by gas chromatography to give Ia as a colorless gas, which was conveniently stored in glass at −78°.

3-Difluoramino-4-fluoro-3,4-diazadecafluorohexane (Ib).—A 400-ml quartz reactor was charged with 1.63 g (6.1 mmol) of decafluoroazoethane[9] and 0.74 g (7.1 mmol) of N_2F_4, and the tube was irradiated at 25° for 1.0 hr. The reaction tube was cooled at −80°, and the volatile products were removed by applying vacuum (1–2 mm). The residual yellow liquid, analyzed by gas chromatography[8] on a 6-ft column at 25°, was found to consist of 61% unchanged decafluoroazoethane (gc retention time, 1.4 min) and 36% Ib (gc retention time, 5.2 min). The product was purified by gas chromatography on the same column to give Ib as a pale yellow liquid. The product could be stored indefinitely at −78°.

Registry No.—Ia, 1840-66-0; Ib, 3829-29-6; $CF_3N{=}NCF_3$, 372-63-4; $C_2F_5N{=}C_2H_5$, 756-00-3; tetrafluorohydrazine, 10036-47-2.

Acknowledgment.—The author is indebted to members of the Physical and Analytical Division for gas chromatography, infrared, mass spectral, and nmr analyses.

Free-Radical 1:5 Rearrangement of the Trichloromethyl Group[1,2]

MELVIN S. NEWMAN AND ROGER M. LAYTON

Evans Chemistry Laboratory of The Ohio State University, Columbus, Ohio 43210

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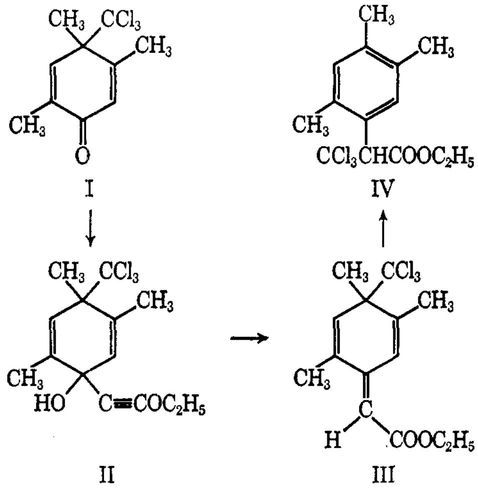
(+)-4-Trichloromethyl-2,4,5-trimethyl-2,5-cyclohexadienone (I) produces (+)-1-ethoxyethynyl-4-trichloromethyl-2,4,5-trimethyl-2,5-cyclohexadienol (II) on treatment with ethoxyethynylmagnesium bromide followed by water. Treatment of (+)-II with acid yields (−)-ethyl 4-trichloromethyl-2,4,5-trimethyl-2,5-cyclohexadienylideneacetate (III). On pyrolysis or photolysis of active III inactive ethyl α-(2,4,5-trimethylphenyl)-β,β,β-trichloropropionate (IV) is formed. Reaction of active I with ethylmagnesium bromide followed by treatment of the product with dilute acid and then heating affords inactive 2,4,5-trimethyl-β,β,β-trichloroisopropylbenzene (VIII). The free-radical nature of these rearrangements is demonstrated and discussed. Resolution of I was accomplished by reaction with active α-(isopropylidenaminooxy)propionic acid (V).

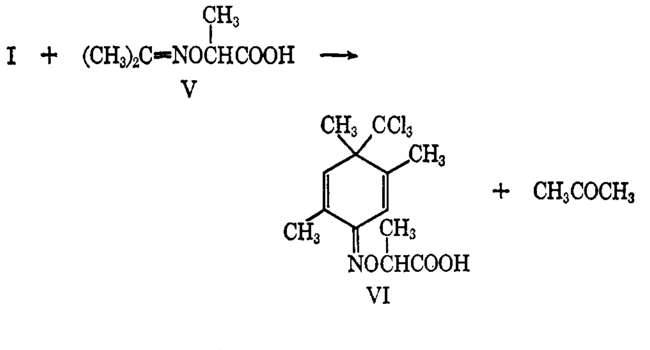
In earlier studies on the behavior of trichloromethyl groups in 4-methyl-4-trichloromethyl-2,5-cyclohexadienones, 1,5 migrations had been observed in several cases.[3] The work herein reported was initiated with the intent to find out more about the mechanism involved in the transformation of 4-trichloromethyl-2,4,5-trimethyl-2,5-cyclohexadienone (I)[4] to ethyl α-(2,4,5-trimethylphenyl)-β,β,β-trichloropropionate (IV) *via* the expected intermediate compounds, II and III (Scheme I).

SCHEME I



Since I and IV each had an asymmetric carbon (but different ones), the use of optically active I was deemed of interest. Accordingly I was resolved by reaction with active α-isopropylidenaminooxypropionic acid (V)[5] to yield a mixture of isomers of VI which was separated by fractional recrystallization. On heating with levulinic acid,[6] the pure isomer of VI was converted into active I. Thus the reagent, V, may prove of value for the resolution of other ketones (Scheme II).

