*Reaction of 2-Chloro-3-phenyltropone and 2-Chloro-7-phenyltropone with Ammonia and Amines**

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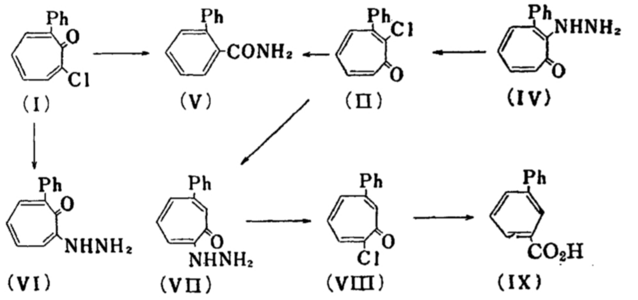
The present writer has been examining the reactivity of 2-phenyltropone[1,2] and taking a great interest in comparing its chemical and physical properties with those of 3- and 4-phenyltropones. As a preliminary step, the synthesis of 3-phenyltropone from 2-phenyltropone was attempted. The objective would be realized if the expected abnormal substitution** could occur in the reaction of ammonia and 2-chloro-3-phenyltropone, easily obtainable from 2-phenyltropone through 3-phenyltropolone. However, such an abnormal substitution of 3- or 7-substituted 2-chlorotropone has not been carried out, although the reaction has been tried often with 4(or 6)- and 5-substituted 2-chlorotropones[3,4]. In the first step of this experiment, therefore, the reaction of not only 2-chloro-3-phenytropone but also 2-chloro-7-phenyltropone with ammonia and amines was examined.

The starting material, the 2-chloro derivatives, were prepared by the reaction of 3-phenyltropolone and thionyl chloride. This afforded a mixture of 2-chloro-7-phenyltropone (I) and 2-chloro-3-phenyltropone(II) in a good yield, in which the quantity of I was 4~5 times as large as that of II. In some cases, a small amount of colorless crystals III, m. p. 86.5°C, was obtained during this reaction. In 1951, Cook and others[5] reported the formation of a *o*-chlorobenzaldehyde, besides 2-chlorotropone, by the reaction of tropolone and thionyl chloride. The analytical values of III also agree with those of the corresponding chlorophenylbenzaldehyde but its infrared spectrum[6] does not exhibit the absorption in the carbonyl region. The ultraviolet absorption spectrum of III, shown in Fig. 1, does not exhibit the absorption in the longer wave length, characteristic of the tropone nucleus[7], so that III must be a compound formed by aromatization, but its structure is still under examination.

The structure of I is proved by the fact that its alkaline hydrolysis affords a biphenyl-2-carboxylic acid and that its hydrogenolysis forms 2-phenyltropone. The structure of II was established by its identity with a compound, obtained by the decomposition of 2-hydrazino-3-phenyltropone (IV) with copper sulfate in hydrochloric acid solution[8]. IV is derived from the structurally known 2-methoxy-3-phenyltropone[9].



Reaction of 2-chloro-3-phenyltropone (II) by standing in ethanolic solution saturated with ammonia at a room temperature

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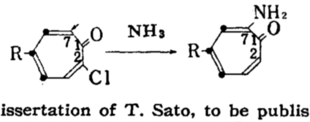
*) Paper presented before the 8th Scientific Meeting of the Chemical Research Institute of Non-aqueous Solution, Tohoku University, October 22, 1956.

[1] T. Mukai, *Sci. Repts. Tohoku Univ., First Ser.*, **38**, 280 (1954).

[2] T. Nozoe, T. Mukai, J. Minegishi and T. Fujisawa, ibid., **37**, 388 (1953).

**) 2-Halotropones react with ammonia to give 2-aminotropones, but it has been found by T. Sato that the replacement of halogen by ammonia does not occur directly, and an abnormal substitution at C_7 rather than at C_2 occurs in the majority of cases (see ref. 3 and 4).



[3] The dissertation of T. Sato, to be published.

[4] T. Nozoe, S. Seto and T. Sato, *Proc. Japan Acad.*, **30**, 473 (1954).

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

[6] Infrared spectra were measured with Perkin-Elmer Model 21 double beam Spectrophotometer by Mr. Yusaku Ikegami of the Chemical Research Institute of Non-aqueous Solution, Tohoku University, to whom the author is deeply indebted.

[7] M. Tsuboi, This Bulletin, **25**, 369 (1952).

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

[9] T. Muroi, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **77**, 1084 (1956).

resulted in its rearrangement to biphenyl-2-carboxamide (V) in a good yield, instead of undergoing the expected abnormal substitution. The reaction of 2-chloro-7-phenyltropone (I) and ethanolic ammonia also ended in the same rearrangement.

