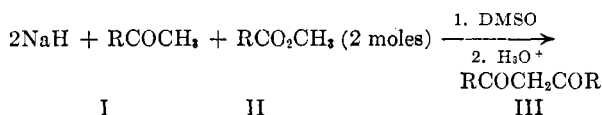


Acylation of Ketones in Dimethyl Sulfoxide¹JORDAN J. BLOOMFIELD²*Department of Chemistry, University of Arizona, Tucson, Arizona*

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Symmetrical β -diketones are readily prepared by allowing methyl esters to react with methyl ketones in dimethyl sulfoxide with sodium hydride as base.

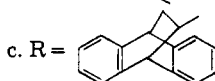
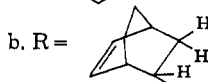
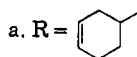
Recently dimethyl sulfoxide and sodium hydride have been shown to be a useful combination of solvent and base for alkylation of malononitrile and 2,4-pentanedione.³ This combination has now proved to be of considerable utility in the acylation of some methyl ketones with methyl esters to produce symmetrical β -diketones.⁴ These conditions failed to produce β -diketone in only one case, the reaction between 4-benzyloxybutanone-2 (Id) and methyl β -benzyloxypropionate (IIId).



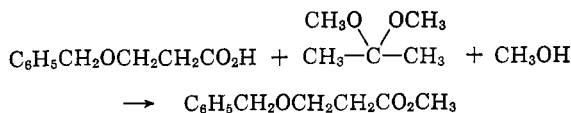
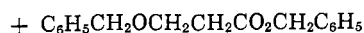
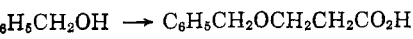
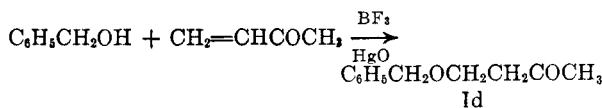
I

II

III



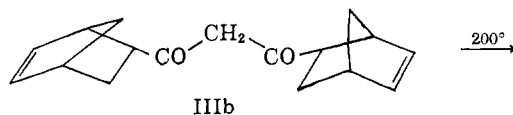
The ketones, Ia-c, and the esters, IIa-c, were prepared by Diels-Alder reactions of methyl vinyl ketone and methyl acrylate, respectively, with butadiene (Ia and IIa), cyclopentadiene (Ib and IIb), and anthracene (Ic and IIc). Compounds Id and IIId were prepared by the reactions outlined below.



Several attempts to prepare Id by reaction of benzyl chloride and 4-hydroxybutanone-2 met with failure. Attempts to prepare the acid chloride of β -benzyloxypropionic acid with thionyl chloride or phosphorus pentachloride also failed. The experimental evidence indicates that the thionyl chloride reaction produced benzyl chloride and β -propiolactone.

The acylation reactions were conducted in dry dimethyl sulfoxide using a molar ratio of sodium hydride to ester to ketone of 2:2:1. A ratio of 1:2:1 gave lower yields of β -diketone.⁶ In one case, with Ia and IIa, in which the reaction was carried out in toluene with sodium methoxide as base, the yield of the β -diketone IIIa isolated as the copper chelate⁷ was 36% compared to a yield of 83% when the reaction was carried out in dimethyl sulfoxide with two equivalents of sodium hydride.

The liquid β -diketones, IIIa and IIIb, were isolated as copper chelates. The regenerated diketones were then vacuum distilled. However, compound IIIb was very readily decomposed at a bath temperature of only 200°. Cyclopentadiene was discovered in the pump traps and the distillate, a nearly colorless liquid, 1-vinyl-3-(5-norborn-2-enyl)-1,4-propanedione, IV, readily polymerized to an insoluble, hard, lucite-like polymer. The polymer had a correct analysis for (C₁₂H₁₄O₂)_n. The pure β -diketone, 1,3-di(5-norborn-2-enyl)-1,3-propanedione (IIIb) was obtained by vacuum distillation in a Hickman still heated in an air bath at not over 150°.



IV

(3) J. J. Bloomfield, *J. Org. Chem.*, **26**, 4112 (1961).

(4) The effectiveness of this combination may rest largely in the fact that sodium hydride converts dimethyl sulfoxide to its strongly basic and soluble conjugate base, an observation published after submission of this paper.⁵

(5) E. J. Corey and M. Chaykovsky, *J. Am. Chem. Soc.*, **84**, 866 (1962).

