Synthesis and Reactions of Cyano- and Carboxytropones

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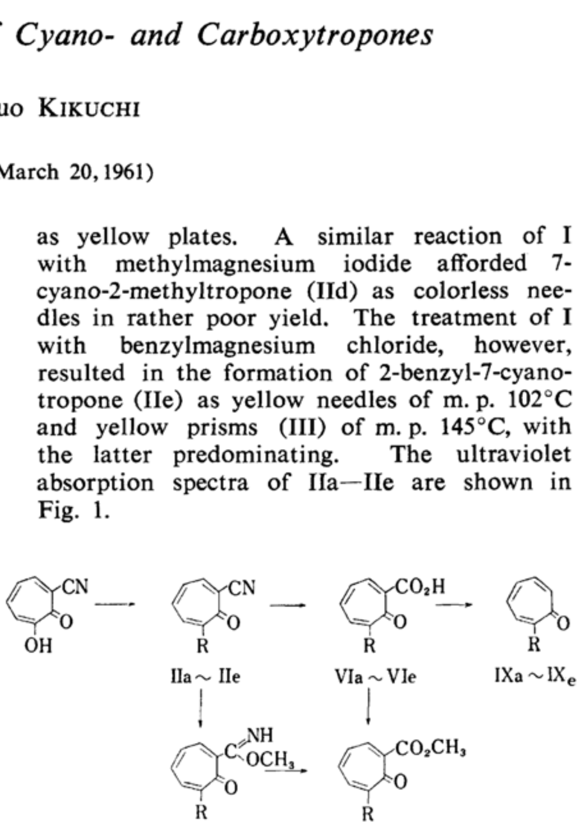
It has been reported that several kinds of cyanotropolones[1-4] can be obtained by the reaction of bromotropolones with cuprous cyanide or with potassium cyanide. In the case of cyanotropone, however, only the synthesis of 2-cyanotropone from 2-bromotropone and cuprous cyanide has been reported.[5]

In the present paper it is shown that several kinds of Grignard reagents react with 3-cyanotropolone (I)[1-4] to give corresponding 2-aryl- or 2-alkyl-7-cyanotropones. In this respect it is interesting to note that the cyano group of I is rather inactive to the Grignard reagents used and that the expected 3-aroyl- or 3-acyltropolones are not obtained.

The reaction of phenylmagnesium bromide and I afforded 7-cyano-2-phenyltropone (IIa) as yellow plates. Proof of the structure of IIa was obtained both by decarboxylation and by decarboxylative bromination of 2-phenyltropone-7-carboxylic acid (VIa) from IIa to yield 2-phenyltropone[6-9] and 7-bromo-2-phenyltropone[8,10], respectively.

Similarly, the reaction of I with α- and β-naphthylmagnesium bromide each afforded 7-cyano-2-α-naphthyltropone (IIb) as yellow needles and 7-cyano-2-β-naphthyltropone (IIc) as yellow plates. A similar reaction of I with methylmagnesium iodide afforded 7-cyano-2-methyltropone (IId) as colorless needles in rather poor yield. The treatment of I with benzylmagnesium chloride, however, resulted in the formation of 2-benzyl-7-cyanotropone (IIe) as yellow needles of m. p. 102°C and yellow prisms (III) of m. p. 145°C, with the latter predominating. The ultraviolet absorption spectra of IIa—IIe are shown in Fig. 1.



R a, C_6H_5; b, α-$C_{10}H_7$; c, β-$C_{10}H_7$; d, CH_3; e, $C_6H_5CH_2$

III was easily reacted both with concentrated hydrochloric acid and with ethanolic hydrogen chloride to give colorless needles (IV) and colorless prisms (V), respectively. Detailed studies on the structures of III, IV and V are now under way.

The cyanotropones (IIa-IIe) obtained above were easily hydrolyzed with sulfuric acid to give corresponding tropone carboxylic acids. Thus, 2-phenyltropone-7-carboxylic acid (VIa), 2-α-naphthyltropone-7-carboxylic acid (VIb), 2-β-naphthyltropone-7-carboxylic acid (VIc), 2-methyltropone-7-carboxylic acid (VId) and

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[1] B. J. Abadir, J. W. Cook, J. D. Loudon and D. K. V. Steel, *J. Chem. Soc.*, **1952**, 2350.

