[Contribution from Hickrill Chemical Research Laboratory]

Reactions of Halotropones and Related Compounds

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The acid-catalyzed displacement by bases in 2-substituted tropones has been investigated. As an example, 2-iodotropone has been obtained from 2-chlorotropone, 2-bromotropone and tropolone *p*-toluenesulfonate by treatment with potassium iodide in acetic acid. The aromatization of 2-chlorotropone to benzoic acid on treatment with hydroxide ion also occurs with 2-bromo- and 2-iodotropone but not with tropolone *p*-toluenesulfonate which is reconverted to tropolone. With phenyllithium no rearrangement is observed, tropolone, its methyl ether and chlorotropone being converted to 2-phenyltropone.

The recent uncovering by Doering and Knox[2] of the rearrangement of chlorotropone (I) and the chloride exchange of tribromotropolone has encouraged further investigation into the chemistry of the halotropones.

The halide displacement reaction has been extended and studied in connection with the preparation of the bromo and iodo analogs. 2-Bromotropone (II) can be prepared conveniently from 2-chlorotropone (I)[2] by treatment with hydrogen bromide in boiling acetic acid. The extent of bromide exchange is determined analytically since mixtures of I and II show no depression on melting and have not been separable by crystallization. 2-Iodotropone (III) results from the action of potassium iodide in wet acetic acid on I or II and from the action of tetraethylammonium iodide in dry acetic acid on I. The structural similarity of the three halotropones is suggested by the ultraviolet spectra (Fig. 1) in which III differs noticeably from I and II and is more strongly supported by comparison of the infrared spectra (Fig. 2). Not only are a considerable number of the bands of essentially equal intensity and wave number, but the others, of which some change in intensity alone and some in both intensity and position, are all similar and have undergone an orderly, progressive alteration in response to the successive replacement of chlorine by bromine and iodine. It should be noted that the halogen–carbon bonds are not manifested as fundamentals, these being out of range of the rock salt prism. The weak intensity of the carbon–hydrogen bond is quite remarkable and may possibly be explained by assuming that the dipole moment of the carbon–hydrogen bond approaches zero in the halotropones as a result of the partial positive charge on the carbon atoms.[3a,b]

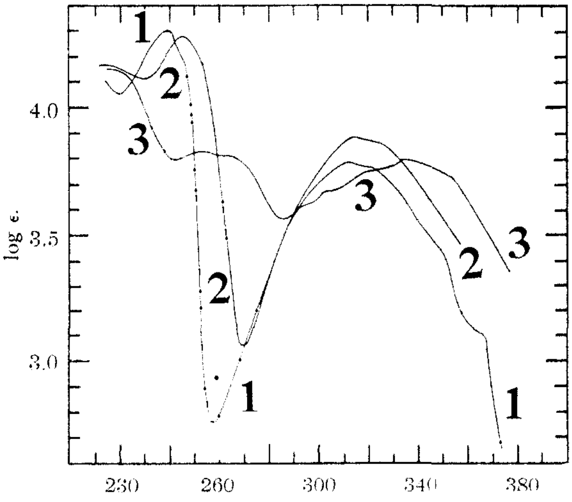
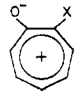
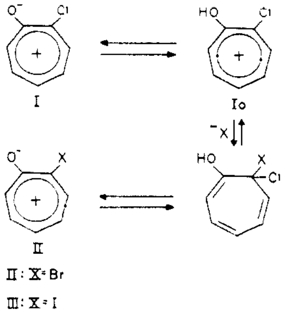


Fig. 1.—Ultraviolet absorption spectra of chloro-(I, curve 1), bromo-(II, curve 2), and iodo-(III, curve 3) tropone in isoöctane.



That the halide displacement reaction is acid-catalyzed can be inferred from the following observations. With potassium bromide instead of hydrogen bromide in boiling, wet acetic acid and for 5 hr., instead of 2 hr., 2 chlorotropone reacts much more slowly, only 16.5% of the chlorine being replaced by bromine. With sodium iodide in acetone at 100° for 3 hr., I is recovered unchanged. It is of interest that acid chlorides, close electronic relatives of 2-chlorotropone, also undergo acid-catalyzed exchange: Staudinger and Anthes[4] report the conversion of benzoyl and acetyl chloride with hydrogen bromide and hydrogen iodide to the corresponding acid bromides and iodides, respectively, whereas Thiele and Haakh[5] find that benzoyl chloride is unchanged on heating with powdered potassium iodide.

The mechanism of the exchange is plausibly expressed as the reaction of halide ion with the conjugate acid of the halotropone (2-chlorohydroxycycloheptatrienylium ion, Ia) to give an intermediate clearly capable of proceeding to the product. The reaction therefore belongs to the



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[2] W. von E. Doering and L. H. Knox, This Journal, **74**, 5683 (1952).

[3] (a) W. von E. Doering and F. L. Detert, *ibid.*, **73**, 876 (1951). (b) See footnote 13 in ref. 2.

[4] H. Staudinger and E. Anthes, *Ber.*, **46**, 1417 (1913).

[5] J. Thiele and H. Haakh, *Ann.*, **369**, 131 (1909).

