The Mannich Base of Troponoid and its Application. VIII. Reaction of 3-Bromo-5-formyl-7-isopropyltropolone

By Kyozo OGURA

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In the preceding paper of this series[1], the synthesis of 3-bromo-5-formyl-7-isopropyltropolone (I) from the Mannich base, 3-bromo-5-piperidinomethyl-7-isopropyltropolone, was described; the present paper concerns the reaction of this aldehyde.

Aldehyde I is highly reactive and is similar to 3, 7-dibromo-5-formyltropolone[2]. It forms an acetal II on merely being warmed in methanol and undergoes a reaction with various amines to form the Schiff base. The reaction of I with aniline, *p*-toluidine, *p*-anisidine and 5-aminotropolone respectively afforded *N*-(3-bromo-7-isopropyltropolon-5-ylmethylene)aniline (III), *N*-(3-bromo-7-isopropyltropolon-5-ylmethylene)-*p*-toluidine (IV), *N*-(3-bromo-7-isopropyltropolon-5-ylmethylene)-*p*-anisidine (V), and *N*-(3′-bromo-7′-isopropyltropolon-5′-ylmethylene)-5-tropolonylamine (VI). The reaction of I and *o*-phenylenediamine afforded 2-(3′-bromo-7′-isopropyltropolon-5′-yl)benzimidazole (VIII) through *N*-(3-bromo-7-isopropyltropolon-5-ylmethylene)-*o*-aminoaniline (VII). The compound VIII was also obtained by the reaction of (3-bromo-7-isopropyltropolon-5-yl)-*N*-(*p*-dimethylaminophenyl)nitrone with *o*-phenylenediamine[1]. The structures of VII and VIII were supported by their ultraviolet spectra. The reaction of I with malononitrile, cyanoacetamide, and ethyl cyanoacetate respectively afforded 3-bromo-5-(β, β-dicyanovinyl)-(IX), 3-bromo-(β-cyano-β-carbamoylvinyl)-(X), and 3-bromo-5-(β-cyano-β-ethoxycarbonylvinyl)-7-isopropyltropolone (XI). The hydrolysis of XI with alkali gave 3-bromo-5-(β-cyano-β-carboxyvinyl)-7-isopropyltropolone (XII). The reaction of I and hippuric acid

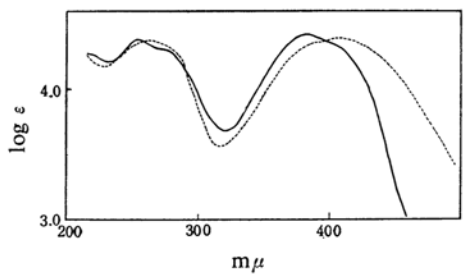
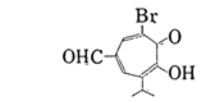
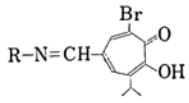


Fig. 1. Ultraviolet spectra of VII(……) and VIII (——) in methanol.

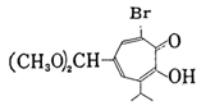
1) K. Ogura, This Bulletin, **34**, 839 (1961).
2) S. Seto and K. Ogura, ibid., **32**, 493 (1959).



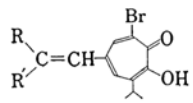
I



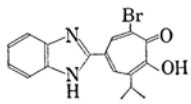
III : R = C_6H_5
IV : R = p-CH_3-C_6H_4
V : R = p-CH_3O-C_6H_4
VI : R =
VII : R = o-H_2N-C_6H_4



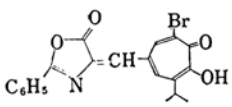
II



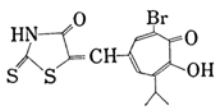
IX : R = R′ = CN
X : R = CN, R′ = $CONH_2$
XI : R = CN, R′ = $COOC_2H_5$
XII : R = CN, R′ = COOH
XIV: R = C_6H_5CONH, R′ = COOH



VIII



XIII



XV

Scheme 1

gave the corresponding azlactone compound (XIII), which was hydrolyzed to 3-bromo-5-(β-benzamido-β-carboxyvinyl)-7-isopropyltropolone (XIV).

