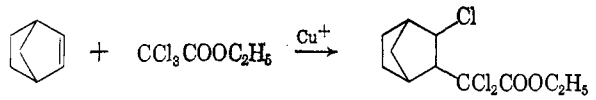
trichloroglutarate (II, 32%) and ethyl 2,2,4-trichlorodecanoate (III, 13–29%) were obtained from ethyl acrylate and 1-octene, respectively, using cuprous chloride as a catalyst.

$$R{-}CH{=}CH_2 + CCl_3COOC_2H_5 \xrightarrow{Cu^+} R{-}CHClCH_2CCl_2COOC_2H_5$$

I, R = CN
II, R = $COOC_2H_5$
III, R = C_6H_{13}

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]

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

$$R{-}CH{=}CH_2 + \cdot CCl_2COOC_2H_5 \longrightarrow R{-}CHCH_2CCl_2COOC_2H_5 \quad (2)$$

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

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.

Acknowledgment—The authors are grateful to Dr. Yoshinobu Odaira for his helpful suggestions.

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

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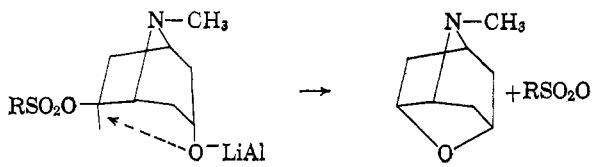
In an attempt to convert scopolamine into tropine, 3-acetoxy-6-methanesulfonoxytropane was prepared from the naturally occurring alkaloid. When this com-

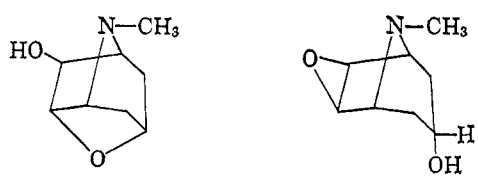
pound was reduced with lithium aluminum hydride a basic compound, whose infrared spectrum was similar but not identical with that of tropine, was isolated. The picrate of this compound possessed a melting point almost identical with that of tropine picrate. Its infrared spectrum, however, was not identical with that of an authentic sample of tropine picrate. Lithium aluminum hydride reduction of impure samples of 6-hydroxyhyoscyamine ditosylate and 6-hydroxyhyoscyamine dimesylate gave rise to the identical basic compound as well as to 2-phenyl-1-propanol.

It appeared that this product might be 3,6-epoxytropane and that it might result from the attack of lithium aluminum hydride on the acetoxy group to form the intermediate I, followed by nucleophilic displacement of the sulfonate group by the alkoxide ion to yield 3,6-epoxytropane II. A somewhat similar



I II

rearrangement has been reported by Fodor[3] who performed a lithium aluminum hydride reduction on scopolamine. Scopoline III rather than the expected scopine IV was isolated. Fodor suggested that this product



III IV

might arise by a backside nucleophilic attack of the lithium aluminum alkoxide complex on the epoxide ring.

In order to verify the structure of the unknown basic product resulting from the lithium aluminum hydride reduction of 3-acetoxy-6-methanesulfonoxytropane, an authentic sample of 3,6-epoxytropane was prepared by the dehydration of 3,6-tropanediol with phosphorus oxychloride, following the procedure of Fodor.[4] The infrared spectra of this sample of 3,6-epoxytropane and that of its picrate were identical with those of the rearranged product and that of its picrate.

Experimental[5]

3-Acetoxy-6-methanesulfonyloxytropane Picrate.—To a solution of 1.0 g. (5.0 mmoles) of 3-acetoxy-6-propanol[4] in 10 ml. of dry pyridine was added 0.6 g. (5.25 mmoles) of methanesulfonyl chloride, and the mixture was warmed on a steam bath for 3 hr. The pyridine was removed *in vacuo*, and the brown residue was dissolved in 20 ml. of water. The aqueous solution was saturated with anhydrous potassium carbonate and then extracted with six 25-ml. portions of chloroform. The chloroform extracts were washed with two 25-ml. portions of water and dried over anhydrous sodium sulfate. The chloroform was removed to afford 1.29 g. (93%) of a viscous brown sirup. This sirup was treated with picric acid in the usual manner to yield the picrate which, after recrystallization from ethanol, melted at 216–217° dec.

Anal. Calcd. for $C_{17}H_{22}N_4O_{12}S$: C, 40.32; H, 4.38; N, 11.06. Found: C, 40.59; H, 4.12; N, 11.00.

