling ether of the two desmotropic forms of 1,1-dibenzoylethane. The diketo form (VIIa) afforded a quantitative yield of 2-methyl-1,3-diphenylpropane-1,3-diol (VIIIa, probably mixture of stereoisomers), while the enol form (IXa)[3] was reduced under identical conditions to give a 79% yield of 2-methyl-1,3-diphenyl-1-propene-3-ol (Xa).



When a shorter reaction time was used in the reduction of the enol form of 1,1-dibenzoylethane (IXa), propiophenone and benzaldehyde were isolated to the extent of 53 and 32%, respectively. This is interpreted as indicating that the reduction had proceeded only up to stage IV, and that some of the product underwent a reverse aldol type re-

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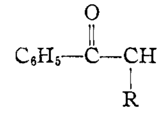
[1] This work was supported by grants to the Detroit Institute of Cancer Research from the Michigan Cancer Foundation, the American Cancer Society, Inc., and The Kresge Foundation.

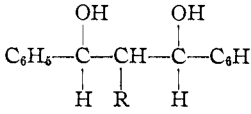
[2] A. S. Dreiding and J. A. Hartman, THIS JOURNAL, **75**, 939 (1953).

[3] C. L. Bickel and R. Morris, *ibid.*, **73**, 1786 (1951).

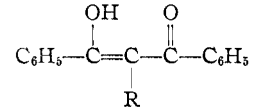
action under the alkaline conditions of isolation.[4]


$C_6H_5-\overset{\overset{O}{\|}}{C}-\underset{\underset{R}{|}}{CH}-\overset{\overset{O}{\|}}{C}-C_6H_5$

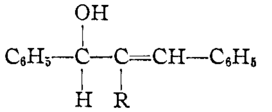
VII


$C_6H_5-\underset{\underset{H}{|}}{\overset{\overset{OH}{|}}{C}}-\underset{\underset{R}{|}}{CH}-\underset{\underset{H}{|}}{\overset{\overset{OH}{|}}{C}}-C_6H_5$

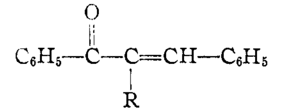
VIII


$C_6H_5-\overset{\overset{OH}{|}}{C}=\underset{\underset{R}{|}}{C}-\overset{\overset{O}{\|}}{C}-C_6H_5$

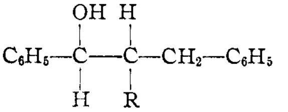
IX


$C_6H_5-\underset{\underset{H}{|}}{\overset{\overset{OH}{|}}{C}}-\underset{\underset{R}{|}}{C}=CH-C_6H_5$

X


$C_6H_5-\overset{\overset{O}{\|}}{C}-\underset{\underset{R}{|}}{C}=CH-C_6H_5$

XI

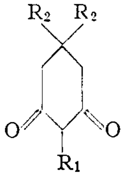

$C_6H_5-\underset{\underset{H}{|}}{\overset{\overset{OH}{|}}{C}}-\underset{\underset{R}{|}}{\overset{\overset{H}{|}}{C}}-CH_2-C_6H_5$

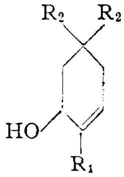
XII

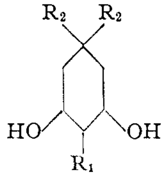
a, R = $CH_3$; b, R = H

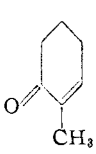
The lower homolog, dibenzoylmethane, which exists almost completely in the enol form (IXb),[5] also suffered the loss of an oxygen during the lithium aluminum hydride reduction in boiling ether to give a monohydric alcohol. In this case, however, the double bond was reduced and the product was an 83% yield of 1,3-diphenylpropane-1-ol (XIIb). This result is not inconsistent with the view that chalcone (XIb) is an intermediate, since Rondestvedt[6] has found that a number of ring substituted chalcones are reduced to hydrochalcols by lithium aluminum hydride in boiling ether. That a reduction of the double bond does not also occur in the same treatment of the enol form of dibenzoylethane (IXa) apparently is due to the methyl group at carbon-2.

