**Acknowledgments.**—The authors wish to express their thanks to Mrs. Gertrude Y. Greenberg for performing a portion of the preparative work reported in this paper and for measuring the ultraviolet absorption spectra and optical rotations. Mrs. Iris J. Siewers and Miss Alice M. Bernardi of the National Heart Institute determined the infrared spectra. The microanalyses were performed under the direction of Dr. W. C. Alford at the Microanalytical Laboratory, NIAMD, National Institutes of Health.

BETHESDA 14, MARYLAND

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[CONTRIBUTION FROM HICKRILL CHEMICAL RESEARCH LABORATORY]

# Rearrangement of Halotropones. Chloride Exchange in Tribromotropolone

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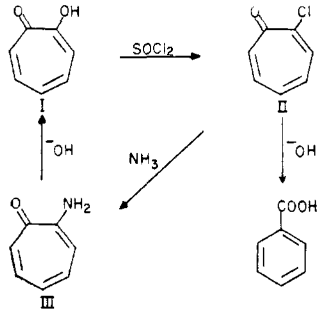
RECEIVED FEBRUARY 20, 1952

Chlorotropone, obtained from tropolone and thionyl chloride, reacts with ammonia normally but slowly to give aminotropone whereas with hydroxide ion benzoic acid is produced rapidly, this being a very facile rearrangement to the aromatic system. Upon treatment with sodium methoxide, 2-methoxy-3,5,7-tribromotropone rearranges to methyl 2,4,6-tribromobenzoate and 2-methoxy-3,5-dibromobenzoic acid. A similar behavior is shown by 2-methoxy-3,5,7-trichlorotropone while 2,3,5,7-tetrachlorotropone rearranges with alkali to 2,3,5-trichlorobenzoic acid. 3,5,7-Tribromotropolone reacts with thionyl chloride to give 2,3,5,7-tetrachlorotropone and with concentrated hydrochloric acid to give 3,5,7-trichlorotropolone. This unusual, acid-catalyzed halide exchange is a unique consequence of the cyclic nature of tropolone and has occasioned the reexamination of the theoretical aspects of the aromatic character of tropolone.

The hydroxyl function of tropolone (I), which simulates the hydroxyl of a carboxylic acid in its acidity and etherification with methanolic hydrogen chloride and an alcohol or phenol in its conversions to an acetate and a benzoate,[2] reacts with thionyl chloride to give 2-chlorotropone (II). The structure of II is firmly established by its conversion to aminotropone (III)[2] with ammonia and by the essential identity of its ultraviolet spectrum with that of tropolone methyl ether (IV) (Fig. 1).



Hydroxide ion, which hydrolyzes III, IV and tropolone acetate to tropolone, reacts with chlorotropone rapidly at 100° to give benzoate ion, no trace of tropolone being detectable. This facile, aromatizing rearrangement of the tropolone system is to be added to an increasingly large group: the benzilic acid type which is difficult with tropolone[2] but which is facilitated by nitro groups[3]; the methoxide-catalyzed rearrangement of tropolone methyl ether to methyl benzoate[2]; the iodinative decarboxylation of tropolone to triiodophenol[2,4]; and the deaminative aromatization of α-aminotropolones to salicylic acids.[6,7]

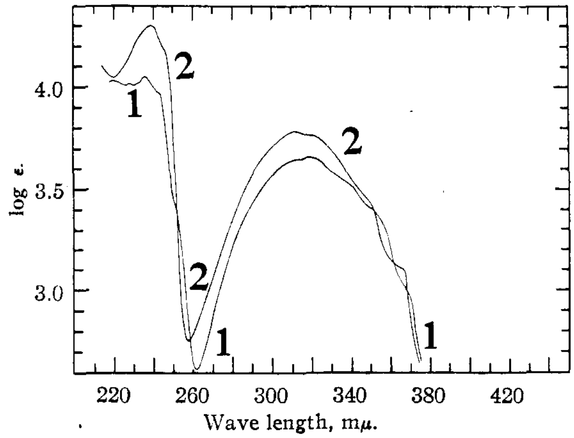


Fig. 1.—Ultraviolet absorption spectra of tropolone methyl ether (IV, curve 1) and of chlorotropone (II, curve 2) in isoöctane.