[2] T. Nozoe, Y. Kitahara and S. Masamune, *Proc. Japan Acad.*, **29**, 17 (1953).

[3] T. Nozoe and Y. Kitahara, ibid., **30**, 204 (1954).

[4] Y. Kitahara, *Sci. Repts. Tohoku Univ., Ser. I*, **40**, 74 (1956).

[5] T. Nozoe, S. Seto and S. Matsumura, *Proc. Japan Acad.*, **28**, 483 (1952).

[6] T. Nozoe, T. Mukai and J. Minegishi, ibid., **27**, 419 (1951).

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

[8] W. E. Doering and J. R. Mayer, ibid., **75**, 2387 (1953).

[9] T. Nozoe, T. Mukai, J. Minegishi and T. Fujisawa, *Sci. Repts. Tohoku Univ., Ser. I*, **37** 388 (1953).

[10] T. Mukai, ibid., **38**, 280 (1954).

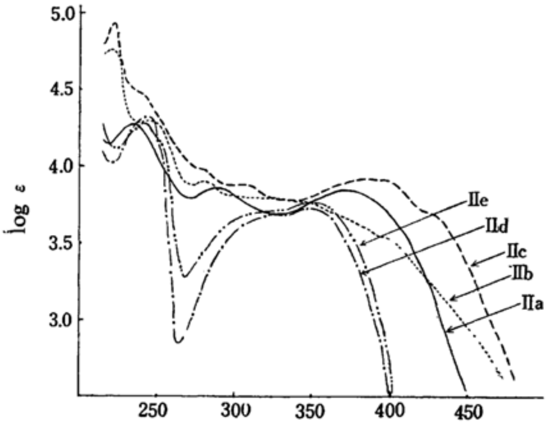


Fig. 1. Ultraviolet absorption spectra of IIa—IIe in methanol.

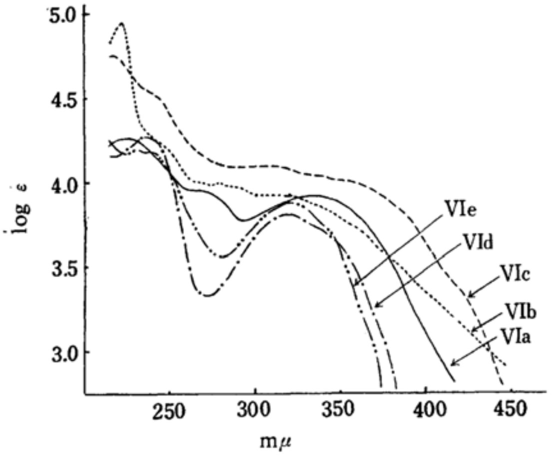


Fig. 2. Ultraviolet absorption spectra of VIa—VIc in methanol.

2-benzyltropone-7-carboxylic acid (VIe) were obtained. The ultraviolet absorption spectra of VIa–VIe are shown in Fig. 2.

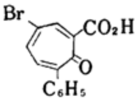
When treated with methanolic hydrogen chloride, 7-cyano-2-phenyltropone (IIa) afforded methyl 2-phenyltropone-7-carboximidate (VIIa) as pale yellow needles, the structure of which was ascertained by the hydrolysis of VIIa with dilute hydrochloric acid to give methyl 2-phenyltropone-7-carboxylate (VIIIa). Similar treatment of 7-cyano-2-α-naphthyltropone (IIb) afforded methyl 2-α-naphthyltropone-7-carboximidate (VIIb) as an oil, the hydrolysis of which afforded methyl 2-α-naphthyltropone-7-carboxylate (VIIIb).

Attempted synthesis of formyltropones by Stephen's method did not succeed.

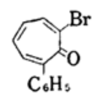
When heated to reflux in acetic anhydride, VIa, VIb and VIc were easily decarboxylated to give 2-phenyltropone (IXa), 2-α-naphthyltropone (IXb)⁾[11] and 2-β-naphthyltropone (IXc)[11] respectively.