The reaction was also applied to three strongly enolic[7] monocyclic β-dicarbonyl compounds, cyclohexane-1,3-dione (XIIIa), 2-methylcyclohexane-1,3-dione (XIIIb) and 5,5-dimethylcyclohexane-1,3-dione (XIIIc).


XIII


XIV

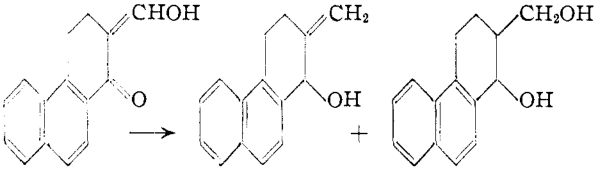

XV


XVI

a, $R_1 = R_2 = H$
b, $R_1 = CH_3$; $R_2 = H$
c, $R_1 = H$; $R_2 = CH_3$

In all three cases the major products were the unsaturated alcohols, XIVa (50%), XIVb (62%) and XIVc (68%). The formation of a small yield of the two stereoisomeric glycols (XVc) in the reduction of XIIIc was demonstrated and the higher boiling fractions observed in the reduction of XIIIa and XIIIb may also have contained some of the corresponding glycols (XVa and XVb). A sample of 2-methyl-2-cyclohexene-1-ol (XIVb), prepared by the lithium aluminum hydride reduction of 2-methyl-2-cyclohexene-1-one (XVI), was identical with the reaction product from XIIIb.

The action of lithium aluminum hydride on 2-hydroxyethylenecyclohexanone has been shown to result in two unsaturated alcohols and some glycol.[2] In contrast, 2-hydroxymethylene-1-keto-1,2,3,4-tetrahydrophenanthrene (XVII) yielded only one unsaturated alcohol, 1-hydroxy-2-methylene-1,2,3,4-tetrahydrophenanthrene (XVIII, 54%), some glycol, 1-hydroxy-2-hydroxymethyl-1,2,3,4-tetrahydrophenanthrene (XIX, 15%) and 13% of 1-keto-2-methyl-1,2,3,4-tetrahydrophenanthrene.[8] Evidence for the structure of XVIII was available from its ultraviolet and infrared absorption spectra and from its catalytic hydrogenation, which yielded one of the steroisomers of 1-hydroxy-2-methyl-1,2,3,4-tetrahydrophenanthrene, identical with a sample prepared by the lithium aluminum hydride reduction of 1-keto-2-methyl-1,2,3,4-tetrahydrophenanthrene.


XVII XVIII XIX

## Experimental[9]

**Reduction of the Diketo Form of 1,1-Dibenzoylethane (VIIa).**—The diketone VIIa was prepared by the method of Abel[10] in the reported yield. The ultraviolet spectrum exhibited a maximum in alcohol at 246 mμ (ε 23700) and a broad plateau with a maximum at 282 mμ (ε *ca.* 2000). The infrared spectrum had a strong band at 5.98 μ (conjugated carbonyl) and showed no absorption characteristic for the enol (see below). When 5.0 g. (0.023 mole) of VIIa was reduced by the addition of the solid to 1.0 g. (0.025 mole) of lithium aluminum hydride in boiling ether followed by refluxing for five hours and the product worked up as described earlier,[2] there was obtained 5.1 g. of a stiff gum, $\lambda_{max}^{alc}$ 246 mμ (ε 960). Evaporative distillation at 175° and 0.2 mm. left no residue in the distilling pot and gave a 96% yield of a mixture of stereoisomeric forms of 2-methyl-1,3-diphenylpropane-1,3-diol (VIIIa) as a colorless clear gum which resisted crystallization from several common organic solvents (reported for one isomer,[11] m.p. 98–99°). The infrared spectrum had a strong band at 2.96 μ (hydroxyl group).