The aldehyde I underwent condensation with rhodanine to form 3-bromo-7-isopropyltropolon-5-ylmethylenerhodanine (XV), but its treatment with alkali failed to produce the corresponding thioketocarboxylic acid but afforded colorless crystals (XVI) of m. p. 249°C(decomp.), corresponding to the molecular formula of $C_{13}H_{12}O_4S$, and a small amount of I. The bromination

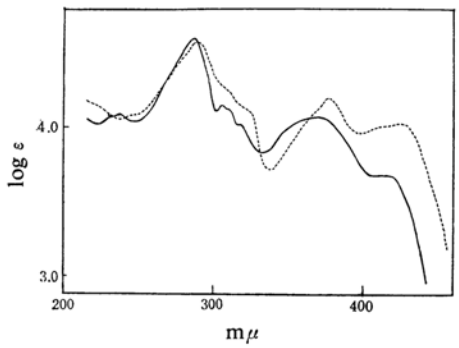
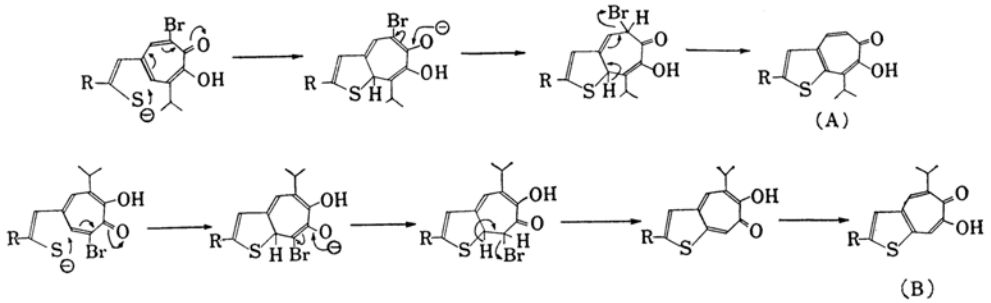


Fig. 2. Ultraviolet spectra of XVI (——) and XVII (·····) in methanol.

of XVI afforded a monobromo compound (XVII) of m. p. 273°C(decomp.). The ultraviolet spectrum of XVI, as indicated in Fig. 2, is not that of a monocyclic tropolone type. The infrared spectrum of XVI showed absorptions for carboxyl group at 2550 and 1672 cm^{-1}. These facts suggest that XVI is a thieno[2, 3-d]tropolone derivative (A or B) formed by the abnormal intramolecular attack of the sulfide anion at the 6- or 4-position of the tropolone ring, with the liberation of the bromide ion from the 3-position.

It may be presumed that the 6-position is sterically hindered by the isopropyl group in 7-position and is liable to be less attacked than the 4-position, so that the product is more likely to be B. Finally, the structure of this product (XVI) was established as 2-carboxy-5-isopropylthieno[2, 3-d]tropolone (B) by the experiments to be described below.

The oxidation of XVI with alkaline potassium permanganate afforded 2, 3, 5-thiophenetricarboxylic acid (XVIII), m. p. 216°C, which formed trimethyl ester XIX, m. p. 83°C with diazomethane. The ester XIX was identified by mixed fusion and through comparison of its ultraviolet and infrared spectra with those of the specimen synthesized by Jones[3]. The



(A)

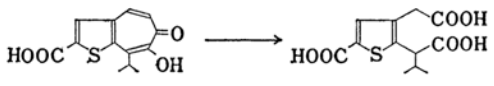
(B)

R = COOH

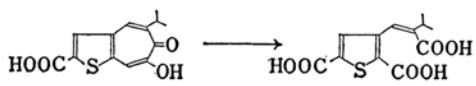
Scheme 2

3) R. G. Jones, *J. Am. Chem. Soc.*, **77**, 4164 (1955).

oxidation of XVI with alkaline hydrogen peroxide afforded a colorless acid substance (XX), m. p. 259°C(decomp.). Elemental analyses of XX gave values corresponding to $C_{12}H_{12}O_6S$, while XX formed a trimethyl ester, (XXI), $C_{15}H_{18}O_6S$, m. p. 86°C, with diazomethane and formed XVIII by oxidation with potassium permanganate. By analogy with the facts known on the oxidation of tropolones with hydrogen peroxide[4-7], it is expected that 8-isopropyl derivative A should afford 2-(α-carboxyisobutyl)-3-carboxymethyl-5-carboxythiophene (A′) and that 5-isopropyl derivative B should give 2, 5-dicarboxy-3-(β-isopropyl-β-carboxyvinyl) thiophene (B′). The ultraviolet spectrum of XX



