[Contribution from the McPherson Chemical Laboratory, The Ohio State University]

Rearrangement Involving Migration of the Trichloromethyl Group[1]

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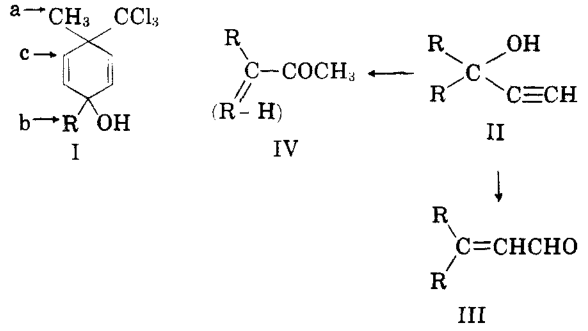
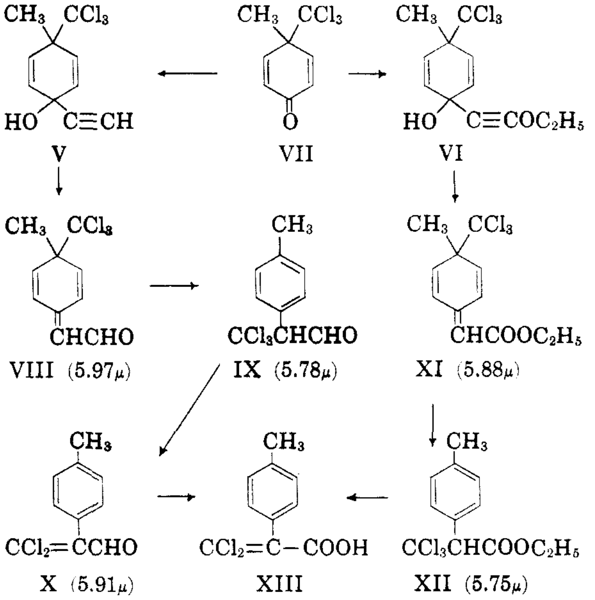
The synthesis of 1-ethynyl-4-methyl-4-trichloromethyl-2,5-cyclohexadienol, V and of 1-ethoxyethynyl-4-methyl-4-trichloromethyl-2,5-cyclohexadienol, VI, are described. On treatment with acid V rearranges to 4-methyl-4-trichloromethyl-2,5-cyclohexadienyleneacetaldehyde, VIII, and this rearranges further to α-(p-tolyl)-β,β,β-trichloropropanal, IX, which was not isolated as it lost hydrogen chloride spontaneously to yield α-(p-tolyl)-β,β-dichloroacrolein, X. On treatment with acid VI rearranges to ethyl 4-methyl-4-trichloromethyl-2,5-cyclohexadienylideneacetate, XI, and this rearranges further to ethyl α-(p-tolyl)-β,β,β-trichloropropionate, XII.

A mechanism for the rearrangement is proposed which involves migration of the trichloromethyl group through an intermediate in which a chlorine atom forms a bridge between two carbon atoms.

Rearrangements involving compounds of type I have been shown to yield products in which the trichloromethyl group has moved to positions a or b[3] or the methyl group has migrated to position c. Ethynyl carbinols of type II have been shown to yield α,β-unsaturated aldehydes, III, when the R groups contain no hydrogen which may eliminate with the hydroxyl, and α,β-unsaturated ketones, IV, when the R groups can provide a hydrogen for water formation.



As a consequence of recent studies on the Zincke and Suhl reaction[4] and on reactions of ethynyl carbinols catalyzed by cation exchange resins[5] we were interested in the behavior of 1-ethynyl-4-methyl-4-trichloromethyl-2,5-cyclohexadienol, V, and 1-ethoxyethynyl-4-methyl-4-trichloromethyl-2,5-cyclohexadienol, VI, on treatment with acidic reagents.