*Anal.* Calcd. for $C_{16}H_{18}O_2$: C, 79.30; H, 7.49. Found: C, 78.64; H, 7.62.

The bis-*p*-nitrobenzoate was formed[12] in a crude quantita-

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[4] Such a reaction is not unreasonable since Abel, *J. Chem. Soc.*, **79**, 930 (1901), found that benzalpropiophenone was formed in only 10% yield when benzaldehyde and propiophenone were allowed to stand in alkaline solution for seven days.

[5] K. H. Meyer, *Ann.*, **380**, 212 (1911); E. Hofling, H. Lieb and W. Schoniger, *Monatsh.*, **83**, 60 (1952).

[6] C. Rondestvedt, Jr., THIS JOURNAL, **73**, 4509 (1951).

[7] G. Schwarzenbach and E. Felder, *Helv. Chim. Acta*, **27**, 1044 (1944).

[8] This ketone may not be a direct product of the lithium aluminum hydride reduction, but may have resulted from a partial isomerization of XVIII during the chromatographic adsorption or other operations involved in the isolation of the products.

[9] All analyses were performed by Micro-Tech Laboratories, Skokie, Ill. The melting points and boiling points are not corrected. We are indebted to the late Dr. W. E. Bachmann, Dr. J. P. Horwitz and Dr. S. Kaufman of the University of Michigan for the samples of cyclohexane-1,3-dione and 2-methylcyclohexane-1,3-dione used in these experiments. 2-Hydroxymethylene-1-keto-1,2,3,4-tetrahydrophenanthrene was prepared from a sample of 1-keto-1,2,3,4-tetrahydrophenanthrene kindly furnished by Dr. W. Dauben of the University of California. We also wish to thank Dr. J. M. Vandenbelt and Mr. Bruce Scott of Parke, Davis and Co. for the measurement and interpretation of some of the absorption spectra.

[10] R. D. Abel, *J. Chem. Soc.*, **101**, 989 (1912).

[11] R. D. Abel, *ibid.*, **79**, 930 (1901).

[12] F. Wild, "Characterization of Organic Compounds," Cambridge University Press, Cambridge, England, 1947, p. 51.

tive yield. Recrystallization from petroleum ether–ether gave colorless needles, m.p. 174.8–176.0° with softening at 172° (reported[13] m.p. 173–174°).

When the reduction was carried out with only 30 minutes refluxing time the results were identical.

**Reduction of the Enol Form of 1,1-Dibenzoylethane (IXa).**—Although isolated from its copper salt,[8] the enol (IXa) appeared to be contaminated with a small amount of the diketo form (VIIa). The latter was removed after three recrystallizations from ether until the intensity of the ultraviolet absorption bands remained constant in freshly prepared solutions, $\lambda_{\max}^{\text{cyclohexane}}$ 244, 330 m$\mu$ ($\epsilon$ 9050, 15320). In ethanol the spectrum was similar but slowly changed to the spectrum of the diketo form described above. The infrared spectrum, determined in carbon tetrachloride, had a weak band at 5.95 $\mu$ which may be due to ketonization of the enol.[14] A broad band of high intensity which extended from 6.3 to beyond 6.6 $\mu$ was also present (chelated enol[14]).

The reduction of IXa was much more vigorous than that of VIIa, evolving a gas, and produced a transitory yellow color. From 3.0 g. (0.0126 mole) of IXa, added to an ethereal solution of 2.0 g. (0.05 mole) of lithium aluminum hydride and heated by five hours refluxing, there was obtained 2.71 g. (96%) of a viscous oil. Evaporative distillation at 137–142° and 0.2 mm. gave 2.22 g. (79%) of **2-methyl-1,3-diphenyl-1-propene-3-ol (Xa)** as a colorless oil, $\lambda_{\max}^{\text{alc}}$ 247 m$\mu$ ($\epsilon$ 16320). The infrared spectrum had a strong band at 2.75 $\mu$ (hydroxyl group) and showed no absorption from 5.8–6.2 $\mu$ (carbonyl group). The product could not be solidified by chromatography followed by another evaporative distillation.

