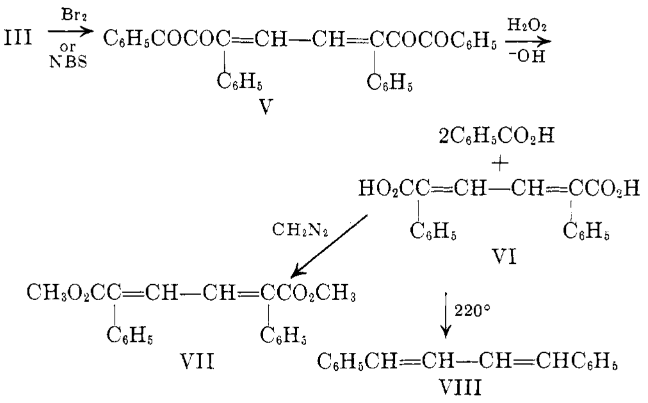
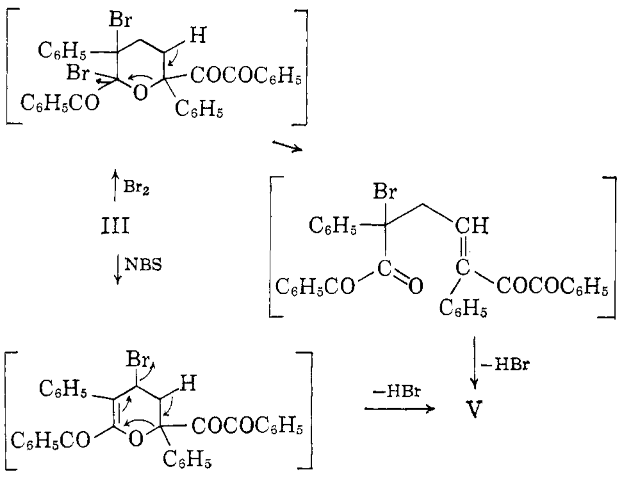


The formation of V from III may be rationalized by several pathways. One possibility would involve the following scheme. The isolation of V from III provides definite evidence for the previous assignment of III.



Experimental[4]

Preparation of 6-Benzoyl-2,5-diphenyl-2-phenylglyoxoyl-3,4-dihydro-2H-pyran (III).—To 18.2 g. (0.081 mole) of 1,3-diphenyl-1,2-propanedione[5] in 80 ml. of methanol was added 25 ml. (0.29 mole) of 37% formalin solution. The mixture was heated to reflux and 0.5 ml. of piperidine in 10 ml. of methanol was added in 5 min. The solution was refluxed 3 hr., poured into water, and extracted with methylene chloride. The organic extract was washed with successive portions of dilute sulfuric acid, 5% sodium bicarbonate solution, and water. Removal of the solvent provided a yellow oil which was heated 10 hr. at 95°. The oil was then triturated with methanol and yielded a yellow solid which was recrystallized from a benzene-*n*-heptane mixture to afford 2.1 g. (11.5%) of dense yellow prisms, m.p. 132–134°. A mixture melting with a sample of III obtained[2] from I melted at 132–134°.

Bromination of 6-Benzoyl-2,5-diphenyl-2-phenylglyoxoyl-3,4-dihydro-2H-pyran (III).—Treatment of 2.0 g. (4.2 mmoles) of III in 100 ml. of refluxing dry carbon tetrachloride with 1.0 g. (6.25 mmoles) of bromine in 50 ml. of carbon tetrachloride provided 1.47 g. (74.6%) of yellow needles, m.p. 166–167° after recrystallization from a benzene–*n*-heptane mixture, lit.[2] m.p. 162–163°.

Anal. Calcd. for $C_{32}H_{22}O_4$: C, 81.68; H, 4.71. Found: C, 81.51; H, 4.62.

When 0.60 g. (1.28 mmoles) of III was treated with a solution of 0.23 g. (1.28 mmoles) of N-bromosuccinimide in carbon tetrachloride containing a trace of benzoyl peroxide, hydrogen bromide was evolved copiously. Purification of the resulting solid provided 0.42 g. (70.0%) of V.

