Some Cationoid Reactions of 4-Ethyltropolone

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Since the steric effect of the side-chain in troponoid compounds is generally larger than in benzenoid compounds, because of a planar, seven-membered ring, tropolone and its homologs often show interesting unexpected behavior in some reactions(1) in which benzenoid compounds react normally. Although the chemical and physical properties of 4-methyl- and 4-isopropyl-tropolone have extensively been studied,(2) the properties of 4-ethyltropolone have scarcely been known; it has been synthesized only in a poor yield from 4-ethylcycloheptane-1, 2-dione.(3) In this paper, we wish to report on a new synthesis of 4-ethyltropolone (I) and on some of its reactions.

4-Ethyltropolone (I) was synthesized from 4-acetyltropolone (II)(4) by the Huang-Minlon reduction. When heated with hydrazine, II afforded the hydrazone (III), which gave I when heated with potassium hydroxide in ethylene glycol. The yield of I from II was about 60%. When the reduction was carried out without the isolation of the hydrazone, I was not obtained, but a polymerized substance was formed. Besides the known copper chelate,(3) I gave a cyclohexylamine and dicyclohexylamine salts.

The azo-coupling of I with *p*-toluenediazonium chloride gave a *p*-tolylazo compound (IV).(3) The nitration of I gave a mononitro (V) or dinitro compound (VI), according to the variation in the reaction conditions. The action of 1-3 molar equivalents of fuming nitric acid on I afforded V, while 1-4 molar equivalents of concentrated nitric acid gave mainly VI. However, in one experiment, in which one molar equivalent of concentrated nitric acid was used, a trinitro compound (VII) was isolated in a poor yield, although these results could not be reproduced. The amino compound (VIII) obtained by the catalytic reduction of V was identical with that derived from the azo compound (IV) by similar reduction. Since IV has an azo group at the 5-position,(5) V and VIII were assumed to be 4-ethyl-5-nitro- and 5-amino-4-ethyltropolone respectively. The amine (VIII) was easily diazotized by sodium nitrite and an acid, and 5-chloro-4-ethyl- (IX) and 5-bromo-4-ethyltropolone (X) were prepared by Sandmeyer reaction. The heating of the dinitro compound (VI) in methanol for a few minutes afforded a colorless neutral compound (XI) in a good yield. On the basis of its ultraviolet absorption spectrum, this compound is considered to be a benzenoid compound produced by the rearrangement reaction. From such a similarity in chemical behavior between VI and 4-methyl-5, 7-dinitro-(6) or 4-isopropyl-5, 7-dinitrotropolone,(7) which afforded methyl 3-methyl-4, 6-dinitrobenzoate and methyl 3-isopropyl-4, 6-dinitrobenzoate in the same treatment, the dinitro compound (VI) and the rearranged product (XI) were assumed to be 4-ethyl-5, 7-dinitrotropolone and methyl 3-ethyl-4, 6-dinitrobenzoate respectively. The trinitro compound (VII) was assumed to be 4-ethyl-3, 5, 7-trinitrotropolone from its ultraviolet and infrared spectra, which are similar to those of 3, 5, 7-trinitrotropolone,(8) although it showed a negative ferric chloride coloration and was stable when heated with alcohol.

The bromination of 4-ethyltropolone (I) with a molar equivalent of bromine in methanol afforded as the main product a monobromo compound (XII)(9) which was different from the monobromo compound (X), besides a dibromo compound (XIII) and a tribromo compound (XIV). On the other hand, when two molar equivalents of bromine were used, besides XIV an isomeric dibromo compound (XV) was obtained in a good yield. When three molar equivalents of

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1) T. Nozoe, *Nature*, **167**, 1055 (1951); *Fortschr. Chem. org. Naturstoffe*, **13**, 233 (1956).

2) Cf. T. Nozoe et al., "Dai Yuki Kagaku (Comprehensive Organic Chemistry)," Vol. 13, Chapters 5—9, Asakura Shoten, Tokyo (1960), esp. pp. 156, 160.

3) T. Nozoe, T. Mukai and S. Matsumoto, *Proc. Japan Acad.*, **27**, 110 (1951).

4) T. Nozoe, K. Takase and M. Ogata, *Chem. & Ind.*, **1957**, 1070.

