Filtration gave a white powder (0.033 g., 8%), m.p. 93–102° dec., which was dried over phosphorus pentoxide under reduced pressure; λ_{max} (ethanol) 255 (ϵ 4.9 × 10^3), 315 mμ (ϵ 3.9 × 10^3), λ_{max} (50% ethanol) 268 mμ (ϵ 5.2 × 10^3).

Anal. Calcd. for $C_{18}H_{21}N_3O_3SCl_2$: C, 50.23; H, 4.92; N, 9.76. Found: C, 50.51; H, 4.77; N, 10.11.

When this compound was chromatographed on Whatman no. 1 paper (solvent, 4:1:5 butanol–acetic acid–water) and the chromatogram developed with fresh 1% sodium nitroprusside in 0.05 *N* sodium hydroxide solution both cysteine ethyl ester and cysteine were identified.

2. **Ethyl Thioglycolate Adduct.**—Ethyl thioglycolate (2.6 g., 0.022 mole) in 20 ml. of 5% sodium hydroxide solution was added to nicotinamide-1-(2,6-dichlorobenzylo)-bromide (1.01 g., 0.00279 mole) in 20 ml. of distilled water. After 10 min. the product (0.96 g., 86%) was removed by filtration, washed with water and dried. Recrystallization from ethanol–benzene gave nearly white crystals, m.p. 131–132°; λ_{max} (ethanol) 255 (ϵ 4.1 × 10^3), 316 mμ (ϵ 2.4 × 10^3); λ_{max} (50% ethanol) 267 mμ (ϵ 3.1 × 10^3).

Anal. Calcd. for $C_{17}H_{18}N_2O_3SCl_2$: C, 50.88; H, 4.52; N, 6.98. Found: C, 50.56, 50.64; H, 4.55, 4.67; N, 6.83, 6.87.

When this adduct was chromatographed on paper as described previously, ethyl thioglycolate was identified.

3. ***n*-Propyl Mercaptan Adduct.**—This addition compound was prepared from *n*-propyl mercaptan in the same way as the adduct of ethyl thioglycolate. The crude yellow product was recrystallized from cold ethanol to give a white powder, m.p. 96–98°, λ_{max} (ethanol) 256 (ϵ 4.3 × 10^3), 316 mμ (ϵ 2.7 × 10^3).

Anal. Calcd. for $C_{16}H_{18}N_2OSCl_2$: C, 53.78; H, 5.08. Found: C, 53.91, 54.03; H, 5.13, 5.27.

Ultraviolet Spectra of Benzyl Mercaptan Adduct in Ethanol–Water Mixtures.—The benzyl mercaptan adduct, m.p. 131–132° (lit.[9a] m.p. 131–133°), was prepared by the same method as the ethyl thioglycolate adduct. The effect of the polarity of the medium on the ultraviolet spectrum of this adduct are summarized in Table I.

TABLE I

ULTRAVIOLET ABSORPTION MAXIMA OF BENZYL MERCAPTAN ADDUCT IN ETHANOL–WATER SOLUTIONS

Water, ml.	Ethanol, ml.	Concn. × 10^4 *M*	λ_{max}, mμ	$\epsilon \times 10^{-3}$	λ_{max}, mμ	$\epsilon \times 10^{-3}$
0	50	1.0	316	4.8	254	7.1
5	45	1.1	315	2.4	257	4.5
10	40	1.5	317	1.6	257	3.9
20	30	1.1	317	0.45	265	3.6
30	20	1.4	317	.14	265	3.8
40	10	0.99	317	.09	265	6.7

Reaction of Benzyl Mercaptan Adduct with Hydrogen Chloride.—The addition compound (*ca.* 0.1 g.) was dissolved in 10 ml. of chloroform, and anhydrous hydrogen chloride was passed through the solution. The white precipitate, m.p. 235° dec., was shown to be nicotinamide-1-(2,6-dichlorobenzylo)-chloride by a mixture m.p. (236°) and by identity of the infrared spectra. Nicotinamide-1-(2,6-dichlorobenzylo)-chloride was prepared by heating a mixture of 2,6-dichlorotoluene (16.1 g., 0.100 mole), sulfuryl chloride (6.8 g., 0.050 mole), and benzoyl peroxide (0.2 g., 0.0008 mole) on the steam bath until gas evolution ceased (1 hour). Nicotinamide (6.1 g., 0.050 mole) and 25 ml. of absolute alcohol were added, and the solution was refluxed for 3 hr. When the reaction mixture was cooled, white crystals (7.8 g., 49%) separated. Two recrystallizations from alcohol-water gave white crystals, m.p. 237–238.5° dec.