(A) (A′)



(B) (B′)

Scheme 3

exhibited absorption maxima at 250 mμ(log ε, 4.19) and 280 mμ(log ε, 4.09), while the infrared spectrum of XXI showed absorptions for the carbonyl group of unsaturated ester and for the carbon-carbon double bond at 1715 and 1643 cm^{-1}. The nuclear magnetic resonance spectrum of XXI had absorption corresponding to one ethylenic proton at 222 c. p. s. (with cyclohexane standard). These facts indicate that this oxidation product XX is 2, 5-dicarboxy-3-(β-isopropyl-β-carboxyvinyl)thiophene (B′) and that

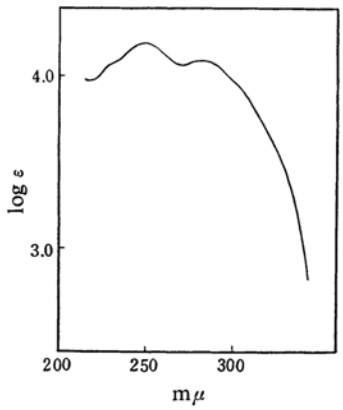


Fig. 3. Ultraviolet spectrum of XX in methanol.

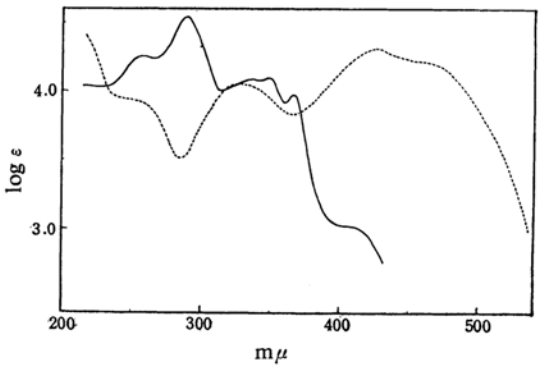
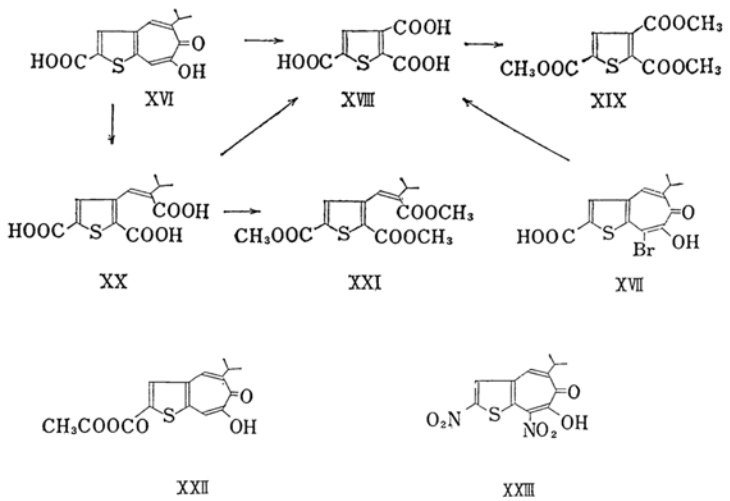


Fig. 4. Ultraviolet spectra of XXII (——) and XXIII (·····) in methanol.



Scheme 4

4) J. W. Cook et al., *J. Chem. Soc.*, **1951**, 503.
5) T. Nozoe et al., *Proc. Japan Acad.*, **30**, 604 (1954).
6) D. S. Tarbell et al., *J. Am. Chem. Soc.*, **74**, 1234 (1952).
7) H. Fernholz et al., *Ann.*, **576**, 131 (1952).

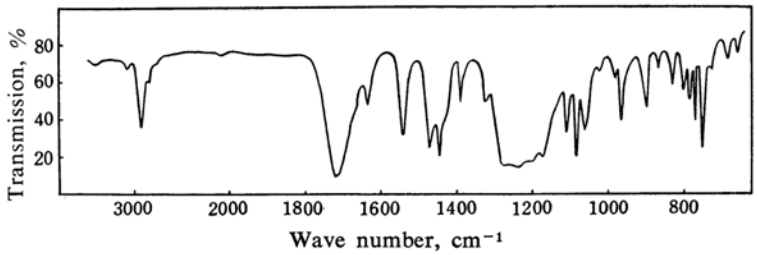


Fig. 5. Infrared spectrum of XXI in KBr disk.