(6) Cf., C. R. Hauser, F. W. Swamer, and J. T. Adams, *Org. Reactions*, **8**, 126 (1954).

(7) See ref. 4, p. 122.

(1) This work was supported under contract AF 33(616)7908 with the Nonmetallic Materials Laboratory of Wright Air Development Division, Wright-Patterson Air Force Base, Ohio. This paper may be reproduced for any purpose of the U.S. Government.

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TABLE I
SUMMARY OF ACYLATION REACTIONS
IN DIMETHYL SULFOXIDE

| Ketone (moles) | Base (moles) | β -Diketone (yield, %) |
|----------------|---------------------------------------|------------------------------|
| Ia (0.2) | NaOCH ₃ (0.2) ^a | IIIa (36) ^b |
| Ia (0.1) | NaH (0.2) | IIIa (56) ^{b,c} |
| Ia (0.5) | NaH (1.0) | IIIa (83) ^b |
| Ib (0.5) | NaH (0.5) | IIIb (42) ^b |
| Ib (0.2) | NaH (0.4) | IIIb (75) ^b |
| Ib (0.4) | NaH (0.8) | IIIb (71) ^b |
| Ib (1.0) | NaH (2.0) | IIIb (79) ^b |
| Ic (0.56) | NaH (0.56) | IIIc (25) ^d |
| Ic (0.2) | NaH (0.4) | IIIc (30.5) ^{b,e} |
| Ic (0.25) | NaH (0.5) | IIIc (47) ^f |
| Ic (0.5) | NaH (1.0) | IIIc (39.5) ^d |
| Ic (1.5) | NaH (3.0) | IIIc (36) ^{d,g} |
| Id (0.1) | NaH (0.2) | IIId (0) |

^a The solvent was toluene in this case. ^b Isolated as the copper chelate. ^c This reaction was worked up by adding acetic acid to the reaction mixture instead of pouring the reaction mixture into cold dilute hydrochloric acid. A powerful stench was noted which was not noticed in the alkylation reactions.³ A bad odor was present in most of the other acylation reaction mixtures but it was usually mild. ^d Isolated directly as the free β -diketone. ^e In this reaction the ketone was added as a slurry in ether. The reaction was carried out so that the ether refluxed vigorously for 9 hr. In the other reactions ether was not present and the reaction was normally conducted (see experimental) at about 70° for 6 to 9 hr. ^f The pure β -diketone was isolated directly in 35% yield; a further 12% was isolated as the copper chelate. ^g This reaction was carried out at 75° for 17 hr. The residue remaining after the usual work-up (the precipitated solid was washed with 4 l. of cold ether in 500-ml. portions, then with 500 ml. of hot 95% ethanol and finally with 1 l. of boiling ether), was dissolved in 2 l. of hot chloroform, filtered, and poured into 2 l. of boiling methanol. The β -diketone was immediately collected, m.p. 208–211°. Concentration of the filtrate to 300 ml. permitted the isolation of 170 g. of a product, m.p. 160–180° from which, however, no further β -diketone could be isolated as the copper chelate. This material has not been further investigated.

Compound IIIc, a high-melting solid, was separated from the other components of the reaction mixture by washing the precipitated solids with large volumes of ether. A filtered chloroform solution of the residue was then poured into boiling methanol. The diketone, which precipitated almost immediately, was usually as pure as material regenerated from the copper chelate.

Experimental⁸

Dimethyl sulfoxide (Crown-Zellerbach) was distilled from calcium hydride through a 3-ft. helix-packed column at 18 mm. just before use. The acylation reactions were carried out under dry, oxygen-free nitrogen in a three-neck flask fitted with a dropping funnel, a thermometer, a Trubore stirrer and, when necessary, a reflux condenser (reactions with ether or toluene). The apparatus was oven-dried (120°) and assembled hot, under nitrogen. Sodium hydride (Metal Hydrides, oil-free) was ground to a powder and weighed in a drybox. The acylation procedures de-

scribed below are typical. In cases where the molar ratio of ketone to sodium hydride was 1:1 the reaction conditions were otherwise the same as those in which this ratio was 1:2. The molar ratio of ester to ketone for reactions in dimethyl sulfoxide was always 2:1.

1,3-Di(3-cyclohexenyl)-1,3-propanedione (IIIa).—Butadiene and methyl vinyl ketone were allowed to react to produce 4-acetylcyclohexene, Ia, in 92% yield,⁹ b.p. 89–90°/30 mm., n_D^{20} 1.4673 (lit.,⁷ b.p. 79.5–80°/20 mm., n_D^{20} 1.4698).

