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, $n^{25}D$ 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, $n^{25}D$ 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, $n^{28}D$ 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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[13] A. J. Birch, E. M. A. Shoukry, and P. Stansfield, *J. Chem. Soc.*, 5376 (1961).

[14] (a) H. H. Zeiss and W. B. Martin, Jr., *J. Am. Chem. Soc.*, **75**, 5935 (1953); (b) D. J. Baisted and J. S. Whitehurst, *J. Chem. Soc.*, 4089 (1961).

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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[1] C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957, p. 247.

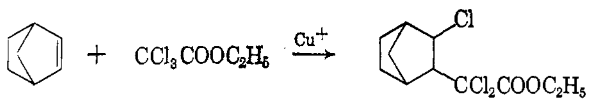
[2] (a) F. Minisci and R. Galli, *Tetrahedron Letters*, 533 (1962); (b) M. Asscher and D. Vofsi, *J. Chem. Soc.*, 2261 (1961); *Chem. Ind.* (London), 209 (1963); M. Asscher, E. Levy, H. Rosin, and D. Vofsi, *Ind. Eng. Chem., Prod. Res. Develop.*, **2**, 121 (1963).

trichloroglutarate (II, 32%) and ethyl 2,2,4-trichlorodecanoate (III, 13–29%) were obtained from ethyl acrylate and 1-octene, respectively, using cuprous chloride as a catalyst.

$$R\text{—}CH{=}CH_2 + CCl_3OOOC_2H_5 \xrightarrow{Cu^+} R\text{—}CHClCH_2CCl_2COOC_2H_5$$

$$\begin{aligned} &\text{I, } R = CN \\ &\text{II, } R = COOC_2H_5 \\ &\text{III, } R = C_6H_{13} \end{aligned}$$

Norbornene also gave a good yield (63%) of 1:1 adduct, ethyl α,α,3-trichloronorbornane-2-acetate (IV), when treated at slightly elevated temperature (120°); however, no effort was made to determine the stereochemistry of IV.



IV

In the reaction of acrylonitrile with ethyl trichloroacetate, cuprous and cupric chloride were also effective as the catalysts, but ferrous, ferric, and cobaltous chloride were ineffective to induce such addition. Addition of hydroquinone to the reaction mixture had no influence on these reactions and this may indicate that a usual radical chain process might be unlikely. These facts could be explained by an oxidation–reduction mechanism, in the same manner as suggested previously.[2]

$$Cu^+ + CCl_3COOC_2H_5 \longrightarrow CuCl^+ + \cdot CCl_2COOC_2H_5 \quad (1)$$

$$R\text{—}CH{=}CH_2 + \cdot CCl_2COOC_2H_5 \longrightarrow R\text{—}\dot{C}HCH_2CCl_2COOC_2H_5 \quad (2)$$

$$R\text{—}CHCH_2CCl_2COOC_2H_5 + CuCl^+ \longrightarrow R\text{—}CHClCH_2CCl_2COOC_2H_5 + Cu^+ \quad (3)$$

Because of the high efficiency of step 3, the telomer formation has been suppressed and 1:1 adducts were obtained exclusively in the copper salts catalyzed addition.

Experimental

Reaction of Acrylonitrile with Ethyl Trichloroacetate.—A mixture of 5.4 g. (0.1 mole) of acrylonitrile, 19.1 g. (0.1 mole) of ethyl trichloroacetate, 0.28 g. (0.002 mole) of cuprous oxide, and 50 ml. of anhydrous ethanol was refluxed for 20 hr. Solvent and unchanged materials were removed by distillation under reduced pressure and precipitated inorganic materials were removed by filtration. The residual oil was distilled to give 9.0 g. (37%) of a colorless oil boiling at 124–126° (6 mm.), which had infrared absorptions at 1726, 1730 (C=O), and 2250 (C≡N) cm.$^{-1}$. This product was identified as ethyl 4-cyano-2,2,4-trichlorobutyrate (I) by further treatment as described below.

Anal. Calcd. for $C_7H_8Cl_3NO_2$: C, 34.38; H, 3.30. Found: C, 34.79; H, 3.28.

Reduction of 2.0 g. of I by heating under reflux with 15 g. of zinc powder in 30 ml. of 95% ethanol for 10 hr. gave 0.3 g. of ethyl 4-cyanobutyrate boiling at 60–80° (6–10 mm.). This was then hydrolyzed by heating under reflux with 15 ml. of concentrated hydrochloric acid for 10 hr. After removal of the water by distillation under reduced pressure, the residual product was extracted with ether and the ether extract was dried over anhydrous sodium sulfate. Removal of ether at aspirator pressure left 0.3 g. of white crystalline solid which, after recrystallization from benzene, formed colorless needles, m.p. 96–97°, undepressed on admixture with authentic glutaric acid.

