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The Synthesis and Reactions of 2-Chloro-5-hydroxytropone*1

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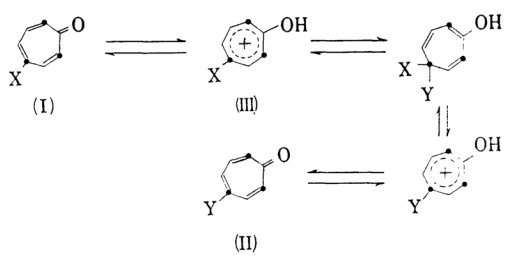
The acid hydrolysis of some polyhalotropones and some reactions of the products were investigated. The treatment of 2, 5-dichlorotropone with hydrochloric or sulfuric acid afforded 2-chloro-5-hydroxytropone (I) and a small amount of 5-chlorotropolone. The compound I gives only one kind of the methyl ether and one kind of the acetyl or benzoyl derivative. From the methyl ether, 5-amino- and 5-methylamino-2-chlorotropone were derived. The methoxyl and the amino groups of these compounds are reactive to alkaline hydrolysis, giving I without any of the skeletal rearrangement usually observed in the alkaline treatment of similar 2-halotropones. The hydrolysis of 2, 4, 7-tribromotropone with hydrochloric acid gave 3, 6-dichlorotropolone and 7-chloro-4-hydroxytropolone.

It is known[1] that 2-halotropones react with alkalis to give benzoic acid derivatives mainly, besides a small amount of tropolones, and that polyhalotropones, under similar treatment, afford benzoic acid and salicylaldehyde derivatives, in addition to considerable amounts of tropolones in some cases.

However, on being heated with strong acids, halotropones, (for example, I; X=halogen), are converted into a conjugated acid cation (III), whose hydrolysis yields hydroxytropone (II; Y=OH) without any rearrangement to benzenoid compounds. When hydrogen halides are used



in this reaction, the exchange of the halogen atom often occurs and a different halotropone (II; Y=halogen) may be obtained besides the products of hydrolysis.[1] Apparently, in the acid treatment of halotropones, halogen atoms located at the 3- or 4-position undergo such reactions easier than those at the 2-position. This is probably due not only to steric interference but also to facile anionoid attack at positions β or δ to the conjugated unsaturated ketone.

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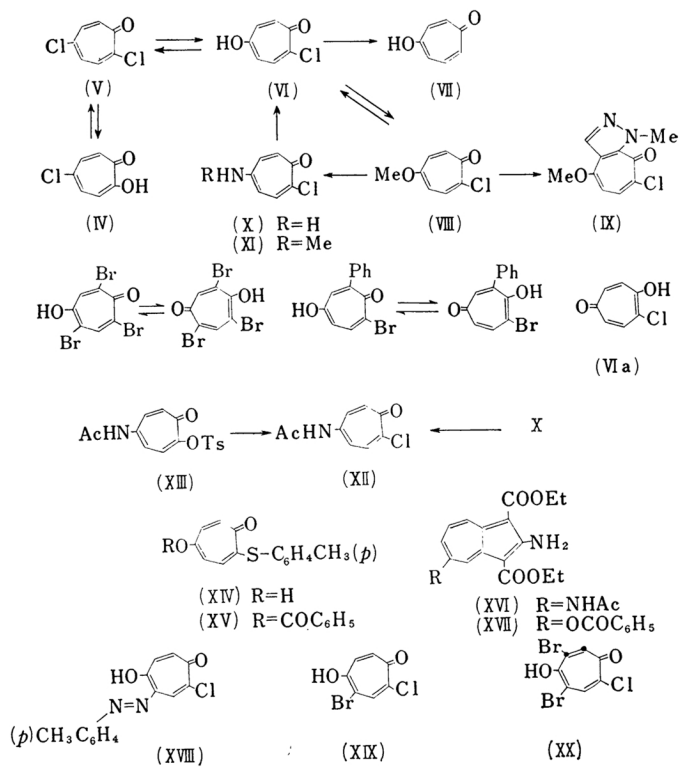
1) T. Nozoe, "Non-Benzenoid Aromatic Compounds," Ed. by D. Ginsburg, Interscience Publishers, New York (1959), p. 410; T. Nozoe et al., "Dai Yuki Kagaku (Comprehensive Organic Chemistry)," Vol. 13, Asakura-Shoten, Tokyo (1960), pp. 181, 217.