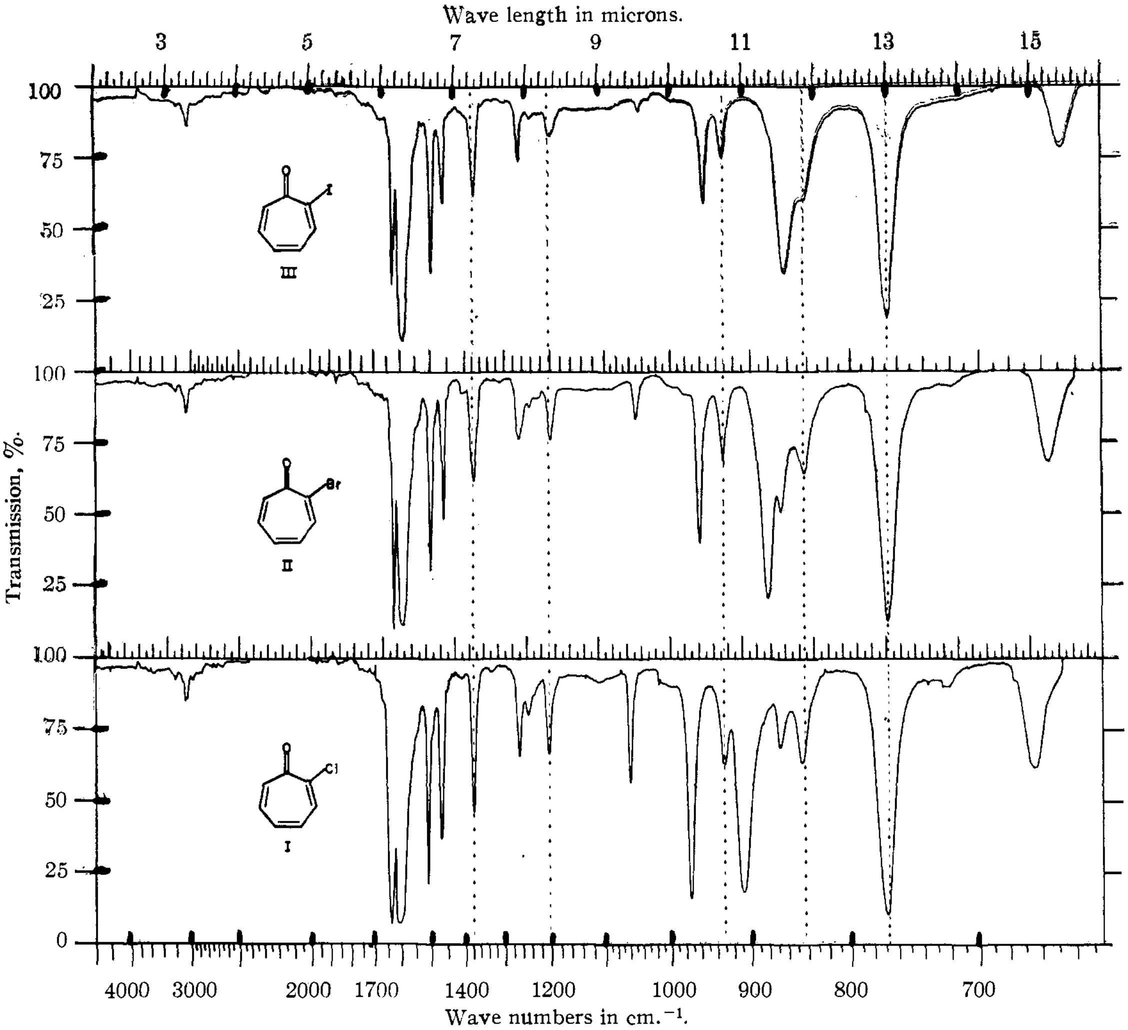

Fig. 2.—These infrared spectra are of 2-chloro(I)-, 2-bromo(II)- and 2-iodo(III)-tropone.

class of displacements in the tropolone series where one nucleophilic reagent displaces another from the 2-position. Acid-catalysis should always activate the tropone ring system to the displacement but can only be *effective* in those cases where the nucleophilic reagent is not too completely converted to its conjugate acid by the acidic catalyst. This displacement reaction is not limited theoretically to the 2-position but, as implied in the representation of the conjugate acid (Ia), should be able to occur at any one of the seven carbon atoms in the tropone nucleus. Pertinent is the recent conclusion of Brown[6] that no definite, *a priori*, theoretical prediction as to the position of nucleophilic attack on cycloheptatrienylium oxide[7] can be arrived at from the molecular orbital treatment. To the extent that one would consider hydroxycycloheptatrienylium ion similar to cycloheptatrienylium oxide[8] and that one would neglect interaction with halogen,[9] these results taken with the examples of Doering and Knox,[2] constitute nucleophilic displacements at four of the seven positions of cycloheptatrienylium oxide and are in support of the theoretical treatment of Brown.

The only other previously known example of the acid-catalyzed displacement involved the etherification of tropolones and the hydrolysis of tropolone methyl ethers. In seeking further examples, it has been found that neither tropolone nor tropolone acetate reacts with hydrogen bromide in acetic acid to give II, nor tropolone acetate with tetraethylammonium iodide in acetic acid to give III. The reverse reaction, the hydrolysis of 2-chlorotropone to tropolone, can be effected by heating for 9 hr. at 150° with dilute hydrochloric acid but does not occur on heating with water alone or with aqueous silver nitrate. The fact that the strongly halophilic acid, silver ion, in no way facilitates the reaction supports the view that

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[6] R. D. Brown, *J. Chem. Soc.*, 2670 (1951).

