Reaction of Troponoids and Organometallic Compounds. V. Reaction of Bromotropolones and Alkylmagnesium Iodides

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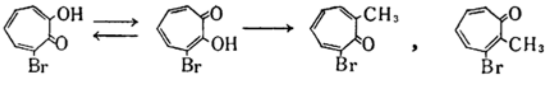
It has been reported in a previous paper[1] of this series that bromo derivatives of tropolone methyl ether react with α- and β-naphthylmagnesium bromides to yield corresponding bromo substitution products of 2-α- and 2-β-naphthyltropones and 2-hydroxyphenyl α- and β-naphthyl ketones.

The present paper deals with an investigation on the reaction of bromotropolones and alkyl Grignard reagents.

Reaction of methylmagnesium iodide and 3-bromotropolone (Ia) yielded colorless plates (IIa) whose ultraviolet spectrum was similar to that of tropone[2] (Fig. 1), suggesting that it is monobromo-2-methyltropone. As 3-bromotropolone is in a " high mobile tautomeric " system as represented with A and A′, two isomeric monobromo-2-methyltropone, i. e. 7-bromo-2-methyltropone (B) and 3-bromo-2-methyltropone (B′) should be obtained by this reaction. Actually, treatment of IIa with dilute alkali gave *o*-toluic acid (IIIa) indicating that IIa is 7-bromo-2-methyltropone (B).



A A′ B B′

However, the reaction of 3,7-dibromotropolone and methylmagnesium iodide under similar condition gave only minute amount of unidentified phenolic substance. Similarly, the reaction of 3, 5, 7-tribromotropolone and methylmagnesium iodide afforded only a small amount of dimethyl 3, 5-dibromo-2-hydroxyphenyl carbinol which was proved to be identical with that synthesized by the reaction of methyl 3, 5-dibromosalicylate and methylmagnesium iodide.

On the other hand, by the reaction of 3, 7-dibromotropolone methyl ether (Ib) and methylmagnesium iodide 3, 7-dibromo-2-methyltropone (IIb) was obtained. By treatment with alkali IIb was submitted to rearrangement to give 3-bromo-*o*-toluic acid (IIIb)[3], debromination of which gave IIIa. The ultraviolet absorption spectrum of IIb (Fig. 1) showed bands characteristic of tropone.

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[1] Part IV: K. Kikuchi, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **81**, 505 (1960).

[2] T. Nozoe, T. Mukai and K. Takase, *Sci. Repts. Tohoku Univ., Ser.* **I**, **39**, 164 (1956).

[3] D. Peltier, *Compt. rend.*, **237**, 357 (1954).

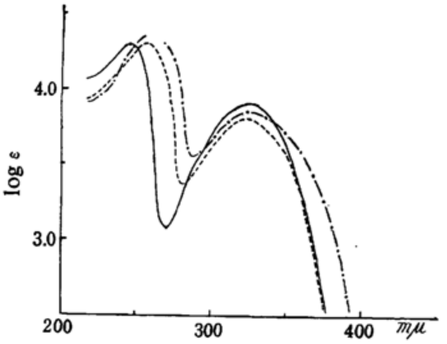
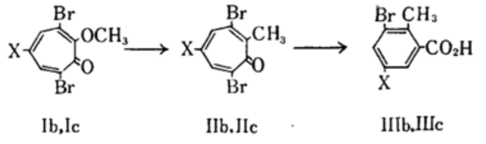


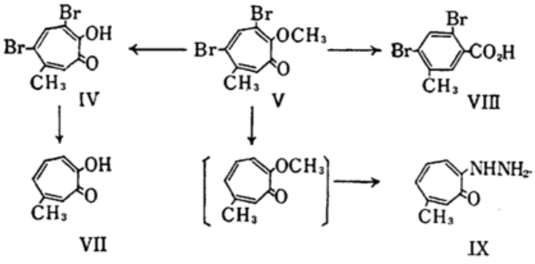
Fig. 1. Ultraviolet absorption spectra of IIa (——), IIb (------) and IIc (—·—·—) in methanol.

