On the Bromination Reaction of Tropone and its Bromine Compounds[1]

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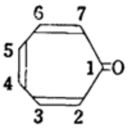
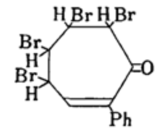
On bromination, tropone is not directly subject to replacement with bromine but intermediately forms a bromine addition product and subsequently forms the true bromine-substitution product by its dehydrobromination and debromination[2,3]. This fact gives a new observation regarding the aromaticity of tropone and is one of the experimental facts that indicate highly unsaturated characteristic of tropone compared to tropolone. It has been noticed, however, that tropones show different modes in the bromine addition according to their structures. For example, bromination of 2-phenyltropone chiefly gave a tetrabromide (I) and indicated that the C_2-C_3 double bond of I was fairly resistant to further bromination owing to the steric hindrance by the phenyl group at C_2 position[3]. Tropone itself was also brominated to form the tetrabromide (II) but its dehydrobromination gave 2,7-dibromotropone and this indicated that the C_4-C_5 double bond of II was resistant to bromine addition[2]. In addition, bromination of 2-bromotropone also afforded 2,7-dibromotropone via the addition product, and this dibromotropone was not further brominated even on application of an excess of bromine in chloroform or acetic acid with heating[2]. These facts also indicated that the C_4-C_5 double bond in tropone ring was inactive to bromine addition or substitution. In 1951, Brown[4] suggested that the C_2 (or C_7) position on the tropone ring will be most easily submitted to electrophilic substitution from his calculation by the molecular orbital method, and this is rather interesting when the above facts are considered.

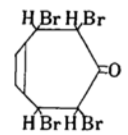
In the present paper, further bromination reaction of tropone and its various bromine-substituted derivatives is reviewed and examinations are made on whether the double bond at C_4-C_5 of II is entirely inactive to bromine addition. Also what effect the bromine atoms present in the tropone ring have on this addition reaction is described.

Tropone invariably affords 2,7-dibromotropone, on causing an excess of bromine to react under heating and it is known to give the tetrabromide (II) when cold[2]. Therefore, different reaction conditions were adopted. Tropone was dissolved in glacial acetic acid or chloroform, an excess of bromine was added, and the mixture was allowed to stand for a long period. The oily addition product obtained by this reaction differs from II and its analytical value agrees with that for a hexabromide. Its dehydrobromination with sodium acetate was found to give chiefly 2,4,7-tribromotropone, though accompanied with 2,7-dibromotropone. It has become clear through this experiment that the addition product obtained here has the structure of III and that the double bond at C_4-C_5 submits to bromine addition under the above conditions. The ultraviolet spectrum of the addition product III is shown in Fig. 1 and there is no marked absorption maximum. Its infrared spectrum[5] has no





(I)



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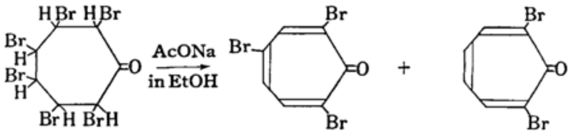

(III)

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[1] This paper was read before the 9th Annual Meeting of the Chemial Society of Japan held in Kyoto on April 5, 1956.

[2] T. Nozoe, T. Mukai and K. Takase, *Science Repts. Tohoku Univ.*, **1**, **39**, 164 (1956).

[3] T. Mukai, ibid., **1**, **38**, 281 (1954).

[4] R. D. Brown, *J. Chem. Soc.*, **1951**, 2670.

[5] Infrared spectrum was measured with Perkin-Elmer Model 21 double beam spectrophotometer by Mr. Yusaku Ikegami of the Chemical Research Institute of Non-aqueous Solutions, to whom the author's deep gratitude is hereby expressed.

marked absorption in the C=C region either. These facts support the conclusion that the addition compound has the saturated ketone structure of III. The absorption of C=O in III appears as two bands* at 1735 and 1706 cm^{-1}. Toda and Kitahara⁶⁾ have found that the equatorial α-bromine atom of bromosuberones shifts its carbonyl band to the higher frequency by 17 cm^{-1} than that of suberone at 1701 cm^{-1}. The absorption at 1735 cm^{-1} is higher in frequency by 34 cm^{-1} than that of suberone, so this is thought to indicate the fact that the two α-bromine atoms of III are in equatorial to C=O.