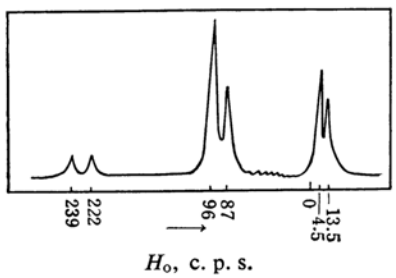
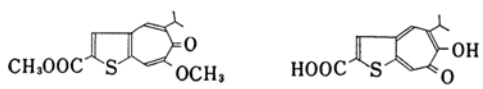


Fig. 6. NMR spectrum of XXI in carbon tetrachloride.

consequently, the position of the isopropyl group in XVI must be 5.

The oxidation of the monobromo compound XVII with potassium permanganate gave 2, 3, 5-thiophenetricarboxylic acid (XVIII), judging from which XVII must be 2-carboxy-5-isopropyl-8-bromothieno [2, 3-d] tropolone. The heating of XVI with acetic anhydride, in the presence of sodium acetate, afforded colorless crystals of m. p. 190°C, $C_{15}H_{14}O_5S$, which showed infrared absorptions of the hydroxyl group at 3160 cm^{-1}, and of the carbonyl group at 1765 and 1730 cm^{-1}. This product was therefore considered to be the anhydride XXII. It reverted to XVI on alkaline hydrolysis. The treatment of XVI with concentrated nitric acid in acetic acid gave yellow needles, of m. p. 185°C, whose elemental analyses and infrared spectrum indicated that this product was 2, 8-dinitro-5-isopropylthieno [2, 3-d] tropolone (XXIII). The ultraviolet spectra of XXII and XXIII are shown in Fig. 4.

The treatment of XVI with diazomethane afforded only one kind of methyl ether XXIV; this is thought to be due to the condensed thiophene ring, as in the case of benzotropolones[6], and there is almost no contribution from the type of XVI′.



XXIV XVI′

Scheme 5

Experimental*

3-Bromo-5-dimethoxymethyl-7-isopropyltropolone (II).—A solution of 20 mg. of I in methanol (1 ml.) was refluxed for 30 min. The evaporation of the methanol left colorless needles. The crystals were collected, with the addition of petroleum ether, and recrystallized from petroleum ether to form colorless rods, m. p. 86~87°C. Yield, 20 mg.

Found: 49.49; H, 5.35. Calcd. for $C_{13}H_{16}O_4Br$: C, 49.38; H, 5.36%.

***N*-(3-Bromo-7-isopropyltropolon-5-ylmethylene)-aniline (III).**—A mixture of I (30 mg.), aniline (15 mg.) and acetic acid (0.1 ml.) was warmed in a water bath, by which the whole first dissolved to form a red solution, but then yellow crystals began to separate out. This mixture was warmed for 30 min., and the crystals were collected and recrystallized from petroleum ether to form yellow scales, m. p. 145~147°C. Yield, 20 mg.

Found: C, 59.71; H, 4.54; N, 3.92. Calcd. for $C_{17}H_{16}O_2NBr$: C, 58.96; H, 4.62; N; 4.05%.

λ_{max}^{MeOH} $m\mu(\log \varepsilon)$: 260(4.50), 340(3.88), 385(4.00).

***N*-(3-Bromo-7-isopropyltropolon-5-ylmethylene)-*p*-toluidine (IV).**—A mixture of I (40 mg.) and *p*-toluidine (20 mg.) in acetic acid (0.1 ml.) was warmed in a water bath for 20 min. and then cooled to room temperature. The crystals that formed were collected and recrystallized from petroleum ether to form yellow needles, m. p. 113~116°C. Yield, 30 mg.

Found: C, 57.71; H, 4.57; N, 3.70; Calcd. for $C_{18}H_{18}O_2NBr.H_2O$: C, 57.15; H, 5.29; N, 3.70%.

λ_{max}^{MeOH} $m\mu(\log \varepsilon)$: 259(4.34), 342(3.78), 390(3.99).