Both V and VI were readily prepared from 4-methyl-4-trichloromethyl-2,5-cyclohexadienone, VII, by treatment with ethynyllithium and ethoxylethynylmagnesium bromide, but only V was obtained in a pure crystalline state. All attempts to isolate pure VI failed, as it could not be crystallized, and on distillation rearrangement products were obtained.

On treatment of V with 10% sulfuric acid at room temperature an oil was obtained which had absorption peaks at 5.78 (s, strong), 5.91 (w, weak), and 5.97 μ (m, medium) but no acetylenic bands near 3 μ ($\equiv$CH) or 4.5 μ ($-C \equiv C-$). On standing at 0°, or more rapidly at higher temperatures, this oil underwent a series of changes as indicated by shifts in the infrared spectra. The 5.91 μ band increased in intensity at the expense of the 5.78 and 5.97 μ bands, which eventually disappeared. These changes were accompanied by evolution of hydrogen chloride. We interpret these changes to be the reactions represented in going from V to VIII (5.97 μ) to IX (5.78 μ) to X (5.91 μ). In agreement with the expected behavior of X the final product yielded a red-orange 2,4-dinitrophenylhydrazone in 85–90% yield which had strong absorption[6] at

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(1) This material was presented before the Organic Division at the meeting of the American Chemical Society in Minneapolis, Minnesota, September, 1955.

(2) This research was supported by a grant from the Ohio State University from funds allocated to the support of fundamental research.

(3) K. von Auwers and W. Julicher, *Ber.*, **55**, 2167 (1922).

(4) M. S. Newman and A. G. Pinkus, *J. Org. Chem.*, **19**, 978 (1954).

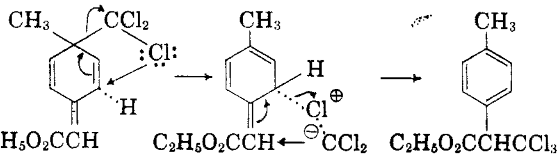
(5) M. S. Newman, *J. Am. Chem. Soc.*, **75**, 4740 (1953).

(6) See E. A. Braude and E. R. H. Jones, J. Chem. Soc., 498 (1945) for ultraviolet absorption spectra of a number of unsaturated aldehyde 2,4-dinitrophenylhydrazones.

377 mμ and gave analytical figures in agreement with those to be expected from the 2,4-dinitrophenylhydrazone of α-(*p*-tolyl)-β,β-dichloroacrolein, X. Furthermore, on oxidation of the final product, α-(*p*-tolyl)-β,β-dichloroacrylic acid, XIII, was obtained. When V was treated with acidic 2,4-dinitrophenylhydrazine reagent, an almost quantitative yield of the deep red 2,4-dinitrophenylhydrazone of (4-methyl-4-trichloromethyl)-2,5-cyclohexadienylene)acetaldehyde, VIII, was obtained.

As stated above, we were unable to obtain a pure sample of VI. However, the oily reaction product from the treatment of VII with ethoxyethynylmagnesium bromide was undoubtedly mostly VI, as it had a strong absorption band at 4.5 μ and almost no absorption in the 5–6 μ region where carbonyl containing impurities would absorb. On standing at 0°, or more rapidly at higher temperatures, bands appeared at 5.75 and 5.88 μ and the band at 4.5 μ decreased in intensity. Eventually only a band at 5.75 μ remained. We interpret these changes to be caused by the rearrangement of VI (4.5 μ) to XI (5.88 μ) to XII (5.75 μ). On alkaline hydrolysis of XII, followed by acidification, the same dichloroacrylic acid, XIII, was obtained as that produced by the oxidation of the dichloroacrolein, X. The ester, XI, was also prepared by the Reformatsky reaction of VII with ethyl bromoacetate, followed by dehydration of the hydroxyester, XV, thus produced. On attempted distillation of XV, dehydration and rearrangement to XII occurred. It is noteworthy that the trichloroester, XII, was stable to the action of pyridine in boiling benzene whereas the trichloroaldehyde, IX, lost hydrogen chloride spontaneously at room temperature.