4-Carbomethoxycyclohexene was prepared, 81–86% yield, following the procedure of Alder and Vogt.¹⁰

The ester, 140 g. (1.0 mole), was added rapidly to a vigorously stirred mixture of sodium hydride, 24 g. (1.0 mole), in 400 ml. of dimethyl sulfoxide. Then the ketone, 62 g. (0.5 mole) was added over 40 min. The temperature which rose to 55° during the addition was maintained at 60° for an additional 3.5 hr. The cooled reaction mixture was poured into 1 l. of ice and water containing 100 ml. of concentrated hydrochloric acid. The organic layer was separated and the aqueous layer extracted twice with 150 ml. of ether. The combined organic solutions were washed twice with 150 ml. of saturated sodium bicarbonate solution, filtered, poured into 1 l. of hot 10% copper acetate monohydrate solution, and stirred overnight after adding 150 ml. of methanol. The precipitated chelate was filtered off and washed with 300 ml. of water, twice with 150 ml. of petroleum ether (b.p. 60–80°), once with 150 ml. of methanol, and finally twice with 250 ml. of ether. The yield of vacuum dried blue powder was 109 g. (83%), m.p. 215.0–215.5°. This solid was stirred for 3 hr. with 1 l. of 10% sulfuric acid and 250 ml. of petroleum ether (b.p. 60–80°). The organic layer was washed with water and with saturated sodium bicarbonate solution, filtered, and dried over anhydrous magnesium sulfate. Distillation at 0.1 mm. gave 84.2 g. (72.4% over-all), b.p. 116–122°, n_D^{20} 1.5367. The analytical sample had b.p. 114–116°/0.1 mm., n_D^{20} 1.5392.

Anal. Calcd. for C₁₅H₂₀O₂: C, 77.73; H, 8.70. Found: C, 77.69; H, 8.64.

The infrared spectrum (neat) shows a strong, broad band at 1625 cm.⁻¹, indicative of a β -diketone.¹¹ Other bands occur at 3070(m), 2970(s), 2880(m), 1445(s), 1365(m), 1295(m), 1260(w), 1225(m), 1190(w), 1140(m), 1050(w), 990(w), 955(w), 928(m), 780(w), and 735(w) cm.⁻¹.

A portion of the chelate was recrystallized twice from benzene to give the analytical sample, m.p. 218.2–219.4°.

Anal. Calcd. for C₃₀H₃₈CuO₄: C, 68.48; H, 7.28. Found: C, 68.66; H, 7.19.

The infrared spectrum (KBr disk) includes bands at 3080(w), 2970(m), 2880(w), 1580(s), 1530(s), 1460(s), 1360(m), 1310(w), 1295(w), 1235(w), 1175(m), 1140(w), 1050(w), 1010(m), 930(m), 920(m), 890(w), 810(w), 780(m), 738(m), and 720(w) cm.⁻¹.

1,3-Di(5-norborn-2-enyl)-1,3-propandione (IIIb).—Equivalent amounts of methyl vinyl ketone and cyclopentadiene were allowed to react in ether in a flask fitted with a Dry Ice condenser to control the vigorous reflux¹² to produce 5-acetylnorborn-2-ene, Ib, in 78–79% yield, b.p. 63–65°/4–5 mm., n_D^{20} 1.4812 (lit.,¹³ b.p. 48–48.5/2 mm., n_D^{20} 1.4841).

A similar reaction with methyl acrylate and cyclopentadiene carried out according to Roberts¹⁴ but modified by using a Dry Ice condenser and allowing the reaction mixture

(9) A. A. Petrov, *J. Gen. Chem. USSR*, **11**, 309 (1941); *Chem. Abstr.*, **35**, 5873^s (1941).

(10) K. Alder and W. Vogt, *Ann.*, **564**, 109 (1949).

(11) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," 2nd ed., John Wiley and Sons, Inc., New York, N. Y., 1958, p. 142.

(12) This is the procedure of Plate and Meerovich¹³ modified by adding ether and using an open flask rather than a sealed tube.

(13) A. F. Plate and T. A. Meerovich, *Bull. acad. sci., URSS, Classe. sci. chim.*, 219 (1947); *Chem. Abstr.*, **42**, 5440c (1948).

(14) J. D. Roberts, E. R. Trumbull, Jr., W. Bennett, and R. Armstrong, *J. Am. Chem. Soc.*, **72**, 3116 (1950).