Reaction of 3, 5, 7-tribromotropolone methyl ether (Ic) and methylmagnesium iodide afforded four kinds of crystals as follows: pale yellow prisms (IIc), m. p. 63~64°C; colorless needles (IV), m. p. 151.5~153°C; colorless needles (V), m. p. 151~152°C and colorless needles (VI), m. p. 116~117°C. The main product was IIc.

Treatment of IIc with alkali afforded an acid (IIIc) whose debromination gave *o*-toluic acid (IIIa). This fact and the analytical values of IIc and IIIc indicate that IIc and IIIc are 2-methyl-3, 5, 7-tribromotropone and 3, 5-dibromo-*o*-toluic acid, respectively. The ultraviolet spectrum of IIc is shown in Fig 1.



IV showed red coloration with ferric chloride characteristic of tropolone and gave yellow sodium salt with aqueous sodium carbonate. On catalytic debromination, IV afforded 4-methyltropolone (VII)[4,5]. Treatment of V with hydrobromic acid in aqueous acetic acid and with aqueous sodium hydroxide afforded IV and 4, 6-dibromo-*m*-toluic acid (VIII)[6], respectively. Catalytic debromination of V on palladium-charcoal gave colorless crystals which, on treatment with hydrazine hydrate, was converted to 2-hydrazino-6-methyltropone (IX)[7]. These experimental results indicate that IV is 3, 5-dibromo-6-methyltropolone and V is 3, 5-dibromo-2-methoxy-6-methyltropone as shown in the following scheme.



It was reported previously that the reaction of 7-bromo-2-methoxytropone and phenylmagnesium bromide afforded phenyltropolone[8], m. p. 96~97°C, as a by-product. Pauson[9] suggested it to be 4-phenyltropolone and later Kitahara[10] presented the mechanism of its formation. The formation of IV and V also could be explained by his mechanism.

Analysis of VI is in agreement with the formula $C_9H_8OBr_2$ and its ultraviolet absorption spectrum (Fig. 2) is quite similar to those of IIa—IIc, and it is suggested that VI has a tropone nucleus. Presumably VI will be 3, 5-dibromo-2, 7-dimethyltropone or 3, 5-dibromo-2, 6-dimethyltropone formed either by the reaction of excess of methylmagnesium iodide with IIc or V, but the determination of the structure was impossible because of limited amount of the material.

Application of ethylmagnesium iodide to Ib afforded 3, 7-dibromo-2-ethyltropone (IId), as in the case of IIb. IId was converted to 3-bromo-2-ethylbenzoic acid (IIId), and the latter was debrominated to 2-ethylbenzoic acid (IIIe). The same reaction of ethylmagnesium iodide with Ic gave no crystalline product even after chromatographic separation on an alumina column. Ethanolic solution of the oil thereby obtained, however, when treated with dilute alkali, resulted in the formation of dibromo-2-ethylbenzoic acid (IIIf) and its ethyl ester (IIIg). From this fact it seems reasonable to assume that 2-ethyl-3, 5, 7-tribromotropone (IIe) was formed in this reaction as in the case of IIc.

Some nucleophilic reactions on IIa, IIb and IIc were next examined.

Heating of IIa and IIb with *p*-toluidine respectively afforded 2-methyl-7-(*p*-toluidino)-tropone (Xa) as yellow prisms and 3-bromo-2-methyl-7-(*p*-toluidino)-tropone (Xb) as yellow plates. The ultraviolet spectrum of Xa was shown in Fig. 2. Similarly, heating of IIa and IIb with aniline respectively gave 7-anilino-2-methyltropone (Xc) as an oil and 7-anilino-3-bromo-2-methyltropone (Xd) as yellow crystals.

Application of hydrazine hydrate to IIa at

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[4] R. D. Haworth, B. P. Moore and P. L. Pauson, *J. Chem. Soc.*, **1948**, 1045.

[5] T. Nozoe, T. Mukai, M. Kunori, T. Muroi and K. Matsui, *Sci. Repts. Tohoku Univ., Ser.* **I**, **35**, 242 (1951).