5) It is known that the azo-coupling to a tropolone ring usually occurs at the 5-position.(1)

6) T. Nozoe, T. Mukai, M. Kunori, T. Muroi and K. Matsui, *Sci. Repts. Tohoku Univ.*, *I*, **35**, 242 (1951); T. Muroi, *Bulletin Yamagata University, Natural Science*, **3**, 155 (1954); R. D. Haworth and P. R. Jefferies, *J. Chem. Soc.*, **1951**, 2067.

7) T. Nozoe, Y. Kitahara, E. Kunioka and K. Doi, *Proc. Japan Acad.*, **26** (9), 38 (1950); E. Sebe, *Sci. Repts. Tohoku Univ.*, I, **36**, 99 (1952).

8) T. Nozoe, M. Oyama and K. Kikuchi, This Bulletin, **36**, 168 (1963).

9) This compound, m. p. 67.5—69°C, was identical with the monobromo compound, m. p. 66°C, formerly obtained by the bromination of 4-ethylcycloheptane-1,2-dione.(3)

bromine were used in the presence of sodium acetate, the tribromo compound (XIV) was obtained in a good yield. The monobromo compound (XII) is assumed to be 7-bromo-4-ethyltropolone on the basis of the following evidence. The azo-coupling of XII gave a crystalline azo compound (XVI).[5] The infrared spectrum of XII is quite similar to that of 7-bromo-4-isopropyltropolone[10] in the region of out-of-plane C-H deformation vibrations. The dibromo compound (XV) is assumed to be 3, 7-dibromo-4-ethyltropolone, since it was also obtained by the bromination of XII and gave a crystalline azo compound (XVII) by azo-coupling. Therefore, another dibromo compound (XIII) is assumed to be 5, 7-dibromo-4-ethyltropolone. The tribromo compound (XIV) is considered to be 3, 5, 7-tribromo-4-ethyltropolone since it was obtained from X, XII and XV by bromination. The formation of the tribromo derivative (XIV) by the bromination of I shows that the steric hindrance of the ethyl group is smaller than that of the isopropyl group,[11] as was expected. On the other hand, the formation of the dibromo compound (XIII) is similar in tendency to the bromination of 4-isopropyltropolone[2,10] rather than to that of 4-methyltropolone.[2]

The treatment of I with iodine, in the presence of potassium carbonate, afforded 4-ethyl-7-iodotropolone (XVIII), the structure of which was based on the following evidence. The azo-coupling of XVIII gave a crystalline azo compound (XIX),[5] and it was known that the iodination of tropolones, under these conditions, generally give 3 (or 7)-iodotropolones. Furthermore, the infrared spectrum of XVIII is similar to that of 7-iodo-4-isopropyltropolone[12] in the region of out-of-plane C-H deformation vibrations.

When heated in acetic acid or ethanol, the 5-arylazo derivatives of 4-isopropyltropolone are known to give, especially in the presence of acid or benzoquinone, the reddish-purple "hinopurpurine," whose structure was established to be 2-aryl-3, 3-dimethyl-2, 3, 5, 6-tetrahydro-5, 6-cyclohepta[c]pyrazoledione (XX).[13] On the other hand, it has been reported[3] that 4-ethyl-5-(*p*-tolylazo)tropolone (IV) gives, on heating in acetic acid in the presence of hydrochloric acid, no hinopurpurin-like, highly colored compound, but an unidentified brown crystals with a m. p. of 210°C. The reexamination of this reaction gave pale yellow needles with a m. p. of 203°C, which were proved