As a more complicated example, 3,5,7-tribromotropolone (V) as its methyl ether (VI) was treated with methoxide ion in boiling, absolute methanol. The major product, as recently reported by Cook, *et al.*,[5] in support of the structure originally proposed[2] for V, is indeed methyl 2,4,6-tribromobenzoate (VII), but a minor product, 3,5-dibromo-2-methoxybenzoic acid (VIII), is produced in significant quantity. That the appearance of VIII as the free acid and not as the expected methyl ester (IX) results from subsequent reaction of IX with methoxide ion is indicated by the fact that methyl 3,5-dibromo-2-methoxybenzoate (IX) reacts with absolute methanolic sodium methoxide to give the acid (VIII) and (presumably) dimethyl ether.[8] In a similar fashion 3,5,7-trichlorotropolone methyl

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[1] Department of Chemistry, Yale University, New Haven, Conn.

[2] W. von E. Doering and L. H. Knox, THIS JOURNAL, 73, 828 (1951).

[3] An effect first discovered by T. Nozoe, Y. Kitahara, K. Yamane and K. Yamaki, *Proc. Japan Acad.*, 26, No. 8, 14 (1950), in the rapid rearrangement of 3,5-dinitro-6-isopropyltropolone.

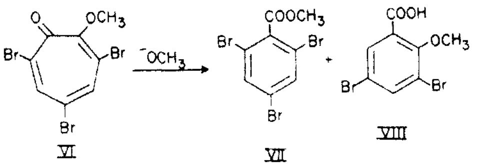
[4] In their first paper on tropolone, Cook, *et al.* [J. W. Cook, A. R. Gibb, R. A. Raphael and A. R. Somerville, *J. Chem. Soc.*, 503 (1951)] maintained that these three rearrangements could not be realized, a position which they reversed in their third.[5]

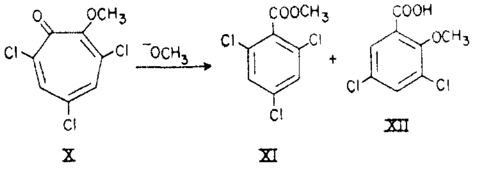
[5] J. W. Cook, A. R. M. Gibb and R. A. Raphael, *ibid.*, 2244 (1951).

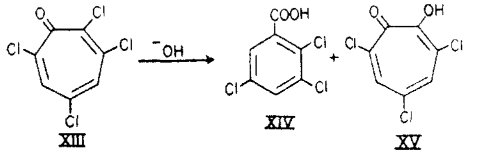
[6] R. D. Haworth and P. R. Jeffries, *ibid.*, 2067 (1951).

[7] T. Nozoe, Y. Kitahara and K. Doi, THIS JOURNAL, 73, 1895 (1951).

[8] See, for examples, J. F. Bunnett, M. M. Robison and F. C. Pennington, *ibid.*, 72, 2378 (1950).

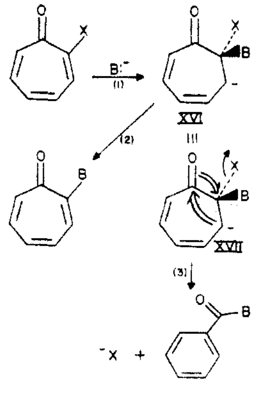






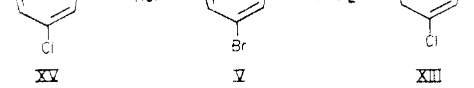
ether (X) rearranges with absolute methanolic sodium methoxide to a mixture of methyl 2,4,6-trichlorobenzoate (XI) and 3,5-dichloro-2-methoxybenzoic acid (XII). 2,3,5,7-Tetrachlorotropone (XIII) is converted by alkali to a mixture consisting mainly of 2,3,5-trichlorobenzoic acid (XIV) and to a small extent of 3,5,7-trichlorotropolone (XV).

In both VI and X a structural situation exists where the molecule may rearrange either as a 2-halotropone with ultrimate elimination of halide ion (products VIII and XII) or as a tropolone methyl ether with the elimination of methoxide ion (VII and XI). The fact that rearrangement occurs preponderantly by elimination of the stronger base, methoxide ion, is inconsistent with the mechanism originally proposed for rearrangements of this type[2] and seems to require an hypothesis in which the relative ease of eliminating $X^-$ is not one of the product-determining factors. A possible hypothesis involves attack of the nucleophilic reagent at carbon atom 2 in the rate-determining step (1) to give an intermediate XVI which can proceed either by direct loss of $X^-$ to the substitution product (2) or by a more complicated rearrangement of electrons and atomic positions, as suggested by XVII, to the derivative of benzoic acid[3]; the driving force being derived from the larger (*ca.* 30 kcal.) residence energy of the benzene system.[9]



The products of reaction of a molecule such as VI are controlled in the first phase (1) by the ratio of the rates of addition of methoxide ion to positions 2 and 7, a ratio which should be relatively insensitive to changes in X, and are controlled in the final phase by the ratio of reactions (2) and (3), each of which would be affected by changes in X in a similar way. The reaction of VI would therefore not be controlled by the expected large difference in reactivity of a carbon–bromine as compared to a carbon–methoxyl bond and would be sensitive to otherwise minor structural changes.