(8) Melting points were taken with total immersion, calibrated thermometers. Boiling points are uncorrected. Infrared spectra were determined on a Perkin-Elmer Infracord. Analyses were by Micro-Tech Laboratories, Skokie, Illinois.

to reflux produced 5-carbomethoxynorborn-2-ene (IIb) in 88–92% yield, b.p. 67–71°/4.5–5.5 mm., n_D^{25} 1.4739 (lit.^{14,15} b.p. 63.5–5.2 mm., n_D^{25} 1.4718¹⁴; b.p. 71–73°/8 mm., n_D^{25} 1.4745¹⁵).

The ester IIb 304 g. (2.0 moles), dissolved in 250 ml. of dimethyl sulfoxide was added to 48 g. of sodium hydride contained in a 2-l. flask. The ketone, 136 g. (1.0 mole), dissolved in 150 ml. of dimethyl sulfoxide was added to the vigorously stirred mixture over 100 min. during which time the temperature rose to 50–55°. The reaction was completed by continued stirring at 60° for 5 hr. The mixture was cooled to room temperature during a further 90 min. and was then poured with stirring into 2 l. of ice and water containing 200 ml. of concentrated hydrochloric acid. After separation of layers the aqueous solution was extracted three times with 300 ml. of ether. The combined organic solution was filtered, washed once with 250 ml. of water, and three times with 250 ml. of saturated sodium bicarbonate solution. The ether was then removed under vacuum and the residue, dissolved in 100 ml. of methanol, was added in a slow stream to 2 l. of a vigorously stirred, hot solution of 10% copper acetate monohydrate. The precipitate was filtered off and washed with water, triturated with 500 ml. of methanol and then filtered off again. The air-dried filter cake was washed thoroughly with 1 l. of water, then with methanol, and finally with ether. The yield of vacuum-dried purple solid was 227 g. (79.1%) m.p. 213–214°. A small portion was crystallized twice from benzene to give the analytical sample, m.p. 222.6–223.4° dec.

Anal. Calcd. for $C_{24}H_{38}CuO_4$: C, 71.12; H, 6.67. Found: C, 70.99; H, 6.67.

The infrared spectrum (KBr disk) of the chelate includes bands at 3100(w), 3005(m), 2900(w), 1528(s), 1570(s), 1465(m), 1438(s), 1360(m), 1338(m), 1322(m), 1175(m), 1030(m), 1000(w), 958(w), 908–920(w), 793(w), 778(w), 718(m), and 708(m) cm^{-1} .

Forty grams of the crude copper chelate was stirred with 200 ml. of 10% sulfuric acid and 100 ml. of ether for 1 hr. The ether layer was washed with 50 ml. of water, 50 ml. of saturated sodium bicarbonate, and then filtered through anhydrous magnesium sulfate. The ether was evaporated and the residue was distilled. Decomposition occurred during the distillation as evidenced by the drop in head temperature with high reflux ratios, the presence of cyclopentadiene in the Dry Ice traps and the presence of a large amount of orange polymer in the pot, most of which was insoluble in chloroform or dimethylacetamide. The fractions collected and stored in ordinary vials at room temperature rapidly polymerized to a soft, transparent, rubbery material, 13.9 g. This material eventually hardened completely to a hard, transparent, somewhat flexible rod which was only partially soluble in chloroform or tetrahydrofuran. A powdered sample, dried at 105°/0.05 mm. for 18 hr., was analyzed.

Anal. Calcd. for $(C_{12}H_{14}O_2)_n$: C, 75.76; H, 7.42. Found: C, 75.76; H, 7.50.

The infrared spectrum (neat) of a twice distilled sample of this polymerizable liquid, IV, b.p. 120°/2.5 mm., n_D^{25} 1.5609, included bands at 3100(w), 3010(s), 2910(w), 1660(s), 1590(s), 1440(m), 1340(m), 1235(m), 1205(s), 1140(s), 1108(m), 1050(m), 990(m), 950(m), 910(m), 850(w), 810(m), 750(w), and 720(m) cm^{-1} .

Pure 1,3-di(5-norborn-2-enyl)-1,3-propanedione (IIIb) was prepared by stirring the copper chelate with 10% sulfuric acid and pentane. The pentane solution was washed with water and then the product was distilled at 0.05–0.1 mm. in a Hickman still with an air bath temperature of 130–150°. The recovery from the chelate varied from 72.0–92.4% of a product m.p. 26–27°, n_D^{25} 1.5559.