SCHEME II



On treatment of active I with ethoxyethynylmagnesium bromide and work-up of the reaction mixture[3c] racemic IV was obtained. Since it was expected that active IV would be obtained, further study of the rearrangement was undertaken. By careful treatment of a similar reaction mixture with cold water, II was obtained in optically active form when active I was used. Because of experimental difficulties in handling II, no pure isomer was obtained. Hence, it is not known if a single diastereoisomer of II was present or not.[7]

On treatment with acid under mild conditions II could be transformed into III which was also active. However, on warming III to about 85° in cyclohexane

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[1] This work formed part of the Ph.D. thesis (1967) of R. Layton who was the recipient of a National Institutes of Health Predoctoral Fellowship, 1966–1967. Kinetic data are listed in the thesis.

[2] Supported in part by a grant from the National Science Foundation.

[3] (a) K. von Auwers and W. Jülicher, *Chem. Ber.*, **55**, 2167 (1922); (b) M. S. Newman and R. L. Tse, *J. Org. Chem.*, **21**, 638 (1956); (c) M. S. Newman and J. A. Eberwein, *ibid.*, **29**, 2516 (1964).

[4] M. S. Newman, D. Pawellek, and S. Ramachandran, *J. Amer. Chem. Soc.*, **84**, 995 (1962).

[5] M. S. Newman and W. B. Lutz, *ibid.*, **78**, 2469 (1956).

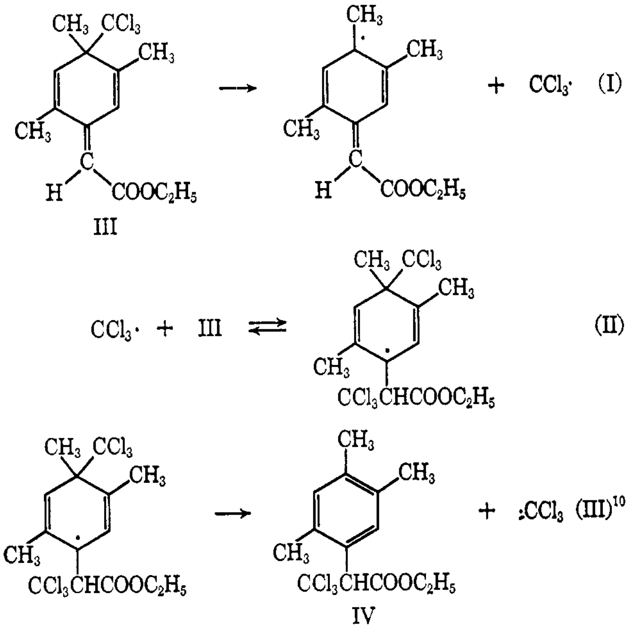
[6] C. H. DePuy and B. W. Ponder, *ibid.*, **81**, 4629 (1959).

[7] M. S. Newman, J. Eberwein, and L. L. Wood, Jr., *ibid.*, **81**, 6454 (1959), showed that only one isomer was formed on treatment of 4-methyl-4-trichloromethyl-2,5-cyclohexadienone with phenylmagnesium bromide.

or on exposure to light III rapidly rearranged to IV which was racemic.

To obtain more information about the rearrangement of III to IV, a study of the rate was undertaken. By measurement of the optical activity, the rate of the thermal rearrangement was shown to be first order with respect to III. As there was an induction period, a free-radical mechanism was suspected. This was confirmed by showing that the rearrangement at 85° could be stopped by the addition of free-radical trapping agents, such as iodine, benzoquinone, and thiophenol; and a nitrogen-purged solution of III in cyclohexane containing a small amount of α,α-diphenyl-β-picrylhydrazyl[8] was slowly decolorized on standing at room temperature. When inactive III in freshly distilled thiophenol was heated at 120 ± 5° and irradiated with 350-W unfrosted light, analysis showed that most of the III remained after 40 hr. Since ethyl 2,4,5-trimethylphenylacetate (VII) was produced in an amount approximately equivalent to the III destroyed, evidence in support of a radical produced by loss of a trichloromethyl group from III was at hand. A sample of authentic VII was prepared from authentic 2,4,5-trimethylbenzyl chloride[9] by conventional procedures.

The above results are in accordance with the reaction scheme indicated by eq III.

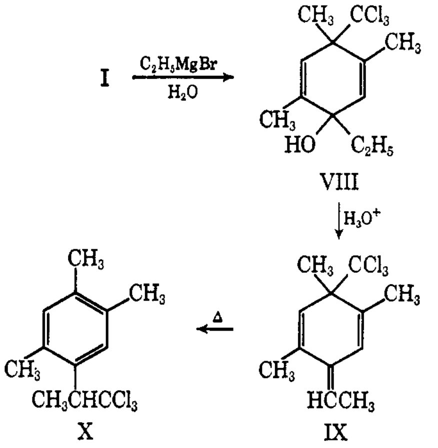


In order that the rate be first order with respect to III, one must assume a chain-terminating reaction between a trichloromethyl radical and III (see Experimental Section for the kinetic analysis). Because of the long-chain length it was not possible to isolate any product resulting from such a chain-terminating step.