[6] R. Fittig, W. Ahrens and L. Mattheides, *Ann.*, **147**, 36 (1868).

[7] P. Akroyd, R. D. Haworth and J. D. Hobson, *J. Chem. Soc.*, **1951**, 3427.

[8] T. Nozoe, T. Mukai and I. Murata, *Proc. Japan Acad.*, **28**, 142 (1952).

[9] P. L. Pauson, *Chem. Revs.*, **55**, 9 (1955).

[10] Y. Kitahara, *Sci. Repts, Tohoku Univ., Ser.* **I**, **39**, 250 (1956).

room temperature afforded yellow needles (XIa) which gave red coloration with ferric chloride. From its analytical value and the ultraviolet absorption spectrum (Fig. 2) it was assumed to be bis-(2-methyltropon-7-yl)-hydrazine (C) or its tautomer (C′) but no further study was made.

C C′

Similar treatment of IIb with hydrazine hydrate yielded colorless needles (XIIa) and yellow needles (XIb). The former was assumed to be 3-bromo-*o*-toluic acid hydrazide from its analytical value and its ultraviolet absorption spectrum (Fig. 2) and the latter to have the analogous structure to XIa. On the other hand, treatment of IIc with hydrazine hydrate gave 3,5-dibromo-*o*-toluic acid hydrazide (XIIb) and the compound corresponding to XIa and XIb was not obtained.

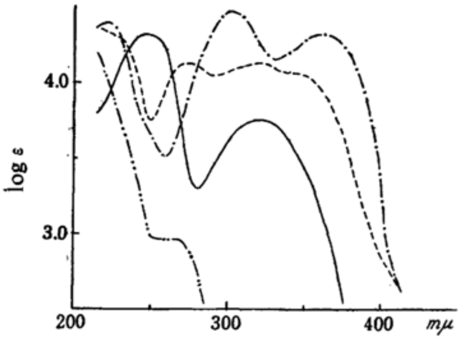

Fig. 2. Ultraviolet absorption spectra of VI (——), Xa (------), XIa (—·—·—·) and XIIa (—··—··—) in methanol.

Several methods[11-15] have already been reported by which 2-halotropones could be converted to tropolones. Application of these methods to IIb and IIc gave no satisfactory results, but by heating of IIb and IIc each with sodium acetate in acetic acid[11] 4-bromo-3-methyltropolone (XIIIa) and 4, 6-dibromo-3-methyltropolone (XIIIb) were obtained respectively only with poor yields.

Experimental

Reaction of 3-Bromotropolone (Ia) and Methylmagnesium Iodide.—To a solution of methylmagnesium iodide prepared from 5.0 g. of methyl iodide, 0.84 g. of magnesium and 20 cc. of absolute ether, a solution of 2.0 g. of Ia dissolved in 20 cc. of dehydrated tetrahydrofuran was added in drops under stirring, while chilling with ice. The mixture was stirred for further five hours under ice-chilling, decomposed with dilute sulfuric acid and extracted with chloroform. The chloroform solution was washed with dilute sodium hydroxide solution by which 320 mg. of Ia was recovered. The chloroform solution was then washed with water, dried and the solvent was removed to give 750 mg. of reddish brown oil. This oil was dissolved in benzene, passed through an alumina column, and 470 mg. of 7-bromo-2-methyltropone (IIa), m. p. 43∼45°C, was obtained. Recrystallization from cyclohexane gave colorless plates, m. p. 46∼47°C.

Found: C, 48.39; H, 3.90. Calcd. for C_8H_7OBr: C, 48.22; H, 3.54%.

Reaction of 7-Bromo-2-methyltropone (IIa) and Alkali.—A mixture of 50 mg. of IIa and 0.5 cc. of 1 N sodium hydroxide was heated on a water bath for one hour. After removal of the insoluble material, the aqueous layer was acidified with dilute hydrochloric acid and the crystals that separated out were recrystallized from dilute ethanol to give colorless crystals (IIIa), m.p. 99∼101°C, undepressed at melting point on admixture with *o*-toluic acid.