Oxidation of V with Alkaline Hydrogen Peroxide.—A solution of 2.0 g. (4.3 mmoles) of V in 35 ml. of purified dioxane was treated with 5 ml. of 30% hydrogen peroxide. To this solution was added 2.3 ml. of 20% sodium hydroxide solution. The addition was carried out drop-wise over a 30-min. period. The solution was stirred overnight, the solvent removed, and the residue was dissolved in water. Acidification of the aqueous solution provided 1.87 g. (85%) of acidic material. Sublimation of the resulting solid afforded 0.97 g. of benzoic acid and 0.90 g. of an acid melting above 300°. The high melting acid (VI) exhibited a maximum at 316 mμ (ε 20,250).

Anal. Calcd. for $C_{18}H_{14}O_4$: C, 73.45; H, 4.79. Found: C, 73.28; H, 4.61.

A 0.90-g. (0.30 mmole) sample of VI was suspended in 25 ml. of dry ether and treated with excess diazomethane solution. Filtration and removal of the solvent afforded 0.85 g. (88.1%) of solid ester. Recrystallization from a benzene–petroleum ether mixture gave VII as needles, m.p. 178–179°; λ_{max} 321 mμ (ε 18,750).

Anal. Calcd. for $C_{20}H_{18}O_4$: C, 74.52; H, 5.63. Found: C, 74.47; H, 5.64

Hydrogenation of 1,4-Dicarbomethoxy-1,4-diphenyl-1,3-butadiene (VII).—A solution containing 0.15 g. (0.47 mmole) of VII in 30 ml. of ethyl acetate consumed 23.0 ml. of hydrogen when stirred at room temperature and atmospheric pressure with 0.10 g. of 10% palladium-on-charcoal catalyst. Recrystallization of the resulting solid from *n*-heptane provided dense prisms melting indefinitely from 95–112°.

Anal. Calcd. for $C_{20}H_{22}O_4$: C, 73.59; H, 6.80. Found: C, 73.88; H, 6.67.

Decarboxylation of 1,4-Dicarboxy-1,4-diphenyl-1,3-butadiene (V).—To 0.60 g. (2.05 mmole) of V was added 0.125 g.-atom of copper powder and 5 ml. of quinoline. The mixture was heated at 220° for 6 hr., diluted with ether, and filtered; the quinoline was removed by extraction with dilute hydrochloric acid. The ether extract was washed with sodium bicarbonate and water. Removal of the solvent provided a yellow oil which was dissolved in petroleum ether and chromatographed on neutral alumina. Elution with petroleum ether provided 0.275 g. of colorless solid, m.p. 145–149°. Recrystallization from benzene–ethanol afforded colorless crystals of VIII, m.p. 152–153°. A mixture melting point with an authentic sample[6] of VIII was not depressed.

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[4] Melting points are uncorrected. Elemental analysis were by Spang Microanalytical Laboratory, Ann Arbor, Mich., and Micro-Tech Laboratories, Skokie, Ill.

[5] H. Fiesselmann and J. Ribka, *Ber.*, **89**, 27 (1956).

[6] B. B. Corson, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1941, p. 229.

Overreduction of Naphthalenic Diethers

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The Birch reaction is a standard method for converting aromatic ethers into unsaturated alicyclic ketones.[1] The reduction of di- and tetrahydronaphthalenic *monoethers* is a basic step in many schemes for the total synthesis of terpenes and steroids. In contrast, the conversion of naphthalenic *diethers* into bicyclic ketones has been almost ignored; to date only 2,6-dimethoxynaphthalene, 2,6-diethoxynaphthalene, and 1,5-dimethoxynaphthalene are known to be reducible in sodium–liquid ammonia solution in the presence of ethanol.[2] Both 2,6-diethers afford the expected 2,6-dialkoxy-1,4,5,8-tetrahydronaphthalenes

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[1] For a comprehensive review of this entire field, see H. Smith, "Organic Reactions in Liquid Ammonia," John Wiley and Sons, Inc., New York, N. Y., 1963, pp. 245–279.

[2] M. Kocor and W. Kotlarek, *Bull. Acad. Polon. Sci. Ser. Sci. Chim.*, **9**, 507 (1961).

which on hydrolysis give 2,6-diketo-1,2,3,4,5,6,7,8-octahydronaphthalene. The 1,5-diether is reduced with the loss of a methoxy group to 1-methoxy-5,8-dihydronaphthalene.