***N*-(3-Bromo-7-isopropyltropolon-5-ylmethylene)-*p*-anisidine (V).**—A mixture of I (20 mg.) and *p*-anisidine (10 mg.) in acetic acid (0.1 ml.) was heated in a water bath for 5 min. and then cooled to room temperature. The crystals that formed were collected and recrystallized from methanol to form yellow needles, m. p. 95~101°C. Yield, 10 mg.

Found: C, 57.39; H, 4.70:, N; 3.91. Calcd. for $C_{18}H_{18}O_3NBr$: C, 57.46; H, 4.79; N, 3.73%.

λ_{max}^{MeOH} $m\mu(\log \varepsilon)$: 259(4.45), 390(4.20).

***N*-(3′-Bromo-7′-isopropyltropolon-5′-ylmethylene)-5-tropolonylamine (VI).**—A mixture of I (20 mg.) and 5-aminotropolone (15 mg.) in acetic acid (0.1 ml.) was heated in a water bath; yellow powder precipitated in 5~6 min. This precipitate was

* All melting points are uncorrected. The microanalyses were carried out by Miss Yoko Endo and Miss Yukiko Endo of this Institute, to whom the author is indebted.

collected and washed with hot methanol and acetic acid, m. p. 203~204°C(decomp.).

Found: C, 55.35; H, 4.06; N, 3.73. Calcd. for $C_{18}H_{16}O_4NBr$: C, 55.40; H, 4.10; N, 3.59%.

λ_{max}^{MeOH} mμ(log ε): 230(4.41), 255(4.52), 420(4.41).

***N*-(3-Bromo-7-isopropyltropolon-5-ylmethylene)-*o*-aminoaniline (VII).**—A mixture of I (40 mg.) and *o*-phenylenediamine (20 mg.) in ethanol (0.1 ml.) was heated in a water bath for a few minutes. The red crystals that precipitated were collected and recrystallized from ethanol to form red prisms, m. p. 104~107°C. Yield, 30 mg.

Found: C, 56.40; H, 4.48; N, 7.55. Calcd. for $C_{17}H_{17}O_2N_2Br$: C, 56.52; H, 4.71; N, 7.75%.

λ_{max}^{MeOH} mμ(log ε): 263(4.37), 406(4.39).

2-(3'-Bromo-7'-isopropyltropolon-5'-yl)benzimidazole (VIII).—A mixture of I (40 mg.) and *o*-phenylenediamine (20 mg.) in 0.1 ml. of acetic acid was heated in a water bath for 5~6 min.; the crystals that formed were collected and recrystallized from methanol to form yellow needles, m. p. 242~243°C(decomp.). Yield, 20 mg.

VIII was also obtained by the use of (3-bromo-7-isopropyltropolon-5-yl)-*N*-(*p*-dimethylaminophenyl) nitrone in place of I and reacted under the same conditions. The compound VII also afforded VIII on being heated in acetic acid.

Found: C, 56.75; H, 3.94; N, 7.68. Calcd. for $C_{17}H_{15}O_2N_2Br$: C, 56.84; H, 4.18; N, 7.81%.

λ_{max}^{MeOH} mμ(log ε): 254(4.39), 383(4.43).

3-Bromo-5-(β, β-dicyanovinyl)-7-isopropyltropolone (IX).—A solution of I (50 mg.), malononitrile (20 mg.), and piperidine (1 drop) dissolved in ethanol (1 ml.) was allowed to stand at room temperature, by which the solution gradually acquired a reddish tint and yellow crystals precipitated out after about 5 hr. After the mixture had been allowed to stand overnight, the crystals were collected, treated with 6 N hydrochloric acid (0.2 ml.), collected on a filter, washed with water, and recrystallized from methanol to form yellow granules, m. p. 145~146°C. Yield, 30 mg.

Found: C, 52.44; H, 3.51; N, 8.30. Calcd. for $C_{14}H_{11}O_2N_2Br$: C, 52.80; H, 3.45; N, 8.78%.

λ_{max}^{MeOH} mμ(log ε): 222(4.20), 280(4.10), 404(4.15), 490(4.70).