On heating a mixture of 2-chloro-7-phenyltropone (I) and hydrazine in ethanol, the structurally known 2-hydrazino-7-phenyltropone[2)] (VI) was obtained in a good yield. On the other hand, the reaction of 2-chloro-3-phenyltropone (II) and hydrazine afforded yellow crystals VII, m. p. 137°C without the rearrangement. The melting points of IV and VII were very close but their admixture showed them to be different substances. The ultraviolet spectrum of VII, shown in Fig. 2, indicated the absorption of a 2-aminotropone type[10)] and its analytical values also agreed with those for a hydrazino compound. The ultraviolet spectra of other hydrazinotropones, IV and VI, are also given in Fig. 2, from which it is seen that the absorption in the longest wavelength region has disappeared in IV alone owing to the steric hindrance of the hydrazino group.

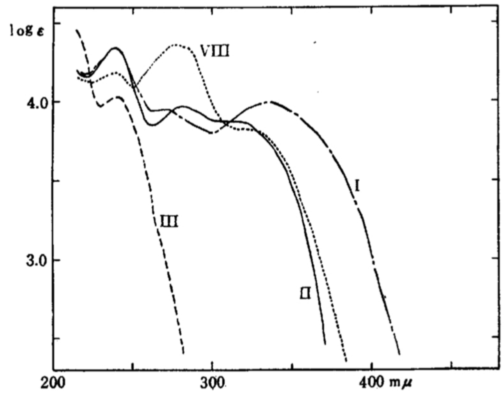


Fig. 1. U. V. Spectra of 2-Chloro-7-phenyltropone (I), 2-Chloro-3-phenyltropone (II), III of m. p. 86.5°C, and 2-Chloro-6-phenyltropone (VIII) in methanol.

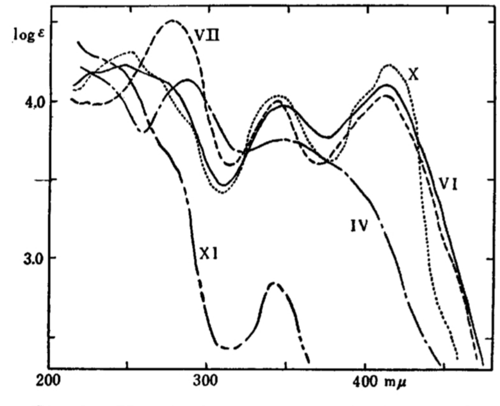
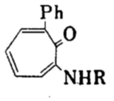


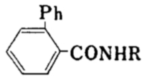
Fig. 2. U. V. Spectra of 2-hydrazino-3-phenyltropone (IV), 2-hydrazino-7-phenyltropone (VI), 2-hydrazino-6-phenyltropone (VII), 2-methylamino-7-phenyltropone (X), and biphenyl-2-carboxymethylamide (XI) in methanol.

Decomposition of VII with copper sulfate in hydrochloric acid medium affords the corresponding chlorotropone VIII which easily undergoes rearrangement on being heated with ethanolic alkali to form biphenyl-3-carboxylic acid (IX)[11)]. It follows that VII and VIII are respectively 2-hydrazino- and 2-chloro-6-phenyltropone. The occurrence of an abnormal substitution with hydrazine was observed for the first time in this compound. It is interesting to note that the reaction with hydrazine is so vastly different from that with ammonia. The ultraviolet spectrum of VIII is given in Fig. 1. It is noted that II and VIII are the chlorine derivatives of 3-phenyltropone, their absorption curve shifts to a shorter wave length region than that of 2-phenyltropone derivatives and they have a maximum near 280 mμ.

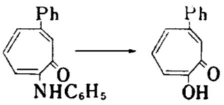
The reaction of I and II with alkyl- and arylamines was next examined. When I or II was heated with methylamine in ethanol solution, I afforded yellow crystals X, m. p. 159°C and II gave pale yellow crystals XI, m. p. 165°C. The ultraviolet spectra of X and XI are indicated in Fig. 2. The spectrum of X exhibits two peaks of high intensity at above 340 mμ, indicating a typical 2-aminotropone type, while that of XI lacks the corresponding absorption, indicating the possibility of an aromatization. Since the analytical values of X agree with those of 2-methylaminotropones and the hydrolysis of X by heating with alkali in ethanolic solution affords 3-phenyltropolone, X must be 2-methylamino-7-phenyltropone. The structure of



(X): R=CH_3
(XV): R=C_6H_5



(XI): R=CH_3
(XII): R=C_6H_5



(XIII) (XIV)

[10)] The absorption in the longer region of ultraviolet spectra of 2-amino- and 2-hydrazinotropones splits into two maxima when measured in methanol (cf. Ref. 2).

[11)] H. Hey, *J. Chem. Soc.*, **1934**, 1966.