For instance, the conversion[2] of 4-bromotropone into 4-hydroxy- or 4-chlorotropone, when it was heated with hydrochloric acid in acetic acid, occured more easily than the conversion of 2-bromotropone into 2-chloro- or 2-hydroxytropone under the same conditions. 3-Bromo-2-chlorotropone gave 2-chloro-3-hydroxytropone and 2, 3-dichlorotropone by a similar treatment, but it did not afford any 3-chlorotropolone.[3] On being heated with concentrated sulfuric acid, 2, 4, 7-tribromotropone[4] and 2-phenyl-4, 5, 7-tribromotropone[5] yielded 4-hydroxy-2, 5, 7-tribromotropone and 5, 7-dibromo-4-hydroxy-2-phenyltropone respectively. The former compound must have been produced by the bromination of 2, 7-dibromo-4-hydroxytropone with bromine that had been generated from the sulfuric acid oxidation of the hydrobromic acid liberated by the initial hydrolysis of 2, 4, 7-tribromotropone.*3

This paper is one of a series devoted to an investigation of the order of relative ease with which halotropones undergo hydrolysis or halogen exchange, and to the utilization of such results in the preparation of 3- or 4-hydroxytropones, whose syntheses have otherwise been difficult. For the present paper, the acid hydrolysis of 2, 5-dichlorotropone and 2, 4, 7-tribromotropone has been investigated, and some reactions of the products have been studied.

2, 5-Dichlorotropone (V),[6] obtained by the reaction of 5-chlorotropolone (IV) and thionyl chloride, on being heated with concentrated hydrochloric acid or concentrated sulfuric acid in acetic acid afforded a considerable amount of pale yellow crystals (VI), m. p. 218°C, and a small amount of 5-chlorotropolone (IV).

The compound VI is acidic and shows a pale green coloration with ferric chloride, but with ferric or cupric ion it does not form a chelate complex which is soluble in chloroform, as is the case with tropolone.

The infrared absorption spectrum of VI in KBr shows OH bands at 3020, 2660 and 2550 cm^{-1} which are assumed to be due to intermolecular hydrogen bonding similar to that found with 4-hydroxytropone.[7,8] The ultraviolet absorption spectrum (Fig. 1) of VI exhibits maxima.

2) a) T. Nozoe, T. Mukai, Y. Ikegami and T. Toda, *Chem. & Ind.*, **1955**, 66; b) T. Nozoe, T. Mukai and Y. Ikegami unpublished work.

3) S. Seto, *Sci. Repts. Tohoku Univ., I*, **37**, 275 (1953).

4) T. Nozoe, Y. Kitahara and H. Abe, *Proc. Japan Acad.*, **29**, 347 (1953).

5) T. Muroi, This Bulletin, **33**, 1166 (1960).

*3 In the early stage of the investigation, it had been explained that the formation of 4-hydroxy-2, 5, 7-tribromotropone proceeded by the direct oxidation of the tropone ring with sulfuric acid. Cf. Ref. 4.

6) T. Sato, *J. Chem. Soc. Japan, Pure Chem. Sect.* (*Nippon Kagaku Zasshi*) **80**, 1771 (1959).

7) R. S. Coffey and A. W. Johnson, *J. Chem. Soc.*, **1958**, 1741.

8) Y. Ikegami, *Kagaku-no-Ryoiki, Extra*, **38**, 46 (1959).

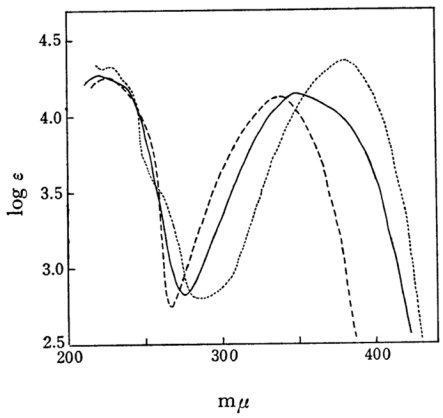


Fig. 1. Ultraviolet absorption spectra.
—— VI in methanol, ····· VI in 0.1 N NaOH,
---- VIII in methanol.