Reduction in sodium–liquid ammonia in the absence of alcohol of the model compounds 1- and 2-naphthyl methyl ether involves both hydrogenation of the aromatic nucleus and reductive cleavage of the methoxy group.[3] The first ether produces a mixture containing α-tetralone, naphthalene, and 1,4-dihydronaphthalene. In contrast, the second ether is converted into a mixture of tetralin and 2-methoxy-5,8-dihydronaphthalene. Similar cases that involve the loss of methoxy during the reduction of a variety of alkyl aryl ethers are known; thus, sodium and ethanol in liquid ammonia convert pyrogallol trimethyl ether into 2,5-dihydroresorcinol dimethyl ether,[4] veratric acid into 3-methoxy-2-cyclohexene-1-carboxylic acid,[5] 3,4,5-trimethoxybenzoic acid into 1,4-dihydro-3,5-dimethoxybenzoic acid,[6] 3,4,5-trimethoxybenzamide and a series of N-alkylated analogs into the corresponding 1,4-dihydro-3,5-dimethoxybenzamides,[6] and 1- and 3-methoxy-2-naphthoic acid into 1,2,3,4,5,8-hexahydro-2-naphthoic acid.[7] Finally, 6-methoxytetralin apparently yields only one product, 6-methoxy-1,2,3,4,5,8-hexahydronaphthalene, by reduction with sodium or lithium and ethanol in liquid ammonia.[8–10]

These observations are recapitulated here since our results show similar loss of the methoxy group. Briefly, 2,7-dimethoxynaphthalene was treated with excess lithium–liquid ammonia in the initial absence of alcohol in the hope of obtaining 2,7-dimethoxy-1,4,5,8-tetrahydronaphthalene. The crude product consisted of *two* substances as demonstrated by thin layer and gas chromatographic data. The mixture was subjected to acid hydrolysis in order to convert the expected enol ether into $\Delta^{1,9}$-octalin-2,7-dione. On work-up, the yellow oil was found to contain *three* products. The ultraviolet spectrum of the mixture showed typical aromatic absorption bands while the infrared spectrum exhibited both conjugated and unconjugated carbonyl maxima.

This mixture was chromatographed to give two main fractions; the first was identified as 6-methoxy-1,2,3,4-tetrahydronaphthalene, while the second was characterized as $\Delta^{1,9}$-octalone-2. The latter material, on the basis of infrared and thin layer evidence, was admixed with a small amount of the unconjugated β,γ-ketone. Clearly, the reduction of 2,7-dimethoxynaphthalene by lithium–liquid ammonia in the initial absence of alcohol did not afford 2,7-dimethoxy-1,4,5,8-tetrahydronaphthalene; instead, the product was a mixture consisting mainly of 2-methoxy-1,4,5,6,7,8-hexahydronaphthalene. Acid hydrolysis of this material then produced both the conjugated and unconjugated ketones. The methoxytetralin was unaffected by the acid and was found again in the characterization of the crude product. This reductive chain can be explained by invoking the sequence 2,7-dimethoxynaphthalene → 2,7-dimethoxy-1,4-dihydronaphthalene → 2,7-dimethoxy-3,4-dihydronaphthalene → 6-methoxytetralin → 2-methoxy-1,4,5,6,7,8-hexahydronaphthalene. Alternatively, allylic cleavage or 1,4-addition of hydrogen to 2,7-dimethoxy-1,2-dihydronaphthalene would yield the same set of products.

In a separate experiment 2-methoxynaphthalene was reduced by excess lithium–liquid ammonia in the presence of methanol. Vapor phase chromatography (DEGS) separated the product into three fractions: hydrocarbon (70%), 6-methoxytetralin (5%), and 2-methoxy-1,4,5,6,7,8-hexahydronaphthalene (25%). Further gas chromatographic examination (CDMS) disclosed that the hydrocarbon fraction contained three components: tetralin (6%), 1,4,5,6,7,8-hexahydronaphthalene (87%), and decalin (7%). The variety of reduced systems encountered here indicated that hydrogenolysis of a methoxy group proceeded in an orderly manner under *forcing* conditions.