The treatment of VIa with 2 mol. equivalents of bromine in acetic acid afforded an acid (X) accompanied with 7-bromo-2-phenyltropone (XI) or with 5,7-dibromo-2-phenyltropone (XII)[12]. The structures of the latter two compounds were identified by respective admixture with authentic samples.

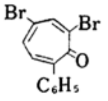
When heated to its decomposition points, X was submitted to decarboxylation to give yellow needles (XIII). Both X and XIII were converted by bromine in acetic acid to 5,7-dibromo-2-phenyltropone (XII). This fact indicates that X and XIII are 5-bromo-2-phenyltropone-7-carboxylic acid and 5-bromo-2-phenyltropone, respectively.



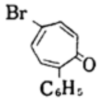
X



XI



XII



XIII

The action of bromine on IIb and IIc gave no satisfactory results.

The action of alkali on 2-phenyltropone-7-carboxylic acid (VIa) was next examined. It was already reported that the action of sodium hydroxide solution on tropone-4-carboxylic acid[12] gave terephthalic acid. The behavior of VIa to alkali, however, was somewhat different. VIa, when heated with dilute sodium hydroxide solution, was easily submitted to rearrangement to form a dibasic acid XIVa of m. p. 217～218°C (decomp.), in good yield. Analysis of XIVa and its dimethyl ester XIVb are in agreement with the formulae $C_{14}H_{12}O_4$ and $C_{16}H_{16}O_4$ respectively. XIVa reduces Fehling's solution and ammoniacal silver nitrate solution. Mild oxidation of XIVa with alkaline-ammoniacal silver nitrate solution gave colorless crystals (XV) which were identified as *o*-biphenylcarboxylic acid. The treatment of XV with concentrated sulfuric acid yielded fluorenone (XVI), which was also obtained directly from XIVa by the action of the same acid under evolution of gas.

XIVa absorbed one mole of hydrogen on palladium-charcoal and on Adam's catalyst to give colorless needles (XVIIa), m. p. 223～225°C (decomp.); dimethyl ester (XVIIb) of XVIIa, m. p. 81～82°C. Analysis of XVIIa and XVIIb are in agreement with the formulae $C_{14}H_{14}O_4$ and $C_{16}H_{18}O_4$, respectively. XVVIIa, when

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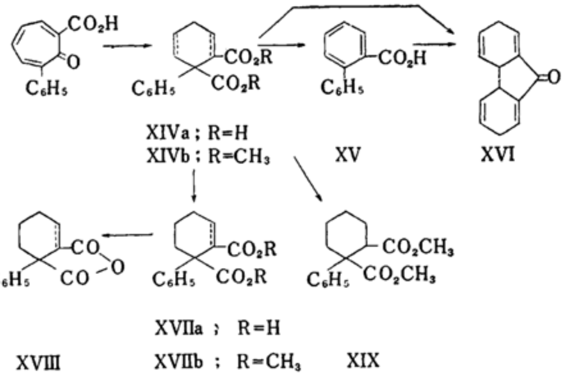
[11] K. Kikuchi, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **77** 1439 (1956).

[12] J. R. Bartels-Keith, A. W. Johnson and A. Langemann, *J. Chem. Soc.*, **1952**, 4461.

heated above its melting point, gave an anhydride (XVIII) of m. p. 125～127°C, which gave the original acid by sodium carbonate solution. The uptake of two moles of hydrogen by XIVa was difficult, but on one occasion, it was reduced on palladium-charcoal to give a small yield of colorless crystals, m. p. 160～170°C which without further purification, was converted to its dimethyl ester (XIX), m. p. 77～78°C. The analysis of XIX is in agreement with the formula $C_{16}H_{20}O_4$.

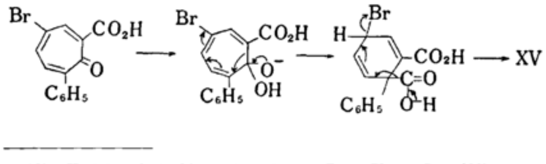


From these facts, it seems almost certain that XIVa is 1-phenylcyclohexadiene-1, 2-dicarboxylic acid but the exact location of double bonds in the cyclohexadiene ring is not clarified yet.