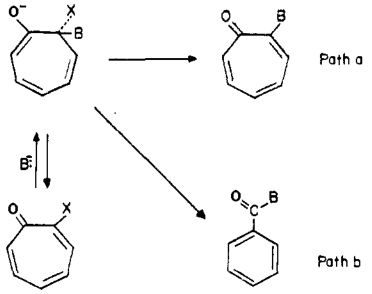
[7] It seems appropriate to employ this name when attention is being directed to the electron distribution and reactive characteristics (Brown agrees that the structure implied in this name is a better *single* representation than that implied in cycloheptatrienone) and otherwise to use the convenient trivial name, tropone [H. J. Dauben and H. J. Ringold, This Journal, **73**, 876 (1951)], but not cycloheptatrienone.

[8] It seems probable that this change would have the effect of making more nearly equal the π-electron densities (q) in the conjugate acid, as represented by a structure of the type Ia.

[9] The halogen atom or a similar, potentially weak base is required in place of hydrogen, if any reaction is to be observed, so that a weak base (halide ion) rather than a strong one (hydride ion) may be eliminated in the final stage of the displacement.

the acid-catalyst functions at the carbonyl oxygen. Tropolone *p*-toluenesulfonate (IV), which can be prepared from tropolone with *p*-toluenesulfonyl chloride in pyridine, reacts with tetraethylammonium iodide in dry acetic acid, but not with sodium iodide in acetone, to give 2-iodotropone. The hydrolysis of IV with dilute, aqueous, methanolic hydrochloric acid leads to tropolone, as expected, and, surprisingly, to a small amount of 2-chlorotropone.

In the reactions of tropolone derivatives with stronger bases, the factors influencing the relative rates of the displacement (path a) and the aromatization (path b) reactions seem to be delicately balanced. With hydroxide ion, 2-bromotropone (II) and 2-iodotropone (III), like 2-chlorotropone (I),[2] give benzoic acid (path b) whereas tropolone *p*-toluenesulfonate (IV) gives tropolone (path a). However, with ammonia both I[2] and IV give aminotropone (path a). A mechanism with which these facts are consistent has already been discussed.[2]



The reaction of tropolone or its derivatives with typical organometallic compounds has not been reported previously and is found now to proceed by path a. Simulating the behavior of carboxylic acids, tropolone itself reacts with phenyllithium to give 2-phenyltropone (V) in good yield. The structural assignment is supported by the facts that V forms a hydrobromide which is, however, less stable than tropone hydrobromide[3a] and that 3 moles of hydrogen are absorbed catalytically giving 2-phenylcycloheptanone, the 2,4-dinitrophenylhydrazone of which was compared with an authentic sample[10] kindly supplied by Dr. C. D. Gutsche. The ultraviolet absorption spectrum (Fig. 3) and the infrared spectrum (Fig. 4) are also consistent with the structure. 2-Chlorotropone (I) reacts with phenylmagnesium bromide or with phenyllithium to give V, unaccompanied, at least in the latter case, by any detectable amount of benzophenone (path b). Tropolone methyl ether also reacts with phenylmagnesium bromide to give V, although the yield is poorer in this case. With *n*-butyllithium, tropolone reacts to give a substance which is assumed to be 2-*n*-butyltropone by analogy with the phenyllithium reaction and from the fact that the ultraviolet absorption spectrum (Fig. 3) is very similar to that of tropone itself. Likewise, the infrared spectrum (Fig. 4) has many features in common with that of tropone, including the most intense band at *ca.* 1580 cm.$^{-1}$. The reaction of tropolone methyl ether and sodiomalonic ester gives a small amount of product, the ultraviolet spectrum of which is shown in Fig. 5.

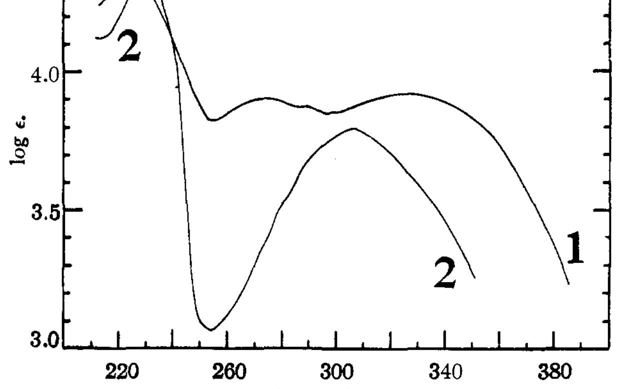


Fig. 3.—Ultraviolet absorption spectra of 2-phenyltropone (V, curve 1) and 2-*n*-butyltropone (curve 2) in isoöctane.