Since IV is racemic, one must assume that the attack of the CCl_3 radical in eq II takes place with equal ease from either face of the plane. Models show that the trichloromethyl group in III does not interfere with approach of a CCl_3 radical from the same side. We assume that the stereochemistry of the unsaturated ester group in III is as shown because of steric factors. Although the ester II is so unstable that complete purification could not be accomplished, the nmr spectrum and thin layer chromatography of the sample used for kinetic study (see Experimental Section) indicated that III has the structure shown and was quite pure. Since III is optically active when optically active I is used as starting material, it is assumed that there is no partial racemization during the steps leading to the formation of III as there is no reason to believe in a change in stereochemistry at the 4 position in any of the steps pictured.

To rule out the argument that IV is formed in an optically active state and is racemized by enolization at a later stage, active I was treated with ethylmagnesium bromide (Scheme III). By suitable treatment the product was converted into 1,1,1-trichloro-2(2,4,5-trimethylphenyl)propane (X). As the latter was also inactive, racemization of IV by enolization seems unlikely since X would not be able to be racemized by an enolization step.

SCHEME III



It had been hoped that the free acid corresponding to IV could be resolved, esterified to form active IV, and submitted to the rearrangement conditions in order to see if active IV would remain active. However, some attempts to prepare the acid failed. Hydrolysis did not occur under acidic conditions and under alkaline conditions loss of hydrogen chloride occurred along with hydrolysis.

When a solution of active III in benzene was exposed to a long-wavelength uv lamp, rearrangement to inactive IV took place. Thus the photochemical reaction occurs with racemization also. The rearrangement was zero order with respect to III. When samples of impure III were left in flasks exposed to the usual laboratory light, rearrangement slowly took place. Hence, the experiments leading to the isolation of pure III had to be done with protection from light.

Further experiments designed to elucidate the stereochemistry of certain 1,3 migrations of CCl_3 groups[11] are under study here as these may prove to be stereospecific because of increased steric factors.

[8] S. Goldschmidt and K. Renn, *Chem. Ber.*, **55**, 628 (1922).

[9] We are grateful to Lauren Dauernheim who supplied us with this material prepared by chloromethylation of 1,2,4-trimethylbenzene.

[10] Equations II and III may be substituted by one equation in which the trichloromethyl radical attacks compound III with simultaneous expulsion of a trichloromethyl radical. The rate would still be first order in compound III were this the case.

[11] M. S. Newman and F. Bayerlein, *J. Org. Chem.*, **28**, 2804 (1963).

Experimental Section[12]

Resolution of 4-Trichloromethyl-2,4,5-trimethyl-2,5-cyclohexadienone (I).—A slow current of pure nitrogen was passed through a refluxing solution of 63.4 g of I,[4] 36.3 g of V,[5] $[\alpha]^{20}\mathrm{D}$ +31.5 ± 0.2° (*c* 8.75, H_2O), and 12 g of *p*-toluenesulfonic acid in 275 ml of 92% acetic acid for 6 hr, when a test with 2,4-DNPH solution[13] showed that acetone was no longer being evolved. The black solution was poured on ice and the organic acidic fraction isolated in the usual way. The residue was taken up in 350 ml of petroleum ether (bp 30–60°). After standing overnight 44 g of tacky crystals remained after decantation of the mother liquor. After decolorization with charcoal in ether, the product was crystallized from benzene–hexane to yield 12.8 g (15%) of colorless needles of α-(4-trichloromethyl-2,4,5-trimethyl-2,5-cyclohexadienylidenaminooxy)propionic acid (VI): mp 155.0–156.5°; $[\alpha]^{20}\mathrm{D}$ −160 ± 1° (*c* 9.56, benzene). Three further recrystallizations from benzene–hexane changed neither the melting point nor the rotation.

Anal. Calcd for $C_{13}H_{16}Cl_3NO_3$: C, 45.8; H, 4.7; N, 4.1. Found: C, 45.9; H, 4.7; N, 4.0.

When the above preparation was repeated using (−)-V, $[\alpha]^{20}\mathrm{D}$ −30 ± 0.2° (*c* 10, H_2O), the product was VI: mp 152.0–153.5°; $[\alpha]^{22}\mathrm{D}$ +154 ± 1° (*c* 4.25, benzene). This was used directly for the preparation of (−)-I (see below).