Anal. Calcd. for $C_{17}H_{20}O_2$: C, 79.65; H, 7.86. Found: C, 79.95; H, 8.14.

The infrared spectrum (neat) includes bands at 3100(w), 3010(s), 2905(w), 1700(w), 1625(s), (β -diketone)¹¹ 1455(m), 1360(s), 1280(m), 1260(m), 1235(m), 1215(m), 1140(m), 1010(m), 980(w), 910(m), 880(w), 865(m), 840(w), 800(w), 775(w), and 710(s) cm^{-1} .

11-Acetyl-9,10-dihydro-9,10-ethanoanthracene (Ic).—Purified anthracene,¹⁶ 200 g. (1.12 moles), methyl vinyl ketone, 115 g. (1.64 moles), toluene, 600 ml., and hydroquinone, 2 g., were heated to 175–180° in a stirred 2-l. autoclave for 12 hr. The reaction mixture, after overnight cooling, was green. It became quite warm when ketone began to precipitate. The contents of the bomb were transferred with the aid of 200–300 ml. of acetone and filtered hot to give an orange solution which was concentrated to about 600 ml. The cooled solution was decanted from the flat plates of anthracene, 13 g. (6.5%), which formed and the crystallization of the ketone was induced by adding a seed. The small cubic crystals were separated while the solution was still warm to give 110 g. (39.6%) m.p. 139–149°. Successive concentrations of the mother liquor gave an additional 120 g. (43.2%) m.p. 128–145° [total, 230 g. (82.8%)]. Recrystallization of 190 g. of adduct from 700 ml. of boiling ethyl acetate gave 143 g. (51.5%) m.p. 147.2–149.6° (lit.¹⁷ 145–148°).

Similar reactions were conducted with practical grade anthracene (Matheson, 90–95%) and gave yields of product m.p. 139–148° varying from 48 to 60%. Concentration of the mother liquors gave additional ketone but repeated recrystallizations did not improve the melting point. Unchanged anthracene was harder to remove in this case. The use of the crude ketone in the β -diketone synthesis did not seem to affect the yield of β -diketone.

Methyl 9,10-Dihydro-9,10-ethanoanthracene-11-carboxylate (IIc).—This ester was prepared in 80.5% yield, m.p. 116.8–117.2°, by reaction of methyl acrylate, 130 g. (1.5 moles), with purified anthracene,¹⁶ 181 g. (1.02 moles), in 600 ml. toluene according to the procedure of Wawzonek.¹⁸ The use of practical grade anthracene usually gave an equally good yield.

1,3-Di(9,10-dihydro-9,10-ethanoanthracenyl-11)-1,3-propanedione (IIIc).—Dimethyl sulfoxide, 300 ml., was added rapidly to a mixture of the ester IIc, 264 g. (1.0 mole), and sodium hydride, 24 g. (1.0 mole), contained in a 2-l. flask. To this vigorously stirred mixture a solution of the ketone, Ic, (m.p. 139–148°), 124 g. (0.50 mole), dissolved in 600 ml. of warm, 55–60°, dimethyl sulfoxide,¹⁹ was added over 2 hr. Stirring was continued for an additional 6 hr. at 70–75° and then the mixture was allowed to cool to room temperature, with continued stirring, overnight.²⁰ The cooled solution was poured into 1.5 l. of water and ice containing 100 ml. of concentrated hydrochloric acid. The solid residue was collected on a large Büchner funnel and washed repeatedly with ether (total about 1.5 l.) to remove unchanged ketone and ester. The residue was dissolved in 400 ml. of warm chloroform. The solution was filtered, concentrated to 300 ml., and then poured into 1 l. of hot methanol. Within 30 sec. a precipitate formed and the entire mass was filtered to give 90 g. of the β -diketone (37.5%) m.p. 210–211.5°. A further 4.7 g. (2%)

(16) L. F. Feiser, "Experiments in Organic Chemistry," D. C. Heath and Co., Boston, Mass., 2nd ed., 1941, p. 345.

(17) T. Shono and R. Oda, *Bull. Inst. Chem. Res., Kyoto Univ.*, **33**, 58 (1955); *Chem. Abstr.*, **50**, 14681e (1956), prepared the ketone by reaction of CH_2MgI with 11-cyano-9,10-dihydro-9,10-ethanoanthracene.

(18) S. Wawzonek and J. V. Hallum, *J. Org. Chem.*, **18**, 288 (1953). These authors report m.p. 117–118°.

(19) The ketone and dimethyl sulfoxide were placed together in the dropping funnel and the mixture was cautiously warmed with a free flame until all the ketone dissolved.