3-Bromo-5-(β-cyano-β-carbamoylvinyl)-7-isopropyltropolone (X).—A solution of I (50 mg.), cyanoacetamide (20 mg.), and piperidine (1 drop) dissolved in ethanol (1 ml.) was refluxed for 3 hr., the solvent was distilled off, and the residue was acidified by the addition of 6 N hydrochloric acid. The yellow, powdery precipitate thereby formed was collected and washed thoroughly with water and methanol, m. p. 233°C(decomp.). Yield, 20 mg.

Found: C, 49.14; H, 3.69; N, 7.61. Calcd. for $C_{14}H_{13}O_3N_2Br$: C, 49.87; H, 3.86; N, 8.31%.

λ_{max}^{MeOH} mμ(log ε): 245(4.06), 275(4.14), 466(4.47).

3-Bromo-5-(β-cyano-β-ethoxycarbonylvinyl)-7-isopropyltropolone (XI).—A mixture of I (50 mg.) and ethyl cyanoacetate (30 mg.) dissolved in ethanol (1 ml.) and with one drop of piperidine added was allowed to stand at room temperature for 2 days, and then the ethanol was evaporated. 6N Hydrochloric acid was added to its reddish syrupy residue; the syrup thereby solidified and formed a yellowish powder. This powder was collected and recrystallized from methanol to form yellow needles, m. p. 106~108°C. Yield, 50 mg.

Found: C, 52.71; H, 4.48; N, 3.43. Calcd. for $C_{16}H_{16}O_4NBr$: C, 52.46; H, 4.37; N, 3.83%.

λ_{max}^{MeOH} mμ(log ε): 245(4.04), 276(4.13), 408(4.25), 476(4.57).

3-Bromo-5-(β-cyano-β-carboxyvinyl)-7-isopropyltropolone (XII).—A mixture of XI (60 mg.) and a 20% aqueous solution of sodium hydroxide (0.5 ml.) was heated in a water bath for a few minutes. The mixture formed a red solution and then precipitated out yellow crystals. The mixture was acidified with 6 N hydrochloric acid, and the yellow precipitate thereby formed was collected by filtration. Recrystallization from methanol afforded yellow prisms, m. p. 210~220°C. Yield, 30 mg.

Found: C, 49.67; H, 3.78; N, 3.70. Calcd. for $C_{14}H_{12}O_4NBr$: C, 49.72; H, 3.58; N, 4.14%.

λ_{max}^{MeOH} mμ(log ε): 265(4.28), 290(4.19).

2-Phenyl-4-(3'-bromo-7'-isopropyltropolon-5'-ylmethylene)-5-oxazolone (XIII).—A mixture of I (100 mg.), hippuric acid (80 mg.), freshly fused sodium acetate (40 mg.), and acetic anhydride (0.5 ml). was heated at 80~90°C for 10 min.; the mixture thereby formed a red solution and an orange precipitate separated. The mixture was cooled and diluted with water (0.2 ml.), and the precipitate was collected by filtration. The precipitate was washed thoroughly with water and methanol, m. p. 190~194°C. Yield, 100 mg.

Found: C, 58.29; H, 3.88; N, 2.92. Calcd. for $C_{20}H_{16}O_4NBr$: C, 57.99; H, 3.87; N, 3.38%.

λ_{max}^{MeOH} mμ(log ε): 258(4.28), 320(4.15), 426(4.21); 510(4.43).

3-Bromo-5-(β-benzamido-β-carboxyvinyl)-7-isopropyltropolone (XIV).—A mixture of 100 mg. of azlactone (XIII) and a 10% sodium hydroxide solution (0.5 ml.) in methanol (0.3 ml.) was heated in a water bath for a a few minutes, the methanol was evaporated, and the residual solution was acidified with 6 N hydrochloric acid. The pale yellow precipitate that formed was collected by filtration and recrystallized from methanol to form a yellow powder, m. p. 220°C(decomp.). Yield, 40 mg.

Found: C, 55.98; H, 4.34; N, 3.08. Calcd. for $C_{20}H_{18}O_5NBr$: C, 55.57; H, 4.17; N, 3.24%.

λ_{max}^{MeOH} mμ(log ε): 262(4.42), 375(4.27).