In the reaction of tribromotropolone (V) with thionyl chloride, designed to form 2-chloro-3,5,7-tribromotropone, the unexpected product, 2,3,5,7-tetrachlorotropone (XIII), was obtained. This structure and the structure 2,3,4,6-tetrachlorotropone, are consistent with the previously mentioned transformation in alkali, but the latter structure would require disruption of the structural relationship of oxygen and halogen atoms during the reaction with thionyl chloride and could scarcely lead to the formation of 3,5,7-trichlorotropolone as one of the alkaline hydrolysis products.



On the conjecture that an acid-catalyzed exchange had been involved, 3,5,7-tribromotropolone (V) was treated with concentrated hydrochloric acid forming 3,5,7-trichlorotropolone (XV). The assigned structure, uniquely consistent with the results of the reaction of the corresponding methyl ether (X) with methoxide ion, is confirmed by the similarity of the ultraviolet spectra of V and XV (Fig. 2) and VI and X (Fig. 3) as well as the infrared spectra (Fig. 4). It is to be inferred *a priori* that the tetrachlorotropone produced in the reaction of V and thionyl chloride results from a similar acid-catalyzed exchange. It seems likely that this new acid-catalyzed halide exchange will be a general reaction of the tropone and tropolone system.

Theoretical consideration leads to the conclusion that this reaction is the first which depends for its occurrence on the cyclic nature of tropolone and is not to be expected of an acyclic analog. The other reactions and properties of tropolone can be qualitatively accommodated on the hypothesis that tropolone is a vinylog of a carboxylic acid or an enolized β-diketone (XVIII). This hypothesis, which is tantamount to erecting a barrier to p-orbital overlap between carbon atoms 1

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(9) The resonance energy of tropolone is calculated by W. N. Hubbard, C. Katz, G. B. Guthrie, Jr., and G. Waddington, This Journal, **72**, 4456 (1952), to be 36 kcal. using the Pauling–Wheland bond energies. This figure, essentially equal to that (38 kcal.) based on the estimated resonance energy of benzoic acid (69 kcal.), is significantly higher than the value deduced by Cook, *et al.*[4] (29 kcal.).

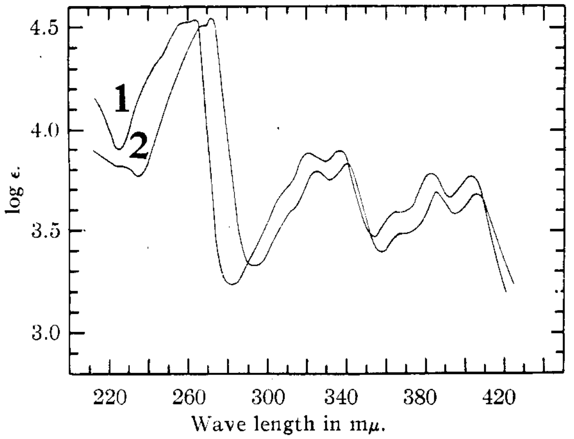


Fig. 2.—Ultraviolet absorption spectra of 3,5,7-trichlorotropolone (XV, curve 1) and 3,5,7-tribromotropolone (V, curve 2) in isoöctane.

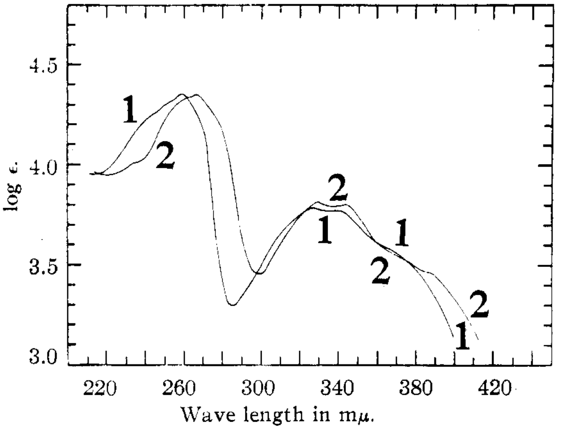
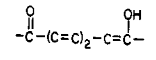