(20) In some cases the reaction mixture was maintained at about 70° for 9 hr. and, after rapid cooling, immediately hydrolyzed. In one case, noted in footnote g to Table I, the reaction was maintained at 75° for 17 hr. These variations do not appear to affect the yield of β -diketone very much.

m.p. 206–210°, was obtained by concentration of the solution. No further product was obtained by treating the extracts with copper acetate solution.

The copper chelate was prepared by stirring a chloroform solution of the diketone with hot 10% copper acetate solution. The blue-gray chelate was insoluble in ordinary organic solvents but would dissolve in warm dimethylacetamide to give a green solution. A small portion, 1 g., of the chelate was dissolved in 35 ml. of dimethylacetamide. This solution was poured into 100 ml. of a 1:1 mixture of ether and methanol. The chelate precipitated as a light blue powder. The melting point depended on the temperature of the bath when the sample was immersed, *e.g.*, m.p. 276.5° dec. when put in bath at 270°; m.p. 280.5° dec. when put in bath at 278°.

Anal. Calcd. for $C_{70}H_{54}CuO_4$: C, 82.21; H, 5.32. Found: C, 81.97; H, 5.54.

The infrared spectrum of the chelate (KBr disk) has bands at 3100(w), 3000(w), 1655(m), 1575(s), 1530(s), 1480(m), 1425(s), 1340(w), 1280(w), 1180(w), 1020(w), and 760(m) cm^{-1} .

A slurry of the chelate in chloroform (about 6 ml. of chloroform for each gram of chelate) was stirred with 10% sulfuric acid until all the chelate dissolved. The organic layer was separated, washed with saturated sodium bicarbonate solution, filtered, and concentrated to about one third the original volume. The hot chloroform solution was poured into two to three times its volume of boiling methanol to give product m.p. 211.8–212.8°. The analytical sample was recrystallized once from ethyl acetate, m.p. 211.6–212.2°, and once from acetone, m.p. 212.1–212.5°.

Anal. Calcd. for $C_{35}H_{28}O_2$: C, 87.47; H, 5.87. Found: C, 87.42; H, 6.15.

In chloroform the infrared spectrum showed bands at 2980(w), 1600(s) (β -diketone),¹¹ 1470(s), 1175(m), 1145(m), 1120(m), 960(w), 945(w), 900(w) and 885(w) cm^{-1} .

β -Benzyloxypropionic Acid and Benzyl β -Benzyloxypropionate.— β -Propiolactone (Celanese), 72 g. (1.0 mole), was added to benzyl alcohol, 680 g. (6.3 moles).²¹ The mixture was magnetically stirred at 75° for 9 hr. and 65° for 9 hr. The excess benzyl alcohol was removed by distillation at 30 mm. and the residue was distilled at 0.01 mm. to give five fractions: a) b.p. 124–127°, n_D^{20} 1.5120, 27.4 g. (15.2%); b) b.p. 125° n_D^{20} 1.5142, 54.5 g. (30.2%); c) b.p. 125–130°, n_D^{20} 1.5158, 25 g. (13.9%); d) 130–152°, 5.2 g. and e) 146–152°, n_D^{20} 1.5372, 56.0 g. (20.8%). Fraction e) was treated with dilute sodium hydroxide to remove traces of β -benzyloxypropionic acid and was then distilled to give benzyl β -benzyloxypropionate, b.p. 144–146°/0.05 mm., n_D^{20} 1.5380.

Anal. Calcd. for $C_{17}H_{18}O_3$: C, 75.53; H, 6.71. Found: C, 75.55; H, 6.81.

The first three fractions were crystallized from ether to give β -benzyloxypropionic acid, m.p. 31.5–33.5°.

Anal. Calcd. for $C_{16}H_{18}O_3$: C, 66.65; H, 6.66. Found: C, 66.81; H, 6.73.

β -Benzyloxypropionic Acid and Thionyl Chloride.—Thionyl chloride (Matheson, practical grade), 20 g., and β -benzyloxypropionic acid, 18.0 g. (0.1 mole), were refluxed for 1 hr. and then allowed to stand overnight. Distillation at 30 mm. gave 8.0 g., b.p. 87°, n_D^{20} 1.5270. ($C_6H_5CH_2Cl$, n_D^{20} 1.5415, $C_3H_4O_2$, n_D^{20} 1.4131). Gas-liquid chromatography showed this product to contain two major components which had retention times corresponding to those for β -propiolactone and benzyl chloride, respectively. The infrared spectrum had strong absorptions at 3180, 1720, 1500, 1460, and 1275 cm^{-1} . These indicate the presence of benzyl and carbonyl radicals. A sample gave a positive halogen test with silver nitrate.