A solution of 12.0 g of the above (−)-VI in 400 ml of 9:1 levulinic acid–1 *N* hydrochloric acid[6] was refluxed for 12 hr. The black solution was poured on ice and the organic product isolated as usual and distilled to yield 8.1 g (90%) of a pale yellow oil, bp 110–112° (2 mm), which soon crystallized. Recrystallization from hexane afforded colorless I, mp 57.5–59.0°, $[\alpha]^{25}\mathrm{D}$ +26.4 ± 0.2° (*c* 8.11, benzene), with little loss. The same procedure applied to (+)-VI (see above) yielded I, mp 55.5–57.5°, $[\alpha]^{20}\mathrm{D}$ −25.5 ± 0.2° (*c* 8.00, benzene), in high yield.

1-Ethoxyethynyl-4-trichloromethyl-2,4,5-trimethyl-2,5-cyclohexadienol (II).—To 57.9 ml of a 0.51 *M* magnetically stirred solution of ethylmagnesium bromide (0.0295 mol) in anhydrous ether was added 2.27 g (0.0325 mol) of freshly distilled ethoxyacetylene.[14] Light brown insoluble ethoxyethynylmagnesium bromide settled out. After refluxing for 20 min, a solution of 5.0 g (0.0197 mol) of inactive I in 50 ml of anhydrous ether was added over a period of 5 min. After stirring 20 min the homogeneous solution was cooled in an ice–salt mixture and decomposed with ice-cold water. The organic phase was separated and dried over anhydrous sodium carbonate, and the solvent was evaporated under reduced pressure in the cold. An ethereal solution of the brownish residue was decolorized with activated charcoal. After removal of the ether 6.3 g of a colorless oil was obtained. This was undoubtedly almost pure II as it absorbed at 2.82 (3546 cm^{-1}, m, OH) and 4.36 μ (2294 cm^{-1}, s, C≡C). There was no absorption in the carbonyl region but, on standing, carbonyl bands began to appear at the expense of the above bands.

Similar results were obtained when (+)-I was used. In a typical run (+)-I, $[\alpha]^{25}\mathrm{D}$ +26.4, yielded II, $[\alpha]^{25}\mathrm{D}$ +36.1 ± 1° (*c* 1.5, benzene, assuming the entire product to be II). Because of the instability of II no analytical sample was obtained, but the ir spectral determinations in this and other runs show that no I remained and, hence, essentially pure dienols (II) were present.

Ethyl 4-Trichloromethyl-2,4,5-trimethyl-2,5-cyclohexadienylideneacetate (III).—In carrying out all experiments from this point on as much work as convenient was done in the absence of light since III is light sensitive.

In a typical experiment a solution at 0° of 6.0 g of the isomers of II in 75 ml of 1:1 ether–benzene was shaken with 75 ml of iced 3 *N* hydrochloric acid, followed by a wash with 5% sodium bicarbonate. After the usual work-up an almost quantitative yield of colorless liquid which proved to be essentially pure III was obtained. No analysis was obtained for this oil, or similar oils from other reactions, as it was sensitive to heat and light. It is dangerous to keep any amount of this oil neat as when rearrangement occurs the heat rapidly builds up. Solutions of III in hydrocarbon solvents were stored below 0° for several weeks in the dark without appreciable change. The above oil (III) had no ir bands at 2.82 or 4.36 μ and did have a single carbonyl band at 5.83 μ (1715 cm^{-1}, s). The ultraviolet spectrum, λ_{max} at 292 mμ (ε 21,400) in 95% ethanol, may be compared with that of diethyl 3-carbethoxymethyl-2-cyclohexenylideneacetate,[15] λ_{max} 298 mμ (ε 21,000), as close a model compound as we could find.

The nmr spectrum of III has three singlets at τ 2.22, 3.87, and 4.37 (1 H each). We assign the 2.22 peak to the hydrogen in the 6 position of III as this would be expected to be deshielded by the carbethoxy group.[16] If this assumption is correct, the stereochemistry of the carboethoxy group as shown in III is correct. The remaining features of the nmr spectrum were as expected and confirm the structure of III. Thin layer chromatography of III on alumina using 10% ethyl acetate in benzene as developer showed that the III (R_f 0.64) prepared as described above was essentially pure as there was only a small second spot (R_f 0.68) which was undoubtedly IV since IV had the same R_f value (0.68). Similar results were obtained when (+)- and (−)-I were used as starting materials. From (+)-I (see above) there was obtained III, $[\alpha]^{20}\mathrm{D}$ −42.0 ± 0.2° (*c* 10.4, benzene).

When the II prepared from (+)-I was converted into III as above described for inactive I, (−)-III, $[\alpha]^{20}\mathrm{D}$ −42.0 ± 0.2° (*c* 10.4, benzene, assuming the entire product to be III), was obtained.