Reaction of 3, 7-Dibromotropolone Methyl Ether (Ib) and Methylmagnesium Iodide.—To a solution of methylmagnesium iodide prepared from 3.0 g. of methyl iodide, 0.5 g. of magnesium and 30 cc. of absolute ether, a solution of 3.0 g. of Ib dissolved in 30 cc. of dehydrated benzene was added in drops and stirring was continued for further two and a half hours. The reaction mixture was poured into dilute sulfuric acid, and the yellow precipitates thereby obtained were filtered off. After washing the organic solvent layer with water, the solvent was removed to give 710 mg. of 3, 7-dibromo-2-methyltropone (IIb). By passing the oily portion through an alumina column 150 mg. of a second crop of IIb was obtained. Recrystallization from ethanol gave colorless needles, m. p. 121∼122°C.

Found: C, 34.29; H, 2.29. Calcd. for $C_8H_6OBr_2$: C, 34.57; H, 2.18%.

Reaction of 3, 7-Dibromo-2-methyltropone (IIb) and Alkali.—Similar treatment of IIb with 1 N sodium hydroxide as in the case of IIa gave colorless plates (IIIb), m. p. 150°C. The reported melting point of 3-bromo-*o*-toluic acid is 153°C.

Found: C, 44.88; H, 3.45. Calcd. for $C_8H_7O_2Br$: C, 44.68; H, 3.28%.

IIIb was debrominated catalytically to *o*-toluic acid (IIIa), m. p. 100∼102°C, and identified by a mixture melting point determination.

Reaction of 3, 5, 7-Tribromotropolone Methyl Ether (Ic) and Methylmagnesium Iodide.—a) To an ice-chilled solution of methylmagnesium iodide prepared from 1.52 g. of methyl iodide, 0.26 g. of magnesium and 15 cc. of absolute ether, 2.0 g. of Ic dissolved in 15 cc. of benzene was added under stirring. The mixture was stirred further for one

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[11] T. Nozoe, Y. Kitahara, T. Ando, S. Masamune and H. Abe, ibid., *Ser.* I, 36, 166 (1952).

[12] W. E. Doering and J. R. Mayer, *J. Am. Chem. Soc.*, 75, 2387 (1953).

[13] S. Seto, *Sci. Repts. Tohoku Univ., Ser.* I, 37, 275 (1953).

[14] S. Seto, ibid., 37, 297 (1953).

[15] W. E. Doering and C. F. Hiskey, *J. Am. Chem. Soc.*, 74, 5688 (1952).

hour and decomposed with dilute sulfuric acid. After washing the organic solvent layer successively with water, 5% sodium hydrogen carbonate solution and water, the solvent was removed and 2.1 g. of red oil was obtained. The oil was redissolved in a mixture of benzene and petroleum ether and passed through a silica column. Three kinds of crystals were thereby obtained; 670 mg. of 2-methyl-3, 5, 7-tribromotropone (IIc), m. p. 62∼64°C; 80 mg. of 3, 5-dibromo-6-methyltropolone (IV), m. p. 148∼150°C; 20 mg. of 3, 5-dibromo-2-methoxy-6-methyltropone (V), m. p. 147∼149°C.

b) To a solution of methylmagnesium iodide prepared from 3.8 g. of methyl iodide, 4.0 g. of Ic dissolved in benzene was added. Treatment of the reaction mixture as in a) gave 920 mg. of IIc, 120 mg. of IV, 75 mg. of V and 20 mg. of dibromodimethyltropone (VI).

IIc was recrystallized from a mixture of benzene and petroleum ether to give colorless needles, m. p. 64∼65°C.

Found: C, 27.26; H, 1.88. Calcd. for $C_8H_5OBr_3$: C, 26.92; H, 1.41%.

Pyridine solution of IIc gives a reddish purple coloration with dilute sodium hydroxide solution.

IV was recrystallized from a mixture of benzene and petroleum ether to give colorless needles, m. p. 151.5∼153°C. Benzene solution of IV gives red coloration with ferric chloride.

