# *The Reaction Products of 2,4,7-Tribromotropone and Anilines*

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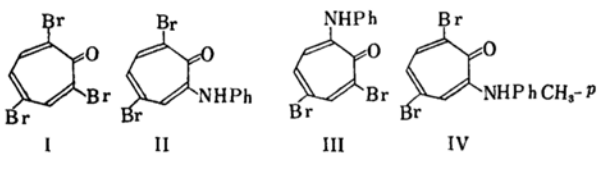
(Received March 11, 1960)

Nozoe and his co-workers[1] have revealed that the treatment of 2,4,7-tribromotropone (I) with aniline or *p*-toluidine affords a mixture of 2-anilino-4,7-dibromotropone (II) and 7-anilino-2,4-dibromotropone (III), or 4,7-dibromo-2-*p*-toluidinotropone (IV) and 2,4-dibromo-7-*p*-toluidinotropone (V); however, the respective components were not separated.

S. Iseda[2], in 1955, reported that the reaction of tribromotropone and aniline or *p*-toluidine resulted in the selective formation of 2-anilinotropone (II) or 2-*p*-toluidinotropone (IV), hydrolyses of which with ethanolic potassium hydroxide easily gave 3,6-dibromotropolone (VI).

The present authors have re-examined these reactions in order to prepare the dibromotropolone and have been able to isolate some reaction products besides the ones described above.

Heating of the tribromotropone (I) and aniline in benzene afforded 7-anilino-2,4-dibromotropone (III) in 21% yield, besides known 2-anilino-4,7-dibromotropone (II) in 66% yield. Separation of both products was easily effected by the application of the difference in their solubilities in chloroform. The structure of the former (III) was clarified through the formation of known 3,5-dibromotropolone (VII) on hydrolysis with alcoholic potassium hydroxide.




It had been found that the reaction of the tribromotropone and sodium acetate in acetic acid affords 3,6- (VI) and 3,5-dibromotropolones[1] (VII). In a similar manner, the above reaction of the tribromotropone and aniline was proved to give not only a 2-substituted but also a 7-substituted product, unlike that observed by Iseda[2].

The reaction of the tribromotropone and *p*-toluidine appeared to result in the formation of more complicated reaction products. Heating of the two compounds in benzene under the same condition as the above gave the 2-*p*-toluidinotropone (IV) in 55% yield and the 7-*p*-toluidinotropone (V) too in 5% yield, as was expected from the reaction in the case of aniline. The structure of the latter V was proved by the formation of known 3,5-dibromotropolone (VII) on its hydrolysis with alcoholic potassium hydroxide.

The ultraviolet absorption spectra of the above four kinds of anilinotropone are shown in Figs. 1 and 2. In general, the 7-anilinotropones (III and V) have absorption maxima in the longer wavelength region than the 2-anilinotropones (II and IV); this fact appears

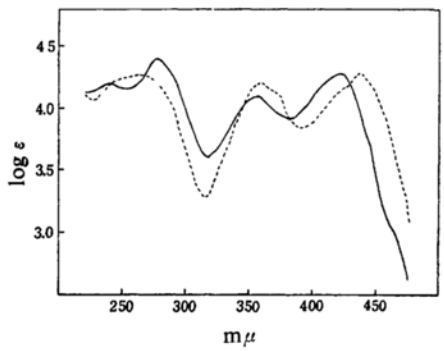



Fig. 1. Ultraviolet absorption spectra.
(——): 2-Anilino-4,7-dibromotropone (II)
(------): 7-Anilino-2,4-dibromotropone (III)

to be probably due to a stronger resonance effect of the bromine atom in the 4-position of the former (III and V) than that in the same position of the latter (II and IV) on the respective mesomeric interaction between the tropone ring and the benzene ring involving a nitrogen atom.

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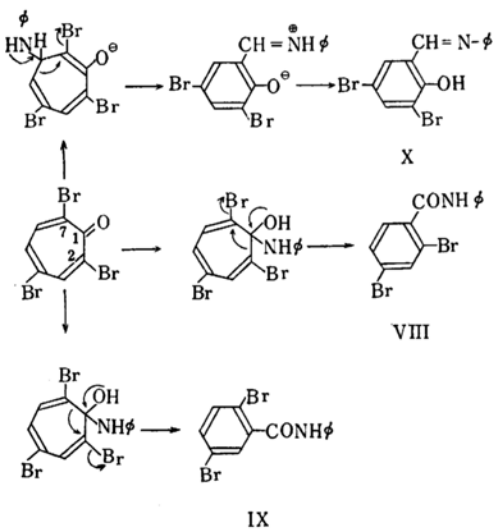
1) T. Nozoe, Y. Kitahara, T. Ando, S. Masamune and H. Abe, *Sci. Repts. Tohoku Univ., Ser. I*, **36**, 166 (1952).
2) S. Iseda, This Bulletin, **28**, 617 (1955).