XI was established by admixture of the methylamide, m. p. 166°C, of biphenyl-2-carboxylic acid, prepared by an unequivocal process.

The reaction with aniline was found to be somewhat more complicated. On heating 2-chloro-3-phenyltropone (II) and aniline in ethanol solution, orange plates XII, m. p. 110°C, were obtained from an easily soluble portion, and yellow crystals XIII, m. p. 173°C, from a sparingly soluble portion. The ultraviolet spectra of XII and XIII are shown in Fig. 3. XII shows absorption of a different type from that of the troponoids while that of XIII is similar to the absorption curve of 2-aminotropones[10]. XII is a neutral substance, is stable to acids and alkalis, and from its analytical values, it is assumed to be the rearrangement anilide of product, biphenyl-2-carboxylic acid. In fact, XII showed no depression of the melting point on admixture with the same anilide, m. p. 110°C, prepared by unequivocal process. Hydrolysis of XIII by heating with alkali in ethanolic solution afforded colorless crystals XIV, m. p. 97°C, an acid substance which gave the coloration with ferric chloride characteristic to tropolones. The ultraviolet spectrum of XIV is also characteristic of that of tropolones[7] as shown in Fig. 3. Previously, Doering and Knox[12] prepared 4-phenyltropolone and gave its melting point at 97°C, and measured its ultraviolet spectrum (in cyclohexane). From the comparison of elemental analytical values and ultraviolet spectra, XIV is undoubtedly 4-phenyltropolone and XIII would then be 2-anilino-6-phenyltropone. This fact indicates clearly that an abnormal substitution occurred in the reaction of II and aniline. This is the first example of an abnormal substitution occuring with an arylamine.

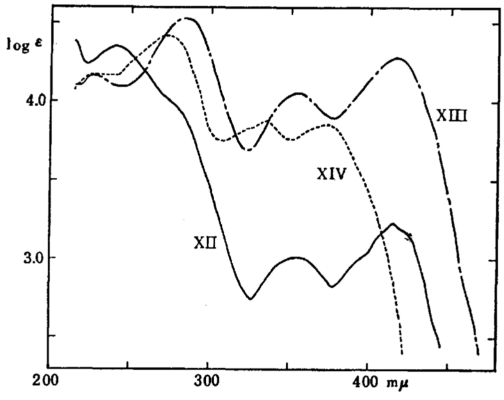


Fig. 3. U. V. Spectra of biphenyl-2-carboxyanilide (XII), 2-anilino-6-phenyltropone (XIII), and 4-phenyltropolone (XIV) in methanol.

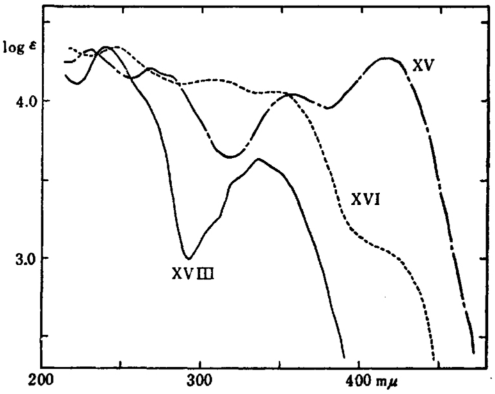


Fig. 4. U. V. Spectra of 2-anilino-7-phenyltropone (XV), the Schiff's Base (XVI), and 2-hydroxy-3-phenylbenzaldehyde (XVIII) in methanol.

In the reaction of 2-chloro-7-phenyltropone (I) and aniline, yellow crystals XV, m. p. 124°C, and colorless crystals XVI, m. p. 103.5°C, are obtained with XVI predominating in yield. The ultraviolet spectra of XV and XVI are indicated in Fig. 4 and from the absorption curve and analytical date, XV was assumed to be 2-anilino-7-phenyltropone. This structure was actually established by the conversion of XV into 3-phenyltropolone (XVII) by alkaline hydrolysis. XVI is a neutral substance and undergoes facile decomposition on being heated in dilute acid or alkali, affording colorless crystals XVIII, m. p. 45.5°C. Although XVIII is an acid substance, it does not dissolve in sodium hydrogen carbonate and exhibits a dark violet coloration with ferric chloride in ethanol, like that of salicylaldehyde. The infrared spectrum of XVIII, exhibits absorptions due to hydroxyl group at 3200 cm^{-1} and that of carbonyl group at 1666 cm^{-1}, which are both displaced to a smaller frequency range. It would be rational to accept this shift by assuming an intramolecular hydrogen bonding between the carbonyl and hydroxyl groups. There is also a C–H stretching vibration of aldehyde group at 2820 and 2730 cm^{-1}. From these facts, the analytical data and ultraviolet absorption in Fig. 4, XVIII is assumed to be 2-hydroxy-3-phenylbenzaldehyde and XVI would then be a Schiff's

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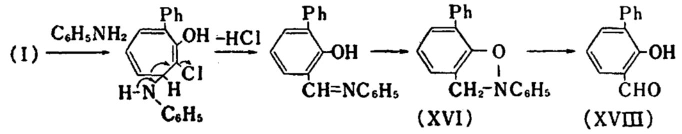
[12] W. von E. Doering and L. H. Knox, *J. Am. Chem. Soc.*, 75, 297 (1953).