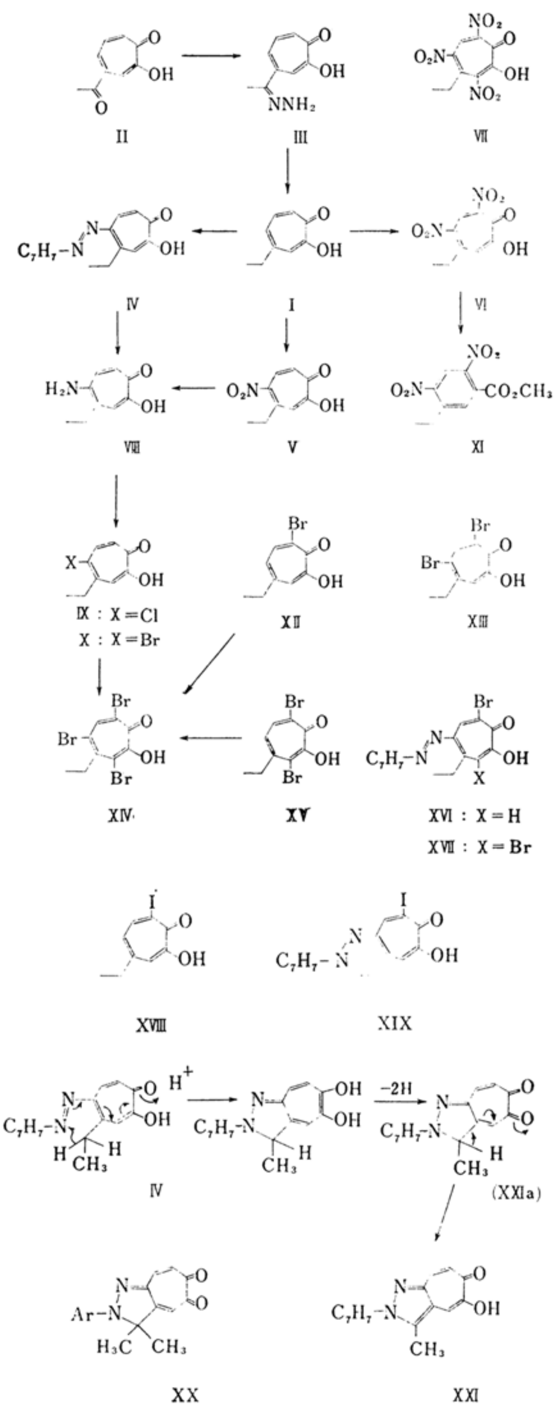

Chart 1. The mechanism of the cyclization reaction of 4-ethyl-5-(*p*-tolylazo)tropolone (IV).

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[10] T. Nozoe, E. Sebe, S. Mayama and S. Iwamoto, *Sci. Repts. Tohoku Univ.*, *I*, **36**, 184 (1952).

[11] 3,5,7-Tribromo-4-isopropyltropolone was only obtained by the heating of the bromine-addition product of 4-isopropyltropolone; T. Nozoe, K. Takase and M. Yasunami, to be published.

[12] T. Nozoe, E. Sebe, L. S. Cheng, S. Mayama and T. J. Hsü, *Sci. Repts., Tohoku Univ.*, *I*, **36**, 299 (1952); Y. Kitahara and T. Arai, *Proc. Japan Acad.*, **27**, 423 (1951).

[13] T. Nozoe, T. Ikemi and T. Ozeki, *Proc. Japan Acad.*, **31**, 455 (1955) and the references therein cited.

to be identical with 5-hydroxy-3-methyl-2-(*p*-tolyl)-6(2*H*)-cyclohepta[c]pyrazolone (XXI)[14] obtained by the ring closure of the *p*-tolylazo derivatives of 4-(1-hydroxyethyl)- or 4-(1-acetamidoethyl)tropolone. The mechanism of the formation of XXI from IV is thought to be similar to that of the hinopurpurin-formation,[13] as is shown in Chart 1, the reaction is facilitated in the presence of iodine or benzoquinone, as was to be expected from the inevitable dehydrogenation process. In this case, however, the hinopurpurin-like diketone (XXIa) easily tautomerizes to the more stable enolic form (XXI), since XXIa, being different from hinopurpurin, has a mobile hydrogen at the 3-position.

Experimental[15]

4-(1-Hydrazonoethyl)tropolone (III).—A mixture of 4-acetyltropolone (II) (16.4 g.), ethanol (20 ml.), and 80% hydrazine hydrate (9 ml.) was heated while being stirred in a boiling-water bath until the orange crystals turned yellow. After they had been allowed to cool, the crystals were collected by filtration and washed with ethanol to give III (16.6 g.) as yellow needles, m. p. 193°C (decomp.).