As a working hypothesis the rearrangement of XI to XII is pictured as follows:



XI XIV XII

The driving force for the rearrangement is probably due to two factors: the increase in stability of XII because of the aromatic ring; and the relief of strain when the trichloromethyl group migrates from the quaternary carbon. The two step turnover of the trichloromethyl group is reminiscent of the second stage in the *para* Claisen rearrangement, originally proposed by Hurd[7] and recently supported by several researches.[8] Work designed to test our hypothesis is being carried out.

EXPERIMENTAL

4-Methyl-4-trichloromethyl-2,5-cyclohexadien-1-one, VII, m.p. 103–104°, was prepared by treating *p*-cresol with carbon tetrachloride in the presence of aluminum chloride.[4]

1-Ethynyl-4-methyl-4-trichloromethyl-2,5-cyclohexadienol, V. After 1.1 g. (0.15 mole) of lithium wire was dissolved in 1.5 l. of liquid ammonia, contained in a 3 l. three-necked flask, packed in mica and fitted with a dry ice condenser, a stainless steel stirrer and a gas inlet tube, dry, pure acetylene was passed in until the solution became colorless. To this solution was added dropwise a solution of 22.6 g. (0.1 mole) of VII in 400 ml. of dry tetrahydrofuran over a period of four hours while maintaining a steady stream of acetylene through the reaction mixture. The latter was allowed to stand overnight and then was decomposed with 10 g. of ammonium chloride. After most of the ammonia had evaporated, water (300 ml.) was added. The organic material was isolated by ether extraction. After removal of the solvent *in vacuo* the residue was recrystallized from a mixture of benzene and Skellysolve B (petroleum ether, b.p. 65–69°) to yield 19.5 g. (78%) of V, m.p. 98–99°.

Anal. Calc'd for $C_{10}H_9Cl_3O$: C, 47.7; H, 3.6; Cl, 42.3. Found: C, 47.9, 47.8; H, 3.6, 3.6; Cl, 42.1, 42.1.

2-(4-Methyl-4-trichloromethyl-2,5-cyclohexadienylene)-acetaldehyde 2,4-dinitrophenylhydrazone, VIIIa. To 0.4 g. of 2,4-dinitrophenylhydrazine in a mixture of 2 ml. of conc'd sulfuric acid, 3 ml. of water and 10 ml. of alcohol was added a solution of 0.376 g. of the ethynyl carbinol V in 10 ml. of alcohol. A red 2,4-dinitrophenylhydrazone was deposited in a few minutes. The product was purified by chromatography through a short column of alumina using benzene as an eluant. Concentration of the benzene solution afforded 0.57 g. (92%) of VIIIa, m.p. 189° (dec.), $\lambda_{\max}$ 404 mμ, log ε, 4.64 (in chloroform).

Anal. Calc'd for $C_{16}H_{13}Cl_3N_4O_4$: C, 44.5; H, 3.0; Cl, 24.7; N, 13.0. Found: C, 44.8; H, 3.1; Cl, 24.8; N, 13.0.

α-(p-Tolyl)-β,β-dichloroacrolein (X). *Acid-catalyzed rearrangement of the ethynyl carbinol*, V. The acidic medium was prepared by adding 3 ml. of water and 10 ml. of tetrahydrofuran (or dioxane, or alcohol) in the cold to 2 ml. of conc'd sulfuric acid..To the above acidic solution was added 0.5 g. of V, in 10 ml. of tetrahydrofuran (or dioxane or alcohol) at 0°. In the case of dioxane, two layers separated and it was necessary to agitate the reaction mixture. The reaction mixture was allowed to stand at room temperature overnight and was then neutralized with a dilute sodium bicarbonate solution and worked up in the usual manner. A yellow oil, showing no ≡C—H absorption in the 3μ region, was obtained: however, this oil exhibited carbonyl absorption bands at 5.78 μ (s), 5.91 μ (w), and 5.97 μ (m). On standing, even at 0°, the 5.91 μ band increased in intensity at the expense of the 5.78 and 5.97 μ bands which eventually disappeared completely. This change was accompanied by the evolution of hydrogen chloride. All attempts to purify the resulting oil which contained X and gave a positive Tollen's test were unsuccessful. However, on treatment with 2,4-dinitrophenylhydrazine reagent, the oil afforded the 2,4-dinitrophenylhydrazone of X, m.p. 234–235°, $\lambda_{\max}$ 3377 mμ, log ε, 4.55 (in chloroform): in 85–90% yield.