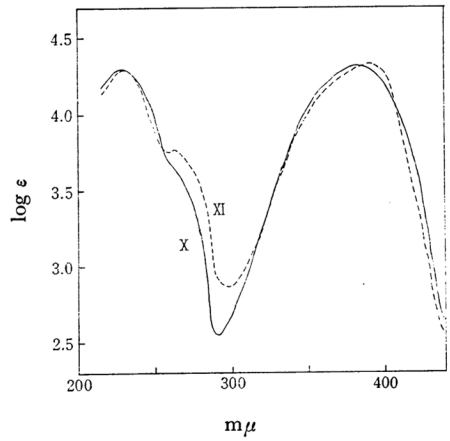


Fig. 2. Ultraviolet absorption spectra of X and XI in methanol.

at wavelengths similar to those observed in the spectrum of 2-bromo-5-hydroxytropone.[7] In addition to the abvoe spectroscopic evidence, VI affords 4-hydroxytropone (VII)[2a,7] on catalytic hydrogenation; therefore, it must be 2-chloro-5-hydroxytropone.

Nozoe et al.[9] and Muroi[10] have reported that a tautomeric relationship exists between 4-hydroxy-2, 5, 7-tribromotropone and 5-hydroxy-2, 4, 6-tribromotropone, and between 5, 7-dibromo-4-hydroxy-2-phenyltropone and 2, 4-dibromo-5-hydroxy-6-phenyltropone, and that in each case the tautomers gave different methyl ethers when allowed to react with diazomethane.

It was thought that VI might also exist as an equilibrium mixture of 2-chloro-5-hydroxytropone and 4-chloro-5-hydroxytropone (VIa); however, the treatment of VI with thionyl chloride afforded only 2, 5-dichlorotropone, and no isomeric 4, 5-dichlorotropone was obtained. Furthermore, compound VI yielded only one acetate, one benzoate and one tosylate, and with diazomethane it afforded only one methyl ether (VIII), besides a nitrogen-containing compound (IX).

Since Nozoe et al.[11] have found that the reaction of halotropones or 4-hydroxytropone with diazomethane gives pyrazolotropone (1-methyl-8-oxocyclohepta[d]pyrazole) derivatives, and since IX was also obtained by the action of diazomethane on the methyl ether (VIII), IX must be the pyrazolotropone derivative, as is shown in the scheme.

The methoxy compound (VIII) was easily hydrolyzed by alkali to give VI. VIII reacts with ammonia and methylamine to afford amino and methylamino compounds (X and XI) respectively; these compounds, on alkaline hydrolysis, yield VI, a reaction similar to the hydrolysis of 2-aminotropone. The ultraviolet absorption spectrum of amino compounds (Fig. 2) are quite different from that of 2-aminotropone,[12] but they are similar to that of 4-aminotropone.[13] The Acetylation of X afforded 5-acetamido-2-chloro tropone (XII), which was also obtained by the action[14] of hydrochloric acid on 5-acetamido-2-tosyloxytropone (XIII); therefore, it is clear that VIII and X are 2-chloro-5-methoxy- and 5-amino-2-chlorotropone respectively.

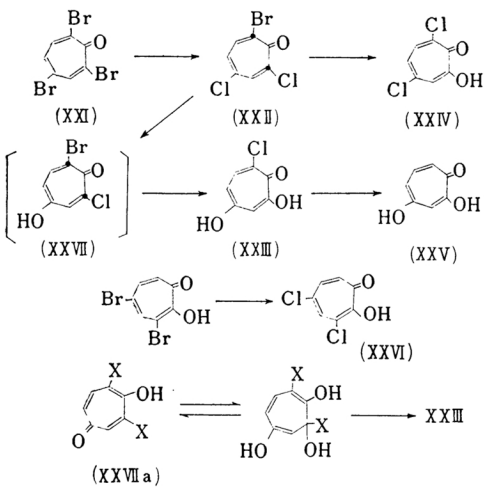
It is known that 5-methoxy-2, 4, 7-tribromotropone,[4] 2, 4-dibromo-5-methoxytropone[15] and 7-bromo-4-methoxy-2-phenyltropone[10] give only the corresponding rearranged compounds, i. e., anisic acid derivatives, upon treatment with alkali or alkoxide, but not the products of a simple hydrolysis, i. e., 4-hydroxytropone derivatives. In contrast to the above, it is noteworthy that the alkaline treatment of the methoxy compound (VIII) afforded only hydroxytropone (VI).