Found: C, 60.51; H, 5.37; N, 15.50. Calcd. for $C_9H_{10}O_2N_2$: C, 60.66; H, 5.66; N, 15.72%.

N-Acetyl Derivative: M. p. 188—189°C, yellow prisms (from glacial acetic acid).

Found: C, 60.43; H, 5.19; N, 12.22. Calcd. for $C_{11}H_{12}O_3N_2$: C, 59.99; H, 5.49; N, 12.72%.

4-Ethyltropolone (I).—To a solution of potassium hydroxide (8.8 g.) in ethylene glycol (40 ml.), III (16.6 g.) was added; the mixture was then heated at 140—150°C for 10 hr. The reaction mixture was poured into water (600 ml.) and acidified with 6 N hydrochloric acid, and the oily substance which separated out was extracted three times with chloroform. The solvent was evaporated and the residue was recrystallized from petroleum ether to give I (4.83 g.) as colorless rhombic prisms, m. p. 42—43°C; reported[3] m. p. 42°C.

Found: C, 72.05; H, 6.55. Calcd. for $C_9H_{10}O_2$: C, 71.98; H, 6.71%. λ_{max}^{MeOH} mμ (log ε); 240 (4.48), 327 (3.87).

Copper Chelate: m. p. 157—158°C, reported[3] m. p. 156°C, pale green crystals (from ethanol).

Found: C, 59.39; H, 4.80. Calcd. for $(C_9H_9O_2)_2$-Cu: C, 59.74; H, 5.01%.

Cyclohexylamine Salt.: m. p. 159—160°C pale yellow crystals (from cyclohexane).

Found: C, 72.64; H, 9.44; N, 5.65. Calcd. for $C_{15}H_{23}O_2N$: C, 72.25; H, 9.30; N, 5.62%.

Dicyclohexylamine Salt.: m. p. 118—119°C, yellow crystals (from cyclohexane).

Found: C, 76.07; H, 9.61; N, 3.59. Calcd. for $C_{21}H_{33}O_2N$: C, 76.09; H, 10.03; N, 4.23%.

4-Ethyl-5-(*p*-tolylazo)tropolone (IV). — Into a solution of I (750 mg.) in pyridine (10 ml.) a solution of *p*-toluene diazonium chloride, prepared by diazotizing *p*-toluidine (600 mg.) in the usual manner, was stirred while the mixture was being cooled an azo compound began to separate during the addition. After the mixture had been stirred for an additional 2 hr., water (10 ml.) was added, and the crystals thereby formed were collected and recrystallized from benzene to give IV (1.27 g.) as red needles m. p. 142—143°C; reported[3] m. p. 141—142°C.

Found: C, 71.38; H, 5.89; N, 10.49. Calcd. for $C_{16}H_{16}O_2N_2$: C, 71.62; H, 6.01; N, 10.44%. λ_{max}^{MeOH} mμ (log ε); 233 (4.42), 292 (4.07), 395 (4.43).

4-Ethyl-5-nitrotropolone (V).—Into a solution of I (300 mg.) in glacial acetic acid (1 ml.), fuming nitric acid (sp. gr. 1.50, 0.1 ml.) was stirred while the mixture was being cooled; a yellow nitro compound began to separate out. After it had been stirred for an additional 2 hr., the reaction mixture was diluted with water (3 ml.) to give V (70 mg.), m. p. 157—163°C, which was recrystallized from methanol to afford pale yellow needles, m. p. 162.5—163°C.

Found: C, 55.51; H, 4.44; N, 6.98. Calcd. for $C_9H_9O_4N$: C, 55.38; H, 4.65; N, 7.18%. λ_{max}^{MeOH} mμ (log ε); 245 (4.57), 325 (4.17), 400 (4.19).

4-Ethyl-5, 7-dinitrotropolone (VI).—Into a solution of I (300 mg.) in glacial acetic acid (1 ml.), concentrated nitric acid (sp. gr. 1.38, 0.5 ml.) was stirred while the mixture was being cooled; yellow crystals then began to separate out. After stirring for an additional 2 hr., water (5 ml.) was added to give VI (150 mg.), m. p. 123—125°C, which was recrystallized from benzene, affording yellow prisms, m. p. 127—128°C.