*Anal.* Calcd. for $C_{16}H_{16}O$: C, 85.67; H, 7.19. Found: C, 85.61; H, 7.35.

Conversion to the **$p$-nitrobenzoate**[12] gave a crude quantitative yield of a tan solid, m.p. 85–90°. After three recrystallizations from petroleum ether as fine colorless needles, the melting point was raised to 90.8–92.0°.

*Anal.* Calcd. for $C_{23}H_{19}NO_4$: C, 73.98; H, 5.12; N, 3.75. Found: C, 73.92; H, 5.52; N, 3.77.

The **3,5-dinitrobenzoate** was crystallized from petroleum ether as pale yellow needles, m.p. 117.6–118.4°.

*Anal.* Calcd. for $C_{23}H_{18}N_2O_6$: C, 66.02; H, 4.34; N, 6.69. Found: C, 66.59; H, 4.70; N, 6.90.

The residue in the first evaporative distillation tube was evaporatively distilled at 185–190° and 0.2 mm. to give 0.35 g. (12%) of a stiff gum which may have contained some of the glycol (VIIIa) but which exhibited absorption at 248 m$\mu$ ($\epsilon$ 16310), indicating that a fair amount of unsaturated alcohol (perhaps a geometrical isomer of Xa) or some similar chromophore must have been present. The material was not further investigated.

**Partial Reduction of the Enol Form of 1,1-Dibenzoylethane (IXa).**—The reaction of 2.62 g. (0.011 mole) of IXa with 2 g. of lithium aluminum hydride in 200 cc. of dry ether at 15° for 20 minutes in the usual manner resulted in a residual oil with a benzaldehyde-like odor, which was distilled to give a mixture of benzaldehyde and propiophenone, b.p. 90–103° at 50 mm., yield 1.18 g., $n^{25}$D 1.5350. The former was separated as the sodium bisulfite derivative which, after decomposition with dilute sulfuric acid, yielded 1.01 g. of an orange 2,4-dinitrophenylhydrazone, m.p. 236–237.5°, not depressed by an authentic sample of the same derivative of benzaldehyde (reported[15] m.p. 237°). This is equivalent to a 32% yield of benzaldehyde.

The filtrate from the bisulfite separation was extracted with ether and concentrated to give 1.84 g. of the red 2,4-dinitrophenylhydrazone of propiophenone, m.p. 135–150°. After two recrystallizations from ethyl acetate–ethanol the melting point was raised to the reported[15] value, m.p. 195–196° alone and when mixed with an authentic sample of the same derivative. The crude yield of derivative was equivalent to a 53% yield of propiophenone.

The residue from the above distillation was evaporatively distilled at 185–190° and 1.5 mm., yield 0.47 g., $\lambda_{\max}^{\text{alc}}$ 248, 286 m$\mu$ ($\epsilon$ 5800, 4650). The peak at 248 m$\mu$ could possibly represent a 35% content of Xa while the peak at 286 m$\mu$ remains unexplained as no further work was done on the material.

**Dibenzoylmethane (IXb)** (this experiment was performed by Mr. D. M. Chern in this Laboratory).—To a mixture of 165 g. (1.1 moles) of ethyl benzoate and 120 g. (1.0 mole) of acetophenone in three liters of dry ether contained in a 5-liter flask under an atmosphere of dry nitrogen was added 46 g. (2.0 moles) of sodium hydride with stirring. After 15 minutes, 2 cc. of absolute ethanol was added and a strong evolution of hydrogen was observed for several hours while the flask was cooled with water. After stirring for two days, the mixture was poured into cold dilute sulfuric acid and the product isolated by ether extraction in the usual way. Recrystallization from methanol afforded IXb as light yellow needles, m.p. 77–78.5° (reported[16] m.p. 77–78°); yield 160 g. (72%).