Base of XVIII and aniline. This assumption was proved to be correct from the facile formation of XVI by heating XVIII and aniline. However, the infrared spectrum of XVI does not exhibit the O-H stretching vibration and the C=N vibration is not distinct, although there is the aromatic C=C vibration at 1616 cm^{-1} (common with XVIII). Considering the fact that XVI is a neutral substance, it is more likely to have an oxazoline structure than that of Schiff's Base.

The formation of a salicylaldehyde derivative by the nucleophilic attack on tropones has already been observed in the reaction of 2,7-dihalotropone with alkali[13] or ammonia[3]. These reactions all belong to the same type and are assumed to have been instigated by the attack of aniline at 3-position of the tropone ring as suggested by Kitahara[14].

The afore-mentioned reactions are examples of ammonia and amines acting as nucleophilic reagents on 2-halo-3-(or 7)-phenyltropone, and the normal and abnormal substitutions and rearrangement reactions have been observed. These reactions are thought to be brought about in different directions by whether the amines attack the 1-position (C=O) of the tropone ring, or the 2-position (C-Cl) or 3- or the 7-position (C-H). Which of these reactions actually occurs depends on the structure of the reacting tropones to be reacted, the basicity and the size of the reagent used. For example, the reaction of ammonia with 2-chloro-7-phenyltropone (I) is principally directed towards its attack on the 1-position (C=O), resulting in aromatization to form V. With methylamine, which has a larger volume than ammonia, the attack occurs at the 2-position (C-Cl), perhaps due to the steric hindrance of the phenyl group at the 7-position a substitution reaction results, forming X. With further increase in the volume of the reagent to aniline, the attack occurs not only at the 2-position (C-Cl) but also at the 3-position (C-H) and results in the formation of XVI. In 2-chloro-3-phenyltropone (II), the steric hindrance of the phenyl and carbonyl groups toward the 2-position becomes so large that the normal substitution at the 2-position does not occur. In the reaction of II and amines, the attacks on the 1-position (C=O) and the 7-position (C-H) invariably occur competitively so that the attack of ammonia and methylamine, due to their volume and basicity, becomes effective on the 1-position (C=O) and rearrangement reaction is likely to occur in the majority. On the contrary, aniline and hydrazine are more liable to attack the 7-position rather than the 1-position and the result is likely to be an abnormal substitution reaction.

The foregoing experimental evidence (especially formation of VII) offers the possibility of deriving 3-phenyltropone from 2-phenyltropone and the writer expects to carry out the preparation of 3-phenyltropone along line.

Experimental[15]

Reaction of 3-Phenyltropolone and Thionyl Chloride. — To a solution of 1.0 g. of 3-phenyltropolone dissolved in 25 cc. of dehydrated benzene, 0.73 g. (1.2 mol. equiv.) of thionyl chloride was added and the mixture was refluxed for 3 hours on a water bath. Benzene was then distilled off, thionyl chloride was removed under reduced pressure, and the dark brown oily residue was dissolved in a mixture of 5 cc. each of chloroform and carbon tetrachloride. This solution was passed through an alumina column (1 cm^2×20 cm.), which was eluted with chloroform, and the effluent was divided into seven fractions. Evaporation of the solvent from each fraction afforded pale yellow to yellow crystals with melting points listed below: (1) m. p. 65∼70°C, (2) 72∼74°C, and (3) 70∼73°C, with a combined yield of 630 mg. (4) 90 mg. of m. p. 55∼65°C. (5) Crystalline but its melting point cannot be determined. (6) 50 mg. of m. p. 80∼87°C. (7) 110 mg. of m. p. 92∼99°C. Fractions 1 to 3 were recrystallized from ethanol to yellow prisms I, m. p. 75°C.

Anal. Found: C, 72.34; H, 4.38. Calcd. for $C_{13}H_9OCl$: C, 72.06; H, 4.14%.

Fractions 6 and 7 were combined and recrystallized from ethanol and afforded pale yellow

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[13] S. Seto, *Sci. Repts. Tohoku Univ., First Ser.*, **37**, 378 (1954).

[14] Y. Kitahara, ibid., **39**, 250 (1956).

[15] All m. p. are uncorrected. The microanalyses were carried out by Miss Ayako Iwanaga and Mr. Shinichi Ohyama of this laboratory to whom the author is indebted.

prisms II, m. p. 103～104°C.