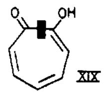
Fig. 3.—Ultraviolet absorption spectra of 3,5,7-trichlorotropolone methyl ether (X, curve 1) and 3,5,7-tribromotropolone methyl ether (VI, curve 2).

and 2 (XIX), permits explanation of the acidity and basicity,[2,10] the displacements at the 2-position,[2] the substitution at the $\alpha$- and $\gamma$-positions,[2] the aromatizing rearrangements and the resonance energy.[9]



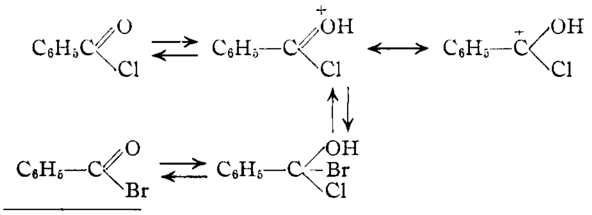
$-\overset{O}{\overset{\|}{C}}-(C{=}C)_2-C{=}\overset{OH}{\overset{|}{C}}-$

XVIII



XIX

The mechanism of the chloride exchange plausibly involves the conjugate acid of the tropolone in which positive charge is borne, in part, by carbon atoms. Those atoms which bear both charge and a bromine atom are subject to attack by chloride and therefore displacement.[11] Combination of the electronic structural hypothesis XIX and this mechanistic hypothesis represents the conjugate acid of tropolone as XX and predicts the possibility of exchange at positions 1, 2, 4 and 6 and no others. One is therefore forced to alter the structural hypothesis so that carbon atoms 3, 5 and 7 bear positive charge. This requirement is satisfied by eliminating the resonance barrier between carbon atoms 1 and 2, a change which has the effect of adding the set of resonance structures XXI to the limited set XX. More precisely one is obliged to permit $p$-orbital overlap between carbon atoms 1 and 2 in the transition state and, if there, presumably also in the unperturbed state.



$$\begin{tikzcd} C_6H_5C\begin{smallmatrix}{\diagup}O\\{\diagdown}Cl\end{smallmatrix} \arrow[r, shift left] & C_6H_5{-}C\begin{smallmatrix}{\diagup}\overset{+}{O}H\\{\diagdown}Cl\end{smallmatrix} \arrow[l, shift left] \arrow[r, leftrightarrow] \arrow[d, shift left] & C_6H_5{-}\overset{+}{C}\begin{smallmatrix}{\diagup}OH\\{\diagdown}Cl\end{smallmatrix} \\ C_6H_5{-}C\begin{smallmatrix}{\diagup}O\\{\diagdown}Br\end{smallmatrix} \arrow[r, shift left] & C_6H_5{-}C\begin{smallmatrix}{\diagup}OH\\{-}Br\\{\diagdown}Cl\end{smallmatrix} \arrow[l, shift left] \arrow[u, shift left] & \end{tikzcd}$$

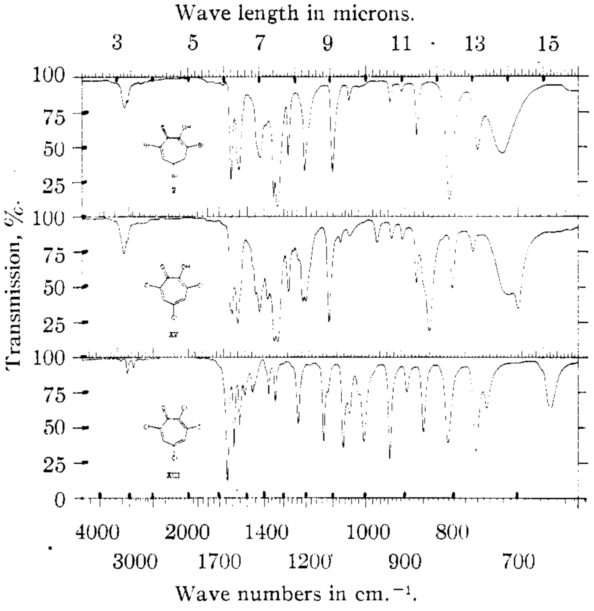
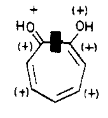
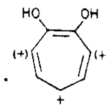


Fig. 4.—Measured with a Baird Infrared Spectrophotometer in both carbon disulfide and carbon tetrachloride in 10% solution with a sodium chloride prism, these composite curves represent the infrared spectra of 3,5,7-tribromotropolone (V), 3,5,7-trichlorotropolone (XV) and 2,3,5,7-tetrachlorotropone (XIII).