Anal. Calc'd for $C_{16}H_{12}Cl_2N_4O_4$: C, 48.6; H, 3.1; Cl, 17.9; N, 14.2. Found: C, 48.7; H, 3.6; Cl, 17.7; N, 14.0.

α-(p-Tolyl)-β,β-dichloroacrylic acid, XIII. To the brown silver oxide formed from 0.6 g. of silver nitrate and 0.3 g. of sodium hydroxide in 10 ml. of water was added gradually a solution of 0.38 g. of crude X in 10 ml. of tetrahydrofuran at 0°. The mixture was stirred at room temperature for four hours and then was diluted with water, filtered, and the filtrate was extracted with ether to remove any non-acid material. The aqueous layer then was acidified carefully in the cold with conc'd hydrochloric acid to yield 0.16 g. (44%) of the acid, XIII, m.p. 85–90°. Recrystallization from a mixture of benzene and Skellysolve B raised its melting

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[7] C. D. Hurd and M. Pollak, *J. Org. Chem.*, **3**, 550 (1939).

[8] H. Schmid and K. Schmid, *Helv. Chim. Acta*, **36**, 489 (1953); S. J. Rhoads and R. L. Crecelius, *J. Am. Chem. Soc.*, **77**, 5057 (1955) and references therein.

point to 119.8–120.6°, (reported[3] m.p. 118–120°). Neut. equiv., Calc'd, 231. Found, 234.

The non-acid fraction yielded about 0.15 g. of a yellow oil, which showed carbonyl absorption at 5.98 μ and gave a positive Tollen's test but its overall infrared absorption spectrum was quite different from that of the starting aldehyde, X.

p-Toluic acid from the aldehyde X. To a solution of 0.3 g. of X in 25 ml. of pyridine was added gradually a solution of 1.4 g. of potassium permanganate in a mixture of 30 ml. of pyridine and 10 ml. of water. This reaction mixture was stirred vigorously at 60–80° for three hours and then was allowed to stand overnight at room temperature. The excess potassium permanganate then was destroyed with sodium bisulfite and the manganese dioxide was removed by filtration. Continuous extraction of the acidified filtrate for 24 hours yielded 50 mg. (31%) of *p*-toluic acid, m.p. 176–180°. After sublimation of the acid it melted at 180.8°. Mixed with an authentic sample of *p*-toluic acid it showed no depression in m.p.

1-Ethoxyethynyl-4-methyl-4-trichloromethyl-2,5-cyclohexadien-1-ol, VI. To 40 ml. of a 1.27 *M* solution of ethylmagnesium bromide (0.05 mole) in anhydrous ether was added a solution of 4 g. (0.057 mole) of ethoxyacetylene[9] in 40 ml. of anhydrous ether. On stirring, the dark brown, insoluble ethoxyethynylmagnesium bromide settled out. The mixture was refluxed for $^1/_2$ hour; then 50 ml. of dry benzene was added to dissolve the dark brown complex. A solution of 10 g. of VII in 70 ml. of dry benzene was added dropwise over a period of $^1/_2$ hour. At the end of the addition, the reaction mixture was refluxed for one hour and finally decomposed with 30 g. of ammonium chloride in 100 ml. of water. The organic layer afforded 11.6 g. (90%) of a dark brown oil which exhibited —C≡C— absorption at 4.5 μ. On standing for a short while carbonyl absorption bands at 5.75 μ and 5.88 μ appeared at the expense of the 4.5 μ —C≡C— band. Hence no attempt was made to distil the ethoxyethynyl carbinol, VI. On further standing, the 5.88 μ band disappeared completely as the 5.75 μ band increased in intensity.