Found: C, 32.95; H, 2.54. Calcd. for $C_8H_6O_2Br_2$: C, 32.68; H, 2.06%.

V was recrystallized from a mixture of benzene and petroleum ether to give colorless needles, m. p. 151∼152°C. Pyridine solution of V colors reddish purple with dilute sodium hydroxide solution.

Found: C, 35.48; H, 3.00. Calcd. for $C_9H_8O_2Br_2$: C, 35.06; H, 2.60%.

VI was recrystallized from ethanol to yield colorless needles, m. p. 116∼117°C. Pyridine solution gives deep reddish purple coloration with dilute sodium hydroxide solution.

Found: C, 36.96; H, 3.03. Calcd. for $C_9H_8OBr_2$: C, 36.98; H, 2.73%.

Reaction of 2-Methyl-3, 5, 7-tribromotropone (IIc) and Alkali.—Similar treatment of IIc with 2 N sodium hydroxide solution as in the case of IIa gave colorless crystals (IIIc), m. p. 195∼197°C.

Found: C, 33.09; H, 2.36. Calcd. for $C_8H_6O_2Br_2$: C, 32.68; H, 2.06%.

IIIc was debrominated to *o*-toluic acid, m. p. 100∼102°C.

Debromination of 3,5-Dibromo-6-methyltropolone (IV).—Catalytic reduction of 40 mg. of IV dissolved in 6 cc. of methanol, in the presence of 50 mg. of sodium acetate and 20 mg. of 5% palladium-charcoal resulted in absorption of 6 cc. of hydrogen. After removal of the catalyst by filtration, the solvent was removed and the crystalline residue was recrystallized from petroleum ether to give colorless crystals, m. p. 70∼72°C. These crystals showed no depression at the melting point on admixture with 4-methyltropolone (VII).

Acid Hydrolysis of 3, 5-Dibromo-2-methoxy-6-methyltropone (V).—A suspension of 18 mg. of V in a mixture of 0.5 cc. of acetic acid and 0.1 cc. of hydrobromic acid (sp. g. = 1.48) was heated on a water bath for one hour. Addition of water separated 14 mg. of colorless crystals, m. p. 150∼151°C. These crystals showed no depression at the melting point on admixture with 3, 5-dibromo-6-methyltropolone (IV).

Reaction of 3, 5-Dibromo-2-methoxy-6-methyltropone (V) and Alkali.—Similar treatment of V with dilute aqueous sodium hydroxide as in the case of IIa afforded colorless plates (VIII), m. p. 181∼183°C, the melting point remaining unchanged on admixture of 4, 6-dibromo-*m*-toluic acid.

Reaction of Hydrazine and the Debromination Product of 3, 5-Dibromo-2-methoxy-6-methyltropone (V).—A solution of 60 mg. of V dissolved in 6 cc. of methanol was catalytically debrominated with the addition of 50 mg. of sodium acetate and 5% palladium-charcoal. After removal of the catalyst by filtration, the solution was diluted with water and extracted with benzene. The benzene layer was washed with water and the solvent was removed. The crystalline residue obtained was dissolved in 0.1 cc. of methanol and two drops of 80% hydrazine hydrate was added. The mixture was warmed on a water bath, cooled and the crystals thereby formed were recrystallized from benzene to give yellow needles, m. p. 121∼123°C, which showed no depression at the melting point on admixture with 2-hydrazino-6-methyltropone (IX).

Reaction of 3, 5, 7-Tribromotropolone and Methylmagnesium Iodide.—To a solution of Grignard reagent prepared from 1.0 g. of methyl iodide, 0.72 g. of 3, 5, 7-tribromotropolone dissolved in dehydrated tetrahydrofuran was added under chilling with ice. After being stirred for five hours, the reaction mixture was decomposed with dilute sulfuric acid and extracted with chloroform. The chloroform extract was treated with dilute sodium carbonate solution by which 250 mg. of 3, 5, 7-tribromotropolone was recovered. The chloroform solution was further treated with dilute sodium hydroxide and the aqueous layer was acidified with dilute hydrochloric acid and extracted with benzene. Benzene extract afforded, after removal of the solvent, 130 mg. of dark red oil, chromatographic separation of which through an alumina column gave 40 mg. of crystals. Recrystallization from ethanol gave colorless plates, m. p. 133∼134°C.