Anal. Calcd. for $C_5H_8O_4$: C, 45.45; H, 6.10. Found: C, 45.50; H, 6.39.

When cuprous chloride (0.002 mole) was used instead of cuprous oxide in the reaction of acrylonitrile and ethyl trichloroacetate, I was obtained in a yield of 20%. The addition of hydroquinone (5.5 g., 0.05 mole) to the reaction mixture had no influence on the reaction.

Cupric chloride (0.002 mole) was also able to give I in a yield of 10%.

When ferrous chloride tetrahydrate (0.002 mole) was used as a catalyst, about half the amount of acrylonitrile used was polymerized under the same conditions and no 1:1 adduct was obtained.

Ferric and cobaltous chloride (0.002 mole) were unable to induce addition and the starting materials were almost completely recovered in these experiments.

Reaction of Ethyl Acrylate with Ethyl Trichloroacetate.—A mixture of 11.0 g. (0.1 mole) of ethyl acrylate, 19.1 g. (0.1 mole) of ethyl trichloroacetate, 0.2 g. (0.002 mole) of cuprous chloride, and 40 ml. of anhydrous ethanol was heated under reflux for 20 hr. By treating the reaction mixture as described above, 6.3 g. (32%) of diethyl 2,2,4-trichloroglutarate (II) was obtained, b.p. 101–105° (3 mm.).

Anal. Calcd. for $C_9H_{13}Cl_3O_4$: C, 37.07; H, 4.49. Found: C, 37.35; H, 4.62

By reduction with zinc powder and 95% ethanol followed by hydrolysis with concentrated hydrochloric acid in the same manner as described above, II gave glutaric acid, m p. 96–97°, undepressed on admixture with an authentic sample.

Anal. Calcd. for $C_5H_8O_4$: C, 45.45; H, 6.10. Found: C, 45.54; H, 5.92.

Reaction of 1-Octene with Ethyl Trichloroacetate.—A mixture of 5.6 g. (0.05 mole) of 1-octene, 9.5 g. (0.05 mole) of ethyl trichloroacetate, 0.1 g. (0.001 mole) of cuprous chloride, and 25 ml. of anhydrous ethanol was heated under reflux for 20 hr. By treating the reaction mixture as described above, 2.0 g. (13%) of ethyl 2,2,4-trichlorodecanoate (III) was obtained, b.p. 103–104° (0.5 mm.). This product has strong infrared absorptions at 1730 (C=O) and 2870 (—CH$_2$—) cm.$^{-1}$.

Anal. Calcd. for $C_{12}H_{21}Cl_3O_2$: C, 47.46; H, 6.97. Found: C, 47.32; H, 7.02.

Reduction of III with zinc powder and 95% ethanol gave ethyl decanoate which was identified by gas chromatography on a 550 cm. silicone column at 188°.

The yield of III was raised to 29% when reaction was carried out at 120°, for 10 hr., in a 50-ml. glass tube placed in a 60-ml. stainless steel bomb.

Reaction of Norbornene with Ethyl Trichloroacetate.—A mixture of 9.2 g. (0.06 mole) of norbornene, 11.5 g. (0.06 mole) of ethyl trichloroacetate, 15 ml. of acetonitrile, and 0.2 g. (0.002 mole) of cuprous chloride in a 50-ml. glass tube was placed in a 60-ml. stainless steel bomb and heated in an oil bath at 120° for 16 hr. By treating the reaction mixture as described above 13 g. (63%) of ethyl α,α,3-trichloronorbornane-2-acetate (IV) was obtained, b.p. 95–101° (0.4 mm.). (In some other experiments this fraction was contaminated with a small amount of white crystals, less than 0.1 g., which was easily separated from the 1:1 adduct by filtration and was recrystallized from hexane, m.p. 140.5–141.5°. This compound was not treated further.) The 1:1 adduct (IV) was redistilled at 96–98° (0.4 mm.), infrared 1730 (C=O) cm.$^{-1}$.

Anal. Calcd. for $C_{11}H_{15}Cl_2O_2$: C, 46.26; H, 5.29; Cl, 37.24. Found: C, 46.13; H, 5.21; Cl, 36.36.

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The Lithium Aluminum Hydride Reduction of 3-Acetoxy-6-methanesulfonoxytropane[1]

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In an attempt to convert scopolamine into tropine, 3-acetoxy-6-methanesulfonoxytropane was prepared from the naturally occurring alkaloid. When this com-