The reaction mixture, from which the foregoing toluidinotropones (IV and V) were removed, afforded furthermore four kinds of reaction product not isolated to date: 2, 4-dibromobenz-*p*-toluidide (VIII), 2, 5-dibromobenz-*p*-toluidide (IX), 3, 5-dibromosalicylidene-*p*-toluidine (X), and an unidentified substance XI of m. p. 158°C.

The toluidide (VIII and IX) was easily converted into the known dibromobenzoic acid, respectively, on treatment with 75% sulfuric acid. The azomethine compound X was identified with a condensation product of 3, 5-dibromosalicylaldehyde and *p*-toluidine. Another reaction product XI has the composition of $C_{14}H_{12}O_2NBr$, the structure of which will be elucidated in future.

It has been found that the tribromotropone (I) converts into benzoic acid derivatives by the action of bases such as dilute alkali or ammonia[1]. Formations of the dibromobenz-*p*-toluidides (VIII and IX) from the tribromotropone may be taken as the products of the benzilic acid type of rearrangement due to a nucleophilic attack of *p*-toluidine on the 1-position of the molecule. Formation of a Schiff's base X recalls that of 3-bromosalicylaldehyde from 2, 7-dibromotropone by the action of alkali[3,4], and the mechanisms of the above reaction can be illustrated as follows:



X

VIII

IX

## Experimental

The ultraviolet absorption spectra were measured in methanol with a Beckman model DU spectrophotometer.

**Reaction of 2, 4, 7-Tribromotropone (I) and Aniline.**—A mixture of the tribromotropone (I, 70 g.), anhydrous sodium acetate (21 g.), aniline (28 g.) and benzene (1400 ml.) was heated under reflux for 3 hr. The residue obtained by the evaporation of the solvent was washed with water and subsequently extracted with chloroform (100 ml). Crystallization of the part less soluble in chloroform gave 2-anilino-4, 7-dibromotropone (II) as yellow needles from benzene, m. p. 197~198°C (reported[2] m. p. 196~197°C) (47.4 g., 66%). The part more soluble in chloroform, after evaporation of the solvent followed by crystallization from benzene, afforded 7-anilino-2, 4-dibromotropone (III) as yellow needles, m. p. 179.5°C (15 g., 21%).

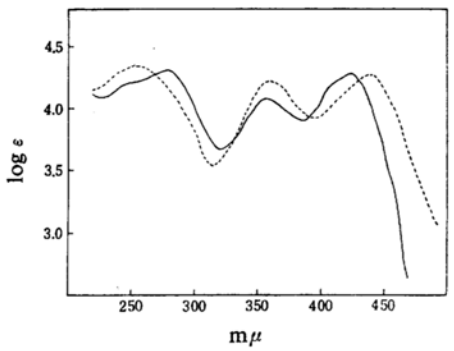



Fig. 2. Ultraviolet absorption spectra.
(——): 4,7-Dibromo-2-*p*-toluidinotropone (IV)
(------): 2,4-Dibromo-7-*p*-toluidinotropone (V)

Found: C, 43.52; H, 2.46; N, 4.10. Calcd. for $C_{13}H_9ONBr_2$: C, 43.96; H, 2.56; N, 3.95%. $\lambda_{max}^{MeOH}$ mμ (log ε): 265 (4.25), 361 (4.18), 438 (4.27).

**Hydrolysis of 7-Anilino-2, 4-dibromotropone (III).**—A mixture of III (280 mg.), ethanol (10 ml.), potassium hydroxide (440 mg.) and water (4 ml.) was heated under reflux for 20 min. It was then diluted with water, acidified with concentrated hydrochloric acid to Congo-red and extracted with chloroform. The extract, after evaporation of the solvent followed by crystallization from methanol, gave 3, 5-dibromotropolone (VII), m. p. 154~155°C, undepressed on admixture with an authentic specimen[5].