β -Benzyloxypropionic Acid and Phosphorus Pentachloride.—Phosphorus pentachloride, 10.8 g. (0.05 mole), was added

in very small portions to a 100-ml. flask containing β -benzyloxypropionic acid, 9.0 g. (0.05 mole). The flask was cooled in cold water. The reaction mixture was allowed to stand for 20 min. and then the phosphorus oxychloride was removed by warming at 35° while maintaining a vacuum of 30 mm. The mixture slowly changed from light yellow to orange. The pressure was gradually reduced to 0.1 mm. and maintained at this pressure for 10 min. The infrared spectrum of a portion of the pot liquid at this point had important peaks at 3040(w), 2900(w), 1800(m), 1750(s), 1500(w), 1455(w), 1360(w), 1260(w), 1175(m), 1100(w), 1075(w), 785(m), and 700(m) cm^{-1} .

The liquid collected in the Dry Ice trap during this treatment, 6.0 g., was distilled at 30 mm. to give only 0.8 g. of product b.p. 60–70°, infrared spectrum, 2900(s), 2700(m), 1810(w), 1725(s), 1650(s), 1630(m), 1500(w), 1440(s), 1305(s), 1250(s), 1075(w), 1055(m), 980(s), 940(m), 870(w), 820(m), 770(w), 700(s), and 680(w) cm^{-1} . The original mixture was heated at 260° under 0.02–0.05 mm. pressure to give 1.5 g. of a pale yellow liquid, b.p. 114°, which had an infrared spectrum very similar to the product above with the exception of the absence of peaks at 1810, 870, and 680 cm^{-1} . Several of the other bands were weaker. New bands were noted at 1200(s) and 735(m) cm^{-1} . Neither spectrum resembled very closely that of the products obtained from the thionyl chloride reaction. Both products of this reaction became very viscous on standing.

4-Benzyloxybutanone-2 (Id).—To a stirred mixture of benzyl alcohol, 54 g., and catalyst (prepared from 1.5 g. of red mercuric oxide, 1.5 ml. of boron trifluoride etherate, and 2 ml. of benzyl alcohol)²² maintained at 100° was added a solution of methyl vinyl ketone, 70 g. (1.0 mole) and benzyl alcohol, 108 g. (1.0 mole). The temperature was maintained at 100° for 0.5 hr. and then allowed to fall to 70° during 2 hr. The mixture was allowed to stand overnight at room temperature. A small amount of free mercury was observed to be present. Solid, anhydrous potassium carbonate was added, and the mixture was filtered. The filtrate was distilled at 0.05 mm. to give 103 g. (63.5%) of recovered benzyl alcohol and then four fractions of 4-benzyloxybutanone-2 were obtained: a) b.p. 87–93°, n_D^{20} 1.5066 (2.8%); b) b.p. 93–95°, n_D^{20} 1.5044, 8.8 g. (5%); c) b.p. 95°, n_D^{20} 1.5061, 26.9 g. (15.1%); and d) b.p. 94–95°, n_D^{20} 1.5090, 20.4 g. (11.4%) (lit.,²³ b.p. 88–91°/0.5 mm., n_D^{20} 1.5040).

Methyl β -Benzyloxypropionate (IId).—A mixture of β -benzyloxypropionic acid, 65 g. (0.36 mole), 50 ml. of 2,2-dimethoxypropane (Dow), 40 ml. of methanol, and 0.1 g. of *p*-toluenesulfonic acid was refluxed for 18 hr.²⁴ The solvent was removed by distillation at atmospheric pressure and the residue, after treatment with sodium bicarbonate solution, was distilled at 0.05 mm. b.p. 81–84°, 57.4 g. (82.1%) n_D^{20} 1.4942. A middle fraction was analyzed.

Anal. Calcd. for $C_{11}H_{14}O_3$: C, 68.02; H, 7.26. Found: C, 67.42; H, 7.35.

Reaction of 4-Benzyloxybutan-2-one (Id) with Methyl β -Benzyloxypropionate (IId).—This reaction was carried out in the manner described for the preparation of compounds IIIa and IIIb. The reaction mixture was very red.

No copper chelate could be prepared from the reaction mixture after the customary work-up. No further investigation of the reaction product was made.