Anal. Calcd. for $C_{13}H_{11}N_2OCl_3$: C, 49.16; H, 3.49. Found: C, 48.94, 49.13; H, 3.61, 3.73.

Reaction of the Benzyl Mercaptan Adduct with Malachite Green.—A solution of malachite green oxalate (0.5 g.) in 10 ml. of absolute ethanol was heated gently while the adduct was added, with stirring, until the solution was decolorized (pale green). Filtration gave a pale green solid (0.5 g.) and a green filtrate. The solid was soluble in water and insoluble in alcohol and ether. Two recrystallizations from alcohol-water and decolorization with charcoal gave off-white crystals, m.p. 229–230° dec. Analysis by sodium fusion demonstrated the presence of nitrogen and chlorine and the absence of sulfur. With silver nitrate solution, the compound gave an acid-soluble white precipitate (silver oxalate). It was concluded that the compound was nicotinamide-1-(2,6-dichlorobenzylo)oxalate.

Anal. Calcd. for $C_{28}H_{22}N_4O_6Cl_4$: C, 51.55; H, 3.40. Found: C, 51.54, 51.81; H, 3.45, 3.68.

The green filtrate deposited white fluffy crystals (0.1 g.), m.p. 120–122° dec. This compound was identified as the benzyl sulfide of malachite green by m.m.p. (122°) with an authentic sample. The sulfide was prepared also by the dropwise addition of 6 *N* sodium hydroxide solution to a solution of malachite green oxalate (0.4 g., 0.0004 mole) and benzyl mercaptan (1 ml., 0.009 mole) in 15 ml. of absolute ethanol until the solution was decolorized. A tan solid was removed by filtration, and the filtrate was diluted with 5 ml. of ethanol and allowed to stand for 2 hr. Filtration gave fluffy white crystals (0.08 g., *ca.* 50%), m.p. 121–123° dec. This compound turned green on standing in air.

Anal. Calcd. for $C_{30}H_{32}N_2S$: C, 79.60; H, 7.13. Found: C, 79.51, 79.65; H, 7.07, 7.26.

1-(2,6-Dichlorobenzyl)-1,6-dihydronicotinamide.[11]—Sodium borohydride (0.207 g., 0.00547 mole) was added during 1 min. to a stirred solution of nicotinamide-1-(2,6-dichlorobenzylo)bromide (1.00 g., 0.00276 mole) in 15 ml. of distilled water. The crude product precipitated and was recrystallized by dissolving it in 15 ml. of ethanol, adding 15 ml. of water, and chilling. The bright yellow, fine crystals (0.512 g., 66%), m.p. 161–163° dec. [lit.[11] m.p. >150° (dec.)], were dried over potassium pentoxide. The ultraviolet maxima in ethanol were at 354 mμ (ϵ 4200) and 263 mμ (ϵ 4300) [lit.[11] (methanol) 355 mμ (ϵ 7450), 265 mμ (ϵ 9840)].

Comparisons of Infrared Spectra.—The infrared spectra in cm.$^{-1}$ of the following compounds are given.

n-Propanethiol adduct of nicotinamide-1-(2,6-dichlorobenzylo)-bromide: 3450 m, 3150 m, 2975 m, 1675 s, 1654 s, 1608 m, 1562 s (1590–1535), 1465 w, 1454 m, 1434 m, 1409 m, 1380 m, 1356 m, 1342 m, 1283 m, 1222 m, 1204 m, 1170 m, 1090 m, 1085 m, 1032 w, 957 w, 947 w, 920 w, 875 w, 823 w, 800 w, 776 m, 767 m, 750 m, 737 m, 704 w, 667 w.