3-Bromo-7-isopropyltropolon-5-ylmethylenerhodanine (XV).—A mixture of I (500 mg.), rhodanine (250 mg.), freshly fused sodium acetate (500 mg.), and acetic acid (3.4 ml.) was heated in a boiling water bath; orange prismatic crystals thereby precipitated out. After the mixture had been heated for 1 hr., water (1 ml.) was added to the mixture, and the crystals were collected and washed with water and methanol. Orange prisms, m. p. 235~240°C. Leaving the filtrate to stand at room temperature further afforded a precipitate of XV. Yield, 700 mg.

Found: C, 44.15; H, 3.10; N, 3.40. Calcd. for $C_{14}H_{12}O_3NS_2Br$; C, 43.55; H, 3.13; N, 3.63%.

λ_{max}^{MeOH} mμ(log ε): 253(4.16), 335(3.96), 430(4.26), 500(4.31).

2-Carboxy-5-isopropylthieno[2, 3-d]tropolone (XVI).—A solution of XV (450 mg.) in a 15% aqueous solution of sodium hydroxide (4 ml.) was heated on a water bath for 1 hr.; the yellow crystals that precipitated out were collected and acidified with 6 N hydrochloric acid, thereby obtaining ca. 20 mg. of I.

The acidification of this filtrate with 6 N hydrochloric acid afforded a colorless precipitate, which was collected after the addition of a small amount of methanol (0.5 ml.). The precipitate was washed with water and methanol and then recrystallized from methanol to form colorless crystals of XVI, m. p. 249°C. Yield, 200 mg.

Found: C, 59.16; H, 4.36. Calcd. for $C_{13}H_{12}O_4S$: C, 59.09; H, 4.58%.

λ_{max}^{MeOH} mμ(log ε); 237(4.09), 287(4.61), 305(4.15), 370(4.08).

2-Carboxy-5-isopropyl-8-bromothieno[2, 3-d]tropolone (XVII).—A solution of bromine (30 mg.) in methanol (0.5 ml.) was added drop by drop into a suspension of XVI (50 mg.) in methanol (2 ml.), while being stirred under ice-cooling, and the whole was stirred at room temperature for 10 min. after the completion of the addition. The crystals that formed were collected and recrystallized from methanol to form pale yellow needles (XVII), m. p. 270~273°C(decomp.). Yield, 20 mg.

Found: C, 45.34; H, 3.30. Calcd. for $C_{13}H_{11}O_4BrS$: C, 45.49; H, 3.21%.

λ_{max}^{MeOH} mμ(log ε): 288(4.58), 377(4.20), 425(4.03).

2, 3, 5-Thiophenetricarboxylic Acid (XVIII).—Into a solution of XVI (100 mg.) dissolved in a 10% sodium hydroxide solution (6.5 ml.), a 5% aqueous solution of potassium permanganate (8 ml.) was stirred drop by drop. After the completion of the addition, the mixture was stirred for 2 hr. and warmed on a water bath for a few min., and the manganese dioxide that had formed was filtered off. The filtrate was concentrated under a reduced pressure to about one-half the original volume, acidified to pH 3~4 by the addition of hydrochloric acid, and extracted three times with ether. The evaporation of ether from the extract left colorless crystals which were collected by filtration, washed with water, and recrystallized from ether to form colorless granular crystals, m. p. 215~216°C. Yield, 30 mg.

Found: C, 38.32; H, 2.40. Calcd. for $C_7H_4O_6S$; C, 38.90; H, 1.87%.

λ_{max}^{MeOH} mμ(log ε): 275(3.97).

Trimethyl 2, 3, 5-thiophenetricarboxylate (XIX).—An excess of diazomethane was added to a solution of XVIII (10 mg.) in ether (1 ml.), and the mixture was allowed to stand in a cold room for 1 hr. The evaporation of the ether left colorless needles which sublimed at 100°C under a reduced pressure. The sublimate afforded colorless needles, m. p. 82~83°C. Yield, 10 mg. This substance showed no depression of melting point on admixture with an authentic sample.

λ_{max}^{MeOH} mμ(log ε): 218(4.11), 274(4.10).

2, 5-Dicarboxy-3-(β-isopropyl-β-carboxyvinyl)-thiophene (XX).—To a solution of XVI (100 mg.) dissolved in 1 N sodium hydroxide (2 ml.), a 35% hydrogen peroxide solution (2 ml.) was added, and the mixture was allowed to stand at room temperature for 2 days. This solution was then acidified (pH 3) with hydrochloric acid and extracted three times with ether, and the extract was concentrated. The colorless crystals that precipitated out were collected and recrystallized form water containing a small amount of ethanol to from colorless prisms, m. p. 256~259°C. Yield 70 mg.