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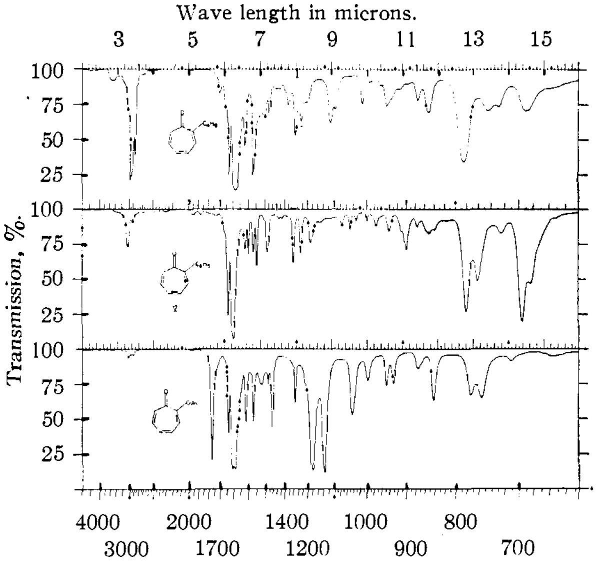

Fig. 4.—These curves are infrared spectra of 2-*n*-butyltropone (top), 2-phenyltropone (V) and tropolone acetate (bottom).

Experimental[11]

2-Bromotropone (II).—A solution of 0.203 g. (0.0015 mole) of 2-chlorotropone (I)[2] in 5 ml. of glacial acetic acid saturated with hydrogen bromide and 5 ml. of glacial acetic acid was refluxed for 2 hr. and concentrated under reduced pressure to a dark, tarry residue which was treated with water and extracted with chloroform. Sublimation of the dried, concentrated chloroform extract afforded a colorless, crystalline solid; 0.251 g., m.p. 56–59.5°. Crystallization from isoöctane afforded 0.200 g. (75%) of II as long, glis-

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(10) C. D. Gutsche, This Journal, **71**, 3513 (1949).

(11) All melting points are corrected. Analyses are by the Schwarzkopf Microanalytical Laboratory, Middle Village, Long Island, New York.

tening needles, m.p. 59.5–60.5°. The analytical sample melts at 60.0–60.5° and, on admixture with 2-chlorotropone (I), melts at 62.0–62.5°.

Anal. Calcd. for C_7H_5OBr: C, 45.4; H, 2.7; Br, 43.2. Found: C, 45.5; H, 2.8; Br, 43.1.

2-Iodotropone (III). (a) From 2-Chlorotropone (I).—A mixture of 0.070 g. (0.0005 mole) of I and 1.66 g. (0.010 mole) of potassium iodide in 9 ml. of acetic acid containing 1 ml. of water was refluxed for 5 hr., diluted with an equal volume of water and concentrated under reduced pressure. The mixture of salt and product was dissolved in hot water and extracted with chloroform. Concentration of the chloroform extract gave a residue which was sublimed (0.094 g.) and crystallized once from cyclohexane to yield 0.063 g. (54.5%) of III as tan platelets, m.p. 68–70°, and, in admixture with the preparation below, m.p. 69.5–70.5°.

Anal. Calcd. for C_7H_5OI: I, 54.7. Found: I, 55.0; Cl, 0.0.

If the crude product is dissolved in cold water instead of hot, a small amount of insoluble, dark-green crystalline solid is obtained which melts at 105.5–106° after crystallization from ethanol. It is decomposed by hot water to III and an aqueous solution giving a precipitate with silver nitrate.

(b) From 2-Bromotropone (II).—II (0.155 g., 0.0008 mole) and potassium iodide (2.8 g., 0.016 mole) were refluxed with 12.5 ml. of glacial acetic acid and 1.5 ml. of water for 5 hr. The mixture was worked as in (a) above, affording, after sublimation and crystallization from cyclohexane, III as tan plates; 0.144 g. (74%), m.p. 71.0–71.5°.

Anal. Calcd. for C_7H_5OI: C, 36.2; H, 2.2; I, 54.7. Found: C, 36.4; H, 2.4; I, 53.8, 55.2.

The mixture m.p. of I (m.p. 65–66°) and III (m.p. 70–71°) was 42.5–56.5° and that of II (m.p. 60–61°) and III (m.p. 70–71°) was 49.0–51°.

(c) From 2-Chlorotropone (I) and Tetraethylammonium Iodide.—A mixture of I (0.050 g., 0.00034 mole) and tetraethylammonium iodide (1.50 g., 0.006 mole) in 5 ml. of acetic acid, dried by refluxing with acetic anhydride, treating with phosphorus pentoxide and distilling, was refluxed for 5 hr. The reaction mixture was diluted with an equal volume of water and concentrated *in vacuo*. Addition of water to the residue left a small amount of insoluble, red material (0.059 g., m.p. 140–142°; also obtained by refluxing tetraethylammonium iodide in acetic acid) which was filtered. Extraction of the filtrate with chloroform gave material sublimation of which afforded crude III (0.051 g.) which was recrystallized three times from cyclohexane to give 0.020 g. (24%), m.p. 69.5–70.5°.

Reaction of I and Potassium Bromide in Aqueous Acetic Acid.—A mixture of I (0.050 g., 0.00036 mole), potassium bromide (0.850 g., 0.0071 mole), 5 ml. of acetic acid and 2 ml. of water was refluxed for 5 hr. Worked in the usual way as in (a) above, 0.048 g. of fine white needles, m.p. 64.5–65.5°, was obtained after one crystallization from cyclohexane. The analysis corresponds to a mixture of chlorotropone (82.5 wt. %) and bromotropone (16.5 wt. %).

Anal. Calcd. for C_7H_5OCl: Cl, 25.2. C_7H_5OBr: Br, 43.2. Found: Cl, 20.9; Br, 7.0.