Similar treatment of 2-α-naphthyltropone-7-carboxylic acid (VIb) with dilute sodium hydroxide gave a dicarboxylic acid (XX)($C_{18}H_{14}O_4$) of m. p. 237～238°C (decomp.), which was converted to benzanthrone (XXI) with concentrated sulfuric acid. XX is considered to be 1-α-naphthylcyclohexadiene-1, 2-dicarboxylic acid formed in a manner similar to that in the case of XIVa.

The reaction of 5-bromo-2-phenyltropone-7-carboxylic acid (X) with dilute alkali, however, gave *o*-biphenylcarboxylic acid (XV). The mechanism of its formation is tentatively assumed as follows.

Recently it was reported[13] that the reaction of 4-bromo-2-phenyltropone and 4-mercapto-2-phenyltropone with alkali gave the same *o*-biphenylcarboxylic acid (XV). It seems interesting that the rearrangement of troponoid compounds is accompanied with the formation of hydroaromatic compounds or with the elimination of substituents other than in 2-(i. e. 7-) position.



Experimental

7-Cyano-2-phenyltropone (IIa).—To a solution of phenylmagnesium bromide, prepared from 9.6 g. of bromobenzene, 1.7 g. of magnesium and 30 cc. of absolute ether, and subsequently diluted with 40 cc. of anhydrous tetrahydrofuran, was added 3.0 g. of powdered 3-cyanotropolone (I) during 10 min. with stirring. The resulting clear solution was stirred for 2.5 hr. at 45～55°C, decomposed with dilute sulfuric acid and extracted with chloroform. The chloroform solution was washed with water, dried and the solvent was removed by distillation. The yellow crystals thereby obtained were recrystallized from a mixture of benzene and petroleum ether to give yellow plates (IIa), m. p. 134～135°C. Yield, 2.22 g.

Found: C, 80.69; H, 3.89; N, 7.04. Calcd. for $C_{14}H_9ON$: C, 81.14; H, 4.38; N, 6.76%.

7-Cyano-2-α-naphthyltropone (IIb).—To a solution of α-naphthylmagnesium bromide, prepared from 2.8 g. of α-bromonaphthalene, 0.34 g. of magnesium and 5 cc. of absolute ether, was added a solution of 0.5 g. of I dissolved in dehydrated dioxane and was stirred for 7 hr. at 75～80°C. After being left overnight, the reaction mixture was decomposed with dilute sulfuric acid and extracted with chloroform. The chloroform extract was washed with water, dried and the solvent was removed. The residual oil provided 0.34 g. of IIb, m. p. 160～162°C. Recrystallization from benzene gave yellow needles, m. p. 163～164°C.

Found: C, 84.52; H, 4.18; N, 5.78. Calcd. for $C_{18}H_{11}ON$: C, 84.03; H, 4.31; N, 5.44%.

7-Cyano-2-β-naphthyltropone (IIc).—To a solution of β-naphthylmagnesium bromide, prepared from 2.8 g. of β-bromonaphthalene, 0.34 g. of magnesium, a small amount of iodine and 5 cc. of absolute ether, was added a solution of 0.5 g. of I dissolved in dehydrated dioxane, and the reaction mixture was treated as in the case of IIb. The residual oil provided 0.42 g. of IIc, m. p. 177～180°C. Recrystallization from dioxane gave yellow plates, m. p. 180～181°C.

Found: C, 84.51; H, 4.01; N, 5.56. Calcd. for $C_{18}H_{11}ON$: C, 84.03; H, 4.31; N, 5.44%.

7-Cyano-2-methyltropone (IId).—To a solution of methylmagnesium iodide, prepared from 2.56 g. of methyl iodide, 0.5 g. of magnesium and absolute ether and subsequently diluted with dehydrated tetrahydrofuran, was added 0.8 g. of powdered I with stirring. After being stirred for another 4 hr. at 45～50°C, the mixture was treated as in the case of IIa to give 0.12 g. of IId. Recrystallization from ethanol gave colorless needles, m. p. 119～120°C.