XX



XXI

This acid-catalyzed exchange is a unique consequence of the *cyclic* arrangement of the conjugated tropolone system and impels one to consider the "aromatic" resonance structures omitted in the simple vinylog hypothesis. As a single structure more adequately approximating the electron distribution of tropolone, the notation

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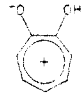
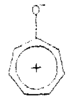
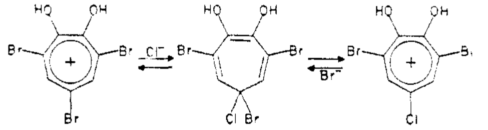
[10] The very weak basicity of benzoic acid [$pK_a$ of the conjugate acid is −7.26: L. A. Flexser, L. P. Hammett and A. Dingwall, THIS JOURNAL, **57**, 2103 (1935)] and the existence of unstable hydrochlorides of dihydroresorcinol and dimethyldihydroresorcinol [G. Merling, *Ann.*, **278**, 20 (1894); A. W. Crossley and P. Haas, *J. Chem. Soc.*, **83**, 494 (1903); A. W. Crossley and H. R. Le Sueur, *ibid.*, **81**, 821 (1902)] constitute a good analogy for the basicity of tropolone.

[11] This mechanism can be illustrated with the analogous conversion of benzoyl chloride to benzoyl bromide with hydrogen bromide [H. Staudinger and E. Anthes, *Ber.*, **46**, 1417 (1913)] and is discussed more fully by W. von E. Doering and Claude F. Hiskey, THIS JOURNAL, **74**, 5688 (1952).

XXII is suggested.[12] By this notation one recognizes the $C_7H_7^+$ cycle as the major source of aromatic resonance energy and cycloheptatrienylium oxide (XXIII)[13,14] as the parent of the new aromatic series, tropolone being related as phenol to benzene.[15] In this notation the previously described mechanism of the chloride exchange is represented by three sequences of the type XXIV, XXV and XXVI.


XXII


XXIII



XXIV XXV XXVI

This investigation was supported in part by a research grant (c-1130) from the National Cancer Institute, of the National Institutes of Health, Public Health Service, and in part by a research grant (DRIR-148) from the Damon Runyon Memorial Fund for Cancer Research.

## Experimental[16]

**2-Chlorotropone** (II).—A mixture of 0.420 g. of tropolone, 9 ml. of dry benzene and 0.28 ml. (10% excess) of thionyl chloride was heated on the steam-bath under reflux for 1.5 hr. Solvent and excess thionyl chloride were removed on the steam-bath under reduced pressure, leaving a crystalline residue which was sublimed at 90° and 4 mm. to give a light yellow sublimate, 0.438 g. (90%), m.p. 62–64°. Recrystallization from isohexane (60–70 ml.) gave 0.366 g. of 2-chlorotropone as long, practically colorless, fluffy needles m.p. 66–67°.

*Anal.* Calcd. for $C_7H_5OCl$: C, 59.8; H, 3.6; Cl, 25.2. Found: C, 60.1; H, 4.0; Cl, 25.1.

II gives no color with alcoholic ferric chloride, is recovered unchanged from its solution in warm water or concentrated aqueous ammonia, and gives no silver chloride when heated on the steam-bath with aqueous silver nitrate.

**Ammonolysis of 2-Chlorotropone** (II).—A mixture of 0.070 g. (0.0005 mole) of II and 7 ml. of 4% absolute methanolic ammonia was heated at 130° in a sealed tube for 8 hr. Removal of solvent on the steam-bath under reduced pressure gave a yellow oil which partially crystallized. Treatment with dry ether dissolved the organic material, leaving a residue of ammonium chloride (0.024 g.). Evaporation of the ether extract gave a crystalline residue which was recrystallized from benzene to give 0.027 g. (45%) of yellow needles, m.p. 94–98°, raised to 102–103° by recrystallization from acetonitrile; m.p. 102–104° in admixture with 2-aminotropone, m.p. 104–105°.[2]

**Rearrangement of II with Alkali.**—A mixture of 0.070 g. of II and 6 ml. of 3 *N* sodium hydroxide was refluxed for 2 hr. The solution was cooled, acidified with dilute sulfuric acid, and extracted with three small portions of ether. Concentration of the ether extract left a residue which was dissolved in chloroform, filtered, and evaporated on the steam-bath. Sublimation of the residue gave a colorless, crystalline sublimate, 0.043 g. (70%), m.p. 120–121°, undepressed in admixture with authentic benzoic acid, m.p. 121–122°.