1-(2,6-Dichlorobenzyl)-1,4-dihydronicotinamide: 3470–3370 w, 3140 w, 2810 w, 1688 m, 1663–1640 m, 1577 (1610–1540) s, 1435 m, 1380 w, 1360 m, 1338 m, 1300 w, 1280 w, 1207 m, 1161 w, 1085 w, 998 w, 952 w, 867 w, 778 w, 764 w, 713 w.

1-(2,6-Dichlorobenzyl)-1,6-dihydronicotinamide: 3375 m, 3190 m, 2775 w, 1680 m, 1643 s, 1598 s, 1580 s, 1562 s, 1435 s, 1430 s, 1385 s, 1359 m, 1340 w, 1317 m, 1308 w, 1282 m, 1220 m, 1201 m, 1178 w, 1162 w, 1128 w, 1021 w, 979 w, 954 w, 870 w, 777 m, 763 w, 729 w, 707 w.

Nicotinamide-1-(2,6-dichlorobenzylo)chloride: 3500 m, 3380 m, 3290 m, 3080 s (3200–2900), 1688 s, 1617 m, 1578 m, 1563 m, 1497 w, 1466 w, 1447 s, 1411 s, 1390 s, 1366 m, 1320 w, 1275 w, 1202 m, 1185 m, 1133 m, 1118 w, 1088 m, 1027 w, 970 w, 948 w, 895 w, 883 w, 852 w, 834 w, 813 m, 793 w, 778 m, 768 m, 755 m, 708 w, 678 m, 672 m.

n-Propanethiol[17]: 4444 w, 2915 s, 2577 w, 2326 w, 1449 s, 1370 m, 1330 w, 1290 m, 1245 s, 1107 w, 1096 w, 920 m, 901 s, 893 s, 813 s, 790 s, 730 s, 704 m.

---

(17) Sadtler Standard Spectra, Midget Ed., Sadtler Research Laboratories, Philadelphia, Pa., no. 328 (1962).

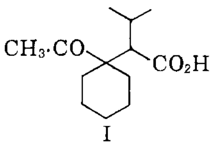
The Conjugate 1:4-Addition of Some Acetylenic Grignard Reagents to Cyclohexylidenemalononitrile

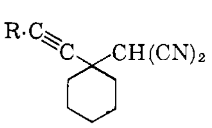
W. PARKER AND R. RAMAGE

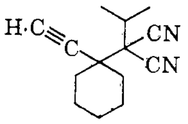
Department of Chemistry, The University of Glasgow, Glasgow, Scotland

Received November 15, 1962

Recently, in another connection, it was found necessary to devise a synthesis of α-(1-acetylcyclohexyl)isovaleric acid (I). By analogy with the well established addition of alkyl Grignard reagents to carbon–carbon double bonds conjugated with electrophilic groupings,[1] the quaternary center of this acid was produced by the addition of ethynylmonomagnesium bromide[2] to cyclohexylidenemalononitrile to give [1-(1-ethynyl)cyclohexyl]malononitrile (II. R = H). Treatment of II (R = H) with isopropyl iodide in the presence of sodium ethoxide gave the alkylated derivative (III) which was converted into the required γ-ketocarboxylic acid (I) by basic hydrolysis followed by acid-catalyzed decarboxylation.


I


II

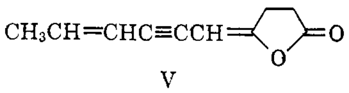

III

A series of such additions[3] then was performed in order to examine this procedure as a general synthetic route to 1,1-disubstituted cyclohexanes. Cyclohexylidenemalononitrile, in the presence of cuprous chloride,[1] was treated with the Grignard reagents of phenylacetylene, 1-octyne, and the tetrahydropyranyl ether of propargyl alcohol and the corresponding [1-(1-alkynyl)-cyclohexyl]malononitriles were isolated in yields ranging from 48% to 17%. When 4-benzoyloxycyclohexylidenemalononitrile was treated with ethynylmonomagnesium bromide, 1-(4-benzoyloxy-1-ethynyl cyclohexyl)malononitrile was obtained as a mixture of the *cis* and *trans* forms.