As has been mentioned above, the methoxyl group of VIII underwent anionoid substitution reaction; however, the reaction of *p*-tolylthiophenol with 2-chloro-5-hydroxytropone (VI) or its benzoyl derivative yielded 2-(*p*-tolylthio)tropone derivatives (XIV or XV respectively). 5-Acetamido-2-chlorotropone (XII) and the benzoyl derivative of VI reacted with ethyl cyanoacetate, in the same way as do 2-chlorotropones, to give 5-acetamido-[16] and 5-benzoyloxyazulene derivatives (XVI and XVII respectively).

9) T. Nozoe, Y. Kitahara, J. Shin and T. Toda, to be published.
10) T. Muroi, This Bulletin, **34**, 178 (1961).
11) T. Nozoe, T. Mukai and T. Asao, to be published.
12) T. Nozoe, S. Seto, H. Takeda, S. Morosawa and K. Matsumoto, *Proc. Japan Acad*, **27**, 556 (1951); *Sci. Repts. Tohoku Univ., I*, **36**, 126 (1952).
13) K. Doi, This Bulletin, **33**, 887 (1960).
14) H. Matsumura, *J. Chem. Soc. Japan, Pure Chem. Sect.* (*Nippon Kagaku Zasshi*), **82**, 623 (1961).
15) T. Mukai, unpublished results.
16) T. Nozoe, K. Takase and M. Tada, This Bulletin, **36**, 1006 (1963).

With diazotized *p*-toluidine, 2-chloro-5-hydroxytropone (VI) reacted, similarly to 4-hydroxytropone, to give the azo compound (XVIII), The bromination of VI yielded 4-bromo-2-chloro-5-hydroxytropone (XIX) and 4, 6(or 4, 7)-dibromo-2-chloro-5-hydroxytropone (XX). The structures of these compounds were assumed to be as above from the reactivity of 4-hydroxytropone[2a]; however, the position of the second bromine atom in XX was not clarified.

When 2, 4, 7-tribromotropone (XXI) was heated with hydrochloric acid in acetic acid at 100°C for one hour, it gave dichloromonobromotropone (XXII), whereas the same solution, on being heated at 135°C for 10 hr., afforded 70% of chlorodihydroxytropone (XXIII) and 10% of dichlorohydroxytropone (XXIV). The compounds XXIII and XXIV were also obtained by a similar acid treatment of XXII. The dihydroxytropone (XXIII) was identified as 7-chloro-4-hydroxytropolone since, on hydrogenolysis, it



gave 4-hydroxytropolone (XXV).[17] Compound XXIV was not identical with 3, 5-dichlorotropolone (XXVI), obtained by the anionoid substitution of 3, 5-dibromotropolone[18] with hydrochloric acid; therefore, it must be 3, 6-dichlorotropolone.

During the treatment of polyhalotropones with acids, the halogen at the γ-position (C_4) undergoes anionoid substitution more easily than that at the α-position (C_2 or C_7); therefore, XXII is assumed to be 7-bromo-2, 4-dichloro- or 2-bromo-4, 7-dichlorotropone.

As has been shown above, the vigorous treatment of XXI or XXII with hydrochloric acid caused the hydrolysis of the halogens at the 2- and 4-positions, but not at the 7-position. This may indicate that the 2- and 4-positions, in both XXI and XXII, are more reactive than the 7-position.

It is considered that XXII undergoes a competitive hydrolysis of the halogen at the 2- and 4-positions to give XXIV and XXVII, and that there is no further hydrolysis of XXIV under these reaction conditions, whereas the further hydrolysis of XXVII proceeds through its tautomeric form (XXXVIIa) to yield XXIII.

Further investigations are being undertaken to clarify the above reaction path, and to study the reactivity of the 4-hydroxy- and 2, 4-dihydroxytropones which were obtained in this work.

Experimental*4

The Treatment of 2, 5-Dichlorotropone (V) with Hydrochloric Acid.—a) A solution of 2, 5-dichlorotropone (2 g.) in acetic acid (15 ml.) containing water (0.1 ml.) was saturated with hydrogen chloride gas; the solution was then kept at 110°C for 10 hr. in a sealed tube. The solvent was removed, and the residue was extracted with benzene. The insoluble part (1.65 g.) was recrystallized from ethanol to give 2-chloro-5-hydroxytropone (VI) as yellow needles, m. p. 217—218°C.

Found: C, 53.69; H, 3.16. Calcd. for $C_7H_5O_2Cl$: C, 53.69; H, 3.20%.

λ_{max}^{MeOH} mμ (log ε): 220(4.27), 350(4.14).