Anal. Found: C, 71.88; H, 4.46. Calcd. for $C_{13}H_9OCl$: C, 72.06; H, 4.14%.

The alumina column was finally eluted with ethanol and evaporation of ethanol from the effluent afforded pale yellow crystals. Low-pressure (3 mmHg) sublimation yielded 20 mg. of colorless crystals, m. p. 73～80°C, which recrystallized from cyclohexane to colorless plates III, m. p. 85.5～86.5°C. $\tilde{\nu}$ (in KBr): 3340, 3300～80, 3040, 2915, 2865, 1467, 1412, 1356, 1313, 1240, 1179, 1113, 1085, 1055, 1038, 845, 788, 757, 701 cm^{-1}.

Anal. Found: C, 71.44; H, 4.77. Calcd. for $C_{13}H_9OCl$: C, 72.06; H, 4.14%.

Hydrolysis of 2-Chloro-7-phenyltropone (I) with Alkali. — A solution of 150 mg. of I dissolved in a mixture of 4 cc. each of ethanol and 4 N potassium hydroxide was refluxed for 4 hours on a water bath. Ethanol was then distilled off, the residue was diluted with water, and extracted with benzene to remove a neutral portion. The aqueous layer was neutralized to weak acid and extracted three times with chloroform. The chloroform extract was washed with water and the solvent evaporated, leaving 120 mg. of yellowish brown oil. The residual oil was distilled under reduced pressure (2 mmHg) at a bath temperature of 140°C and the colorless oily distillate crystallized immediately to 90 mg. of crystals melting at 75～85°C. Recrystallization from petroleum ether—benzene mixture afforded colorless crystals, m. p. 107～109°C, undepressed on admixture with biphenyl-2-carboxylic acid, m. p. 109～110°C.

Catalytic Reduction of 2-Chloro-7-phenyltropone (I).—To a solution of 50 mg. of I dissolved in 5 cc. of methanol, 50 mg. of sodium acetate and 20 mg. of 5% palladium-carbon were added and the mixture was hydrogenated at ordinary temperature and pressure. The absorption of hydrogen was quite slow and only 8.1 cc. (1.5 mol. equiv.) was absorbed in 5 hours. The catalyst was filtered off, the residue was diluted with water, and the solution was extracted with benzene. Evaporation of the benzene gave 40 mg. of a pale yellow oil which crystallized on inoculation of 2-phenyltropone crystal. The crystalline mixture was allowed to stand with a small quantity of methanol and afforded needles, m. p. 81～83°C. The mixed m. p. 82～84°C on admixture with 2-phenyltropone, m. p. 84°C. Similar catalytic reduction of 2-chloro-3-phenyltropone (II) ended in the recovery of II and no product was obtained that would form a hydrochloride or a picrate.

Formation of 2-Hydrazino-3-phenyltropone (IV).—To a solution of 120 mg. of 2-methoxy-3-phenyltropone⁹⁾, m. p. 77～78°C, dissolved in a mixture of 4 cc. of ether and 1 cc. of methanol, 0.1 cc. of 80% aqueous solution of hydrazine hydrate was added and the mixture was allowed to stand overnight in a refrigerator. This solution was treated with water and the separated ether layer was evaporated at room temperature from which 120 mg. of orange yellow crystals were obtained. Recrystallization from ethanol afforded 70 mg. of deep yellow prisms IV, m. p. 140°C.

Anal. Found: N, 12.97. Calcd. for $C_{13}H_{12}NO_2$: N, 13.20%.

Formation of 2-Chloro-3-phenyltropone (II) from 2-Hydrazino-3-phenyltropone (IV).—A solution of 300 mg. of IV dissolved in 4 cc. of concentrated hydrochloric acid was added in a few minutes into a heated solution of 3 g. of copper sulfate dissolved in 3 cc. of water. Some evolution of nitrogen was observed but a fair amount of tarry substance separated out. After boiling for 5 minutes, the solution was cooled and extracted with chloroform. The chloroform extract was washed with water, passed through an alumina column, and the column was eluted with chloroform. The pale yellow crystals, m.p. 93～95°C, obtained on evaporation of chloroform, were recrystallized from ethanol to pale yellow plates, m. p. 104～105°C, undepressed on admixture with 2-chloro-3-phenyltropone (II), m. p. 104°C, as described above.

Reaction of 2-Chloro-3-phenyltropone (II) and Ammonia.—A solution of 100 mg. of II dissolved in 3 cc. of ethanol saturated with ammonia at room temperature was placed in a vessel, sealed tightly, and left to stand at room temperature for 50 hours. The color of the solution changed from yellow through brown to pale yellow. Ethanol was evaporated under reduced pressure at room temperature and 60 mg. of pale yellow crystals, m. p. 173～174°C, so obtained were recrystallized from benzene to colorless needles V, m. p. 174～174.5°C, undepressed on admixture with an authentic sample of biphenyl-2-carboxamide, m. p. 174°C.