Found: C, 74.41; H, 4.66; N, 9.72. Calcd. for C_9H_7ON: C, 74.47; H, 4.86; N, 9.65%.

Reaction of 3-Cyanotropolone (I) and Benzylmagnesium Chloride.—To a solution of Grignard reagent prepared from 3.78 g. of benzyl chloride, 0.75 g. of magnesium and 15 cc. of absolute ether

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[13] T. Muroi, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **80**, 303 (1959).

and diluted with 15 cc. of dehydrated tetrahydrofuran, was added 1.5 g. of I with stirring. The mixture was stirred for another 2 hr. at 45~50°C, decomposed with dilute sulfuric acid and extracted with chloroform. The chloroform extract was washed with water, the solvent was removed under reduced pressure, and 530 mg. of yellow crystals (III) thereby obtained, were collected by filtration. Chromatographic separation of the filtrate over silica gel gave 40 mg. of III and 120 mg. of 2-benzyl-7-cyanotropone (IIe).

IIe was recrystallized from ethanol to give pale yellow prisms, m. p. 101~102°C.

Found: C, 81.16; H, 4.72; N, 6.51. Calcd. for $C_{15}H_{11}ON$: C, 81.43; H, 5.01; N, 6.33%.

III was recrystallized from ethanol to give yellow prisms, m. p. 144~145°C.

Found: C, 79.81; H, 6.22; N, 4.51. Calcd. for $C_{22}H_{19}O_2N$: C, 80.22; H, 5.81; N, 4.25%.

Reaction of Compound (III) and Concentrated Hydrochloric Acid.—The addition of 0.5 cc. of concentrated hydrochloric acid to 100 mg. of III at room temperature gave viscous syrup which soon solidified to colorless crystals. They were collected by filtration and recrystallized from a large amount of *n*-butanol to give colorless microneedles (IV), m. p. 225°C (decomp.).

Found: C, 76.04; H, 6.62; N, 4.24. Calcd. for $C_{22}H_{21}O_3N$: C, 76.06; H, 6.09; N, 4.03%.

Reaction of Compound (III) and Ethanolic Hydrogen Chloride.—The addition of 0.5 cc. of ethanol, saturated with hydrogen chloride, to 100 mg. of III at room temperature yielded a clear solution. After being left for 10 min., the solvent was removed and the crystals that were obtained were recrystallized from ethanol to give colorless prisms (V), m. p. 173~174°C.

Found: C, 76.25; H, 6.98; Calcd. for $C_{24}H_{25}O_3 \cdot N$: C, 76.77; H, 6.71%.

2-Phenyltropone-7-carboxylic Acid (VIa).—A mixture of 1.7 g. of IIa and 17 cc. of 75% sulfuric acid was heated at 140~150°C for one hour and the mixture was poured onto ice. The crystals that separated out were recrystallized from ethanol to give yellow plates, m. p. 107~108°C. Yield, 1.6 g.

Found: C, 74.18; H, 4.47. Calcd. for $C_{14}H_{10}O_3$: C, 74.33; H, 4.46%.

Methyl Ester (VIIIa).—Obtained by the reaction of VIa and ethereal diazomethane. Recrystallization from methanol gave yellow needles, m. p. 99~100°C.

Found: C, 74.88; H, 4.87. Calcd. for $C_{15}H_{12}O_3$: C, 74.99, H, 5.03%.

p-Toluidide.—Obtained by the usual method. Recrystallization from ethanol gave orange-yellow crystals, m. p. 121~122°C.

Found: N, 4.56. Calcd. for $C_{21}H_{17}O_2N$: N, 4.44%.

2-α-Naphthyltropone-7-carboxylic Acid (VIb).—Obtained by heating a mixture of 100 mg. of IIb, 1 cc. of 50% sulfuric acid and 1 cc. of glacial acetic acid at 150~160°C for one hour. Recrystallization from ethanol gave orange yellow prisms, m. p. 139~140°C. Yield, 80 mg.

Found: C, 78.01; H, 4.51. Calcd. for $C_{18}H_{12}O_3$: C, 78.25; H, 4.38%.