**3,5,7-Tribromotropolone Methyl Ether (VI).**—A solution of 0.270 g. (0.00075 mole) of tribromotropolone (V), m.p. 123°, was dissolved in 20 ml. of dry ether containing a few drops of methanol and treated with ethereal diazomethane until a drop of the reaction mixture gave no coloration with alcoholic ferric chloride. Solvent was carefully evaporated under nitrogen at 30–40° giving a light yellow residue which was dried *in vacuo* at room temperature, dissolved in boiling isohexane, and filtered from a small amount of insoluble material. VI crystallized as long, yellow needles, 0.207 g. (74%), m.p. 123–123.5°. Concentration of the mother liquor to 2 ml. gave an additional 0.022 g., m.p. 118–120°.

*Anal.* Calcd. for $C_8H_5O_2Br_3$: C, 25.8; H, 1.4; Br, 64.3; $OCH_3$, 8.3. Found: C, 26.0; H, 1.4; Br, 64.0; $OCH_3$, 8.4.

**Rearrangement of 3,5,7-Tribromotropolone Methyl Ether (VI).**—A solution of 0.164 g. (0.00044 mole) of VI in 13 ml. of absolute methanol containing 0.130 g. of dissolved sodium was refluxed on the steam-bath for 30 min. Removal of solvent on the steam-bath under reduced pressure gave a mixture of oil and salts which was cooled in ice and treated with 20 ml. of ether and 5 ml. of cold water. The ether layer was separated and the aqueous layer was extracted twice with 5-ml. portions of ether. The combined ether extracts were washed free of alkali with 3 1-ml. portions of cold water, dried over magnesium sulfate, and evaporated. The light yellow, oily residue, dried overnight *in vacuo*, weighed 0.121 g. (74% calculated as methyl tribromobenzoate) and crystallized on short standing at 4°. Recrystallization from a small amount of ethanol gave methyl 2,4,6-tribromobenzoate (VII) as colorless needles: 0.083 g., m.p. 65–67° raised to 68–69° after two recrystallizations from isohexane.

*Anal.* Calcd. for $C_8H_5O_2Br$: C, 25.8; H, 1.4; Br, 64.3; $OCH_3$, 8.3. Found: C, 25.9; H, 1.6; Br, 64.1; $OCH_3$, 8.5.

The ether-extracted alkaline solution and water washings were combined, acidified with 2 *N* nitric acid, and extracted with 3 5-ml. portions of ether. The ether extract was washed with 3 1-ml. portions of cold water, dried over magnesium sulfate and evaporated. The vacuum-dried, crystalline residue, 0.044 g., was recrystallized from a small amount of ethanol to give 0.018 g. (20%) of 3,5-dibromo-2-methoxybenzoic acid (VIII) as almost colorless needles, m.p. 195–196° (lit.[17] 193–194°).

*Anal.* Calcd. for $C_8H_6O_3Br_2$: C, 31.0; H, 2.0; Br, 51.5; $OCH_3$, 10.0. Found: C, 31.3; H, 2.1; Br, 51.2; $OCH_3$, 10.0.

From the aqueous acidic layer and water washings, aqueous silver nitrate precipitated 0.024 g. of silver bromide (30% of theory based on elimination of one mole of bromide ion).

**Reaction of Methyl 3,5-Dibromo-2-methoxybenzoate (IX) with Methoxide Ion.**—3,5-Dibromo-2-methoxybenzoic acid, 0.018 g., was treated with ethereal diazomethane and the solvent evaporated to give the ester as colorless needles, m.p. 47–49° (lit.[18,19] 52–53°). This was refluxed on the steam-bath with 2 ml. of absolute methanol containing 0.015 g. of dissolved sodium and the reaction mixture worked as described above. No neutral material was isolated. The acidic product, 3,5-dibromo-2-methoxybenzoic

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[12] This notation, a circle inscribed in a polygon, represents a system of cyclic molecular orbitals composed of as many *p*-orbitals as there are carbon atoms peripheral to the circle and occupied by an equal number of electrons plus the number of included negative charges or minus the number of positive charges. This notation implies generalized but not equal delocalization of charge and electrons and is adapted from the notation proposed by Kauffmann, "Die Valenzlehre," Enke, Stuttgart, Germany, 1911, p. 539, to represent benzene. It is adopted in preference to the dotted-line notation of the Thiele-type proposed by T. Nozoe, *Science Repts. Tohoku Univ., First Ser.*, **34** [4], 199 (1950), and Dauben and Ringold[13] for tropolone and tropone (XXIII), respectively, on the grounds of greater convenience and the lack of any previous, prejudicing history of use in other connections. Both notations have the virtue of representing to some extent the molecular orbital picture of an electron cloud without resort to writing a number of extreme structures.