Ethyl α-(2,4,5-Trimethylphenyl)-β,β,β-trichloropropionate (IV).—Pure IV[3c] was obtained in every experiment starting from active or inactive I, II, or III. In all cases the product (IV) was optically inactive when measured at the sodium d line and the mercury green line. One feature of the nmr spectrum of IV is of interest. There is an octet (2 H) centered at τ 5.91. These peaks are due to the fact that the methylene hydrogens, normally a quartet (as in III), are nonequivalent because of a nonadjacent asymmetric center.[17]

Photochemical Rearrangement of III.—When 5 ml of a 10% solution of (+)-III, $[\alpha]^{19}\mathrm{D}$ +41.2 ± 0.2° (*c* 10, benzene), in cyclohexane in a Pyrex flask was placed in direct sunlight for 6 hr there remained no optical activity at 5893 and 4960 Å. The product was essentially pure IV.

The rate of the photochemical rearrangement was studied as follows. A 3% solution of III, $[\alpha]^{20}\mathrm{D}$ −42.0 ± 0.2° (*c* 10.4, benzene), in benzene was placed in a 1-dm Pyrex polarimeter tube and was allowed to stand in the dark at 20° for 3 hr. No change in rotation had occurred in this time. Beside the polarimeter tube was mounted a small long-wavelength uv source[18] so that readings could be taken without disturbing the photolysis. After an induction period of about 25 min after the uv light was turned on the rotation began to change. The data are listed in Table I. The observed rotation (assumed to be proportional to concentration in the range in question) was plotted against time to give a line which had a slope of about -3.5×10^{-3} deg min^{-1}. The zero-order rate constant, k_0, was calculated from eq 1 to be 2.6×10^{-4} mol l.$^{-1}$ min^{-1}.

$$k_0 = -\frac{\mathrm{d[III]}}{\mathrm{d}t} = \frac{-C}{[\alpha]l}\,\frac{\Delta\alpha\ (\mathrm{obsd})}{\Delta t} = \frac{-C\ (\mathrm{slope})}{[\alpha]l} \qquad (1)$$

(l = tube length in decimeters [α] = specific rotation, and C = conversion factor to change concentration units from grams per milliliter to moles per liter)

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[12] Melting points of all samples were taken with a Thomas–Hoover 6406-M capillary melting point apparatus. The thermometer was corrected by comparison with the melting range of standards. Boiling points are uncorrected. Microanalyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn. The infrared absorption spectra were determined on a Perkin-Elmer Infracord spectrophotometer, Model 137. Infrared absorptions are described as strong (s), medium (m), and weak (w). Ultraviolet absorption spectra were measured with a Cary Model 14 recording spectrophotometer, using 1-cm matched cells. Nuclear magnetic resonance (nmr) spectra were determined relative to tetramethylsilane at 60 Mc with the Varian Associates high-resolution spectrophotometer, purchased in part with funds from the National Science Foundation. Carbon tetrachloride solutions were used, unless noted otherwise. An Aerograph Hy-Fi Model 600-C gas chromatograph was used for gas–liquid partition chromatographic analysis. The phrase "worked up in the usual manner" refers with minor variations to the handling of organic solutions in the following manner. The organic solution was washed successively with water and saturated sodium chloride solution and dried by filtering through a bed of anhydrous magnesium sulfate, and the solvent was removed *in vacuo*.

[13] R. Shriner, R. Fuson, and D. Curtin, "The Systematic Identification of Organic Compounds," 4th ed, John Wiley and Sons, Inc., New York, N. Y., 1962, p 111.

[14] Obtained from Chemical Samples Co., Columbus, Ohio.

[15] M. W. Cronyn and J. E. Goodrich, *J. Amer. Chem. Soc.*, **74**, 3331 (1952).

[16] L. M. Jackman, "Applications of N.M.R. Spectroscopy in Organic Chemistry," Pergamon Press Inc., New York, N. Y., 1959, p 121.

[17] This phenomenon has been observed before, *e.g.*, J. J. Looker, *J. Org. Chem.*, **31**, 2973 (1966), and ref 8–10 therein.

[18] "Mineralight" Model SL 3660 (filter removed), Ultra-Violet Products, Inc., Pasadena, Calif.

TABLE I

PHOTOCHEMICAL REARRANGEMENT OF (−)-III TO IV
($k_0 = 2.55 \times 10^{-4}$ mol l.$^{-1}$ min^{-1})

Time, min[a]	$-\alpha$ (obsd)
0	1.20 ± 0.03
45	1.00
105	0.86
165	0.60
225	0.45

[a] The relative time was adjusted to compensate for an indefinite induction period.

Thermal Rearrangement of III.—Two 10% solutions of III, $[\alpha]^{19}\text{D}$ +41.2 ± 0.2° (*c* 10.0, benzene), in cyclohexane and benzene, respectively, were sealed into ampoules and heated in an oil bath at 95° in darkness for 1 hr. Neither solution showed any optical activity at 5893 or 4960 Å. When similar solutions were sealed and no heating was done, the rotation was essentially unchanged after 24 hr. In a similar reaction in cyclohexane in which heating was at 100° for 30 min the reaction mixture was examined by glpc with a 5 ft × 0.125 in. 5% SE-30 silicone on 60–80 mesh Chromosorb W[19] column. In addition to the solvent there was only one main product, IV: retention time, 14.3 min at 165°. There was no peak corresponding to ethyl 2,4,5-trimethylphenylacetate (VII) or hexachloroethane, but there was a small peak for chloroform.