Reaction of I and Sodium Iodide in Acetone.—A mixture of I (0.050 g., 0.00036 mole), and sodium iodide (0.160 g., 0.0011 mole) in 3 ml. of dry acetone was heated at 100° for 3 hr. in a sealed tube. Freed of acetone, the residue was extracted with boiling cyclohexane and filtered, to give unreacted I, 0.039 g. (78%), as fine needles, m.p. 65–66.5°.

Anal. Calcd. for C_7H_5Cl: Cl, 25.2. Found: Cl, 25.3; I, 0.0.

Tropolone and Hydrogen Bromide.—A mixture of 0.050 g. of tropolone, 1.0 ml. of acetic acid saturated with hydrogen bromide and 1.0 ml. of acetic acid was warmed on the steam-bath for 4 hr. The product was concentrated at reduced pressure, diluted with water and extracted with chloroform. Removal of the chloroform left an oil which was crystallized from isohexane to yield, 0.029 g. (58%) of unchanged tropolone, m.p. 49.0–51.0°. The mother liquor gave an additional 0.014 g. (28%) of tropolone.

Reaction of Tropolone Acetate (a) with Hydrogen Bromide.—A mixture of 0.040 g. of tropolone acetate (prepared in 92% yield from tropolone, acetic anhydride and a trace of freshly fused sodium acetate; infrared absorption spectrum is in Fig. 4), 1.0 ml. of acetic acid saturated with hydrogen bromide and 1.0 ml. of acetic acid was warmed on the steam-bath for 2 hr. Removal of the acetic acid *in vacuo* under reduced pressure left a residue from which 0.023 g. (62%) of tropolone copper complex was obtained.

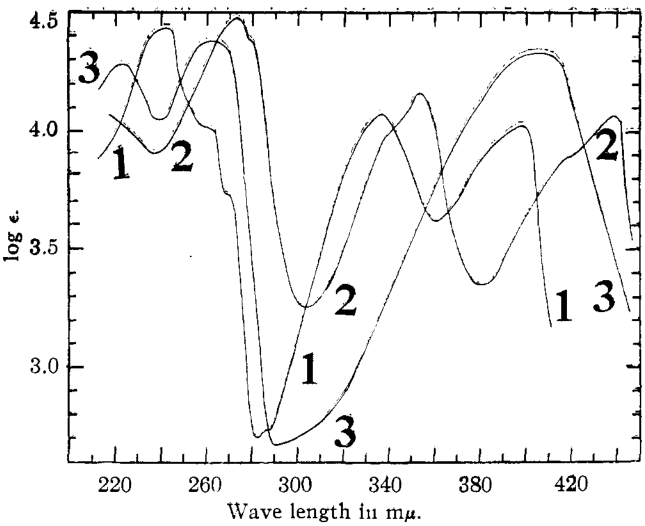

Fig. 5.—These curves represent the ultraviolet absorption spectra of aminotropone (1), 3,5,7-tribromoaminotropone (2), and the tropolone methyl ether–sodiomalonic ester product (3) in 95% ethanol solution.

(b) With Tetraethylammonium Iodide.—A mixture of 0.058 g. of tropolone acetate and 1.50 g. of tetraethylammonium iodide in 5 ml. of dry acetic acid was refluxed for 5 hr. and then afforded only copper tropolone, 0.037 g. (69%).

Reaction of 2-Chlorotropone (II). (a) Aqueous Acid.—A solution of 0.140 g. of I in 10 ml. of 2.4 *N* hydrochloric acid was heated at 150° in a sealed tube for 9 hr. and extracted with chloroform to give material from which 0.088 g. (58%) of tropolone copper complex, m.p. 318° with dec., was obtained.

When the reaction was carried out at 100° for 1 hr. only starting material was recovered.

(b) Water.—2-Chlorotropone (0.140 g.) was heated with 10 ml. of distilled water at 150° in a sealed tube for 9 hr. By the usual procedure there was obtained 0.012 g. (8%) of tropolone copper complex, m.p. 314° with dec., after crystallization from chloroform and by sublimation of the chloroform residue 0.080 g. (57%) of unchanged I, m.p. 65–66.5°, was obtained.

(c) Aqueous Silver Nitrate.—A mixture of 0.122 g. (0.00087 mole) of I, 0.148 g. (0.00087 mole) of silver nitrate and 10 ml. of distilled water was heated at 150° in a sealed tube for 9 hr. giving 0.015 g. of silver chloride (12% of the theoretical amount). The aqueous solution (*p*H 1) was extracted with chloroform, the chloroform extract being shaken with aqueous cupric acetate. No crystals of tropolone copper complex were obtained on concentration of the chloroform solution and sublimation of the residue gave 0.098 g. (80%) of unchanged I, m.p. 65–66°. There remained a pasty green solid, 0.019 g., which did not sublime.

Tropolone *p*-Toluenesulfonate (IV).—After 23 hr. at room temperature, a solution of 0.150 g. (0.0012 mole) of tropolone and 0.240 g. (0.0012 mole) of *p*-toluenesulfonyl chloride in 0.5 ml. of dry pyridine had deposited crystals of tropolone *p*-toluenesulfonate. These were stirred with 10 ml. of cold water, filtered and washed well with water (yield 0.278 g.). Two recrystallizations from 95% ethanol gave 0.246 g. (72.5%) of colorless needles, m.p. 156.5–157.5°. There was recovered 0.020 g. of tropolone as the copper complex. The analytical sample of IV melts at 159–159.5°.