Methyl Ester (VIIIb).—Yellow prisms of m. p. 105~106°C.

Found: C, 78.17; H, 4.72. Calcd. for $C_{19}H_{14}O_3$: C, 78.60; H, 4.85%.

2-β-Naphthyltropone-7-carboxylic Acid (VIc).—Obtained as in the case of VIb. Recrystallization from *n*-butanol gave reddish orange microcrystals, m. p. 189~190°C.

Found: C, 78.17; H, 4.38. Calcd. for $C_{18}H_{12}O_3$: C, 78.25; H, 4.38%.

Methyl Ester.—Yellow plates, m. p. 81~82°C.

Found: C, 78.53; H, 5.07. Calcd. for $C_{19}H_{14}O_3$: C, 78.60; H, 4.85%.

2-Methyltropone-7-carboxylic Acid (VId).—Obtained as in the case of VIa. Recrystallization from ethanol gave colorless plates, m. p. 146~147°C.

Found: C, 65.75; H, 4.72. Calcd. for $C_9H_8O_3$: C, 65.85; H, 4.91%.

2-Benzyltropone-7-carboxylic Acid (VIe).—Obtained as in the case of VIa. Pale yellow needles of m. p. 128~129°C.

Found: C, 74.76; H, 4.75. Calcd. for $C_{15}H_{12}O_3$: C, 74.99; H, 5.03%.

Methyl 2-Phenyltropone-7-carboximidate (VIIa).—A mixture of 100 mg. of IIa and 2 cc. of absolute methanol was saturated with dry hydrogen chloride under ice-chilling, and the resulting clear red solution was left overnight at 0°C. Benzene and water were added successively to the solution, and the aqueous layer was neutralized cautiously with cold dilute aqueous solution of sodium carbonate. The crystals that separated out were collected by filtration, yield 70 mg. Recrystallization from ether gave pale yellow needles (VIIa) m. p. 85~86°C.

Found: N, 6.04. Calcd. for $C_{15}H_{13}O_2N$: N, 5.85%.

Picrate.—Reddish orange prisms, m. p. 141~142°C.

Found: N, 12.03. Calcd. for $C_{21}H_{16}O_9N_4$: N, 11.96%.

Acid Hydrolysis of VIIa.—A solution of 30 mg. of VIIa in 2 N hydrochloric acid was warmed on a water bath for 10 min. and cooled. The crystals that separated out were collected by filtration and recrystallized from methanol to give yellow crystals, m. p. 98~100°C. These crystals showed no depression of melting point on admixture with VIIIa.

Methyl 2-α-Naphthyltropone-7-carboximidate (VIIb).—Similar treatment of IIb as in the case of IIa provided VIIb as an oil which could not be solidified. This oil was subjected to acid hydrolysis with 2 N hydrochloric acid by which yellow crystals, m. p. 105~106°C were obtained. These crystals showed no depression of melting point on admixture with VIIIb.

Decarboxylation of 2-Phenyltropone-7-carboxylic Acid (VIa).—A solution of 50 mg. of VIa in 0.5 cc. of acetic anhydride was heated to reflux for 1.5 hr., shaken with water to decompose the acetic anhydride and extracted with benzene. The benzene extract was washed with 2 N sodium carbonate and water, dried and the solvent was evaporated. The pale yellow crystals (IXa) m. p. 82~83°C thereby obtained showed no depression of melting point on admixture with 2-phenyltropone.

Decarboxylation of 2-α-Naphthyltropone-7-carboxylic Acid (VIb).—Treatment of VIb similar to that in the case of VIa yielded pale yellow crystals m. p. 110°C which showed no depression of melting point on admixture with an authentic sample of 2-α-naphthyltropone (IXb).

Decarboxylation of 2-β-Naphtyltropone-7-carboxylic Acid (VIc).—Treatment of VIc similar to that in the case of VIa yielded pale yellow crystals of m. p. 132∼134°C, undepressed on admixture with an authentic sample of 2-β-naphthyltropone (IXc).