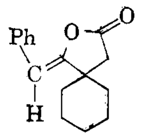
The naturally occurring polyacetylenic acid (IV) is readily transformed at pH 7 into the corresponding γ-enol lactone[4] (V), and this fact suggested that a similar mechanism could account for the unexpected hydration of the triple bond in this series. Alkaline hydrolysis of [1-(1-phenylethynyl)cyclohexyl]malononitrile (II. R = Ph), followed by thermal decarboxylation and treatment with diazomethane, afforded a mixture of the γ-enol lactone (VI) and the keto ester (VII. R = CH_3) which was separated by chromatography on activated alumina.

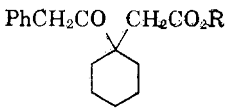
$CH_3CH{=}CHC{\equiv}CC{\equiv}CCH{=}CHCO_2H$

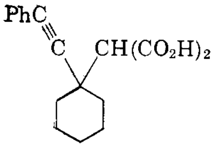
IV

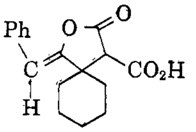

V

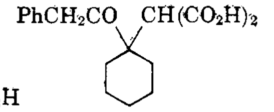
These facts were indicative of the triple bond hydration proceeding *via* the γ-enol lactone (VI) rather than the corresponding δ-enol lactone. The formation of VI and VII (R = H) from the basic hydrolysis and thermal decarboxylation of II (R = Ph), therefore, is envisaged as proceeding through the ethynylmalonic acid (VIII) which would then undergo isomerisation to the related enol lactone (IX). Incomplete hydrolysis of this material would give a mixture of IX and the ketomalonic acid (X), both of which can lose carbon dioxide on heating to furnish the two final products VI and VII (R = H).


VI


VII


VIII


IX


X

Experimental[5]

Cyclohexylidenemalononitrile was prepared in the usual manner[7] by refluxing cyclohexanone (64.5 g.) and malononitrile (40 g.) with ammonium acetate (4.6 g.) and acetic acid (7.5 g.) in benzene. Normal isolation procedure gave the required product (70.4 g.), b.p. 86° (2 mm.), n^{25}_{D} 1.5100.

4-Benzoyloxycyclohexylidenemalononitrile.—A mixture of 4-benzoyloxycyclohexanone (12 g.), malononitrile (3.3 g.), ammonium acetate (0.5 g.), and acetic acid (0.7 g.) in benzene (50 ml.) was heated under reflux for 15 hr. under a Dean and Stark water separator. The cooled reaction mixture was washed with saturated sodium bicarbonate solution and water, dried, and the solvent removed to give **4-benzoyloxycyclohexylidenemalononitrile** which crystallized from methanol in prisms, m.p. 135–136°; ν_{max} (Nujol mull) 1720 cm.$^{-1}$ (benzoate) and 2230 cm.$^{-1}$ (conjugated nitrile).

Anal. Calcd. for $C_{16}H_{14}N_2O_2$: C, 72.15; H, 5.3; N, 10.5. Found: C, 71.95; H, 5.5; N, 10.5.

[1-(1-Ethynyl)cyclohexyl]malononitrile (II. R = H).—A warm solution of ethylmagnesium bromide (from magnesium, 6.0 g.) in dry tetrahydrofuran (200 ml.) was transferred under nitrogen to a dropping funnel and added over 3 hr. to a stirred saturated solution of acetone-free acetylene in tetrahydrofuran (500 ml.). Acetylene was passed through the solution during this addition and for a further hour. Freshly prepared cuprous chloride (5 mole %), followed by cyclohexylidenemalononitrile (7.5 g.) in dry tetrahydrofuran (100 ml.), was added over 3 hr. to the solution of ethynylmonomagnesium bromide held in a nitrogen atmosphere and the reaction mixture then was stirred for 20 hr. at 20°. The Grignard complex was decomposed with saturated ammonium chloride solution and the reaction mixture extracted with ether. The combined ethereal extracts were washed with saturated brine solution, dried, and the solvent removed to give a red oil. An ethanolic solution of the crude product was treated with potassium cyanide (1 g.) in a minimum volume of water and stirred for 4 hr. The reaction mixture then was diluted with water, and isolated in the usual manner by ether extraction. Removal of the solvent followed by fractional distillation of the residual oil gave **[1-(1-ethynyl)cyclohexyl]malononitrile** (4.2 g., 48%), b.p. 74° (0.1 mm.), n^{25}_{D} 1.4824; ν_{max} (liquid film) 3300, 2270, and 2100 cm.$^{-1}$.