Anal. Calcd. for $C_{14}H_{12}O_4S$: S, 11.60. Found: S, 11.83.

Reactions of Tropolone *p*-Toluenesulfonate (IV). (a) With Tetraethylammonium Iodide.—IV (0.095 g., 0.00034 mole) and tetraethylammonium iodide (1.50 g., 0.006 mole) were refluxed 5 hr. in 5 ml. of dry acetic acid, diluted with 5 ml. of water, heated on the steam-bath for 90 min. to hydrolyze unreacted IV, and concentrated *in vacuo*. Addition of water, filtration and extraction of the aqueous solution with chloroform afforded 0.008 g. (15%) of tropolone copper complex. The chloroform mother liquor was evaporated to dryness and from the residue there was obtained a tan sublimate (0.041 g.) which after crystallization from cyclohexane yielded 0.027 g. (34%) of 2-iodotropone (III), m.p. 70.5–71.0°, and m.p. 70.5–71.0° in admixture with authentic material.

(b) **With Sodium Iodide.**—A mixture of 0.103 g. (0.00037 mole) of IV and 0.168 g. (0.0011 mole) of sodium iodide in 5 ml. of dry acetone was heated at 100° for 3 hr. in a sealed tube. Removal of the acetone, addition of water and filtration of the unreacted sulfonate afforded 0.097 g. of IV, which was crystallized from ethanol to give 0.089 g. (86.5%) of material, m.p. 158–159.5°.

(c) **With Aqueous Acid.**—A mixture of 0.125 g. (0.0045 mole) of IV, 4 ml. of 3 *N* hydrochloric acid and 2 ml. of methanol was refluxed for 3 hr. There was obtained in the usual manner 0.042 g. (61%) of tropolone as the copper complex. Sublimation of the chloroform residue yielded 4 mg. of 2-chlorotropone (I) which, after two recrystallizations from cyclohexane, melts at 65–66° and does not depress the m.p. of an authentic sample.

Reaction of 2-Bromotropone (II) and Hydroxide.—II (0.050 g.) was heated on the steam-bath with 2 ml. of 1 *N* sodium hydroxide for 1 hr. The cooled, yellow solution was shaken with chloroform, acidified with dilute sulfuric acid and extracted again with chloroform. The latter chloroform extract gave no coloration with alcoholic ferric chloride but a solid on evaporation which crystallized from cyclohexane as colorless needles; 0.014 g. (42%), m.p. 121.0–122.5°, and mixed m.p. with benzoic acid 121.5–122.5°.

Reaction of 2-Iodotropone (III) and Hydroxide.—III (0.070 g., 0.00030 mole) was heated at 100° with 2 ml. of 1 *N* sodium hydroxide for 1 hr. Acidification with dilute sulfuric acid precipitated material which was extracted with ether. Removal of the ether, sublimation and crystallization from cyclohexane afforded 0.019 g. (52%) of benzoic acid, m.p. 121.5–122.5° (mixed m.p. 122–123°).

Alkaline Hydrolysis of Tropolone *p*-Toluenesulfonate (IV).—IV (0.530 g., 0.0019 mole) was refluxed with 25 ml. of 10% alcoholic potassium hydroxide for 5 min. After the bulk of the ethanol distilled, there was obtained 0.225 g. (76%) of tropolone as the copper complex, m.p. 320–321° with dec., by the usual procedure.

Ammonolysis of Tropolone *p*-Toluenesulfonate (IV).—IV (0.300 g., 0.0011 mole) in 15 ml. of 5% ammonia in dry methanol was heated in a sealed tube at 110–120° for 6 hr. The material remaining after removal of the methanol was triturated with water, the insoluble fraction being extracted with ether. The dark brown oil (0.047 g.) obtained on removal of the ether only partially crystallized when seeded with 2-aminotropone and was dissolved in 0.2 ml. of acetic acid and treated with 0.190 g. of bromine in 0.2 ml. of acetic acid. The yellow crystals of tribromo-2-aminotropone which deposited in a thick mass were stirred with water and filtered (0.077 g., 53.5%). Recrystallization from ethanol afforded a sample, m.p. 203.0–203.5°, which did not depress the m.p. of the authentic sample below.

Tribromo-2-aminotropone.—2-Aminotropone (0.015 g., 0.00008 mole) of 0.1 ml. of acetic acid was brominated with a solution of 0.065 g. (0.00036 mole) of bromine in 0.2 ml. of acetic acid at room temperature. The solvent and excess bromine were removed in a vacuum desiccator and the remaining solid was crystallized from ethanol to yield 0.022 g. (50%) of tribromo-2-aminotropone as yellow needles, m.p. 203.5–204.5°.

Anal. Calcd. for $C_7H_{14}ONBr_3$: C, 23.5; H, 1.1; N, 3.9; Br, 67.0. Found: C, 23.3; H, 1.4; N, 3.9; Br, 66.7.

The ultraviolet spectra of 2-aminotropone and tribromo-2-aminotropone are given in Fig. 5.

N-Benzoyl-2-aminotropone.—A mixture of 0.020 g. of 2-aminotropone, 0.1 ml. of pyridine and 0.2 ml. of benzoyl chloride was heated on the steam-bath for 5 min. The crystalline product was triturated with 5% aqueous carbonate, dried and crystallized from ethanol; 0.025 g. (67%), m.p. 122–124°. The analytical sample of N-benzoyl-2-aminotropone was obtained as tan needles, m.p. 125–126°.