Bromination of VIa.—a) To a solution of 50 mg. of VIa in 0.5 cc. of acetic acid was added 70 mg. of bromine. After standing for 5 hr. the whole was heated for 10 min. on a water bath, diluted with water and extracted with benzene. The benzene extract was washed with dilute sodium carbonate solution and the aqueous layer was acidified with dilute hydrochloric acid by which 30 mg. of 5-bromo-2-phenyltropone-7-carboxylic acid (X) was obtained as yellow needles. Recrystallization from ethanol raised the melting point to 174∼175°C (decomp.).

Found: C, 55.10; H, 3.11. Calcd. for $C_{14}H_9O_3Br$: C, 55.11; H, 2.96%.

The benzene layer was washed with water, dried and the solvent was evaporated. Residual oil provided some crystals on standing which were recrystallized from cyclohexane to give pale yellow plates (XI), m. p. 78∼80°C. These crystals showed no depression of melting point on admixture with 7-bromo-2-phenyltropone.

b) Similar treatment of 50 mg. of VIa with 70 mg. of bromine, except when heating was prolonged to one hour, afforded 20 mg. of X and several milligrams of pale yellow needles (XII) m. p. 131∼132°C, which showed no depression of melting point on admixture with 5, 7-dibromo-2-phenyltropone.

Decarboxylation of X.—Acid (X), when heated to its melting point and subsequently sublimed under reduced pressure, was easily decarboxylated to give 5-bromo-2-phenyltropone (XIII). Recrystallization from ethanol gave pale yellow needles, m. p. 130∼131°C.

Found: C, 59.34; H, 3.17. Calcd. for $C_{13}H_9OBr$: C, 59.79; H, 3.47%.

Bromination of X.—To a solution of 40 mg. of X in acetic acid was added 40 mg. of bromine and the mixture, after standing for one hour, was heated on a water bath for one hour, diluted with water and extracted with benzene. The benzene extract was washed successively with water, 2 N sodium carbonate and water, and the solvent was removed. The crystals thereby obtained were recrystallized from ethanol to give yellow needles (XII), m. p. 130∼131°C, with undepressed melting point on admixture with 5, 7-dibromo-2-phenyltropone (XII).

Bromination of XIII.—To a solution of 30 mg. of XIII dissolved in 0.5 cc. of acetic acid was added 50 mg. of bromine and the mixture was allowed to stand for two days. The mixture was then diluted with water, extracted with benzene and the benzene solution was washed successively with water, 2 N sodium carbonate and water. The residual oil, obtained upon removal of the solvent, was heated on a water bath for 30 min. and cooled. The crystals thereby obtained were repeatedly recrystallized from ethanol to give yellow crystals (XII) m. p. 127∼130°C, with undepressed melting point on admixture with 5, 7-dibromo-2-phenyltropone.

Reaction of VIa and Alkali.—A solution of 100 mg. of VIa dissolved in 1 cc. of 1 N sodium hydroxide was heated on a water bath for an hour, treated with active charcoal and then acidified with 2 N hydrochloric acid by which 80 mg. of 1-phenylcyclohexadiene-1, 2-dicarboxylic acid (XIVa) was obtained. Recrystallization from dilute ethanol gave colorless prisms, m. p. 216∼217°C (decomp.).

Found: C, 68.60; H, 4.96. Calcd. for $C_{14}H_{12}O_4$: C, 68.84; H, 4.95%. Neutral equivalent as a dibasic acid, 122; Found. 126.

These crystals gradually reduced Fehling's solution and the ammonical silver nitrate solution.

Dimethyl Ester (XIVb).—Obtained by the reaction of XIVa and ethereal diazomethane. Recrystallization from methanol gave colorless prisms, m. p. 95∼96°C.

Found: C, 70.41; H, 5.64. Calcd. for $C_{16}H_{16}O_4$; C, 70.57; H, 5.92%.