Ethyl α-(p-tolyl)-β,β,β-trichloropropionate, XII. *Rearrangement of the ethoxyethynyl carbinol* VI. The ester, XII was obtained by allowing the crude VI to stand at room temperature overnight: to stand at 0° for 5–6 days: or to be in contact with acid as described below. A solution of 7 g. of the crude VI in 60 ml. of ether was mixed with 60 ml. of 10% sulfuric acid. The heterogeneous mixture was stirred vigorously at room temperature for four hours and the ether layer was then worked up in the usual manner to give a dark brown oil which crystallized on scratching. Recrystallization from alcohol yielded 5.2 g. (74.3%) of the trichloro ester XII, m.p. 73.4–74.4°.

Anal. Calcd. for $C_{12}H_{13}Cl_3O_2$: C, 48.7; H, 4.4; Cl, 36.0. Found: C, 48.8; H, 4.6; Cl, 36.0.

Alkaline hydrolysis of this ester, XII, afforded 92.7% of the α-(*p*-tolyl)-β,β-dichloroacrylic acid, XIII, m.p., 120.8–121.4°.

Ethyl α-(p-tolyl)-β,β-dichloroacrylate, b.p. 130.5–131° at 3 mm., n_D^{26} 1.5394, was obtained in 91% yield by treating the XII with one equivalent of sodium ethoxide.

Anal. Calc'd for $C_{12}H_{12}Cl_2O_2$: C, 55.6; H, 4.6; Cl, 27.4. Found: C, 55.8; H, 4.7; Cl, 27.6.

The dichloro ester was also obtained in about 50% yield from the silver salt of the dichloroacid and ethyl iodide. Alkaline hydrolysis of the dichloro ester afforded a 70% yield of the acid XIII, m.p., 121–122°.

Ethyl 2-(4-methyl-4-trichloromethyl-2,5-cyclohexadien-1-ol) acetate, XV. A mixture of 45 g. (0.2 mole) of VII and 33.4 g. (0.2 mole) of ethyl bromoacetate in 400 ml. of benzene and 200 ml. of toluene was heated until about 100 ml. of solvent was removed by distillation. Then 26 g. of clean dry zinc was added and the reaction allowed to proceed vigorously. After the usual isolation procedure there was obtained 50.2 g. (80%) of the crude XV, an oil which could not be crystallized. It exhibited hydroxyl absorption at 2.88 μ and carbonyl absorption at 5.75 μ. Attempts to distil the hydroxy ester *in vacuo* resulted in complete conversion into the trichloro ester XII, m.p. 73–74°.

Ethyl 2-(4-methyl-4-trichloromethyl-2,5-cyclohexadienylene)-acetate, (XI). To 15.7 g. of the crude hydroxy ester XV at 0° was added 100 ml. of ice-cold formic acid. After shaking for 5–10 minutes at 0°, the mixture was diluted with water, carefully neutralized with sodium hydroxide, and extracted with ether. The ethereal extract was dried over potassium carbonate. On removal of ether under reduced pressure, 14 g. (95%) of the crude α,β-unsaturated ester XI, a dark oil exhibiting absorption at 5.75 μ (w) and 5.86 μ (s), was obtained. This ester did not undergo any rearrangement when kept over anhydrous potassium carbonate at 0°. All attempts to distil this ester XI *in vacuo* resulted in the formation of the trichloro ester XII, m.p., 73–74°.

α-(p-Tolyl)-β,β,β-trichloropropionic acid. Crude ester XI (1.5 g.) was treated with 5 g. of potassium hydroxide in 100 ml. of aqueous alcohol at room temperature for $2^1/_2$ hours. Working up the reaction mixture in the usual manner yielded 0.8 g. of the trichloro acid, m.p. 168–169°, (reported[3] m.p., 168–169°). Neut. equiv., Calc'd: 267.5. Found, 266.

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(9) We wish to thank Mr. Gerald Kahle for a sample of ethoxyacetylene.