Found: C, 35.05; H, 3.25. Calcd. for $C_9H_{10}O_2Br_2$: C, 34.87; H, 3.25%.

These crystals showed no depression at the melting point on admixture of dimethyl 3, 5-dibromo-2-hydroxyphenyl carbinol prepared from the reaction of methyl 3, 5-dibromosalicylate and methylmagnesium iodide.

Reaction of 3, 7-Dibromotropolone Methyl Ether (Ib) and Ethylmagnesium Iodide.—To a solution of ethylmagnesium iodide, prepared from 3.2 g. of ethyl iodide, a solution of 3.0 g. of Ib in benzene was added with stirring at 0°C, and the reaction mixture was treated as in the reaction of Ib and methylmagnesium iodide. 3, 7-Dibromo-2-ethyltropone (IId) was obtained as colorless needles, m. p. 81∼82°C. Yield, 730 mg.

Found: C, 37.28; H, 3.02. Calcd. for $C_9H_8OBr_2$: C, 36.98; H, 2.73%.

IId, when heated on a water bath for three hours, with the addition of dilute aqueous solution of sodium hydroxide, was rearranged to give colorless plates (IIId), m. p. 100~101°C.

Found: C, 47.10; H, 4.00. Calcd. for $C_9H_9O_2Br$: C, 47.18; H, 3.96%.

IIId was catalytically debrominated to 2-ethylbenzoic acid (IIIe), m. p. 64~65°C.

Reaction of 3, 5, 7-Tribromotropolone Methyl Ether (Ic) and Ethylmagnesium Iodide.—To a solution of ethylmagnesium iodide, prepared from 1.68 g. of ethyl iodide, 2.0 g. of Ic in benzene was added. After being stirred for one hour under ice-chilling, the reaction mixture was treated as in the case of Ic and methylmagnesium iodide. With the recovery of 350 mg. of 3, 5, 7-tribromotropolone, 1.7 g. of dark red oil was obtained. This oil was dissolved in a mixture of benzene and petroleum ether and passed through a silica column, but none of each fraction of the eluents gave crystalline products.

The red oil (800 mg.), obtained from easily eluated fraction, was then warmed with a mixture of 1 cc. of ethanol and 1.5 cc. of 2 N sodium hydroxide for several minutes and chilled with ice. From the alkali-soluble part 220 mg. of dibromo-2-ethylbenzoic acid (IIIf) was obtained. Recrystallization from ethanol raised the melting point to 145~146°C.

Found: C, 35.01; H, 2.62. Calcd. for $C_9H_8O_2Br_2$: C, 35.10; H, 2.62%.

Alkali-insoluble part gave 300 mg. of ethyl dibromo-2-ethylbenzoate (IIIg). Recrystallization from ethanol raised the melting point to 45~46°C.

Found: C, 38.85; H, 3.57. Calcd. for $C_{11}H_{12}O_2Br_2$: C, 39.32; H, 3.60%.

IIIf was debrominated to 2-ethylbenzoic acid (IIIe), m. p. 63~64°C, and was esterified to IIIg with ethanol in the presence of concentrated sulfuric acid.

2-Methyl-7-(*p*-toluidino)-tropone (Xa). — A mixture of 50 mg. of 7-bromo-2-methyltropone (IIa) and 50 mg. of *p*-toluidine was heated at 120~130°C for ten minutes, diluted with benzene and the benzene solution was washed successively with dilute sulfuric acid and water. The crystalline residue, obtained upon removal of benzene, was recrystallized from ethanol to give yellow prisms, m. p. 75~76°C.

Found: N, 6.40. Calcd. for $C_{15}H_{15}ON$: N, 6.22%.