[13] H. J. Dauben and H. J. Ringold, THIS JOURNAL, **73**, 876 (1951).

[14] W. von E. Doering and F. L. Detert, *ibid.*, **73**, 876 (1951).

[15] It is the view of M. J. S. Dewar, *Nature*, **166**, 790 (1950), that tropolone is the parent of the aromatic system.

[16] All m.ps. are corrected. The microanalyses are by the Schwarzkopf Microanalytical Laboratory, Middle Village, Long Island, New York. The ultraviolet absorption spectra were measured in a Beckman model DU spectrophotometer.

[17] N. W. Hirwe and B. V. Patil, *Proc. Indian Acad. Sci.*, **5A**, 321 (1937); *C. A.*, **31**, 6216 (1937).

[18] A. Peratoner, *Gazz. chim. ital.*, **16**, 418 (1886).

[19] H. Gilman, W. Langham and F. Moore, THIS JOURNAL, **62**, 2333 (1940).

acid amounted to 0.016 g., m.p. 195–196° after recrystallization from cyclohexane.

**3,5,7-Trichlorotropolone Methyl Ether (X).**—A solution of 0.348 g. (0.0015 mole) of trichlorotropolone (XV, *vide infra*) in 25 ml. of dry ether containing a few drops of methanol was treated with ethereal diazomethane until a drop of the reaction mixture gave no coloration with alcoholic ferric chloride. Evaporation of the solvent under nitrogen and crystallization of the solid residue from isohexane gave 0.304 g. (85%) of X, m.p. 91–92° raised to 91.5–92.5° after a second recrystallization from isohexane. Concentration of the mother liquor and cooling gave a second crop of 0.013 g., m.p. 83–89°.

*Anal.* Calcd. for $C_8H_5O_2Cl_3$: C, 40.1; H, 2.1; Cl, 44.4; $OCH_3$, 13.0. Found: C, 40.4; H, 2.3; Cl, 44.2; $OCH_3$, 12.6.

**Rearrangement of 3,5,7-Trichlorotropolone Methyl Ether (X).**—A solution of 0.180 g. (0.00075 mole) of X in 24 ml. of absolute methanol containing 0.24 g. of dissolved sodium was refluxed on the steam-bath for 30 min. The reaction mixture was worked precisely as described for the rearrangement of tribromotropolone methyl ether. The oily neutral product weighed 0.142 g. (79% calculated as methyl trichlorobenzoate) and crystallized completely on short standing at 4°. Recrystallization from 1 ml. of isohexane gave methyl 2,4,6-trichlorobenzoate (XI) as colorless needles, m.p. 43–44°, raised to 44° after a second recrystallization from isohexane.

*Anal.* Calcd. for $C_8H_5O_2Cl_3$: C, 40.1; H, 2.1; Cl, 44.4; $OCH_3$, 13.0. Found: C, 40.4; H, 2.4; Cl, 44.0; $OCH_3$, 12.6.

The acidic product was dried *in vacuo*, 0.032 g. (19%) was sublimed at 100–110° and 2 mm. and recrystallized from cyclohexane to give 3,5-dichloro-2-methoxybenzoic acid (XII) as colorless needles; 0.018 g., m.p. 166–166.5° (lit.[20] 166–167°).

*Anal.* Calcd. for $C_8H_6O_3Cl_2$: C, 43.5; H, 2.7; Cl, 32.1; $OCH_3$, 14.0. Found: C, 43.7; H, 3.0; Cl, 32.0; $OCH_3$, 14.3.

From the aqueous acidic layer and water washings, aqueous silver nitrate precipitated 0.024 g. of silver chloride (22% of theory for the elimination of one mole of chloride ion).