Anal. Calcd. for $C_{14}H_{11}O_2N$: C, 74.7; H, 4.9; N, 6.2. Found: C, 74.4; H, 5.2; N, 6.1.

2-Phenyltropone (V). (a) **From Tropolone.**—To an ethereal solution of phenyllithium, prepared from 0.460 g. of lithium and 5.14 g. of bromobenzene, there was added rapidly 0.800 g. of tropolone dissolved in 20 ml. of absolute ether. The resulting dark green solution was refluxed for 15 min., and decomposed with 3 *N* sulfuric acid. The oily ether extract was treated with boiling cyclohexane, filtered and concentrated. Sublimation of the residue yielded 0.969 g. (81%) of 2-phenyltropone (V), m.p. 79–83°. One crystallization from cyclohexane gave 0.841 g. (70%) of stout yellow needles, m.p. 83.5–85.5°. An analytical sample was prepared by further recrystallization, m.p. 84.5–85.5°.

Anal. Calcd. for $C_{13}H_{10}O$: C, 85.7; H, 5.5. Found: C, 85.7; H, 5.8.

Treatment of a dry, ethereal solution of V with anhydrous hydrogen bromide precipitates an unstable, solid hydrobromide salt which can be reconverted to the free base by dissolving in hot water, V crystallizing on cooling.

(b) **From 2-Chlorotropone** (I).—To a stirred solution of phenylmagnesium bromide, prepared from 0.065 g. (0.0027 mole) of magnesium and 0.423 g. (0.0027 mole) of bromobenzene in 10 ml. of ether, there was added rapidly 0.303 g. (0.002 mole) of I in 10 ml. of ether. A precipitate formed, disappeared and, as the last portion of I was added, a heavy precipitate reappeared. After refluxing for 15 min., the reaction mixture was decomposed with a solution of 0.290 g. of ammonium chloride in 5 ml. of water. The dried ethereal solution yielded an oily solid, which after crystallization and sublimation afforded 0.233 g. (59%) of V, m.p. 83.5–85.0°.

To an ethereal solution of phenyllithium, prepared from 0.140 g. (0.020 mole) of lithium and 1.57 g. (0.010 mole) of bromobenzene, there was added 0.140 g. (0.001 mole) of I dissolved in 10 ml. of ether. The brown solution was stirred under gentle refluxing for 15 min., the resulting complex being decomposed with 8 ml. of 3 *N* sulfuric acid. The yellow, ethereal layer was washed with a saturated salt solution, dried over magnesium sulfate and concentrated to a viscous, brown oil from which a yellow oil sublimed, which partially crystallized when seeded with V. Crystallization from cyclohexane afforded 0.064 g. of crude V, m.p. 74–78°. There was obtained from the mother liquor a mixture of oil and crystals (0.085 g.) which upon purification through the hydrobromide salt and crystallization from cyclohexane yielded 0.023 g. of V, m.p. 83–85°. The ether-soluble material from the preparation of the hydrobromide was washed well with water, dried and recovered. The infrared spectrum of this oily solid (0.045 g.) showed no band in the carbonyl region, eliminating benzophenone as a possible constituent.

(c) **From Tropolone Methyl Ether.**—To a stirred solution of phenylmagnesium bromide, prepared from 0.054 g. (0.0022 mole) of magnesium and 0.345 g. (0.0022 mole) of bromobenzene in 10 ml. of ether, there was added 0.120 g. (0.00088 mole) of tropolone methyl ether dissolved in 10 ml. of ether. A precipitate formed during the addition. After being stirred at room temperature for 15 min., the complex was decomposed with ammonium chloride, the ether layer being separated, dried and evaporated. The residue yielded 0.145 g. of a sticky, yellow solid on sublimation. Recrystallization from benzene followed by sublimation gave 0.020 g. of V, m.p. 82.5–84.0°.

Hydrogenation of 2-Phenyltropone (V).—V (0.020 g.) was hydrogenated in 2 ml. of 95% ethanol over 7 mg. of platinum oxide. The reaction was stopped after 3.1 molar equivalents of hydrogen had been absorbed. The 2,4-dinitrophenylphenylhydrazone from 0.009 g. of the reduction product melts at 169.4–170.2° and does not show a depressed m.p. on admixture with an authentic sample of the 2,4-dinitrophenylhydrazone of 2-phenylcycloheptanone. At a temperature slightly above its melting point the derivative resolidifies and melts again at 179.5°.

2-*n*-Butyltropone.—To a stirred ethereal solution of *n*-butyllithium, from 0.278 g. (0.040 mole) of lithium and 2.74 g. (0.020 mole) of *n*-butyl bromide, there was added rapidly 0.488 g. (0.004 mole) of tropolone dissolved in 25 ml. of ether. The solution was stirred at room temperature for 30 min. and diluted with 14 ml. of 3 *N* sulfuric acid. The ether layer was washed with water, dried over magnesium sulfate and concentrated to an oil which was evaporatively distilled in a molecular distillation apparatus at 50° and 2–3 mm. 2-*n*-Butyltropone (0.539 g., 83%) distilled as a colorless liquid which turned a light yellow on standing. For analysis the material was redistilled.