$\lambda_{max}^{0.1N\ NaOH}$ mμ (log ε): 228(4.33), 260^{sh} (3.52), 381-(4.37).

From the benzene-soluble part, 5-chlorotropolone (IV) (200 mg.) was obtained after being recrystallized from methanol.

b) After a solution of 2, 5-dichlorotropone (3 g.) in acetic acid (27 ml.) and concentrated hydrochloric acid (15 ml.) in a sealed tube had been allowed to stand at 100°C for 10 hr., the solvent was evaporated. By treating the residue described above, 2.2 g. of VI and 300 mg. of IV were obtained.

The Treatment of 2, 4, 7-Tribromotropone (XXI) with Hydrochloric Acid.—a) A solution of 2, 4, 7-tribromotropone (500 mg.) in acetic acid (10 ml.) saturated with hydrochloric acid gas was kept in a sealed tube at 100°C for 10 hr. The colorless needles precipitated out by cooling the solution in an ice box were recrystallized from cyclohexane, yielding colorless needles (XXII), m. p. 149—150°C.

Found: C, 32.70; H, 1.25. Calcd. for $C_7H_3OBrCl_2$: C, 32.12; H, 1.91%.

b) A solution of XXI (500 mg.) in a mixture of acetic acid (4 ml.) and concentrated hydrochloric acid (3 ml.) was kept in a sealed tube at 135—140°C for 10 hr. The residue which was obtained by removing the solvent was dissolved in water and extracted with benzene and then with ethyl acetate. The yellow powder obtained from the extract with ethyl acetate was washed with benzene, and the insoluble part (130 mg.) was recrystallized from dilute ethanol giving yellow long prisms, 3-chloro-6-hydroxytropolone

17) T. Nozoe and Y. Kitahara, *Proc. Japan Acad.*, **30**, 214 (1954); Y. Kitahara, *Sci. Repts. Tohoku Univ., I*, **39**, 258 (1956).
18) T. Nozoe, Y. Kitahara, K. Yamane and A. Yoshikoshi, *Proc. Japan Acad.*, **27**, 18 (1951).

*4 All melting points are uncorrected.

(XXIII), m. p. 242°C.

Found: C, 48.71; H, 3.13. Calcd. for $C_7H_5O_3Cl$: C, 48.72; H, 2.92%.

λ_{max}^{MeOH} mμ (log ε): 255(4.47), 340(3.81), 367(3.93).

The residue obtained by removing the solvent from the benzene extract was recrystallized from cyclohexane affording crystals of 3, 6-dichlorotropolone (XXIV), m. p. 129—130°C.

Found: C, 44.26; H, 2.36. Calcd. for $C_7H_4O_2Cl_2$: C, 44.02; H, 2.11%.

λ_{max}^{MeOH} mμ (log ε): 252(4.39), 336(3.98), 377(3.75), 388(3.75), 397^{sh}(3.68), 428(3.31).

The Treatment of XXII with Hydrochloric Acid.—A solution of XXII (500 mg.) in acetic acid (5 ml.) and concentrated hydrochloric acid (3 ml.) was heated around 140°C for 10 hr. in a sealed tube. The solvents were removed under reduced pressure, and the residue was separated into a soluble part (260 mg.) and an insoluble part in benzene. The former was sublimed under reduced pressure to give 114 mg. of sublimate, which was then recrystallized from dilute ethanol to give XXIII, m. p. 240—242°C. The insoluble part in benzene was sublimed in vacuo to afford 30 mg. of the sublimate, which was then recrystallized from methanol, giving XXIV, m. p. 129—130°C. The infrared spectra of both of the compounds were superimposable upon those of XXIII and XXIV respectively, which had been obtained before.

The Reduction of 7-Chloro-4-hydroxytropolone (XXIII).—A solution of XXIII (50 mg.) and sodium acetate (25 mg.) in ethanol (6 ml.) was submitted to catalytic hydrogenation in the presence of 5% Pd-C (20 mg.); 9 ml. of hydrogen was thus absorbed. The residue obtained by removing the solvent was sublimed in vacuo, yielding yellow crystals, m. p. 191—194°C. Recrystallization from acetic acid gave yellow crystals (10 mg.), m. p. 221—223°C, these crystals showed no depression of melting point on admixture with 4-hydroxytropolone (XXV), m. p. 225—226°C, obtained by the alkaline hydrolysis of 3-bromotropolone.[9]

3, 5-Dichlorotropolone. — A solution of 3, 5-dibromotropolone (100 mg.) in acetic acid (4 ml.) and concentrated hydrochloric acid (3 ml.) was refluxed for 10 hr. The solvent was removed, and the residue was recrystallized from benzene-cyclohexane, affording micro needles of 3, 5-dichlorotropolone (XXVI), m. p. 138—139°C.