A 10% solution of inactive III in cyclohexane was divided into three 4-ml portions in three vials covered with aluminum foil. To one was added about 3% of iodine, to another 3% of benzoquinone. The three tightly stoppered vials were heated in an oil bath at 90–95°, and aliquots were withdrawn from time to time. The pure sample was almost completely rearranged to IV in 75 min as judged by ir analysis. The other two samples showed no change from III.

A solution of 3.5 g of III in 35 ml of freshly distilled thiophenol was heated at 115–125° and irradiated with a 350-W unfrosted light. After 40 hr the reaction solution was dissolved in ether-benzene (1:1), washed with sufficient 10% sodium hydroxide to remove all of the thiophenol, and then worked up in the usual manner. The infrared spectrum of the residue indicated that a large fraction of III was still present. The residue in methylene chloride was analyzed by gas–liquid partition chromatography with a 5 ft × 0.125 in. 5% SE-30 silicone oil on Chromosorb W, analytical column at 165°. A large peak (retention time, 14.3 min) appeared which was doubtlessly the regular rearrangement product IV produced by the rearrangement of III on the chromatography column. One other major peak appeared (retention time, 3.7 min). When authentic ethyl 2,4,5-trimethylphenylacetate (VII) which had a retention time of 3.7 min was added to the solution being analyzed, the peak increased in intensity and remained symmetrical. The areas[20] under the respective peaks indicated a 7:3 ratio of IV to VII.

A magnetically stirred portion of the residue in a small sublimation apparatus at 0.2-mm pressure was heated in an oil bath at 85–90°. The small fractions that slowly condensed on the cold finger were examined by infrared analysis. Heating was interrupted while the cold finger was removed, and the cold finger was rinsed with acetone before the collection of another fraction. The infrared spectrum of the first two fractions were identical with that of VII.

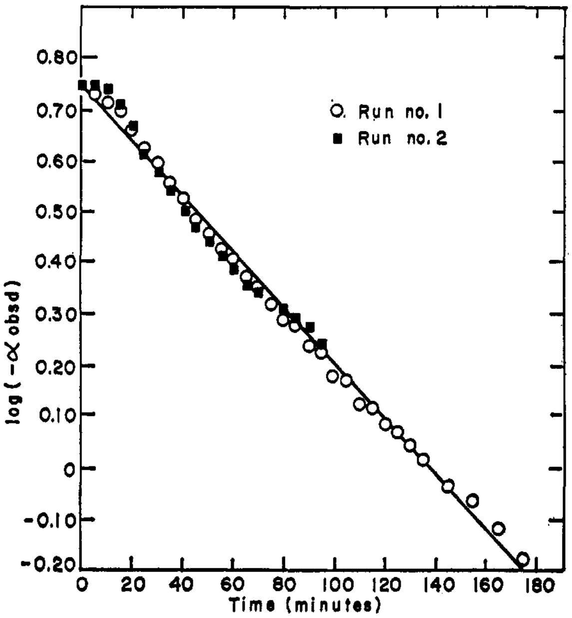

Figure 1.—A plot of log ($-\alpha_{\text{obsd}}$) *vs.* time for the thermal rearrangement of (−)-III to IV at 85°.

$$\log \alpha \text{ (obsd)} = \frac{-k_1 t}{2.30} + \text{constant} \qquad (2)$$

The rate of the thermal rearrangement was measured in a 2-dm jacketed polarimeter tube at 85°. A 7% solution of III, $[\alpha]^{20}\text{D}$ −42.0 ± 0.2° (*c* 10.4, benzene), in purified *n*-decane[21] was introduced into the tube which was fitted by a rubber stopper through which a syringe needle was inserted in order to prevent compression. The needle was withdrawn after about 20 min when thermal equilibrium was established. There was an induction period of about 30 min during which the rotation did not change. The data for change in rotation with time were plotted in Figure 1 to give a straight line which had a slope of -5.40×10^{-3} min^{-1}. The first-order rate constant, k_1, was calculated from eq 2 above to be 1.24×10^{-2} min^{-1}.