It would appear that the variety of compounds observed in our reductions must be due to two types of reductions which take place in the same reaction; first, a metal–ammonia reduction undoubtedly gives certain new products (*e.g.*, demethoxylated and partially reduced compounds); and second, the addition of alcohol to the blue solution yields a metal–alcohol–ammonia combination that further reduces the intermediates derived from the metal–ammonia reduction. Naturally, the exact product or products seen in such a Birch reduction sequence will depend on solvent, alkali metal, molar ratios, proton donor liquids, and reaction time. All of these factors tend to hinder the easy prediction of structure and quantity of overreduced reaction products in specialized situations.

Experimental[11]

Methylation of Naphthols.—The literature procedure[12] employing a basic aqueous solution of the naphthol to which was added dimethyl sulfate produced 2,7-dimethoxynaphthalene [m.p. 136–137°, $\lambda_{\max}^{\text{ethanol}}$ 235 mμ (log ϵ 4.99), lit.[10] m.p. 138°] and 2-methoxynaphthalene [m.p. 72–73°, $\lambda_{\max}^{\text{ethanol}}$ 226.5 mμ (log ϵ 4.98), lit.[12] m.p. 72°].

Reduction of 2,7-Dimethoxynaphthalene. A.—To a blue solution of 7.0 g. of lithium (1.01 g.-atoms) in 500 ml. of ammonia, 4.66 g. (0.025 mole) of 2,7-dimethoxynaphthalene was added with stirring over a period of 30 min. After stirring further for 1 hr. at $-30°$, 20 ml. of reagent grade methanol was introduced dropwise to the blue solution to produce a colorless medium. After the ammonia had evaporated overnight at room temperature, water (250 ml.) was added to the residual gray slurry. The aqueous solution was extracted with three 175-ml. portions of ether and the combined ether extracts were washed with water (1 l.) and saturated salt solution. After drying with anhydrous magnesium sulfate, the ether was removed under reduced pressure on the rotary evaporator, providing 3.96 g. of a yellow oil (*ca.* 85%). Distillation of the sample (75–85° at 1 mm.) afforded a colorless liquid containing two components, 6-methoxytetralin and 2-methoxy-1,4,5,6,7,8-hexhydronaphthalene. Analytical v.p.c. on a diethylene glycol succinate (DEGS) column (2 m., on Chromosorb P at 145°, 15 lb. of N_2 pressure) revealed the two substances in almost equal amounts at 3.0 and 4.8 min. Thin-layer chromatography (ether–hexane, 1:1) showed one spot (R_f 0.70), while hexane as an eluent produced two connected spots (R_f 0.71 and 0.65). In neither instance did a retention time or an R_f value correspond to the starting material.

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[5] A. J. Birch, J. Cymerman-Craig, and M. Slaytor, *Australian J. Chem.*, **8**, 512 (1955).

[6] M. E. Kuehne and B. F. Lambert, *J. Am. Chem. Soc.*, **81**, 4278 (1959).

[7] E. L. Eliel and T. E. Hoover, *J. Org. Chem.*, **24**, 938 (1959).

[8] A. J. Birch, *J. Chem. Soc.*, 430 (1944).

[9] A. J. Birch, A. R. Murray, and H. Smith, *ibid.*, 1945 (1951).

[10] A. L. Wilds and N. A. Nelson, *J. Am. Chem. Soc.*, **75**, 5360 (1953).

[11] Melting points and boiling points are uncorrected.

[12] O. Fischer and W. Kern, *J. prakt. Chem.* **94**, 34 (1916).

B.—The procedure of A was exactly repeated using 2.50 g. (0.013 mole) of 2,7-dimethoxynaphthalene and 6.0 g. (0.86 g.-atom) of lithium in 500 ml. of liquid ammonia. After the addition of 55 ml. of methanol and evaporation of the ammonia, the ether extraction afforded 3.1 g. of a yellow oil. The distilled colorless liquid (b.p. 90–91° at 2.5 mm.) seemed homogeneous using both t.l.c. (ether–hexane 1:1, R_f 0.70) and v.p.c. (3.0 min., with 5% at 4.8 min.) methods; $\lambda_{\max}^{\text{ethanol}}$ 280 mμ (log ϵ 2.53) and 288 mμ (log ϵ 2.49). The n.m.r. spectrum (in $CDCl_3$) of this slightly impure compound integrated for three methoxy protons (δ 3.55) and slightly more than six saturated protons (δ 1–2).