3-Bromo-2-methyl-7-(*p*-toluidino)-tropone (Xb).— Obtained from 3, 7-dibromo-2-methyltropone (IIb) and *p*-toluidine as in the case of Xa, and recrystallized from ethanol to give orange yellow prisms, m. p. 105~106°C.

Found: N, 4.89. Calcd. for $C_{15}H_{14}ONBr$: N, 4.59%.

7-Anilino-2-methyltropone (Xc).—Obtained from IIa and aniline as in the case of Xa as a red oil. Picrate of Xc was obtained by the usual method and recrystallized from methanol to give yellow microneedles, m. p. 159~160°C.

Found: N, 12.98. Calcd. for $C_{20}H_{16}O_8N_4$: N, 12.72%.

7-Anilino-3-bromo-2-methyltropone (Xd). — Obtained from IIb and aniline by the same method as above, and recrystallized from ethanol to give yellow crystals, m. p. 109~110°C.

Found: N, 4.95. Calcd. for $C_{14}H_{12}ONBr$: N, 4.83%.

Reaction of 7-Bromo-2-methyltropone (IIa) and Hydrazine.—To a solution of 50 mg. of IIa dissolved in 0.1 cc. of ethanol was added 50 mg. of 80% hydrazine hydrate. After being warmed slightly on a water bath, the reaction mixture was acidified with dilute sulfuric acid. Yellow crystals that separated were collected by filtration and recrystallized from ethanol and then from *n*-butanol to give yellow needles (XIa), m. p. 200~201°C. Ethanolic solution of XIa colors red with ferric chloride.

Found: C, 71.52; H, 5.91; N, 10.57. Calcd. for $C_{16}H_{16}O_2N_2$: C, 71.62; H, 6.01; N, 10.44%.

Reaction of 3, 7-Dibromo-2-methyltropone (IIb) and Hydrazine.—To a solution of 100 mg. of IIb dissolved in 0.6 cc. of benzene was added 100 mg. of 80% hydrazine hydrate and the whole was allowed to stand overnight. The crystals that separated out were recrystallized from ethanol to give colorless needles (XIIa), m. p. 157~158°C.

Found: N, 12.15. Calcd. for $C_8H_9ON_2Br$: N, 12.23%.

The filtrate was acidified with dilute sulfuric acid and the crystals that separated out were recrystallized from a mixture of dioxane and *n*-butanol to give yellow needles (XIb), m. p. 283~284°C.

Found: C, 45.10; H, 3.35. Calcd. for $C_{16}H_{14}O_2N_2Br_2$: C, 45.08; H, 3.31%.

Reaction of 2-Methyl-3, 5, 7-tribromotropone (IIc) and Hydrazine.—A solution of IIc in benzene was treated with hydrazine hydrate as in the case of IIb. The crystals obtained were recrystallized from ethanol to give colorless needles (XIIb), m. p. 175~176°C.

Found: N, 9.50. Calcd. for $C_8H_8ON_2Br_2$: N, 9.09%.

4-Bromo-3-methyltropolone (XIIIa).—A mixture of 100 mg. of IIb, 80 mg. of anhydrous sodium acetate and 1 cc. of glacial acetic acid was heated at 180~200°C for one hour. The solution was then diluted with water, warmed further for a half hour, extracted with benzene and the benzene solution was treated with dilute aqueous sodium hydroxide. Yellow sodium salt that separated out was collected by filtration and acidified with hydrochloric acid. XIIIa thereby liberated was recrystallized from ethanol to give pale brownish crystals, m. p. 100~102°C; yield was very poor (about 5 mg.). XIIIa gives red coloration with ferric chloride.

Found: C, 45.30; H, 3.27. Calcd. for $C_8H_7O_2Br$: C, 44.68; H, 3.28%.

4, 6-Dibromo-3-methyltropolone (XIIIb). — Obtained from 40 mg. of IIc as in the case of XIIIa and recrystallized from ethanol to give pale yellow needles, m. p. 121~123°C; yield was about 5 mg.

Found: C, 33.04; H, 2.59. Calcd. for $C_8H_6O_2Br_2$: C, 32.68; H, 2.06%.

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