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.

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Anomalous Reduction of Malonic Esters with Lithium Aluminum Hydride

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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%

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

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

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yield, 1-hydroxymethylcyclohexene in a 21% yield, and the expected 2-hydroxymethylcyclohexanol in only an 11% yield. We were able to use all these intermediates to advantage for the synthesis of 3-methylenecyclohexene.[5] The mechanism postulated for this reaction, based partly on the fact that 2-hydroxymethylenecyclohexanone gives the identical products, involves the normal reduction of the ester to the aldehyde, followed by the formation of the corresponding enolate which could undergo attack at either carbonyl group to produce a doubly charged anion which, although stable to further attack by hydride ion, can lose an oxygen ion by analogy with the mechanism for the base-catalyzed dehydration of aldols. One could write a similar mechanism for the reduction of malonic esters. In order to demonstrate that this anomalous reduction would occur with other malonic esters, ethyl methylmalonate was reduced with lithium aluminum hydride to produce, in addition to the expected diol, a 5.2% yield of methallyl alcohol. The methallyl alcohol was identified by vapor phase chromatography and infrared analysis.

Finally as an example that would give an increased opportunity for this anomalous reduction, bimalonic ester, ethyl 1,1,2,2-ethanetetracarboxylate, was reduced as previously described[6] and the forerun from the reductive acetylation was examined carefully. From this reduction was obtained a 15% yield of 2,3-di(acetoxymethyl)-3-butenyl acetate, together with the expected tetraacetate. The structure of this olefin triacetate was proved by pyrolysis to the known 2,3-di(acetoxymethyl)-1,3-butadiene[6] and by independent synthesis by the pyrolysis of 2,3-di(acetoxymethyl)-1,4-diacetoxybutane.

An attempt to isolate 2-phenylallyl alcohol from the reduction of ethyl phenylmalonate failed. It may be that this substituted styrene is formed but is polymerized before isolation.

Experimental[7]

Methallyl Alcohol from Reduction of Ethyl Methylmalonate.—To a slurry of 27.5 g. (0.737 mole) of lithium aluminum hydride and 300 ml. of dry ether in a 1-l., three-necked flask, fitted with a reflux condenser, a dropping funnel, and a stirrer, was added a solution of 75.6 g. (0.435 mole) of ethyl methylmalonate in 100 ml. of ether at a rate such as to maintain gentle reflux of the solvent acid. After the mixture had been heated under reflux for an additional 18 hr., it was poured onto a mixture of ice and dilute hydrochloric acid. The aqueous phase was extracted for 2 days in an exhaustive extractor and the extracts, together with the original ether layer, were dried over anhydrous magnesium sulfate. Distillation of this solution through a 10-in., helix-packed column gave 1.9 g. (5%) of methallyl alcohol, b.p. 112–115°, n^{25}_{D} 1.4228 (reported[8] b.p. 111.5–112°, n^{25}_{D} 1.4232), and 28.1 g. (72%) of 2-methyl-1,3-propanediol, b.p. 90–93° (4 mm.), n^{25}_{D} 1.4436 (reported[9] b.p. 213–214°, n^{20}_{D} 1.4445). Vapor phase chromatography of this sample of methallyl alcohol at 88° on di-*n*-decyl phthalate column gave a single symmetrical peak with the same retention time as that of an authentic sample of methallyl alcohol.

2,3-Di(acetoxymethyl)-3-butenyl Acetate from the Reduction of Ethyl 1,1,2,2-Ethanetetracarboxylate.—To a slurry of 100 g. (2.63 moles) of lithium aluminum hydride in 3 l. of ether was added dropwise a solution of 318 g. (1 mole) of ethyl 1,1,2,2-ethanetetracarboxylate in 3 l. of ether. After 2 l. of *n*-butyl ether had been added, the mixture was heated under reflux for 8 days. Most of the ethyl ether was removed by distillation with the concurrent addition of an additional 2 l. of *n*-butyl ether. After 500 ml. of glacial acetic acid had been added to decompose the excess hydride, followed by the addition of 1000 ml. of acetic anhydride, the mixture was heated under reflux for 6 days. During this period the mixture became so thick that stirring had to be discontinued and an additional 2 l. of *n*-butyl ether was added. The salts were removed from the solution by filtration and the solvent was removed from the filtrate by distillation. Fractionation of the residue through a 10-in. Vigreux column gave a forerun, b.p. 90–115° (0.2–0.4 mm.), and 151 g. (48%) of 2,3-di(acetoxymethyl)-1,4-diacetoxybutane, b.p. 160–165° (1.8 mm.), m.p. 66–68° (reported[6] 67–68°). The forerun, which contained some solid tetraacetate, was filtered and the solid was washed with ether. The combined filtrates were refractionated through a 10-in., helix-packed column to yield 39 g. (15%) of 2,3-di(acetoxymethyl)-3-butenyl acetate, b.p. 107.5–109° (0.2–0.3 mm.), n^{25}_{D} 1.4499 [reported[6] b.p. 138–139° (2 mm.), n^{25}_{D} 1.4518].

Anal. Calcd. for $C_{12}H_{18}O_6$: C, 55.81; H, 6.96; sapon. equiv., 86. Found: C, 55.98; H, 7.16; sapon. equiv., 85.

The olefin triacetate produced by the pyrolysis of 2,3-di(acetoxymethyl)-1,4-diacetoxybutane was identical to that prepared by the reductive acetylation of ethyl 1,1,2,2-ethanetetracarboxylate.

Pyrolysis of 2,3-Di(acetoxymethyl)-3-butenyl Acetate.—At a rate of 28 drops per min., 35 g. (0.135 mole) of 2,3-di(acetoxymethyl)-3-butenyl acetate was dropped through the pyrolysis tube heated at 490° while the system was flushed with a slow stream of oxygen-free nitrogen.[6] After an ether solution of the pyrolysate was extracted with water, the organic layer was dried over anhydrous magnesium sulfate. (Titration of an aliquot of the aqueous extracts indicated that 55% of the theoretical amount of acetic acid had been eliminated.) The ether was removed by distillation and the residue was fractionated through a 10-in., helix-packed column to give 10.9 g. (41%) of 2,3-di(acetoxymethyl)-1,3-butadiene, b.p. 61–63° (0.25 mm.), m.p. 62–63° (reported[6] m.p. 63–64°), and 14.1 g. of recovered starting material. A mixture melting point determination of this solid with an authentic sample of the diene–diacetate prepared from the pyrolysis of the tetraacetate[6] showed no depression.

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Reactions of Phenyl-Substituted Methanes and Ethanes with Lithium or *n*-Butyllithium

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The chemistry of triphenylmethyllithium has been studied and reviewed recently by Tomboulain.[1] In that investigation, the organometallic compound was prepared in varying yields by reactions of triphenylmethyl chloride with lithium in a variety of solvents. We are now reporting the preparation of this reagent by the reaction of triphenylmethane with lithium or *n*-butyllithium, as well as by the lithium cleavage of 1,1,1,2-tetraphenylethane in tetrahydrofuran (THF) or in mixtures of diethyl ether and THF. Also reported at this time are some related reactions involving toluene, diphenylmethane, and *sym*-tetraphenylethane.

Although lithium wire in THF had been employed previously in the metalation of fluorene,[2a] 9-phenylfluorene[2a,3] and cyclopentadiene,[2a] and in the cleavage

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