**Reduction of Dibenzoylmethane (IXb).**—The reduction of 10.0 g. (0.045 mole) of IXb with 5 g. (0.12 mole) of lithium aluminum hydride was a vigorous reaction accompanied by the evolution of a gas. After refluxing for five hours, the product was isolated and distilled through a small Vigreux column to give 7.81 g. (83%) of 1,3-diphenylpropane-1-ol (XIIb), b.p. 132–133° at 0.1 mm. (reported[17] b.p. 168–174° at 5 mm.); $\lambda_{\max}^{\text{alc}}$ 252 m$\mu$ ($\epsilon$ 760). The infrared spectrum showed a strong band at 2.93 $\mu$ (hydroxyl group) and no absorption in the carbonyl region.

The distillate solidified on chilling and recrystallization from petroleum ether gave fine silky needles, m.p. 28.9–29.8° (reported[18] m.p. 45.5° for a racemic mixture prepared by mixing equal quantities of the two enantiomorphs).

*Anal.* Calcd. for $C_{15}H_{16}O$: C, 84.86; H, 7.59. Found: C, 84.90; H, 7.89.

The $p$-nitrobenzoate crystallized from petroleum ether as silky needles, m.p. 90.6–91.2° (reported[19] m.p. 88–89°).

The phenylurethan crystallized from petroleum ether as fine short needles, m.p. 82–84° (reported[20] m.p. 83–84°).

The undistilled residue in the pot solidified on cooling, yield 0.97 g. (10.4%). Evaporative distillation at 200° and 0.2 mm. gave 0.86 g. of an oil which on rubbing with petroleum ether was converted to a soft solid, m.p. 80–86°. Recrystallization from petroleum ether afforded 1,3-diphenylpropane-1,3-diol (VIIIb), m.p. 94–97° (reported[17] m.p. 94–98°). The broad melting point may be due to contamination with another stereoisomer.

**Reduction of Cyclohexane-1,3-dione (XIIIa).**—The reduction of 2.0 g. (0.017 mole) of the cyclic diketone (XIIIa) with an equal weight of lithium aluminum hydride followed by evaporative distillation gave 0.8 g. (50%) of 2-cyclohexene-1-ol (XIVa) which was collected at 120° and 45 mm. (reported[21] b.p. 85° at 25 mm.); $n^{25}$D 1.4790.

The $\alpha$-naphthylurethan crystallized from petroleum ether as long fine needles, m.p. 155–156° (reported[22] m.p. 156°).

The phenylurethan crystallized from petroleum ether as stout needles, m.p. 106–107° (reported[21] m.p. 106–107°).

An additional 0.11 g. remained in the distillation tube. It was not further investigated.

**Reduction of 2-Methylcyclohexane-1,3-dione (XIIIb).**—From 1.16 g. of XIIIb and 2 g. of lithium aluminum hydride was obtained 0.63 g. (62%) of 2-methyl-2-cyclohexene-1-ol by evaporative distillation at 125° and 25 mm., $n^{25}$D 1.4838 (reported[23] b.p. 80° at 18 mm. and $n^{22}$D 1.4855).

The distilling pot contained 0.074 g. of a residue which was not investigated.

The dibromide of XIVb crystallized from petroleum ether as fine silky needles, m.p. 74.8–75.4° (reported[23] m.p. 75° but not analyzed).

*Anal.* Calcd. for $C_7H_{12}Br_2O$: Br, 58.76. Found: Br, 58.67.

When mixed with the dibromide of the isomeric 2-methyl-

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[13] J. Meisenheimer, *Ann.*, **446**, 76 (1926).

[14] R. S. Rasmussen, D. D. Tunnicliff and R. R. Brattain, THIS JOURNAL, **71**, 1068 (1949).