Reaction of 4-Hydroxybutanone-2 with Benzyl Chloride.—(a) Benzyl chloride, 12.6 g. (0.1 mole), 4-hydroxybutanone-2, 8.8 g. (0.1 mole), dimethyl sulfoxide, 50 ml., and

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potassium carbonate, 13.8 g. (0.1 mole), were mixed and allowed to stand at room temperature for 5 hr., 70° for 6 hr. and at 100° for 10 hr. The mixture was cooled, poured into water, and extracted with ether. The ether was dried with anhydrous magnesium sulfate, filtered, and evaporated to leave a viscous, nonvolatile orange liquid.

(b) In a 1-l. three-neck flask fitted with dropping funnel, Trubore stirrer, and condenser were placed 100 ml. of dry dimethyl sulfoxide and 4.8 g. (0.2 mole) of sodium hydride. Then benzyl chloride, 25.2 g. (0.2 mole), and 4-hydroxybutanone-2, 17.6 g. (0.2 mole), in 100 ml. of dry ether were added over 10 min. with external cooling. The mixture was stirred 22 hr. at room temperature and then poured into 600 ml. of water containing 10 ml. of concentrated hydrochloric

acid. Extraction and treatment as above gave only orange viscous oil.

(c) A reaction similar to (b), but in ether instead of dimethyl sulfoxide, turned to a viscous, rubbery mass within 20 min. After standing overnight the mixture became less rubbery and the stirrer could be moved. No volatile product could be isolated.

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Acetylenic Amines. IV

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A method of preparing 1,1-diaryl- and 1-aryl-1-alkylpropargylamines is reported. This consists of preparing from the acetylenic alcohol, the 1,3-dichloropropylene derivatives, followed by treatment of this compound with the appropriate amine; this 3-chloroallylamine was then dehydrohalogenated to give the desired acetylenic amine.

Tertiary acetylenic chlorides, $RR^1C(Cl)C\equiv CH$ are known only where R and R^1 are aliphatic groups.^{1,2}

Thus, the Hennion synthesis³⁻⁵ of acetylenic amines [$RR^1C(NHR)^2C\equiv CH$] has been limited to products in which R and R^1 are aliphatic groups. The reaction of the aromatic acetylenic carbinols (R and/or $R^1 = C_6H_5$, etc.) with hydrochloric acid, thionyl chloride, etc., has been claimed to produce chloroallenes² or dimers⁶ thereof.

Treatment of the chloroallene with a primary or secondary amine gives the conjugated Schiff's base rather than the α -acetylenic amines. Isolation of compounds of the Schiff's base type has been accomplished⁵ when the crude aliphatic chloroacetylenes were treated with lithium *t*-butylamide.

In the present study it was found that in a large-scale preparation of 3-ethylamino-3-methyl-1-butyne from the crude chloroacetylene, a considerable amount of high-boiling basic material was present. From this fraction there was isolated a material which appeared to be an ethylenic amine with one chlorine atom in the molecule. This compound was assigned the structure (IIa. $R^2 = C_2H_5$) from its elemental analyses; the structure was confirmed with infrared and n.m.r. spectra. It has been

reported⁷ that, when 3-methylbutyn-3-ol was treated with hydrochloric acid, among the products obtained was a dichloro-3-methylbutene. Of the two possible structures, Ia and IV, the authors favored structure Ia. This dichlorobutene (Ia) could react with the amine to give the product IIa.

If this be the case, it should be possible also in the aromatic series to add an additional mole of hydrogen chloride to the chloroallene to give the dichloride Ib.

The treatment of an ether solution of 3,3-diphenyl-1-propyn-3-ol with dry hydrogen chloride at room temperature gave a yellow solution from which the chloroallene could be isolated. Treatment of the product, at this point, with *t*-butylamine gave only the conjugated Schiff's base, the structure of which was confirmed by reduction to *N*-(*t*-butyl)-3,3-diphenylpropylamine. However, addition of more hydrogen chloride at 5-6° caused a color change to green, and the crude dichloropropene Ib could be isolated readily from this mixture. Treatment of Ib with ethylamine gave IIB, which was easily isolated by vacuum distillation of the basic fraction. Dehydrohalogenation of IIB with sodamide in liquid ammonia then gave the desired acetylene IIIB.

The infrared spectra were sufficient to assign the structures of the acetylenic amines, and these assignments were confirmed by the n.m.r. spectra. However, the structure of the intermediate chloro compounds II was not as readily established. In attempting to confirm the assignment of the chlo-

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