Reaction of 2-Chloro-7-phenyltropone (I) and Ammonia. — A mixture of 120 mg. of I in 3.7 cc. of ethanol saturated with ammonia was allowed to stand in a sealed vessel for 50 hours. Ethanol was evaporated under a reduced pressure at room temperature and 80 mg. of brown crystals, m. p. 148～160°C (sint. 120°C), were recrystallized from benzene to 50 mg. of colorless needles V, m. p. 174～174.5°C, undepressed on admixture with biphenyl-2-carboxamide.

Reaction of 2-Chloro-7-phenyltropone (I) and Hydrazine. — To a solution of 50 mg. of I dissolved in 1.5 cc. of ethanol, 0.06 cc. of 80% hydrazine hydrate solution was added and the mixture was refluxed for 30 minutes on a water bath. The ethanolic solution was concentrated to about one-half and cooled. From this 45 mg. of golden yellow needles, m. p. 195～197°C, separated out. The crystals were recrystallized from ethanol to VI, m. p. 199～200°C¹⁶⁾, which showed no depression on admixture with the structurally known 2-hydrazino-7-phenyltropone, m. p. 192°C (decomp.)¹⁶⁾. Benzylidene compound²⁾ of VI: m. p. 150°C.

$\lambda_{\max}^{\mathrm{MeOH}}$ mμ (log ε): 240 (4.38), 273 (4.20), 280 (4.14), 442 (4.56).

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16) VI was reported as melting at 192°C (cf. Ref. 2), but it is corrected to m. p. 200°C.

Reaction of 2-Chloro-3-phenyltropone (II) and Hydrazine.—To a solution of 100 mg. of II dissolved in 3 cc. of ethanol, 0.10 cc. of 80% hydrazine hydrate solution was added and the mixture was refluxed for 30 minutes on a water bath. Evaporation of ethanol and cooling of the residue separated 80 mg. of golden yellow crystals, m. p. 100∼130°C, which were recrystallized from cyclohexane to 60 mg. of orange scales VII, m.p. 136∼137°C.

Anal. Found: N, 13.28. Calcd. for $C_{13}H_{12}ON_2$: N, 13.20%.

Benzylidene compound of VII: Yellow needles, m. p. 203°C.

Anal. Found: N, 9.52. Calcd. for $C_{20}H_{16}ON_2$: N, 9.33%.

$\lambda_{\max}^{\mathrm{MeOH}}$ mμ (log ε): 238(4.25), 285(4.42), 377(4.26), 438(4.59).

Formation of 2-Chloro-6-phenyltropone (VIII) from 2-Hydrazino-6-phenyltropone (VII) and its Aromatization. — A suspension of 80 mg. of VII and 1.5 cc. of concentrated hydrochloric acid was added to a heated solution of 1.5 g. of copper sulfate dissolved in 1.5 cc. of water. After boiling 30 minutes, the solution was diluted with water and extracted with benzene. The benzene extract was washed with water and passed through an alumina column. Evaporation of benzene eluate afforded 45 mg. of a yellowish crystals m. p. 110∼112°C, which were recrystallized from ethanol to pale yellow needles VIII, m. p. 113∼114°C.

Anal. Found: C, 71.72; H, 4.39. Calcd. for $C_{13}H_9OCl$: 72.06; H, 4.14%.

A solution of 40 mg. of VIII in 2 cc. of 10% ethanolic potassium hydroxide solution was refluxed for 30 minutes, ethanol was distilled off, 2 cc. of water was added to the residue, and the mixture was heated for a further 10 minutes. A small amount of brown precipitate that separated out was filtered off, the filtrate was acidified with 6 N sulfuric acid, and the white precipitate so formed was collected by filtration, yielding 20 mg. of colorless crystals, m. p. 145∼153°C. The crystals were recrystallized from benzene-petroleum ether to colorless plates IX, m. p. 162∼163°C. The reported melting point for biphenyl-3-carboxylic acid is 162∼164°C[11].

Reaction of 2-Chloro-7-phenyltropone (I) and Methylamine.—To a solution of 100 mg. of potassium hydroxide dissolved in 2.5 cc. of ethanol, 180 mg. of methylamine hydrochloride was added and potassium chloride that separated out was removed by filtration. To this filtrate, 100 mg. of I was added and the mixture was refluxed for 3 hours on a water bath. The residue obtained on evaporation of ethanol was recrystallized from ethanol to 45 mg. of yellow plates X, m. p. 159°C.

Anal. Found: N, 6.97. Calcd. for $C_{14}H_{13}ON$: N, 6.63%.