[15] R. L. Shriner and R. C. Fuson, "The Systematic Identification of Organic Compounds," 3rd ed., John Wiley and Sons, Inc., New York, N. Y., 1948, pp. 229 and 263.

[16] C. F. H. Allen, *Org. Syntheses*, **20**, 32 (1940).

[17] J. Sprague and H. Adkins THIS JOURNAL, **56**, 2669 (1934).

[18] L. Hewitt and J. Kenyon, *J. Chem. Soc.*, **127**, 1094 (1925).

[19] P. Pfeiffer, E. Kalckbrenner, W. Kunze and K. Levin, *J. prakt. Chem.*, **119**, 109 (1928).

[20] F. Straus and H. Grindel, *Ann.*, **439**, 276 (1924).

[21] P. D. Bartlett and G. F. Woods, THIS JOURNAL, **62**, 2933 (1940).

[22] H. Hoch and O. Schroder, *Naturwissenschaften*, **24**, 159 (1940)

[23] E. Urion, *Compt. rend.*, **199**, 363 (1934).

enecyclohexanol[2] (m.p. 75–76°), the melting point was depressed by 20°.

The phenylurethan of XIVb crystallized from petroleum ether as stout needles, m.p. 91.5–92.8° (reported[24] m.p. 204°).

*Anal.* Calcd. for $C_{14}H_{17}NO_2$: C, 72.69; H, 7.41; N, 6.06. Found: C, 72.63; H, 7.51; N, 6.28.

An alternate preparation of XIVb consisted of the lithium aluminum hydride reduction of 2-methyl-2-cyclohexene-1-one[25] (XVI) in a 70% yield, b.p. 73–75° at 18 mm., $n^{25}D$ 1.4823.

The dibromide and phenylurethan of this sample had the same melting points alone and when mixed with the respective derivatives obtained by the reduction of XIIIb.

**Reduction of 5,5-Dimethylcyclohexane-1,3-dione (XIIIc).**—The reduction of 20 g. of XIIIc (Eastman Kodak Co. White Label) by 7.0 g. of lithium aluminum hydride gave 12.3 g. (68%) of **5,5-dimethyl-2-cyclohexene-1-ol (XIVc)**, b.p. 83–84° at 17 mm., $n^{25}D$ 1.4688.

The **dibromide** crystallized from petroleum ether as short stout needles, m.p. 58.8–59.6°.

*Anal.* Calcd. for $C_8H_{14}Br_2$: C, 33.59; H, 4.93; Br, 55.88. Found: C, 33.93; H, 5.03; Br, 55.85.

The **3,5-dinitrobenzoate** crystallized from petroleum ether as fine needles, m.p. 137.6–138.6°.

*Anal.* Calcd. for $C_{15}H_{16}N_2O_6$: C, 56.24; H, 5.04; N, 8.75. Found: C, 56.32; H, 5.17; N, 8.58.

An additional 0.77 g., which remained as a residue in the evaporative distillation, was fractionally crystallized from ether and petroleum ether to give the two stereoisomeric forms of 5,5-dimethylcyclohexane-1,3-diol (XVc). One form was recrystallized from petroleum ether to give long needles, m.p. 147.6–148° (reported[17] m.p. 146°, but not analyzed).

*Anal.* Calcd. for $C_8H_{16}O_2$: C, 66.62; H, 11.18. Found: C, 65.81; H, 11.24.

The other form crystallized from ether–petroleum ether as large flat plates, m.p. 102.0–103.2° (reported[17] m.p. 102–104°).

**Reduction of 2-Hydroxymethylene-1-keto-1,2,3,4-tetrahydrophenanthrene (XVII).**—One gram of the formyl ketone[26] (m.p. 83–85°) was reduced with an equal weight of lithium aluminum hydride to give 1.1 g. of a pink solid which was taken up in a small amount of benzene and chromatographed on 40 g. of activated alumina by eluting in 50-cc. fractions with the indicated solvents.