Acid Hydrolysis of the Reduced Materials. A.—From the reduction A (above) 2.75 g. of the mixture was added with stirring to 250 ml. of methanol, 15 ml. of water, and 2 ml. of hydrochloric acid. After standing 2 hr. at room temperature, 500 ml. of water was added and the aqueous material was extracted with three 250-ml. portions of ether. The combined ethereal extracts were washed in turn with dilute sodium carbonate solution, water, and saturated salt solution. After drying with magnesium sulfate and removing the ether on the rotary evaporator, there remained a yellow oil (2.20 g., 91%). Analysis by v.p.c. (DEGS, 145°, 15 lb.) indicated the presence of three components: 3.8 min. (<10%), 4.8 min. (35%), and 10.6 min. (55%); t.l.c. (ether–hexane, 1:1) revealed three components (R_f values: 0.70, 0.50, and 0.35). The infrared spectrum showed carbonyl absorption at 6.0 μ (with a shoulder at 5.85 μ) and an intense aromatic C=C stretch at 6.25 μ. The ultraviolet spectrum exhibited three maxima: 280 mμ (log ϵ 3.04), mol. wt. = 192; 288 mμ (log ϵ 3.01), mol. wt. = 192; and 232 mμ (log ϵ 3.94), mol. wt. = 150.

This mixture (2.15 g.) was placed directly on a column of 100 g. of silica (L. Light Co.) previously packed in hexane. Using continuous gradient elution, 25-ml. portions were taken with the following results: fractions 1–19, 0.175 g., yellow, eluted with hexane–benzene; fractions 20–34, 0.470 g., colorless, benzene; fractions 35–48, 0.220 g., colorless, benzene–ether (9:1); fractions 49–64, 1.265 g., colorless, benzene–ether (1:1); fractions 65–79, 0.020 g., yellow, ether. The colorless liquid, $n^{25}\mathrm{D}$ 1.5420, b.p. 77–78° (0.9 mm.), obtained from the second set of fractions appeared homogeneous by v.p.c. (DEGS, 145°, 15 lb., 4.8 min.) and on t.l.c. (ether–hexane, 1:1) as one spot (R_f 0.72). The infrared spectrum had an intense C=C stretch absorption at 6.25 μ, while the ultraviolet spectrum contained only two maxima: 279.5 mμ (log ϵ 3.31) and 288 mμ (log ϵ 2.25). The n.m.r. spectrum (in $CDCl_3$) integrated for three aromatic protons (δ 6.55–7.10), three methoxy protons (δ 3.72), four benzilic protons (δ 2.69), and four saturated protons (δ 1.56–1.95). This data fitted a structure assignment for 6-methoxy-1,2,3,4-tetrahydronaphthalene.[13]

Material from the fourth set of fractions appeared homogeneous by v.p.c. [DEGS, 145°, 15 lbs., 10.6 min.; phenyldiethanolamine succinate (PDEAS), 180°, 25 lb., 17.5 min.], but on t.l.c. (ether–hexane, 1:1) two components were evident (R_f 0.35 and 0.50). The liquid, $n^{28}\mathrm{D}$ 1.5215, b.p., 81–82° (0.6 mm.), possessed a carbonyl absorption in the infrared spectrum at 6.00 μ with a weak shoulder at 5.85 μ; in the ultraviolet spectrum there were maxima at 307 mμ (log ϵ 1.77) and 2.38 mμ (log ϵ 4.18). Two derivatives were made: the semicarbazone, m.p. 204.0–204.5°, $\lambda_{\max}^{\text{ethanol}}$ 268 mμ (log ϵ 4.52); and the 2,4-dinitrophenylhydrazone, m.p. 173.0–173.2°, $\lambda_{\max}^{\text{chloroform}}$ 390 mμ (log ϵ 4.46).

This information was in accord with the corresponding literature values for $\Delta^{1,9}$-octalone-2 and its derivatives (plus the contaminant, β,γ-unsaturated ketone).[14] In addition, a comparison of our α,β-unsaturated ketone with an authentic sample of the $\Delta^{1,9}$-octalone-2 containing some β,γ-ketone produced identical R_f values in three solvent systems (ether, ether–hexane, benzene–acetone) and the same retention times on two different vapor phase chromatographic columns (DEGS and PDEAS). A mixture melting point of the dinitrophenylhydrazones from the two sources showed no depression.