**Rearrangement of 2,3,5,7-Tetrachlorotropone (XIII).**—To a solution of 0.293 g. (0.00012 mole) of tetrachlorotropone (XIII, *vide infra*) in 5 ml. of hot absolute ethanol, 2.5 ml. of 10% ethanolic potassium hydroxide was added. The greenish-yellow solution turned yellow immediately and rapidly deposited a precipitate. The bulk of the ethanol was removed on the steam-bath in a current of nitrogen, giving a light yellow residue which was suspended in water (2–3 ml.) and acidified with dilute sulfuric acid. The precipitated acid was separated by centrifugation, dried *in vacuo*, and crystallized from cyclohexane to give 0.119 g. (53%) of 2,3,5-trichlorobenzoic acid (XIV) as colorless needles, m.p. 162–163°, raised to 162.5-163.5° after a second recrystallization from cyclohexane (lit.[21] 163°); m.p. 165–167° in admixture with an authentic sample[22] m.p. 165–167°. The identity of the acid was further confirmed by comparison of its infrared spectrum with that of the authentic sample.

*Anal.* Calcd. for $C_7H_3O_2Cl_3$: C, 37.3; H, 1.3; Cl, 47.1. Found: C, 37.5; H, 1.5; Cl, 46.9.

The amide, obtained from the acid with thionyl chloride and ammonia in 63% yield, melted at 208–209° after two recrystallizations from acetonitrile (lit.[21] 204–205°).

*Anal.* Calcd. for $C_7H_4ONCl_3$: C, 37.5; H, 1.8; Cl, 47.4; N, 6.2. Found: Cl, 37.4; H, 1.9; Cl, 46.9; N, 6.1.

Evaporation of the cyclohexane mother liquors afforded an oily residue which gave an intense green coloration with alcoholic ferric chloride. This residue was dissolved in a chloroform extract of the aqueous acidic solution from which the crude trichlorobenzoic acid had precipitated. The chloroform solution was shaken with a saturated, aqueous solution of cupric acetate, and separated, the aqueous layer being extracted with warm chloroform until a colorless extract was obtained. The combined green chloroform extracts (30–40 ml.) were concentrated until the appearance of turbidity (6–8 ml.). On cooling, a greenish-yellow salt crystallized in small needles, 0.045 g., m.p. 315–316° with vigorous decomposition.

Treatment of this copper salt dissolved in 25 ml. of warm chloroform with gaseous hydrogen sulfide, followed by filtration through "Super-Cel" and evaporation gave a solid that crystallized from pentane in yellow needles; 0.027 g., m.p. 127–128° which was raised to 128–128.5° after sublimation at 110–115° and 4 mm., m.p. 127–128° in admixture with trichlorotropolone (XV, *vide infra*), m.p. 127–128°.

**2,3,5,7-Tetrachlorotropone (XIII).**—A mixture of 0.595 g. (0.0017 mole) of 3,5,7-tribromotropolone (V, m.p. 123°), 7 ml. of dry benzene and 1.5 ml. (10-fold excess) of thionyl chloride was refluxed on the steam-bath for 2 hr. Removal of solvent and excess thionyl chloride on the steam-bath under reduced pressure gave a pale yellow, solid residue which was crystallized from cyclohexane to give 0.342 g. (87%) of XIII as light, yellowish-green crystals, m.p. 113–114°. Sublimation at 100–105° and 4 mm. followed by crystallization from cyclohexane gave 0.293 g. of XIII, m.p. 115–116°.

*Anal.* Calcd. for $C_7H_2OCl_4$: C, 34.5; H, 0.8; Cl, 58.2. Found C, 34.8; H, 1.0; Cl, 58.3.

**3,5,7-Trichlorotropolone (XV).**—A mixture of 0.720 g. (0.002 mole) of tribromotropolone (V, m.p. 123°), 20 ml. of glacial acetic acid, and 8 ml. of concentrated hydrochloric acid was heated for 20 hr. in a sealed tube at 150°. Removal of solvent on the steam-bath under reduced pressure, and crystallization of the yellow solid from ethanol gave 0.348 g. (77%) of trichlorotropolone (XV) as long, fluffy greenish-yellow needles, m.p. 126–127°. Concentration of the mother liquor and cooling gave an additional 0.049 g., m.p. 112–116°. Sublimation at 110° and 2 mm. followed by crystallization from ethanol raised the m.p. to 127–128°.

*Anal.* Calcd. for $C_7H_3O_2Cl_3$: C, 37.3; H, 1.3; Cl, 47.2. Found: C, 37.5; H, 1.2; Cl, 46.7; Br, trace.

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[22] Kindly supplied by Dr. A. G. Norman, Chief, C Division, Chemical Corps Biological Laboratories, Camp Detrick, Frederick, Md.