First-order kinetics for the thermal rearrangement of III to IV can be explained by assuming a termination reaction for CCl_3 radicals which involves III. This termination reaction could be an abstraction, abnormal addition, or disproportionation. The kinetic consequences of this type of termination reaction are derived below. The proposed chain mechanism can be represented by eq i–iii.

initiation

$$\text{III} \xrightarrow{k_1} \cdot CCl_3 + R\cdot \qquad (i)$$

propagation

$$\text{III} + \cdot CCl_3 \underset{k_3}{\overset{k_2}{\rightleftarrows}} (\text{III-}CCl_3)\cdot \xrightarrow{k_4} \text{IV} + \cdot CCl_3 \qquad (ii)$$

termination

$$\text{III} + \cdot CCl_3 \xrightarrow{k_5} \text{unreactive radical (+ other possible reactions)} \qquad (iii)$$

Assuming the steady-state condition for the formation of $\cdot CCl_3$ and $(\text{III-}CCl_3)\cdot$ then

$$0 = k_1[\text{III}] - k_2[\text{III}][\cdot CCl_3] + k_3[(\text{III-}CCl_3)\cdot] + k_4(\text{III-}CCl_3)\cdot] - k_5[\text{III}][\cdot CCl_3]$$

$$0 = k_2[\text{III}][\cdot CCl_3] - k_3[(\text{III-}CCl_3)\cdot] - k_4[(\text{III-}CCl_3)\cdot]$$

The sum of the last two equations is

$$k_1[\text{III}] = k_5[\text{III}][\cdot CCl_3]$$

so

$$[\cdot CCl_3] = k_1/k_5$$

Assuming long chains

$$\frac{-d[\text{III}]}{dt} = k_4[(\text{III-}CCl_3)\cdot] = \frac{k_4 k_2}{k_3}[\text{III}][\cdot CCl_3]$$

therefore

$$\frac{-d[\text{III}]}{dt} = \frac{k_1 k_2 k_4}{k_3 k_5}[\text{III}]$$

Ethyl 2,4,5-Trimethylphenylacetate (VII).—A mixture of 10.0 g of 2,4,5-trimethylbenzyl chloride[9] and 21.5 g of powdered cuprous cyanide was heated at 145–150° for 30 min.[22] The cooled mixture was triturated with benzene. After removal of

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[19] A Johns-Manville Products Corp. crushed firebrick product.

[20] The areas were estimated by taking the product of the height and the half-height width, assuming the peaks to be perfect triangles.

[21] *n*-Decane was purified by stirring with concentrated H_2SO_4 for 2 days followed by distillation over CaH_2.

[22] A. Modification of the procedure of S. Wawzonek, and H. Hsu, *J. Amer. Chem. Soc.*, **68**, 2741 (1946).

solvent from the filtered solution there was obtained 6.6 g (70%) of 2,4,5-trimethylbenzyl cyanide,[23] bp 105–115° (0.2 mm). Hydrolysis of 5.4 g of the cyanide in 90 ml of 60% sulfuric acid for 15 hr, followed by a conventional work-up, afforded 4.0 g (66%) of pure recrystallized 2,4,5-trimethylphenylacetic acid,[23] mp 128–129°. Esterification by treatment of the acid chloride with ethanol yielded pure VII, bp 90–92° (0.2 mm), in 75% yield.

Anal. Calcd for $C_{13}H_{18}O_2$: C, 75.7; H, 8.8. Found: C, 75.5; H, 8.9.

1,1,1-Trichloro-2-(2,4,5-trimethylphenyl)propane (X).—To a solution of 5.94 g of I in 25 ml of ether was added dropwise with stirring a solution of 0.05 mol of ethylmagnesium bromide in 50 ml of ether. After 15 min the reaction mixture was cooled and treated slowly with ice. The cold ether layer was washed with cold sodium carbonate, and the solvent was removed under reduced pressure in the cold. Infrared examination of the product (mainly VIII) showed that no I was present and OH bands in the 2.8–3.0-μ region were strong. A solution of this crude carbinol mixture[24] in 75 ml of ether was shaken with cold 3 N hydrochloric acid, and the ether solution was then worked up in the usual way, keeping cool and in the dark. The nmr spectrum indicated that the product contained a preponderance of one (presumably the isomer shown) isomer of IX. No elemental analyses for VIII or IX were attempted because of the sensitivity of these compounds to heat.

The nmr spectrum of IX (which was undoubtedly quite pure) had two multiplets for the vinyl hydrogens, one centered at τ 3.63 (1 H) and one centered at τ 4.40 (2 H). The 4-methyl group appeared as a singlet at τ 8.42 (3 H) and the remaining methyl groups as multiplets centerd at τ 7.90, 8.15, and 8.72 (9 H).

A solution of the above semibenzene IX in 5 ml of hexane was exposed to sunlight for several hours. The solvent was then removed under reduced pressure and the residue distilled to yield 4.35 g (70%) of yellow oil, bp 81–83° (0.1 mm).

A careful fractionation afforded a pure colorless sample of X which had nmr peaks as follows: τ 2.79, 3.20 (1 H each, aromatic), a quartet centered at τ 5.92 (1 H, benzylic); a doublet centered at τ 8.39 (3 H, aliphatic CH_3); a singlet at τ 7.91 (3 H aromatic CH_3); and a partly resolved doublet at τ 7.81 (6 H, aromatic CH_3).