The first five fractions eluted with benzene contained a total of 0.12 g. (13%) of colorless crystals. Recrystallization of 0.106 g. from petroleum ether gave 0.071 g. of 1-keto-2-methyl-1,2,3,4-tetrahydrophenanthrene as clusters of colorless needles, m.p. 69.4–71.0° with softening at 67°. When mixed with an authentic sample, the melting point was 70–73° (reported[27] m.p. 73–74°), $\lambda_{max}^{alc}$ 213, $245_{inf}$, 251, $274_{inf}$, 286, 295 mμ (ε 17500, 40150, 49500, 7500, 9950 and 7490) which was identical with an authentic sample. The infrared spectrum of this product showed no absorption for hydroxyl group and a strong band at 5.97 μ (conjugated carbonyl).

Fractions 6–12, eluted with benzene, contained 0.027 g. of a material which resisted crystallization and was not investigated.

Fractions 13–26, eluted with 1:1 benzene–ether, afforded 0.469 g. (54%) of colorless crystals which, on recrystallization from petroleum ether and then cyclohexane, gave **1-hydroxy-2-methylene-1,2,3,4-tetrahydrophenanthrene (XVIII)** as fine silky needles, m.p. 106.0–107.0°; $\lambda_{max}^{alc}$ 230, $254_{inf}$, $262_{inf}$, 272, 280, $291_{inf}$, mμ (ε 86600, 4400, 5300, 6150, 6400 and 4700). The infrared spectrum indicated absorption peaks at 3.15 μ (hydroxyl group), 6.06 μ (double bond) and 11.02 μ (terminal double bond[28]).

*Anal.* Calcd. for $C_{15}H_{14}O$: C, 85.68; H, 6.71. Found: C, 85.85; H, 6.88.

Fractions 32–38 were eluted with 25% methanol in ether and contained 0.158 g. (15%) of the crude diols (XIX) possibly a mixture of *cis* and *trans* isomers. Purification by fractional crystallization with petroleum ether yielded only a few milligrams of one stereoisomer of **1-hydroxy-2-hydroxymethyl-1,2,3,4-tetrahydrophenanthrene (XIX)** as fine needles, m.p. 141–142°, which was sacrificed for analysis.

*Anal.* Calcd. for $C_{15}H_{16}O_2$: C, 78.91; H, 7.06. Found: C, 79.32; H, 7.73.

**Catalytic Hydrogenation of 1-Hydroxy-2-methylene-1,2,-3,4-tetrahydrophenanthrene (XVIII).**—The catalytic reduction of 0.076 g. of XVIII with 0.010 g. of platinum oxide in 10 cc. of methanol gave an 88% yield of what appears to be predominantly one stereoisomer of **1-hydroxy-2-methyl-1,2,3,4-tetrahydrophenanthrene**, m.p. 89–93°. An analytical sample was recrystallized from petroleum ether to give short silky needles, m.p. 95.6–96.6°. Admixture with XVIII depressed the melting point to 85–87°.

*Anal.* Calcd. for $C_{15}H_{18}O$: C, 84.86; H, 7.59. Found: C, 84.87; H, 7.74.

**Reduction of 1-Keto-2-methyl-1,2,3,4-tetrahydrophenanthrene.**—The lithium aluminum hydride reduction of this phenanthrene gave a 90% yield of the crude mixture of alcohols, m.p. 85–90°. Attempted purification by fractional crystallization was unsuccessful and the product was chromatographed on activated alumina. Fractions 3 and 4 (30 cc.), eluted with benzene–ether (1:1), produced a 10% yield of solids which after recrystallization from petroleum ether formed fine silky needles, m.p. 94.2–95.8°, and did not depress the melting point of the saturated alcohol obtained in the previous experiment. Further elution with ether returned the remainder of the material which, after recrystallization from petroleum ether as colorless needles, melted between 87–93°. No further attempt was made to purify this mixture or to determine the amounts of the *cis* and *trans* isomers.

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