Ethanol was evaporated from the recrystallization mother liquor, the residue was dissolved in benzene, and the solution was passed through an alumina column. From the benzene eluate, 30 mg. of yellow crystals, m. p. 75°C, was obtained and this was identified to be I by mixed fusion.

Hydrolysis of 2-Methylamino-7-phenyltropone (X) with Alkali.—A solution of 25 mg. of X dissolved in a mixture of 1.5 cc. of ethanol and 4 N potassium hydroxide was refluxed for 6 hours on a water bath, ethanol was evaporated, and the residue was diluted with water. This was extracted with benzene and 20 mg. of pale brown crystals, m. p. 105∼110°C, obtained on evaporation of benzene were recrystallized from ethanol to crystals of m. p. 113°C, undepressed on admixture with an authentic sample of 3-phenyltropone, m. p. 118°C[2].

Reaction of 2-Chloro-3-phenyltropone (II) and Methylamine.—A solution of 100 mg. of II dissolved in a solution of 130 mg. of methylamine hydrochloride and 100 mg. of potassium hydroxide dissolved in 2.5 cc. of ethanol was sealed in a glass tube and heated for 3 hours at 100°C. The ethanol was evaporated from the mixture, the residue was extracted with benzene and the solid residue obtained on evaporation of benzene was recrystallized from ethanol to pale yellow needles XI, m. p. 162∼164°C.

The oily acid chloride obtained on refluxing biphenyl-2-carboxylic acid with thionyl chloride in benzene was added to ethanolic solution of methylamine and the mixture was warmed on a water bath, from which biphenyl-2-carboxymethylamide was obtained as colorless crystals, m. p. 165∼167°C. This showed no depression of the melting point on admixture with XI.

Reaction of 2-Chloro-3-phenyltropone (II) and Aniline. — A solution of 180 mg. of II and 400 mg. of aniline dissolved in 5 cc. of ethanol was refluxed for 3 hours on a water bath. Ethanol was then evaporated, the residue cooled, and 40 mg. of yellow crystals, m. p. 165∼167°C, obtained from it were recrystallized from benzene to XIII, m. p. 172∼173°C.

Anal. Found: C, 83.79; H, 5.42; N, 5.53. Calcd. for $C_{19}H_{15}ON$: C, 83.49; H, 5.53; N, 5.13%.

The ethanolic solution left after separation of the crystals was extracted with benzene, the benzene extract was shaken with 1 N hydrochloric acid solution to remove remaining aniline, and washed with water. The benzene solution was then passed through an alumina column and the column was eluted with benzene. The effluent was divided into two fractions and evaporation of benzene from the initial fraction left 100 mg. of pale orange oil. The latter fraction afforded 40 mg. of similar oil. Both oils crystallized immediately and respectively afforded crystals of m. p. 97∼101°C and 102∼105°C. These were combined and recrystallized from cyclohexane to 90 mg. of colorless prisms XII, m. p. 109∼110°C.

Anal. Found: C, 83.14; H, 5.46; N, 5.38. Calcd. for $C_{19}H_{15}ON$: C, 83.49; H, 5.53; N, 5.13%.

The alumina column was further eluted with ethanol and 10 mg. of yellow crystals, m. p. 165∼167°C, were obtained, which showed no depression of the melting point on admixture with XIII.

Biphenyl-2-carboxylic acid chloride was refluxed with aniline in benzene and colorless crystals (from ethanol), m. p. 110°C, thereby obtained showed no depression of the melting point on admixture with XII.

Hydrolysis of 2-Anilino-6-phenyltropone (XIII).—To a solution of 30 mg. of XIII dissolved in 2.5 cc. of ethanol, 2.5 cc. of 3 N potassium hydroxide solution was added and the mixture was refluxed for 8 hours on a water bath. Ethanol was evaporated from the mixture, water was added to the residue, and this was extracted with benzene.

Alkaline aqueous solution was neutralized with dilute hydrochloric acid and the turbid solution that resulted was extracted three times with chloroform. The extract was washed with water and the solvent was evaporated, leaving 20 mg. of brown oil which crystallized immediately. Its recrystallization from ethanol afforded colorless needles XIV, m. p. 97°C.

Anal. Found: C, 78.23; H, 5.38. Calcd. for $C_{13}H_{10}O_2$: C, 78.77: H, 5.09%.

This substance colors red with aqueous solution of ferric chloride and the color transits to the chloroform layer. The reported melting point of 4-phenyltropolone is 97°C[12].