B.—The procedure of acid hydrolysis in A (above) was applied to 132 mg. of the liquid obtained in the B reduction. The yield of yellow oil was 94 mg. (78%) which by v.p.c. (DEGS, 155°, 15 lbs.) showed three components: 3.1 min. (6%), 3.9 min. (12%), and 7.7 min. (82%); t.l.c. showed three spots (R_f values: 0.75, 0.45, and 0.35; ether–hexane 1:1). The ultraviolet spectrum revealed the presence of 6-methoxytetralin and of the α,β-unsaturated ketone. The 2,4-dinitrophenylhydrazone gave no depression with that prepared in A (above). The infrared spectra of the ketone and the dinitrophenylhydrazone were virtually superimposable with those obtained in A (above).

Reduction of 2-Methoxynaphthalene.—Using conditions similar to those mentioned above, 2.51 g. (0.016 mole) of 2-methoxynaphthalene in 200 ml. of liquid ammonia was treated with 3.0 g. (0.43 g.-atom) of lithium and gave, after addition of 30 ml. of methanol and evaporation of the ammonia overnight, a white slurry. The usual work-up afforded 2.55 g. of a yellow oil (*ca.* 99%) which by t.l.c. (ether–hexane, 1:1) appeared to contain two major components (R_f 1.0 and 0.70); however, v.p.c. (DEGS, 140°, 15 lb.) showed three components: 1.2 min. (70%), 3.8 min. (25%), and 6.2 min. (5%). The second and third components were shown to be identical by v.p.c. comparison to 2-methoxyhexahydronaphthalene and 2-methoxytetralin, respectively. Also, on acid hydrolysis with aqueous methanol (mineral acid) and addition of 2,4-dinitrophenylhydrazine solution, a dinitrophenylhydrazone was formed which proved identical with those prepared above by mixture melting point and by comparison of infrared spectra.

A sample of distilled material (102–104° at 16 mm.) was chromatographed preparatively through a cyclohexanedimethanol succinate (CDMS) column (on Chromosorb W at 145° with helium flow rate of 60 ml./min.). Three hydrocarbon fractions were isolated at 6.6 min. (7%), 14.6 min. (87%), and 18.9 min. (6%). The first of these was proved to be decalin (retention time on DEGS and infrared spectrum in chloroform), while the last was tetralin (retention time on DEGS and ultraviolet spectrum in ethanol). The second and largest component, $n^{28}\mathrm{D}$ 1.5110, possessed a molecular weight of 134 (by mass spectroscopy) showed *cis* protons in the infrared spectrum (out-of-plane bending, 658 cm.$^{-1}$), and was transparent in the ultraviolet down to 220 mμ. The n.m.r. spectrum exhibited three types of protons: vinyl (δ 5.72), doubly allylic (δ 2.53), and saturated and allylic (δ 1.5–2.2); this data agreed with the literature data for 1,4,5,6,7,8-hexahydronaphthalene.[3]

Anal. Calcd. for $C_{10}H_{14}$: C, 89.5; H, 10.5. Found: C, 89.8; H, 10.6.

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Copper Salts Induced Addition of Ethyl Trichloroacetate to Olefins

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Peroxide-induced addition of alkyl polyhalides to olefins is well known.[1] Recently addition of carbon tetrachloride and chloroform to olefins using catalytic amounts of metallic salts was reported and the oxidation–reduction mechanism was suggested for this kind of addition.[2]

Experiments reported in this note show that ethyl trichloroacetate can also be added to olefins in the presence of a catalytic amount of copper salts. From acrylonitrile, ethyl acrylate, 1-octene, and norbornene, good yields of 1:1 adducts, ethyl 2,2,4-trichlorocarboxylates, have been obtained.

When acrylonitrile (0.1 mole) and ethyl trichloroacetate (0.1 mole) were heated under reflux in ethanol for 20 hr. in the presence of 0.002 mole of cuprous oxide, ethyl 4-cyano-2,2,4-trichlorobutyrate (I) was obtained in a yield of 37%. In the same manner, diethyl 2,2,4-

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