**Reaction of Tribromotropone (I) and *p*-Toluidine.**—A mixture of the tribromotropone (40 g.), anhydrous sodium acetate (11.6 g.), *p*-toluidine (13 g.) and benzene (700 ml.) was heated under reflux for 3 hr. The residue obtained by evaporation of the solvent was washed with water and extracted with acetone to separate into the less soluble A and the more soluble B portion. The fraction A, 37.3 g., after two recrystallizations from benzene, afforded 4, 7-dibromo-2-*p*-toluidinotropone (IV) as yellow needles, m. p. 194.5°C (reported[2] m. p. 196°C) (24 g., 55%). The benzene mother-liquor, after chromatographic purification (benzene—alumina) followed by two fractional recrystallizations from the same solvent, gave a more soluble product, 2, 4-dibromo-7-*p*-toluidinotropone (V) as yellow needles, m. p. 177°C (2.4 g., 5.6%).

Found: C, 45.68; H, 3.08; N, 3.67. Calcd. for

3) S. Seto, *Sci. Repts. Tohoku Univ., Ser. I*, **37**, 377 (1953).
4) Y. Kitahara, ibid., **39**, 250 (1956).
5) T. Nozoe, Y. Kitahara, K. Doi and T. Arai, *Bull. Chem. Research Inst. Non-Aqueous Solns., Tohoku Univ.*, **7**, 13 (1957).

$C_{14}H_{11}ONBr_2$: C, 45.54; H, 3.01; N, 3.79%. $\lambda_{max}^{MeOH}$ mμ (log ε): 250 (4.35), 361 (4.22), 440 (4.28).

From the same source a less soluble product XI was obtained as yellow plates, m. p. 157.5～158°C (2.3 g).

Found: C, 55.38; H, 4.02; N, 4.58. Calcd. for $C_{14}H_{12}O_2NBr$: C, 54.92; H, 3.95; N, 4.58%. $\lambda_{max}^{MeOH}$ mμ (log ε): 240 (4.17), 283 (4.37), 345 (3.99), 350 (4.01), 400 (4.20).

The fraction B, after evaporation of the solvent, crystallization from ethyl acetate and chromatographic purification (benzene—alumina) followed by several recrystallizations from benzene, yielded the following three products in the order of decreasing of solubilities in the solvent:

2,5-Dibromobenz-*p*-toluidide (IX), colorless needles, m. p. 155～155.5°C (0.25 g.),

Found: C, 45.64; H, 2.85; N, 3.80. Calcd. for $C_{14}H_{11}ONBr_2$: C, 45.54; H, 3.01; N, 3.79%.

2,4-Dibromobenz-*p*-toluidide (VIII), colorless needles, m. p. 174°C (0.2 g.),

Found: C, 45.27; H, 2.70; N, 3.89%.

3,5-Dibromosalicylidene-*p*-toluidine (X), orange needles, m. p. 129.5°C (0.44 g.).

Found: C, 45.58; H, 2.92; N, 4.00%.

**Hydrolysis of 2,4-Dibromo-7-*p*-toluidinotropone (V).**—A mixture of the tropone (V, 90 mg), ethanol (5 ml.), potassium hydroxide (200 mg.), and water (3 ml.) was heated under reflux for 30 min., then acidified with dilute hydrochloric acid to Congo-red, and extracted with chloroform. The extract gave 3,5-dibromotropolone (VII, 40 mg.), m. p. 154～155°C, undepressed on admixture with an authentic sample[5].

**Hydrolysis of 2,4-Dibromobenz-*p*-toluidide (VIII).**—A mixture of the toluidide (VIII, 70 mg.) and 75% sulfuric acid (5 ml.) was heated at 130°C for 30 min. The solid obtained by pouring the reaction mixture onto crushed ice gave 2,4-dibromobenzoic acid, m. p. 166～169°C, undepressed on admixture with an authentic specimen[6].

**Hydrolysis of 2,5-Dibromobenz-*p*-toluidide (IX).**—Hydrolysis of IX under the same condition as the above yielded 2,5-dibromobenzoic acid, m. p. 151～153°C, undepressed on admixture with an authentic sample[7].

**3,5-Dibromosalicylidene-*p*-toluidine (X).**—A mixture of 3,5-dibromosalicylaldehyde[8] (30 mg.), *p*-toluidine (20 mg.) and ethanol (2 ml.) was heated under reflux for one hour. The reaction mixture, when cooled, afforded Schiff's base X as orange needles, m. p. 129～129.5°C, undepressed on admixture with the reaction product X of the tribromotropone and *p*-toluidine.

We gratefully acknowledge our debt to the Ministry of Education for the Grant in Aid for Fundamental Scientific Research and to Messrs. S. Ohyama, K. Kato, A. Iwanaga and S. Azumi for the microanalyses.

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6) A. K. Miller, *J. Chem. Soc.*, **61**, 1033 (1892).
7) H. Hubner, *Ber.*, **10**, 1705 (1877).
8) E. Tummeley, *Ann.*, **251**, 179 (1889).