Found: C, 45.12; H, 3.16; N, 11.45. Calcd. for $C_9H_8O_6N_2$: C, 45.01; H, 3.36; N, 11.67%. λ_{max}^{MeOH} mμ (log ε); 246 (4.44), 405 (4.14).

4-Ethyl-3, 5, 7-trinitrotropolone (VII). — To a solution of I (300 mg.) in glacial acetic acid (1 ml.), concentrated nitric acid (sp. gr. 1.38, 0.15 ml.) was added, and the mixture was stirred for 2 hr. with cooling. After dilution with water, the crystals (100 mg.), m. p. 75—82°C, thereby formed were collected and recrystallized from methanol to give VII as pale yellow prisms, m. p. 84—85.5°C.

Found: C, 37.77; H, 2.49; N, 14.58. Calcd. for $C_9H_7O_8N_3$: C, 37.90; H, 2.47; N, 14.74%. λ_{max}^{MeOH} mμ (log ε); 255 (3.99), 357 (4.15).

Another experiment under the same conditions gave the dinitro compound (VI) in a poor yield.

5-Amino-4-ethyltropolone (VIII).—*a) From the Azo Compound (IV).*—A suspension of IV (1.07 g.) in methanol (12 ml.) was shaken, in the presence of platinum oxide (20 mg.), with hydrogen at room temperature and at atmospheric pressure; 205 ml. of hydrogen was absorbed after 1 hr. The catalyst was filtered off, the solvent was evaporated, and the residue was recrystallized from methanol to give VIII (530 mg.) as yellow needles, m. p. 168—169°C.

Found: C, 65.39; H, 6.54; N, 8.48. Calcd. for $C_9H_{11}O_2N$: C, 65.44; H, 6.71; N, 8.48%. λ_{max}^{MeOH} mμ (log ε); 240 (4.38), 360 (4.13), 390 (4.15).

b) From the Nitro Compound (V).—A solution

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[14] T. Nozoe, K. Takase and K. Suzuki, This Bulletin, 38, 362 (1964).

[15] All melting points are uncorrected.

of V (40 mg.) in methanol (5 ml.) was shaken with hydrogen in the presence of platinum oxide; 17 ml. of hydrogen was absorbed after 17 min. The catalyst and the solvent were removed, and the residue was recrystallized from methanol to give VIII (20 mg.) as yellow needles, m. p. 168—169°C.

5-Chloro-4-ethyltropolone (IX).—To a solution of VIII (330 mg.) in 50% aqueous dioxane (5 ml.), concentrated sulfuric acid (0.3 ml.) was added, and then a solution of sodium nitrite (150 mg.) in water (0.5 ml.) was stirred in while the mixture was being cooled. After additional stirring (30 min.), the diazotized solution was stirred into a solution of cuprous chloride (680 mg.) in concentrated hydrochloric acid (3.8 ml.). After additional stirring (1 hr.), the mixture was diluted with water (25 ml.); the copper chelate thereby formed was collected and dried (480 mg.). This copper chelate was suspended in chloroform, hydrogen sulfide gas was passed throughly and the copper sulfide thereby formed was filtered off. The evaporation of the solvent from the filtrate left crystals, which were then recrystallized from methanol to give IX (300 mg.) as pale yellow needles, m. p. 128—129°C.

Found: C, 58.51; H, 4.92. Calcd. for $C_9H_9O_2Cl$: C, 58.54; H, 4.91%. λ_{max}^{MeOH} mμ (log ε); 243 (4.50), 336 (4.12), 365 (3.81), 379 (3.82).

5-Bromo-4-ethyltropolone (X).—A diazotized solution of VIII (330 mg.), prepared as described in the above experiment, was stirred into a solution of cuprous bromide (700 mg.) in concentrated hydrobromic acid (3.8 ml.). The copper chelate thereby formed was decomposed with hydrogen sulfide as described in the above experiment, and the crystals thereby obtained were recrystallized from methanol to give X (350 mg.) as yellow needles, m. p. 128—129°C.

Found: C, 46.69; H, 4.08. Calcd. for $C_9H_9O_2Br$: C, 47.18; H, 3.96%. λ_{max}^{MeOH} mμ (log ε); 244 (4.46), 340 (4.20), 383 (3.79), 401 (3.78).