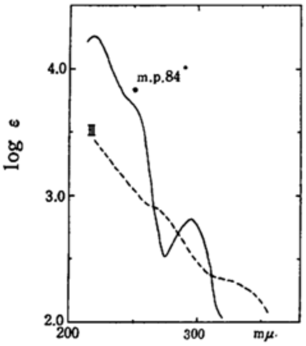

Fig. 1. U. V. absorption spectra of addition product III in cyclohexane and of compound melted at 84°C in methanol.

The addition product III was dissolved in glacial acetic acid and refluxed or heated in an oil bath to 140~150°C without a solvent(7). In this case, hydrogen bromide and bromine were evolved and in both cases, only 2,7-dibromotropone was obtained and not the 2,4,7-tribromo compound.

Similarly, when 2-bromotropone(8) and bromine in glacial acetic acid solution are allowed to stand over a long period of time, a pentabromo-compound is obtained. Dehydrobromination of this addition product by heating in ethanol, in the presence of sodium acetate, easily affords 2,4,7-tribromotropone, from which it is certain that this addition product has the structure shown by IV. It is known from this that the bromine addition occurs not at the C_2-C_3 double bond but at C_4-C_5 double bond. Decomposition of IV by heating in acetic acid results in evolution of hydrogen bromide and bromine, and 2,7-dibromotropone alone is obtained, while its decompostition by heating without a solvent chiefly gives 2,7-dibromotropone accompanied by a small amount of 2,4,7-tribromotropone. It should be noted that in these cases also elimination of free bromine has occurred at C_4–C_5 bond.

(IV)

(V)

Bromination of tropone and 2-bomotropone under heating affords 2,7-dibromotropone, as mentioned earlier, and there is a possibility that the dibromo compound is formed through the addition products, III and IV. In order to confirm this point, sodium acetate was added in this bromination but the 2,7-dibromotropone was invariably obtained and not the 2,4,7-tribromotropone. Therefore, it may be concluded that bromination with heating does not form addition products like III and IV.

Application of an excess of bromine to acetic acid solution of 4-bromotropone(9) results in direct substitution reaction and 2,4,7-tribromotropone is obtained, the bromine addition compounds being obtained with difficulty. In this case, the use of chloroform in place of acetic acid as a solvent affords pentabromo compound as the addition product and this addition product invariably forms 2,4,7-tribromotropone, either by heating in ethanol with sodium acetate or by heating without a solvent or in acetic acid solution. These facts support the structure of V for the addition compound. Decomposition of V in ethanol in the presence of sodium acetate gives, besides 2,4,7-tribromotropone, colorless crystal melting at 84°. This latter substance is stable and neutral and its ultraviolet and infrared spectra are shown respectively in Figs. 1 and 2. From this ultraviolet spectrum, it is seen that the substance no longer retains a tropone ring(10) but its structure remains unsolved.

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* It may owe to the presence of two conformationally different isomers.

6) T. Toda. and Y. Kitahara, to be published. (From the dissertation of T. Toda, Tohoku University) cf. E. J. Corey, *J. Am. Chem. Soc.*, **75**, 2301 (1953).

7) These reaction conditions were taken in order to compare them with that used in the troponization (bromination-dehydrobromination) of suberone. cf. T. Nozoe, Y. Kitahara, T. Ando, S. Masamune and H. Abe, *Science Repts. Tohoku Univ.*, **1**, **36**, 166 (1952); *Proc. Japan Acad.*, **27**, 415 (1951).

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

9) T. Nozoe, T. Mukai, Y. Ikegami and T. Toda, *Chem. & Ind.*, **1955**, 66.

10) M. Tsuboi, This Bulletin, **25**, 369 (1952).

The infrared spectrum of V exhibits an absorption band of C=C at 1605 cm^{-1} and of C=O group at 1738 cm^{-1}. The latter band is 37 cm^{-1} higher in frequency than C=O band of suberone at 1701 cm^{-1} and this will indicate the fact that the two α-bromine atoms of V are located in the equatorial position[6].

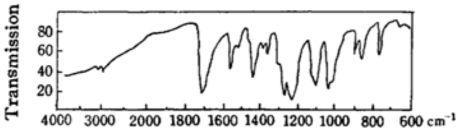
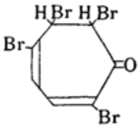
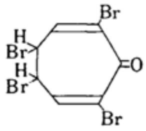


Fig. 2. I. R. absorption spectrum of compound melting at 84°C in KBr.