The structure of X was further substantiated by mass spectrophotometry. Molecular ions of weights 264–270 were obtained, the variations being attributable to the chlorine isotopes. No satisfactory elemental analyses for X were obtained owing to the lack of stability. The analyses for C, H, and Cl added to 100%, but the chlorine values were lower than required by the formula $C_{12}H_{15}Cl_3$ owing to loss of HCl.

Registry No.—(+)-I, 16214-72-5; (−)-I, 16214-73-6; (+)-II, 16214-74-7; (−)-III, 16214-75-8; (±)-IV, 16214-76-9; (+)-VI, 16214-77-0; (−)-VI, 16214-78-1; VIII, 16214-79-2; (±)-IX, 16214-80-5; (±)-X, 16214-81-6.

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(23) L. I. Smith and C. W. MacMullen, *J. Amer. Chem. Soc.*, **58**, 629 (1936).

(24) We assume that a mixture of stereoisomeric carbinols was present because of the complexity of the nmr spectrum. In another case[7] only one isomer was formed.

Studies on the Bromination of Isoprene

VICTOR L. HEASLEY, CHARLES L. FRYE, ROBERT T. GORE, JR., AND PAUL S. WILDAY

Department of Chemistry, Pasadena College, Pasadena, California 91104

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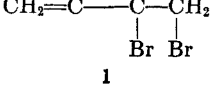
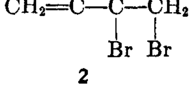
A study of the bromination of isoprene under various conditions is reported. Although previous reports stated that bromination of isoprene gave exclusively *trans*-1,4-dibromo-2-methyl-2-butene (**4**), it has been shown that, depending on the conditions, varying amounts of the following dibromides are also formed: *cis*-1,4-dibromo-2-methyl-2-butene (**3**), 3,4-dibromo-3-methyl-1-butene (**2**), and 3,4-dibromo-2-methyl-1-butene (**1**). The formation of **1**, **3**, and **4** was confirmed by comparison with authentic isomers, using infrared and vpc analysis. The unambiguous syntheses of **3** and **4** are reported. The presence of **2** was based on infrared and vpc studies, and on its rearrangement to **3** and **4**. The equilibration mechanism probably involves a covalent transition state in which the rearranging bromine atom is attached to carbon atoms at both ends of the allylic system, as proposed by Hatch, *et al.*, for the equilibration of 3,4-dibromo-1-butene and *trans*-1,4-dibromo-2-butene. In the addition of bromine to isoprene, in nonpolar solvents, it is suggested that π complexes (four of them are possible from attack of bromine on either end of the *s-cis* and *s-trans* forms of the isoprene molecule) are initially formed that break down to give bromonium ions in which the charge is highly dispersed across the whole allylic system. The bromonium ions from the *s-cis* and *s-trans* forms of isoprene would give **3** and **4**, respectively, by attack of tribromide ion on the terminal, vinyl carbon atom. Dibromide **2** (or **1**, depending on which end of the isoprene molecule was originally attacked) could be formed by opening of the three-membered ring.

Several researchers have reported that the product obtained from the bromination of isoprene is exclusively 1,4-dibromo-2-methyl-2-butene,[1] and that it has the *trans* configuration.[2,3] While studying the allylic diazide, prepared from isoprene dibromide, we became suspicious that this dibromide was not exclusively the *trans* isomer.[4] In order to establish the composition of the dibromide product from isoprene and to begin a mechanistic investigation of diene bromination, of which little is known, we undertook a study of the bromination of isoprene. Theoretically four dibromides, whose structures are shown below, are possible from the addition of bromine to isoprene. The formation of tetrabromide would be expected to be minimal since butadiene is reported to give no tetrabromide[5] and 2,3-dimethyl-1,3-butadiene in only small amounts.[6]


$CH_2{=}C(CH_3){-}CH(Br){-}CH_2Br$

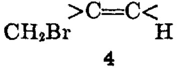
1


$CH_2{=}CH{-}C(CH_3)(Br){-}CH_2Br$

2


$(CH_3)(CH_2Br)C{=}C(H)(CH_2Br)$

3


$(CH_3)(CH_2Br)C{=}C(CH_2Br)(H)$

4

Results and Discussion

The results of our study on the bromination of isoprene under various conditions are shown in Table I. The percentages of the dibromides were determined by

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(2) A. A. Petrov, *J. Gen. Chem. USSR*, **13**, 741 (1943).

(3) Y. M. Slobodin, *ibid.*, **24**, 444 (1954).

(4) C. A. VanderWerf and V. L. Heasley, *J. Org. Chem.*, **31**, 3534 (1966).

(5) L. F. Hatch, P. D. Gardner, and R. E. Gilbert, *J. Amer. Chem. Soc.*, **81**, 5943 (1959).

(6) O. J. Sweeting and J. R. Johnson, *ibid.*, **68**, 1057 (1946).