Methyl 3-Ethyl-4, 6-dinitrobenzoate (XI).—A solution of VI (100 mg.) in methanol (1 ml.) was heated for 2 min., affording XI (80 mg.) as colorless prisms, m. p. 64—65°C, after recrystallization from ether.

Found: C, 47.56; H, 3.81; N, 10.90. Calcd. for $C_{10}H_{10}O_6N_2$: C, 47.25; H, 3.97; N, 11.02%.

The Bromination of I.—*a) With a Molar Equivalent of Bromine.*—Into a solution of I (1.00 g.) in methanol (5 ml.), bromine (1.07 g.) in methanol (2 ml.) was stirred while the mixture was being cooled. After additional stirring (3 hr.), the mixture was allowed to stand overnight and then diluted with water. The crystals (1.47 g.) thereby formed were collected by filtration and fractionally recrystallized from methanol to give *7-bromo-4-ethyltropolone (XII)* (560 mg.), m. p. 63—66°C, which was further recrystallized from petroleum ether, affording colorless needles, m. p. 67.5—69°C, reported[3] m. p. 66°C.

Found: C, 47.23; H, 3.74. Calcd. for $C_9H_9O_2Br$: C, 47.18; H, 3.96%. λ_{max}^{MeOH} mμ (log ε); 256 (4.59), 330 (3.91), 380 (3.84).

The crystalline substance, obtained from the filtrate by the evaporation of the solvent, was dissolved in benzene and shaken with a 5% sodium hydrogen carbonate solution; the sparingly soluble sodium salt thereby formed was then collected by filtration. This salt was dissolved in hot water and acidified with 6 N hydrochloric acid, and the crystals thereby formed were collected and recrystallized from methanol to give *5, 7-dibromo-4-ethyltropolone (XIII)* (20 mg.) as pale yellow needles, m. p. 115—116°C.

Found: C, 35.44; H, 2.52. Calcd. for $C_9H_8O_2Br_2$: C, 35.02; H, 2.61%.

The benzene layer left after the removal of the sodium salt was shaken with a 5% sodium carbonate solution, and the sodium salt thereby formed was collected by filtration. This salt was dissolved in hot water and acidified with 6 N hydrochloric acid, and the crystals thereby formed were collected and recrystallized from methanol to give *3, 5, 7-tribromo-4-ethyltropolone (XIV)* (20 mg.) as greenish yellow prisms, m. p. 96.5—97°C.

Found: C, 28.09; H, 1.65. Calcd. for $C_9H_7O_2Br_3$: C, 27.94; H, 1.82%. λ_{max}^{MeOH} mμ (log ε); 272 (4.35), 352 (3.93), 430 (3.80).

b) With Two Molar Equivalents of Bromine.—Into a solution of I (450 mg.) in methanol (10 ml.), bromine (960 mg.) in methanol (2 ml.) was stirred while the mixture was being cooled. After the mixture had been allowed to stand overnight, the solvent was evaporated and the residue was recrystallized from petroleum ether to give *3, 7-dibromo-4-ethyltropolone (XV)* (350 mg.) as pale yellow prisms, m. p. 90—90.5°C.

Found: C, 35.38; H, 2.51. Calcd. for $C_9H_8O_2Br_2$: C, 35.02; H, 2.61%. λ_{max}^{MeOH} mμ (log ε); 267 (4.48), 339 (3.73), 383 (3.59), 415 (3.64).

The crystals obtained by the removal of the solvent from the mother liquor were fractionally recrystallized from methanol to give XIV (20 mg.).

c) With Three Molar Equivalents of Bromine.—Into a solution of I (300 mg.) and sodium acetate (820 mg.) in methanol (6 ml.), bromine (960 mg.) in methanol (4 ml.) was stirred while the mixture was being cooled. After additional stirring (3 hr.), the mixture was allowed to stand overnight; the crystals thereby formed were collected and recrystallized from methanol to give XIV (550 mg.) as greenish yellow prisms, m. p. 96.5—97°C.

The crystals obtained by the removal of the solvent from the mother liquor were fractionally recrystallized from methanol to give a small amount of XV.

