21. Tropone and Its Derivatives. IV.¹⁾
Rearrangement Reactions of 2, 4, 7-Tribromotropone-1
by Alkaline Reagents.

By Tetsuo NOZOE, Yoshio KITAHARA, Satoru MASAMUNE,
and Shôzô YAMAGUCHI.

Chemical Institute, Faculty of Science, Tôhoku University,
Sendai, Japan.

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The present authors previously reported²⁾ on the formation of tribromotropone (I), m.p. 184.5–185°, in a good yield by the bromination of cycloheptanone, with several bromotropolones as a by-product. It was also shown that acetolysis of (I) gave dibromotropolones in a good yield. One of the authors (Nozoe)³⁾ previously assumed that tropolone might be considered a vinilog of carboxylic acid. According to this idea, (I) may be considered an acid bromide of carboxylic acid. Based on this assumption, it seemed of interest to examine the reaction of (I) with various reagents and that with basic reagents, especially potassium hydroxide, sodium acetate and organic bases, were taken up. Some interesting results were obtained which are described in the following.

As previously reported²⁾, application of sodium acetate to glacial acetic acid solution of (I) yielded o, p-dibromotropolone (II), m.p. 152–153.5°, and a dibromotropolone (III), m.p. 118–120°. Application of diazomethane to (III) in ether yielded two kinds of isomeric methyl ethers, one of prisms (IV), m.p. 119° (Anal. Calcd. for $C_8H_6O_2Br_2$: C, 32.56; H, 2.05. Found: C, 32.60; H, 2.20), and the other (V), m.p. 104° (Anal. Calcd. for $C_8H_6O_2Br_2$: C, 32.56; H, 2.05. Found: C, 32.50; H, 2.12). (IV) easily underwent rearrangement by the application of sodium methoxide in methanol, the reaction proceeding at a room temperature, subsequent hydrolysis giving 2, 5-dibromobenzoic acid, m.p. 157°, in a 30% yield, which was confirmed by mixed fusion with the synthetic specimen⁴⁾. (V) is comparatively stable at a room temperature, its rearrangement finally proceeding after being refluxed on a water bath for 5 hours, subsequent hydrolysis giving the same 2, 5-dibromobenzoic acid in an 80% yield. It follows, therefore, that the assumption made in the previous report regarding the structure of these two compounds was confirmed as o, m'-dibromotropolone (A) for (III) and 2, 4, 7-tribromotropone (B) for (I). Interpreting these results in facilities of rearrangement in the same way as in the case of two isomeric o-

bromotropolone methyl ethers⁵⁾, the structure of (C) and (D) will be likely assumed to be (IV) and (V), respectively.

Dauben and Ringold⁶⁾ report of obtaining 2,5-dibromobenzoic acid from the products obtained by the treatment of (I) by alcoholic potassium hydroxide. Application of alcoholic potassium hydroxide to (I) at a room temperature resulted in vigorous reaction taking place, and fractional recrystallization of the acid product as phenacyl esters yielded some prisms (VI), m.p. 128–128.5°, and a very small amount of prisms (VII), m.p. 81–82°. (VI) and (VII) showed no depression of the melting point when fused respectively with the phenacyl ester, m.p. 128.5–129° (Anal. Calcd. for $C_{15}H_{10}O_3Br_2$: C, 45.23; H, 2.51. Found: C, 45.10; H, 2.67), of 2,5-dibromobenzoic acid (F)⁷⁾, and a very small amount of phenacyl ester, m.p. 81–82° (Anal. Calcd. for $C_{15}H_{10}O_3Br_2$: C, 45.23; H, 2.51. Found: C, 45.00; H, 2.71), of 2,4-dibromobenzoic acid (G)⁷⁾. The mechanism of this reaction will be explained by the assumption of a benzylic acid rearrangement of the following order:

It was previously reported that the treatment of (I) with liquid ammonia or with alcoholic ammonia gave ammonium bromide and a mixture of dibromobenzoic acid amides²⁾, the mixture being very difficult to be separated into pure components. The amide mixture was derived to phenacyl ester of the corresponding acids via hydrolysis with 75% H_2SO_4 at 160–170° for 6 hrs., and recrystallization and mechanical separation of the esters under a microscope yielded some colorless long needles (VIII), m.p. 142–143.5° (Anal. Calcd. for

$C_{15}H_{10}O_3Br_2$: C, 45.23; H, 2.51. Found: C, 45.02; H, 2.26), and a small amount of colorless prisms (IX), m.p. 126–127°. Mixed fusion of (VIII) and (IX) gave obvious depression of the melting point. By mixed fusion, (IX) was proved to be the phenacyl ester of 2,5-dibromobenzoic acid (F) while (VIII) unexpectedly proved to be the phenacyl ester, m.p. 144.5–145.5°, of 3,5-dibromobenzoic acid (H)⁴⁾, and not of 2,4-dibromo compound.

(I) having undergone a simple benzylic acid type rearrangement by such a strong base as potassium hydroxide, has not only undergone rearrangement but induced migration of the bromine atom from ortho to meta position by such a weak base as ammonia, and this is a remarkable phenomenon that should be well-remembered. It has been the usual practice, both here and abroad, to determine the structure of tropolones by the rearrangement of these to aromatic compounds but, since it has been learned that there are instances where such rearrangement of bromine compounds are accompanied by the migration of bromine atoms, these structural determinations must also be interpreted with caution.

It seemed interesting to examine whether such rearrangement reactions would occur with comparatively weak organic bases, such as toluidine, or it would result in condensation by the liberation of HBr, as occurred in acetolysis. By the heating of (I) in benzene with p-toluidine (1.2 mol.) and sodium acetate (1.2 mol.) on a water bath, the reaction proceeds smoothly and sodium bromide and yellow solution are obtained. The evaporation of this yellow benzene solution to a smaller volume yields yellow crystals (X), m.p. 178–184°. Catalytic reduction of (X) in benzene with palladium-charcoal, absorbs 2 moles of hydrogen to yield yellow prisms (XI), m.p. 108.5–109.5° (Anal. Calcd. for $C_{14}H_{13}ON$: N, 6.63. Found: N, 6.71). This substance is assumed to be a toluididotropone (K). Decision on alkyl- and arylaminotropolones will be reported in near future.

It is assumed that the seat of attack of the above-mentioned bases in (I) is the C_1 -, C_2 - and C_7 -positions. The bases such as potassium hydroxide and ammonia are sufficiently strong to rearrange at the attack of C_1 , while weaker ones, i.e., acetate and toluidide ion are inadequate to effect it and only displacement at C_2 or C_7 takes place.

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