Anal. Calcd. for $C_{11}H_{14}O$: C, 81.4; H, 8.7. Found: C, 81.5; H, 8.7.

2-*n*-Butyltropone does not give a picrate but when dry hydrogen bromide is bubbled through an ethereal solution, there separates an oily hydrobromide which solidifies in the cold. The salt is unstable but can be crystallized from acetonitrile as a crystalline solid which, after drying in the air, liberates the original tropone.

2-*n*-Butyltropone, 0.0355 g., was hydrogenated at atmospheric pressure with 0.022 g. of 10% palladium-on-charcoal. in 5 ml. of absolute ethanol. Hydrogen absorption ceased after 3.3 mole equivalents. The ethanol was distilled from the filtered solution and the oily 2-*n*-butylcycloheptanone was converted to its 2,4-dinitrophenylhydrazone which crystallized as golden, irregular plates from ethanol; m.p. 80.0–81.5°.

Anal. Calcd. for $C_{17}H_{24}O_4N_4$: C, 58.6; H, 6.9; N, 16.1. Found: C, 58.8; H, 6.8; N, 16.0.

Tropolone Methyl Ether and Sodiomalonic Ester.—Tropolone methyl ether (0.129 g., 0.00095 mole) was added to a solution of diethyl malonate (0.152 g., 0.00095 mole) in 2 ml. of 0.475 *N* methanolic sodium methoxide. The resulting light orange solution was refluxed on the steam-bath for 40 min., after which time the color had turned a dark brown. Distillation of the methanol left a residue which was diluted with water and filtered. From the ether extract of the filtrate, 0.027 g. of a solid was obtained which crystallized from ethanol in fine, orange needles, m.p. 172.5–173.5°.

Anal. Calcd. for $C_{11}H_6O_4$: C, 64.7; H, 4.0. Found: C, 64.2; H, 4.2.

The ultraviolet spectrum is reported in Fig. 5.

The infrared spectra reported in Figs. 2 and 4 were obtained on a Baird Associates Infrared Spectrophotometer, with a sodium chloride prism. In the case of the solid materials the curves are composed from two spectra, one in carbon tetrachloride and the other in carbon disulfide, at 10% concentration and in 0.1-mm. cells. The liquids were measured neat in 0.025-mm. cells.

The ultraviolet spectra were measured in a Beckmann Instrument Co. Model DU ultraviolet spectrophotometer in the usual manner.

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Dipole Moments and Near Ultraviolet Absorption of Some Monosubstituted Benzenes—The Effect of Solvents and Hydrogen Bonding

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The effect of the solvent on near ultraviolet absorption spectra and dipole moments was studied with aniline, dimethylaniline, phenol and anisole. It was found that both the dipole moment and the shift of the absorption spectrum increase with the refractive index of the solvent, in the case of no specific interaction such as hydrogen bonding. The values of these two quantities are anomalously large when hydrogen bonding is formed between solute and solvent molecules. The effect of hydrogen bonding was studied in detail with phenol and aniline, by the use of mixed solvents which were made by adding a small quantity of the proton acceptor molecules to a normal solvent. The values of ΔF and ΔE due to hydrogen bonding between phenol and several proton acceptors were obtained by the near ultraviolet absorption measurement. From the present experimental results and the theory of the electron migration effect developed by Sklar and Herzfeld, it was concluded that this effect plays an important role in the solvent effect on the dipole moments and the near ultraviolet absorption spectra of phenol, anisole, aniline and dimethylaniline.

Introduction

The effects of substituents on the physical and chemical properties of the benzene molecule have been studied in terms of a resonance and an inductive effect by several workers.[1-6] It has been found that in some monosubstituted benzene molecules, such as phenol or aniline, the resonance effect is especially important in interpreting their dipole moments and near ultraviolet absorption spectra. In these molecules the near ultraviolet absorption spectra usually shift toward the side of longer wave lengths than those of benzene, and the values of the dipole moments are much different from those of the corresponding aliphatic molecules. It is often pointed out that these behaviors are principally due to the resonance effect.[1]

In the present paper, the contribution of the resonance effect to the near ultraviolet absorption spectra and the dipole moments of monosubstituted benzenes is studied by the use of the molecular orbital method developed by Sklar[2] and Herzfeld.[3] The results of these theoretical studies are used in the discussion on the effects of the solvent upon the dipole moment and the absorption spectrum, aniline, dimethylaniline, phenol and anisole being chosen as the materials for research.

Experimental

Purification of Materials.—The details for the purification of aniline, dimethylaniline, phenol, anisole and methanol have been reported previously.[7,8] Hydroquinone dimethyl ether was purified by recrystallization from methanol and ethanol (m.p. 56.3°). The solvents were purified by the method given in "Organic Solvents."[9]

Measurements and Calculations.—The determination of the dielectric constant of various solutions was made by a double beat apparatus described previously.[7] The molecular polarization at infinite dilution $P_{2\infty}$ was calculated by the Halverstadt and Kumler method.[10] From the value of $P_{2\infty}$, the dipole moment was calculated as $\mu = 0.0127\sqrt{(P_{2\infty} - MR_D)T}$.[11]

Near ultraviolet absorption spectra of phenol, anisole, aniline and dimethylaniline in various solvents were determined with a Beckman quartz spectrophotometer model DU and with an E_2 type spectrograph made by the Institute of

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