Lithium Aluminum Hydride Reduction of 3-Acetoxy-6-methanesulfonyloxytropane.—To a suspension of 3 g. of lithium aluminum hydride in 75 ml. of freshly distilled tetrahydrofuran was added dropwise with mechanical stirring a solution of 1.2 g. (4.3 mmoles) of 3-acetoxy-6-methanesulfonyloxytropane in 50 ml. of freshly distilled tetrahydrofuran, and the mixture was then refluxed with continued stirring for 5 hr. The solution was cooled in an ice bath and the excess lithium aluminum hydride was decomposed by addition of 6 ml. of water and 6 ml. of 10% sodium hydroxide solution. The crystalline lithium aluminate was removed by filtration and the filter cake was washed with three 20-ml. portions of hot tetrahydrofuran. The combined tetrahydrofuran filtrates were then evaporated *in vacuo*. The residue was dissolved in 20 ml. of 20% sodium hydroxide and the aqueous solution was continuously extracted with ether for 15 hr. The ether extract was dried over anhydrous sodium sulfate and then evaporated to yield 0.4 g. of a light yellow oil.

The picrate of this oil melted at 284–286° dec. after recrystallization from a mixture of equal parts of ethanol and acetone.

Anal. Calcd. for $C_{14}H_{16}N_4O_8$: C, 45.66; H, 4.38; N, 15.21. Found: C, 45.22; H, 4.38; N, 15.15.

3,6-Epoxytropane.—One gram (64 mmoles) of 3,6-tropanediol was gently refluxed with 10 ml. of phosphorus oxychloride for 1 hr. The excess phosphorus oxychloride was removed *in vacuo* and the dark brown residue was poured over 10 g. of ice. The aqueous solution was saturated with potassium carbonate and extracted with three 15-ml. portions of ether. The ether extracts were dried over anhydrous magnesium sulfate and the solvent was evaporated to yield 0.53 g. (59.6%) of a light green oil of 3,6-epoxytropane, which was converted to the picrate in the usual manner, m.p. 285–287° dec. after recrystallization from absolute ethanol–acetone.

The hydrobromide salt, prepared by reacting 3,6-epoxytropane with anhydrous hydrogen bromide, melted at 278–280° after recrystallization from ethanol–ether, lit.[4] m.p. 280°.

Anal. Calcd. for $C_8H_{14}BrNO$: C, 43.66; H, 6.41; Br, 36.31; N, 6.36. Found: C, 43.39; H, 6.42; Br, 36.20; N, 6.40.

Conversion of 6-Hydroxyhyoscyamine to 3,6-Epoxytropane.—To a solution of 2.28 g. (7.5 mmoles) of 6-hydroxyhyoscyamine in 15 ml. of dry pyridine was added 3.0 g. (15.2 mmoles) of *p*-toluenesulfonyl chloride, and the mixture was warmed on a steam bath for 3 hr. The pyridine was removed *in vacuo* and the brown residue was dissolved in 20 ml. of water. The aqueous solution was saturated with anhydrous potassium carbonate and then extracted with six 25-ml. portions of chloroform. The chloroform extracts were combined, washed with water, and dried over anhydrous sodium sulfate. The chloroform was removed by distillation to yield 2.69 g. (59%) of a viscous brown sirup. While it was not possible to obtain this compound in a pure form, its infrared spectrum indicated that it was the ditosyl derivative of 6-hydroxyhyoscyamine.

When 2.62 g. (4.3 mmoles) of the crude ditosyl derivative of 6-hydroxyhyoscyamine was reduced with 5 g. of lithium aluminum hydride following the procedure described for the reduction of 3-acetoxy-6-methanesulfonyloxytropane, and the products were separated by extraction with dilute hydrochloric acid, 0.58 g. (48%) of 2-phenyl-1-propanol and 0.53 g. (60%) of 3,6-epoxytropane were obtained. The 2-phenyl-1-propanol possessed an infrared spectrum identical with that of an authentic sample. The 3,6-epoxytropane was identified as its picrate, m.p. 285–287°.

(1) Abstracted from a thesis submitted by F. A. Turner to the Graduate College of the University of Illinois in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

(2) National Science Foundation Cooperative Graduate Fellow, 1959–1961.

(3) G. Fodor and O. Kovacs, *J. Chem. Soc.*, 2341 (1953).

(4) D. Bobo, G. Fodor, *et. al.*, *ibid.*, 3461 (1959).

(5) All melting points were obtained by the capillary tube method and are corrected. Microanalyses were performed by Weiler and Strauss Microanalytical Laboratories, Oxford, England.