Reaction of 2-Chloro-7-phenyltropone (I) with Aniline. — A solution of 600 mg. of I and 1.8 g. of aniline dissolved in 6 cc. of ethanol was refluxed for 6 hours on a water bath. Evaporation of the solvent left 250 mg. of yellow crystals, m. p. 97~98°C. Ethanol was added to the filtrate, which was further refluxed for 3 hours, and 100 mg. of yellow crystals, m. p. 97~98°C, was obtained. The mother liquor left here will be designated as A. The two crops of the above crystals were combined, dissolved in carbon tetrachloride and passed through a short alumina column. Evaporation of carbon tetrachloride from the effluent afforded 250 mg. of orange plates, m. p. 101~102°C, and its recrystallization from ethanol gave XVI, m. p. 103~103.5°C. $\tilde{\nu}$ (in KBr): 3030, 1616, 1583, 1488, 1455, 1427, 1372, 1293, 1280, 1202, 1173, 1100, 1075, 1023, 1000, 980, 940, 906, 849, 830, 757, 692, 650 cm^{-1}.

Anal. Found: N, 5.29. Calcd. for $C_{19}H_{15}ON$: N, 5.13%.

XVI is insoluble in either dilute acid or alkali. The mother liquor (A) was dissolved in benzene, shaken with 1 N hydrochloric acid to remove excessive aniline, the benzene layer was washed thoroughly with water, and the benzene evaporated, leaving 190 mg. of yellow crystals, m. p. 89~106°C. The crystals were dissolved in a mixture of 5 cc. each of ethanol and 2 N hydrochloric acid and the mixture was refluxed for 30 minutes on a water bath. Ethanol was evaporated, residual solution was extracted with benzene after addition of water, and the benzene extract was shaken with dilute sodium hydroxide solution to remove an acid portion. The alkaline extract will be designated as B. The benzene extract was washed with water and the solvent evaporated, giving 150 mg. of yellow crystals, m. p. 110~113°C. Recrystallization from ethanol afforded 90 mg. of yellow prisms XV, m. p. 122~124°C.

Anal. Found: N, 5.22. Calcd. for $C_{19}H_{15}ON$: N, 5.13%.

The extract B was neutralized, acidified and extracted with chloroform. The extract was washed thoroughly with water; and evaporation of the solvent left 20 mg. of pale brown oil which soon solidified to colorless crystals, m. p. 38~40°C. This substance is probably identical with XVIII described below.

Hydrolysis of 2-Anilino-7-phenyltropone (XV) with Alkali.—A solution of 50 mg. of XV dissolved in a mixture of 4 cc. of ethanol and 2 cc. of 6 N potassium hydroxide was refluxed for 6 hours on a water bath. Ethanol was evaporated from this mixture, water was added to the residual solution, and extracted with benzene to remove a neutral portion. The aqueous alkali solution was acidified with dilute hydrochloric acid and extracted with chloroform. The extract was washed with water ; evaporation of hlorcoform afforded 30 mg. of pale yellow crystals, m. p. 97~100°C. Its recrystallization from ethanol gave yellowish prisms, m. p. 114~116.5°C, which showed no depression with authentic 3-phenyltropolone, m. p. 118°C[2].

Hydrolysis of Schiff's Base (XVI).—A solution of 110 mg. of XVI dissolved in a mixture of 4 cc. of ethanol and 2 cc. of 6 N potassium hydroxide was refluxed for 1 hour. Ethanol was evaporated from this solution, water was added and then extracted with benzene to remove a neutral portion. The aqueous alkali solution was acidified and extracted with chloroform. The extract was washed with water, the chloroform evaporated, and 80 mg. of pale brown oily residue crystallized immediately, showing m. p. 40~42°C. Recrystallization from ethanol afforded colorless plates XVIII, m. p. 45.5~46°C. $\tilde{\nu}$ (in KBr) 3200, 3040, 2820, 2730, 1666, 1611, 1495, 1472, 1453, 1433, 1384, 1303, 1264, 1214, 1167, 1097, 1065, 1026, 911, 829, 794, 761, 720, 693 cm^{-1}.

Anal. Found: C, 78.33; H. 5.11. Calcd. for $C_{13}H_{10}O_2$: C, 77.98; H, 5.09%.

The halogen test is negative with XVIII and it does not transit to an alkali layer on shaking its benzene solution with saturated solution of sodium hydrogen carbonate. Ethanolic solution of XVIII becomes dark violet with ferric chloride.

Hydrolysis of 80 mg. of XVI by heating in a mixture of 2 cc. of each of ethanol and 2 N hydrochloric acid for 30 minutes also affords 50 mg. of XVIII, m. p. 45°C.

Reaction of 2-Hydroxy-3-phenylbenzaldehyde (XVIII) and Aniline. — A mixture of 80 mg. of XVIII and 200 mg. of aniline was heated on a water bath for 20 minutes and the resulting dark red oil separated crystals on being cooled. The addition of a small amount of ethanol afforded 90 mg. of almost colorless scales, m. p. 103°C, undepressed on admixture with XVI, m.p. 103.5°C.

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