Anal. Calcd. for $C_{11}H_{12}N_2$: C, 76.7; H, 7.0; N, 16.3. Found: C, 76.6; H, 6.75; N, 16.6.

[1-(1-Phenylethynyl)cyclohexyl]malononitrile (II. R = Ph).—Phenylacetylene (10.2 g.) in dry tetrahydrofuran (20 ml.) was added to a stirred solution of ethylmagnesium bromide (from magnesium 2.4 g.) in tetrahydrofuran (250 ml.) and the reaction mixture heated under reflux for 2 hr. The cooled reaction

---

[1] J. Munch-Peterson, *J. Org. Chem.*, **22**, 170 (1957).

[2] E. R. H. Jones, L. Skattebol, and M. C. Whiting, *J. Chem. Soc.*, 4765 (1956).

[3] E. P. Kohler and M. Reimer, *Am. Chem. J.*, **33**, 333 (1905); *Chem. Zentr.*, **I**, 1389 (1905).

[4] P. K. Christiansen, N. A. Sorensen, I. Bell, E. R. H. Jones, and M. C. Whiting, *Festschr. Arthur Stoll*, 545 (1957); I. Bell, E. R. H. Jones, and M. C. Whiting, *J. Chem. Soc.*, 1313 (1958); P. K. Christiansen, *Acta Chem. Scand.*, **11**, 582 (1957).

[5] All melting points were determined on a Kofler hot stage and are corrected. Boiling points are uncorrected. Ultraviolet absorption spectra refer to ethanol solutions and were measured with a Unicam S.P. 500 spectrophotometer. Infrared spectra were determined on the Perkin-Elmer Infracord and Perkin-Elmer 13 spectrophotometers. The alumina used for chromatography was acid washed and activated and graded according to the method of Brockmann and Schodder.[6] Light petroleum refers to the fraction, b.p. 40–60°, unless stated otherwise.

[6] H. Brockmann and H. Schodder, *Ber.*, **74**, 73 (1941).

[7] A. C. Cope and K. E. Hoyle, *J. Am. Chem. Soc.*, **63**, 733 (1941).

mixture then was treated with cuprous chloride (5 mole %) followed by a solution of cyclohexylidenemalononitrile (7.5 g.) in tetrahydrofuran (25 ml.). After heating under reflux for 4 hr., the Grignard complex was decomposed with a saturated solution of ammonium chloride, extracted with ether, and the combined ethereal extracts washed with water and dried. Removal of the solvent gave a viscous gum which solidified on trituration with light petroleum to give **[1-(1-phenylethynyl)cyclohexyl]malononitrile** (5 g., 39%), which crystallized from light petroleum in needles, m.p. 62–63°.

Anal. Calcd. for $C_{17}H_{16}N_2$: C, 82.2; H, 6.5; N, 11.3. Found: C, 82.35; H, 6.4; N, 11.2.

[1-(1-Octynyl)cyclohexyl]malononitrile.—1-Octyne (11 g.) in dry tetrahydrofuran (50 ml.) was added to a solution of ethylmagnesium bromide (from magnesium 2.4 g.) in tetrahydrofuran (85 ml.) and the reaction mixture heated under reflux in an atmosphere of nitrogen for 20 hr. Cuprous chloride (5 mole %) was added to the reaction mixture held at 0°, followed by a slow addition of cyclohexylidenemalononitrile (9.0 g.) in a solution of tetrahydrofuran. The stirred solution was held at room temperature for 18 hr. and then heated under reflux for 8 hr. before being worked up as in the previous experiment. The resultant crude oil was fractionally distilled to give **[1-(1-octynyl)cyclohexyl]malononitrile** (7.0 g. 44%) as a colorless oil, b.p. 112° (0.1 mm.), $n^{21}\text{D}$ 1.4785.