Found: C, 44.00; H, 2.50. Calcd. for $C_7H_4O_2Cl_2$: C, 44.02; H, 2.11%.

The Reduction of 2-Chloro-5-hydroxytropone (VI).—A solution of VI (100 mg.) and sodium acetate (55 mg.) in methanol (9 ml.) was submitted to catalytic hydrogenation using 5% Pd-C (40 mg.) as a catalyst; 13 ml. of hydrogen was thus absorbed. The removal of the solvent left yellow crystals, which were then sublimed under reduced pressure. The recrystallization of the sublimate from methanol afforded yellow needles (50 mg.), m. p. 210°C (decomp.), which showed no depression of melting point on admixture with authentic 4-hydroxytropone (VII).

5-Acetoxy-2-chlorotropone.—After a solution of 2-chloro-5-hydroxytropone (100 mg.) and acetic anhydride (3 ml.) had been heated at 110°C for one hour, the solution was poured onto ice and extracted with benzene; the extract was dried over sodium sulfate, and the solvent was removed. The residue was recrystallized from cyclohexane, giving 5-acetoxy-2-chlorotropone (80 mg.) as colorless needles, m. p. 101.5—102°C.

Found: C, 54.81; H, 3.34. Calcd. for $C_9H_7O_3Cl$: C, 54.42; H, 3.55%.

5-Benzoyloxy-2-chlorotropone.—To a solution of 2-chloro-5-hydroxytropone (500 mg.) in pyridine (4 ml.), benzoyl chloride (450 mg.) was added, the mixture was then poured onto ice. The crystals (800 mg.) which precipitated out were recrystallized from ethanol to afford 5-benzoyloxy-2-chlorotropone (650 mg.) as colorless needles, m. p. 153—154°C.

Found: C, 64.48; H, 3.31. Calcd. for $C_{14}H_9O_3Cl$: C, 64.50; H, 3.48%.

2-Chloro-5-tosyloxytropone.—To a solution of 2-chloro-5-hydroxytropone (600 mg.) in pyridine (6 ml.), *p*-toluenesulfonyl chloride (740 mg.) was added. After having been allowed to stand at room temperature for 20 min., the solution was poured onto ice to give colorless crystals (680 mg.), m. p. 110—115°C. Recrystallization from ethanol afforded 2-chloro-5-tosyloxytropone (600 mg.) as colorless needles, m. p. 119—120°C.

Found: C, 54.46; H, 3.30. Calcd. for $C_{14}H_{11}O_4SCl$: C, 54.11; H, 3.57%.

The Reaction of VI with Thionyl Chloride.—By gentle refluxing the suspended mixture of VI (100 mg.) in thionyl chloride (2 ml.), VI was gradually dissolved. After 30 min., the excess thionyl chloride was removed in vacuo; the residue was extracted with benzene, and the extract was washed with water and dried. The crystals which were obtained after passing the benzene solution through an alumina column were sublimed and then recrystallized from cyclohexane, yielding pale yellow needles (65 mg.). This crystals showed no depression of melting point on admixture with 2, 5-dichlorotropone.

The Methylation of VI with Diazomethane.—To a suspension of VI (2 g.) in ether (30 ml.), an ethereal solution of diazomethane prepared from *N*-nitrosomethylurea (2 g.) was added; the mixture was then allowed to stand in an ice box for 50 hr. The starting material (700 mg.) was recovered as an insoluble part by filtration, the solvent was removed from the filtrate in vacuo, and the residue was dissolved in ether and passed through an alumina column. From the rapidly-eluted fraction by ether, crystals (1.1 g.), m. p. 85—90°C, were obtained, and recrystallization from cyclohexane afforded colorless plates, m. p. 91—92°C, of 2-chloro-5-methoxytropone (VIII).

Found: C, 56.42; H, 3.99. Calcd. for $C_8H_7O_2Cl$: C, 56.34; H, 4.04%.

λ_{max}^{MeOH} mμ (log ε): 225(4.25), 338(4.13).

From the latter fraction of elution, crystals (50 mg.), m. p. 190—193°C, were obtained. Recrystallization from ethanol gave colorless needles (IX), m. p. 195—196°C.