Oxidation of XIVa.—A solution of 50 mg. of XIVa dissolved in 1.5 cc. of alkaline-ammoniacal silver nitrate solution (prepared by dissolving 0.3 g. of silver nitrate in 3 cc. each of concentrated aqueous ammonia and 10% sodium hydroxide solution) was heated on a water bath for 30 min. After removal of the precipitate that formed, the filtrate was acidified and the crystals that separated out were collected by filtration. Recrystallization from dilute ethanol gave colorless prisms (XV), m. p. 108∼109°C. Treatment of XV with concentrated sulfuric acid at room temperature yielded crystals (XVI), m. p. 80∼82°C. XV and XVI were identified as *o*-biphenylcarboxylic acid and fluorenone, respectively, by the mixture melting point determination.

Action of Concentrated Sulfuric Acid on XIVa.—Addition of 0.3 cc. of concentrated sulfuric acid to 30 mg. of XIVa at room temperature resulted in deep reddish purple solution under evolution of gas. After being warmed slightly on a water bath, the reaction mixture was poured onto crushed ice. The crystals that separated out were collected by filtration and recrystallized from dilute ethanol to give yellow prisms (XVI), m. p. 80∼82°C, with undepressed melting point on admixture with fluorenone.

Catalytic Reduction of XIVa.—a) A solution of 250 mg. of XIVa dissolved in 10 cc. of methanol was catalytically reduced at ordinary temperature and pressure, with the addition of 30 mg. of Adam's catalyst. Absorption of hydrogen was 35 cc. After removal of the catalyst by filtration, methanol was removed, and the crystalline residue was recrystallized from methanol to give colorless needles (XVIIa) of m. p. 223∼224°C (decomp.). Yield, 100 mg.

Found: C, 67.77; H, 5.53. Calcd. for $C_{14}H_{14}O_4$; C, 68.28; H, 5.73%.

Dimethyl Ester (XVIIb).—Colorless needles, m. p. 81∼82°C.

Found: C, 69.68; H, 6.25. Calcd. for $C_{16}H_{18}O_4$: C, 70.05; H, 6.61%.

Anhydride (XVIII).—Acid (XVIIa) was heated above its melting point for one minute and cooled. The crystalline mass was recrystallized from methanol to give colorless needles of m. p. 125∼127°C.

Found: C, 72.71; H, 5.17. Calcd. for $C_{14}H_{12}O_3$: C, 73.67; H, 5.30%.

b) A solution of 150 mg. of XIVa dissolved in 5 cc. of methanol was catalytically reduced at ordinary temperature and pressure, with the addition of 100 mg. of palladium-charcoal (5%). The absorption of hydrogen was about 30 cc. After removal of the catalyst by filtration, methanol was removed, and the crystalline residue was washed with a small amount of ether. These crystals of m. p. 160∼170°C were, without further purification, converted to their dimethyl ester (XIX) by the action of ethereal diazomethane. Recrystallization from methanol gave colorless prisms, m. p. 77∼78°C. These crystals showed depression of the melting point on admixture with XVIIb.

Found: C, 69.88; H, 7.13. Calcd. for $C_{16}H_{20}O_4$: C, 69.54; H, 7.30%.

Reaction of 2-α-Naphthyltropone-7-carboxylic Acid (VIb) and Alkali.—Similar treatment of VIb as in the case of VIa gave 1-α-naphthylcyclohexadiene-1, 2-dicarboxylic acid (XX) as colorless prisms, m. p. 237∼238°C (decomp.).

Found: C, 73.68; H, 5.00. Calcd. for $C_{18}H_{14}O_4$: C, 73.46; H, 4.80%.

Action of Sulfuric Acid on XX.—Similar treatment of XX with concentrated sulfuric acid as in the case of XIVa gave yellow needles (XXI), m. p. 169∼170°C, with undepressed melting point on admixture with benzanthrone.

Reaction of 5-Bromo-2-phenyltropone-7-carboxylic Acid (X) and Alkali.—A solution of 20 mg. of X dissolved in 0.4 cc. of 1 N sodium hydroxide was heated for one hour on a water bath and acidified with dilute hydrochloric acid. The crystals thereby obtained were collected by filtration and recrystallized from ethanol to give colorless crystals (XV), m. p. 105∼108°C, with undepressed melting point on admixture with *o*-biphenylcarboxylic acid. By treatment with concentrated sulfuric acid, XV was converted to fluorenone (XVI) and identified by mixture melting point determination.

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