Anal. Calcd. for $C_{17}H_{24}N_2$: C, 79.65; H, 9.45; N, 10.95. Found: C, 79.75; H, 9.45; N, 10.8.

[1-(1-Tetrahydropyranyloxypropargyl)cyclohexyl]malononitrile.—3-Tetrahydropyranyloxy-1-propyne (14 g.) in dry tetrahydrofuran (25 ml.) was added to a solution of ethylmagnesium bromide (from magnesium, 2.4 g.) and the reaction mixture heated under reflux for 8 hr. under nitrogen and then chilled to 0°. Cuprous chloride (5 mole %) then was added followed by a slow addition of cyclohexylidenemalononitrile (9 g.) in tetrahydrofuran (20 ml.) and the reaction mixture stirred for 4 hr. at room temperature and then heated under reflux for 20 hr. The usual work-up procedure gave a dark red viscous liquid which was fractionally distilled to give **[1-(1-tetrahydropyranyloxypropargylcyclohexyl]malononitrile** (3 g. 17%) as a colorless oil, b.p. 140° (0.05 mm.), $n^{21}\text{D}$ 1.4920.

Anal. Calcd. for $C_{17}H_{22}N_2O_2$: C, 71.3; H, 7.75; N, 9.8. Found: C, 71.6; H, 7.95; N, 10.1.

[1-(4-Benzoyloxy-1-ethynyl)cyclohexyl]malononitrile.—4-Benzoyloxycyclohexylidenemalononitrile (30 g.) in dry tetrahydrofuran (250 ml.) was added to a solution of ethynylmonomagnesium bromide (prepared as in the previous experiment from magnesium 12 g.) and the whole stirred in a nitrogen atmosphere at 4° for 44 hr. Decomposition of the Grignard complex and isolation of the product gave a dark red gum which was adsorbed on alumina (grade I, 900 g.) from benzene–light petroleum (5:1). Elution with the same solvent gave starting material (5 g.) and then elution with benzene afforded **[1-(4-benzoyloxy-1-ethynyl)cyclohexyl]malononitrile** (4.3 g.), which crystallized from carbon tetrachloride in prisms, m.p. 129–130°; $\nu_{\max}$ (potassium chloride disk) 3300, 2270, and 1720 cm.$^{-1}$.

Anal. Calcd. for $C_{18}H_{16}N_2O_2$: C, 73.95; H, 5.5; N, 9.6. Found: C, 73.75; H, 5.2; N, 9.8%.

Further elution with benzene–chloroform (4:1) gave the other isomer of **[1-(4-benzoyloxyl-1-ethynyl)cyclohexyl]malononitrile** (2.6 g.), which crystallized from methanol as prisms, m.p. 177–178°.

Anal. Found: C, 74.2; H, 5.3; N, 9.65%.

[1-(1-Ethynyl)cyclohexyl]isopropylmalononitrile (III).—A solution of [1-(1-ethynyl)cyclohexyl]malononitrile (2.3 g.) and sodium ethoxide (from sodium 0.33 g.) in dry ethanol (20 ml.) was heated under reflux for 3 hr. and chilled to −15°. Isopropyl iodide (2.5 g.) was then added and the reaction mixture again heated under reflux for 16 hr. After removal of most of the ethanol, water was added and the solution extracted with ether and combined ethereal extracts washed with water, dried, and the solvent removed to furnish **[1-(1-ethynyl)cyclohexyl]isopropylmalononitrile** (0.9 g.), which crystallized from light petroleum in prisms, m.p. 88–89°.

Anal. Calcd. for $C_{14}H_{18}N_2$: C, 78.45; H, 8.45; N, 13.05. Found: C, 78.8; H, 8.35; N, 13.25.