Found: C, 53.80; H, 3.84; N, 12.24. Calcd. for $C_{10}H_9O_2N_2Cl$: C, 53.47; H, 4.04; N, 12.48%.

5-Hydroxy-2-(*p*-tolylthio)tropone (XIV).—A solution of VI (156 mg.), *p*-thiocresol (152 mg.) and sodium hydroxide (45 mg.) in ethanol (20 ml.) was refluxed for 30 min. A small amount of the precipitate was removed, and the filtrate was evaporated, leaving a yellow solid, which was then washed with water and

recrystallized from methanol, yielding 95 mg. of yellow micro prisms (XIV), m. p. 231—232°C (decomp.).

Found: C, 68.76; H, 4.72. Calcd. for $C_{14}H_{12}O_2S$: C, 68.84; H, 4.95%.

5-Benzoyloxy-2-(*p*-tolylthio)tropone (XV). — A solution of 5-benzoyloxy-2-chlorotropone (245 mg.), *p*-thiocresol (152 mg.) and sodium hydroxide (45 mg.) in ethanol (20 ml.) was refluxed for 10 hr. The solvent was removed, and the residue was dissolved in water, extracted with benzene, and dried. The crystals obtained by removing the benzene were recrystallized from methanol; 150 mg. of greenish yellow plates (XV), m. p. 159—160°C, were thus obtained.

Found: C, 72.59; H, 4.57. Calcd. for $C_{21}H_{16}O_3S$: C, 72.40; H, 4.63%.

5-Amino-2-chlorotropone (X).—a) A solution of 2-chloro-5-methoxytropone (VIII) (100 mg.) in ethanol (20 ml.) saturated with ammonia was allowed to stand at room temperature for 3 days. The removal of the solvent afforded crystals (90 mg.), m. p. 187—190°C, which were then recrystallized from methanol, giving 5-amino-2-chlorotropone (X) as yellow needles, m. p. 204—205°C.

Found: C, 53.75; H, 3.85; N, 9.21. Calcd. for C_7H_6ONCl: C, 54.04; H, 3.89; N, 9.00%.

λ_{max}^{MeOH} mμ (log ε): 230(4.28), 260^{sh}(3.67), 383(4.32).

b) After a mixture of VIII (200 mg.) and liquid ammonia (5 ml.) had been kept at room temperature overnight, the excess ammonia was removed. The residue was dissolved in chloroform, passed through an alumina column, and recrystallization from methanol gave yellow needles (80 mg), m. p. 203—204°C, which showed no depression of melting point on admixture with 5-amino-2-chlorotropone obtained in procedure a).

2-Chloro-5-methylaminotropone (XI). — A solution of VIII (130 mg.) and a 28% aqueous solution of methylamine (0.2 ml.) in methanol (3 ml.) was kept at room temperature for 4 days. The solvent was removed, and the residue was recrystallized from ethanol-ether, giving 2-chloro-5-methylaminotropone (80 mg.) as yellow plates, m. p. 148—149°C.

Found: C, 56.98; H, 4.79; N, 8.20. Calcd. for C_8H_8ONCl: C, 56.65; H, 4.77; N, 8.26%.

λ_{max}^{MeOH} mμ (log ε): 230(4.29), 365(3.75), 390(4.32).

5-Acetamido-2-chlorotropone (XII).—a) After a solution of X (50 mg.) in acetic anhydride (0.5 ml.) had been refluxed for 10 min., the acetic anhydride was removed; the recrystallization of the residue from ethanol afforded XII (50 mg.) as colorless needles, m. p. 210—212°C.

Found: C, 54.56; H, 4.03; N, 7.09. Calcd. for $C_9H_8O_2NCl$: C, 54.70; H, 4.03; N, 7.09%.

λ_{max}^{MeOH} mμ (log ε): 223(4.23); 248(4.15), 269^{sh}(3.91), 350(4.17), 370^{sh}(4.06).

b) After a suspension of 5-acetamido-2-tosyloxytropone (220 mg.) in dioxane (10 ml.) had been saturated with dry hydrogen chloride gas, it was warmed at 80°C for 5 min. The tosyloxytropone had disappeared; it was replaced by colorless crystals. After the reaction mixture had been cooled in an ice box for 2 hr., the precipitate was filtered, affording colorless crystals (120 mg.), which were then recrystallized from ethanol to gave colorless needles, m. p. 210—212°C; these needles showed no depression of melting point on admixture with the sample obtained in procedure a).