The Bromination of 5-Bromo-4-ethyltropolone (X).—To a solution of X (100 mg.) in methanol (3 ml.), bromine (70 mg.) was added, and the mixture was stirred for 3 hr. The crystals obtained by the addition of water were fractionally recrystallized from petroleum ether to give XIV (40 mg.) as greenish yellow prisms, m. p. 96—97°C; together with the X (40 mg.) was also recovered.

The Bromination of 7-Bromo-4-ethyltropolone (XII).—To a solution of XII (100 mg.) in methanol (3 ml.), bromine (70 mg.) was added, and the mixture was stirred for 3 hr. The crystals obtained by the addition of water were recrystallized from petroleum ether to give XV (60 mg.) ; m. p. 96—97°C.

The Bromination of 3, 7-Dibromo-4-ethyltropolone (XV).—To a solution of XV (100 mg.) in methanol (3 ml.), bromine (60 mg.) was added in the presence of sodium acetate (100 mg.) ; the mixture was then stirred for 3 hr. with cooling. The crystals obtained by the addition of water were collected and recrystallized from methanol to give XIV (40 mg.), m. p. 96—97°C.

4-Ethyl-7-iodotropolone (XVIII).—Into a solution of I (300 mg.) and potassium carbonate (610 mg.) in water (1.5 ml.), a solution of iodine (560 mg.) and potassium iodide (560 mg.) in water (1.5 ml.) was stirred while the mixture was being cooled; the potassium salt separated out. After additional stirring (1 hr.), the excess iodine was destroyed by the addition of sodium sulfite and a yellow potassium salt was collected by filtration. This salt was dissolved in hot water and acidified with 6 N hydrochloric acid ; the crystals thereby formed were collected and recrystallized from petroleum ether to give XVIII (490 mg.) as yellow needles, m. p. 76—76.5°C.

Found : C, 38.56 ; H, 3.38. Calcd. for $C_9H_9O_2I$: C, 39.15 ; H, 3.28%. λ_{max}^{MeOH} (log ε) ; 230 (4.12), 260 (4.32), 265 (4.33), 340 (3.91), 383 (3.88).

***p*-Tolylazo Compounds of XII, XV and XVIII.**—They were obtained by the treatment described in the experiment with 4-ethyl-5-(*p*-tolylazo)tropolone (IV).

a) 7-Bromo-4-ethyl-5-(p-tolylazo)tropolone (XVI).—This was obtained from XII as red needles (from benzene), m. p. 181.5—182°C, in a 78% yield.

Found : C, 55.52 ; H, 4.24 ; N, 7.97. Calcd. for $C_{16}H_{15}O_2N_2Br$: C, 55.33 ; H, 4.32 ; N, 8.07%.

b) 3, 7 - Dibromo - 4-ethyl - 5 - (p-tolylazo)tropolone (XVII).—This was obtained from XV as reddish orange needles (from benzene), m. p. 151°C, in an 85% yield.

Found : C, 45.09 ; H, 3.04 ; N, 6.61. Calcd. for $C_{16}H_{14}O_2N_2Br_2$: C, 45.06 ; H, 3.31 ; N, 6.57%.

c) 4-Ethyl-7-iodo-5-(p-tolylazo)tropolone (XIX).—This was obtained from XVIII as dark red needles (from methanol), m. p. 181—182°C, in an 85% yield.

Found : C, 48.14 ; H, 3.68 ; N, 7.07. Calcd. for $C_{16}H_{15}O_2N_2I$: C, 48.73 ; H, 3.81 ; N, 7.11%.

5-Hydroxy-3-methyl-2-(*p*-tolyl)-6(2*H*)-cyclohepta[*c*]pyrazolone (XXI).—To a solution of IV (100 mg.) in ethanol (10 ml.), 6 N hydrochloric acid (0.3 ml.) was added ; this mixture was then heated under reflux for 6 hr. The solvent was evaporated, and the residue was recrystallized from ethanol to give XXI (30 mg.) as pale yellow needles, m. p. 202—203°C ; this was identified with an authentic specimen[14] by admixture and by a comparison of their infrared spectra.

When this reaction was carried out with the addition of iodine, XXI was obtained in a 50% yield.

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