α-(1-Acetylcyclohexyl)isovaleric Acid (I).—Sufficient ethanol was added to a mixture of [1-(1-ethynyl)cyclohexyl]isopropylmalononitrile (0.6 g.) and 30% aqueous potassium hydroxide solution (25 ml.) to give a homogeneous solution and the whole was then heated under reflux until no more ammonia was evolved. The reaction mixture then was acidified with dilute sulfuric acid and warmed at 100° for 20 min. to effect decarboxylation of the intermediate malonic acid. The cooled solution was thoroughly extracted with ether and the combined ethereal extracts then were washed with water, dried, and the solvent removed to give **α-(1-acetylcyclohexyl)isovaleric acid** (0.575 g.), which crystallized from ethyl acetate–light petroleum (b.p. 60–80°) in prisms, m.p. 108–109°.

Anal. Calcd. for $C_{13}H_{22}O_3$: C, 69.0; H 9.8. Found: C, 69.15; H, 9.55.

Alkaline Hydrolysis of [1-(1-Phenylethynyl)cyclohexyl]malononitrile (II. R = Ph).—A mixture of II [R = Ph (2.2 g.)] and 20% aqueous potassium hydroxide solution (100 ml.) was heated under reflux until no more ammonia was evolved. The solution then was acidified, extracted with ether, and the combined ethereal extracts washed with water and dried. Removal of the solvent gave a gum which was heated *in vacuo* at 100° for 2 hr. A portion of the product (1 g.) was esterified with ethereal diazomethane and the resulting ester then adsorbed on alumina (grade III) from light petroleum (b.p. 60–80°). Elution with light petroleum (b.p. 60–80°)–benzene (5:1) yielded the γ-enol lactone VI (0.2 g.), which crystallized from *n*-hexane in needles, m.p. 111–112.5°; $\nu_{\max}$ (potassium chloride disk) 1800 cm.$^{-1}$ (γ-enol lactone), 1670 cm.$^{-1}$ (enol double bond); $\lambda_{\max}$ 256 mμ (ϵ 24,000).

Anal. Calcd. for $C_{16}H_{18}O_2$: C, 79.3; H, 7.5. Found: C, 79.05; H, 7.4.

Further elution with light petroleum (b.p. 60–80°)–benzene (4:1) afforded the keto ester (VII. R = CH_3) as a colorless oil, (0.6 g.), b.p. (bath temp.) 120° (0.05 mm.), $n^{25}\text{D}$ 1.5238; $\nu_{\max}$ (liquid film) 1730 and 1710 cm.$^{-1}$.

Anal. Calcd. for $C_{17}H_{22}O_3$: C, 74.4; H, 8.1. Found: C, 74.2; H, 8.25.

Acknowledgment.—The authors are indebted to Professor R. A. Raphael for many helpful discussions during this work. R. R. gratefully acknowledges a Maintenance Award from the Department of Scientific and Industrial Research.

Anomalous Reduction of Malonic Esters with Lithium Aluminum Hydride

William J. Bailey, Matthew E. Hermes,[1] and
William A. Klein[2]

*Department of Chemistry, University of Maryland,
College Park, Maryland*

Received October 15, 1962

During the one-step reduction and acetylation of triethyl 1,1,2-ethanetricarboxylate with lithium aluminum hydride and acetic anhydride, 2-methylene-1,4-diacetoxybutane was formed in a 16% yield along with the expected 1,4-diacetoxy-2-(acetoxymethyl)butane in a 52% yield.[3] Since there was no reason to expect elimination of acetic acid from a primary acetate under these conditions, it appeared likely that the unsaturated derivative was formed during the reduction of the substituted malonic ester with lithium aluminum hydride. Dreiding and Hartman[4] showed that certain substituted acetoacetic esters, such as 2-carbethoxycyclohexanone, were reduced through the enolate.

For the reduction of 2-carbethoxycyclohexanone the products were 2-methylenecyclohexanol in a 52%

---

[1] Office of Naval Research Fellow, 1956–1957; National Science Foundation Fellow, 1957–1959.

[2] Office of Naval Research Fellow, 1951–1954; Union Carbide Fellow, 1954–1955.

[3] W. J. Bailey, W. G. Carpenter, and M. E. Hermes, *J. Org. Chem.*, **27**, 1975 (1962).

[4] A. S. Dreiding and J. A. Hartman, *J. Am. Chem. Soc.*, **75**, 939 (1953).