5-Acetamido-2-tosyloxytropone (XIII).—To a solution of 5-acetamidotropolone (550 mg.) in pyridine (2.5 ml.), *p*-toluenesulfonyl chloride (1 g.) was added, and the mixture was heated at 80°C for one hour. Water (50 ml.) was added, and the precipitate was filtered, washed with water, and recrystallized from ethanol to give 1.1 g. of XIII as pale yellow micro plates, m. p. 177—178°C.

Found: C, 57.26; H, 4.65; N, 3.90. Calcd. for $C_{16}H_{15}O_5NS$: C, 57.66; H, 4.54; N, 4.20.

λ_{max}^{MeOH} mμ (log ε): 228(4.42), 262^{sh}(4.03), 344(4.16).

Diethyl 2-Amino-5-acetamidoazulene-1, 3-dicarboxylate (XVI).—To a solution of ethyl cyanoacetate (180 mg.) in a sodium ethoxide solution prepared from ethanol (10 ml.) and sodium (20 mg.), XII (140 mg.) was added; the mixture was then kept at room temperature for 3 days. The solvent was removed in vacuo, water was added, and the insoluble part was recrystallized from ethanol, giving yellow crystals (110 mg.), m. p. 178—180°C. This was identified as diethyl 2-amino-5-acetamidoazulene-1, 3-dicarboxylate[16] by a mixed melting point determination and by a comparison of their infrared spectra.

Diethyl 2-Amino-5-benzoyloxyazulene-1, 3-dicarboxylate (XVII).—To a solution of sodium ethoxide prepared from 70 mg. of sodium in anhydrous ethanol (20 ml.), ethyl cyanoacetate (560 mg.) and 5-benzoyloxy-2-chlorotropone (520 mg.) were added. After the mixture had been kept at room temperature for a day, the solvent was removed, water was added, and the solution was extracted with chloroform and then dried. The extract was passed through an alumina column, and 100 mg. of yellow crystals, m. p. 124—127°C, were obtained. Recrystallization from ether gave yellow crystals (XVII), m. p. 129—130°C.

Found: C, 67.65; H, 5.19; N, 2.91. Calcd. for $C_{23}H_{21}O_6N$: C, 67.80; H, 5.20; N, 3.44%.

λ_{max}^{MeOH} mμ (log ε): 245(4.66), 317(4.78), 327(4.88), 370(3.94), 390(3.96), 450(3.44).

When the original water layer was acidified with 2 N sulfuric acid, 180 mg. of a precipitate was obtained. This precipitate was dissolved in methanol and treated with charcoal; yellow crystals, m. p. over 300°C, were thus obtained. The structure of these crystals was not determined.

2-Chloro-5-hydroxy-4-(*p*-tolylazo)tropone (XVIII). — To a stirred solution of VI (156 mg.) and potassium hydroxide (80 mg.) in water (3 ml.), diazotized *p*-toluidine prepared from 118 mg. of *p*-toluidine was added drop by drop. The precipitate was filtered and washed with water, giving 250 mg. of a reddish solid. Recrystallization from benzene-cyclohexane afforded deep red micro needles (XVIII), m. p. 176—177°C.

Found: C, 61.56; H, 3.65; N, 10.45. Calcd. for $C_{14}H_{11}O_2N_2Cl$: C, 61.20; H, 4.04; N, 10.21%.

The Bromination of 2-Chloro-5-hydroxytropone. —To a stirred solution of VI (312 mg.) in acetic acid (8 ml.), bromine (700 mg.) in acetic acid (1 ml.) was added drop by drop at room temperature. The reaction mixture was then allowed to stand overnight, giving 320 mg. of a precipitate. The recrystallization of the precipitate from dilute ethanol afforded pale yellow needles of 2-bromo-4-chloro-5-hydroxytropone (XIX), m. p. 178—179°C.

Found: C, 35.27; H, 2.20; Calcd. for $C_7H_4O_2ClBr$: C, 35.70; H, 1.64%.

The filtrate obtained from the original reaction mixture was evaporated, and the residue was extracted with ethyl acetate. Crystals obtained from the extract were recrystallized from dilute ethanol, affording pale yellow crystals (XX), m. p. 211—212°C.

Found: C, 28.07; H, 1.63. Calcd. for $C_7H_3O_2ClBr_2$: C, 26.72; H, 0.96%.