Found: C, 50.39; H, 4.12. Calcd. for $C_{12}H_{12}O_6S$: C, 50.71; H, 4.26%.

λ_{max}^{MeOH} mμ(log ε): 250(4.19), 280(4.09).

2,5-Dimethoxycarbonyl-3-(β-isopropyl-β-methoxycarbonylvinyl)-thiophene (XXI).—An excess of diazomethane was added to a solution of XX (100 mg.) dissolved in ether (5 ml.), and the mixture was allowed to stand at room temperature. The evaporation of the ether left an oily residue which crystallized after being allowed to stand in a cold room with methanol (0.3 ml.). The crystals, m. p. 76~79°C, were collected and sublimed at 100°C under a reduced pressure to form colorless prisms, m. p. 84~86°C. Yield, 60 mg.

Found: C, 54.92; H, 5.58. Calcd. for $C_{15}H_{18}O_6S$: C, 55.21; H, 5.56.

λ_{max}^{MeOH} mμ(log ε): 248(4.21), 282(4.16).

Permanganate Oxidation of XX.—Into a solution of XX (25 mg.) dissolved in a 1 N sodium hydroxide solution (0.5 ml.), a 5% potassium permanganate solution was stirred drop by drop at room temperature, until the color of the permanganate persisted. The manganese dioxide that formed was filtered off, the filtrate was acidified (pH 3) with hydrochloric acid, and the mixture was extracted with ether, by which ca. 5 mg. of XVIII was obtained.

Permanganate Oxidation of XVII.—To a solution of XVII (80 mg.) dissolved in a 5% sodium hydroxide solution (5 ml.), a solution of potassium permanganate (150 mg.) in water (3 ml.) was added drop by drop, and the mixture was stirred until the permanganate color faded. The reaction mixture was treated as in the oxidation of XVI, and XVIII was obtained.

2-Acetoxycarbonyl-5-isopropylthieno[2, 3-d]tropolone (XXII).—A mixture or XVI (20 mg.), freshly fused sodium acetate (10 mg.), and acetic anhydride (0.2 ml.) was heated at 120°C for 30 min. The acetic anhydride was evaporated, water (0.5 ml.) and a drop of 15% sodium hydroxide were added to the residue, and the yellow solution so formed was acidified with hydrochloric acid. The oil that separated crystallized gradually. The crystals were collected by filtration and recrystallized from methanol to form colorless granular crystals, m. p. 186~190°C. Yield, 10 mg.

Found: C, 58.71; H, 4.60. Calcd. for $C_{15}H_{14}O_5S$: C, 58.82; H, 4.61%.

λ_{max}^{MeOH} mμ(log ε): 257(4.25), 289(4.55), 335(4.09), 350(4.10), 367(3.98).

2, 8-Dinitro-5-isopropylthieno[2, 3-d]tropolone (XXIII).—Concentrated nitric acid (0.8 ml.) was added to a solution of XVI (100 mg.) dissolved in acetic acid (16 ml.). After being allowed to stand

at room temperature for 30 min., the mixture was poured into cracked ice. The precipitate that formed was collected, washed with water, and recrystallized from methanol to form yellow needles, m. p. 184~185°C. Yield, 15 mg.

Found: C, 46.19; H, 3.65; N, 9.55. Calcd. for $C_{12}H_{10}O_6N_2S$: C, 46.46; H, 3.25; N, 9.03%.

λ_{max}^{MeOH} mμ(log ε): 328(4.06), 424(4.33).

2-Methoxycarbonyl-5-isopropyl-7-methoxythieno-[2, 3-d]tropone (XXIV).—An excess of an ether solution of diazomethane was added to a solution of XVI dissolved in dioxane (1 ml.) and allowed to stand in a cold room overnight. The colorless crystals that formed were collected and recrystallized from benzene to form colorless needles, m. p. 168~169°C. Yield, 70 mg.

Found: C, 61.94; H, 5.35. Calcd for $C_{15}H_{16}O_4S$: C, 61.64; H, 5.52%.

λ_{max}^{MeOH} mμ(log ε): 230(4.04), 280(4.59), 347(4.21), 375(4.09).

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