The behavior of 2,5-dibromotropone[9] toward bromination is similar to that of 4-bromotropone, that is, it forms 2,4,7-tribromotropone on standing with bromine in acetic acid solution at room temperature. However, the use of chloroform as a solvent also affords the tetrabromo-compound. This addition compound always forms 2,4,7-tribromotropone, either on dehydrobromination with sodium acetate or on heating alone or in acetic acid solution.



(VI)



(VII)

From these facts, the structure represented by VI is given to this addition compound, and also, in this case the double bond with the bromine is found to be resistant to bromine addition. The infrared spectrum of VI exhibits absorptions at 1658 cm^{-1} for C=O and at 1613 cm^{-1} for C=C, and these values seem approximately as suitable as those for such a conjugated, unsaturated ketone. The bromine addition compound of tropones having bromine atom at C_4 or C_5 position, as in V and VI, tends to decompose and the ultraviolet spectra of V and VI in a polar solvent like methanol exhibit absorption similar to that of 2,4,7-tribromotropone resulting from the decomposition. It is assumed that the failure to obtain addition compounds from the bromination of 4-bromo- and 2,5-dibromotropone in acetic acid solution may be related to this instability.

When 2,7-dibromotropone[8] is allowed to stand with an excess of bromine in acetic acid solution at room temperature for a long period, a tetrabromo compound crystallizes out. Heating with sodium acetate in ethanol solution, affords 2,4,7-tribromotropone together with 2,7-dibromotropone. This proves that the structure of the addition compound is correctly represented by VII. The infrared spectrum of VII has absorptions for conjugated C=O and C=C respectively at 1656 and 1613 cm^{-1}. Heating VII alone or in acetic acid solution results in evolution of bromine and only 2,7-dibromotropone is formed and this also indicates that bromine is easily eliminated from C_4–C_5 bond.

The foregoing bromination reaction of tropones may be summarized as follows: 1) Bromine addition of tropone seems to proceed in a stepwise manner, the addition being facile up to two moles, but addition to the C_4–C_5 double bond requires a long period. This is thought to be due to the increased repulsion between the bromine atoms and between the carbonyl group and bromine atom by the formation of hexabromo compound (III) by the third mole of bromine. 2) Further addition of bromine to bromotropones does not occur in the double bond carrying the bromine atom and this is probably due to increased repulsion between bromine atoms by the formation of a geminated dibromo-structure[11]. 3) The bromine atoms attached to the C_4–C_5 positions tends to be easily liberated as bromine, while those bonded to C_2–C_3 and C_6–C_7 positions are liberated as hydrogen bromide. 4) It is difficult to derive tropone, 2-bromotropone, and 2,7-dibromotropone by bromination into 2,4,7-tribromotropone without going through the addition compounds.

The important point in connection with the foregoing bromination reaction of tropone is the troponization of suberone by the action of bromine[7]. This is one of the fundamental reactions in the preparation of tropones but, because the reaction is so complicated, its reaction mechanism has not been clarified as yet. Therefore, several polybromosuberones that form as intermediates during this reaction have been isolated and their troponization reaction has been examined[12]. The bromine addition compounds formed in the present series of experiments may also be regarded as allied substances of polybromo compounds of suberone, but

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[11] The addition compound having geminated two bromine atoms was obtained on the bromination of 2-phenyltropone. cf. Ref. 3.

[12] Paper presented at the Local Meeting of Tohoku district of the Chemical Society of Japan held in Yamagata on June 28, 1954.

it should be noted that there is a fair difference between the compounds of these two series as to the position and configuration of the bromine atom. It is interesting that troponization of suberone by bromination affords 2, 4, 7-tribromo-, 2, 5-dibromo-, and 4-bromotropones[9], and not 2-bromo- or 2, 7-dibromotropones, while the bromine addition compounds obtained by the bromination of tropone invariably are 2-bromo-[2] and 2, 7-dibromotropone rather than 2, 4, 7-tribromotropone.

Experimental[13]

Bromination of Tropone.—*a*) *In carbon tetrachloride solution.*—To a solution of 150 mg. of tropone dissolved in 3 cc. of carbon tetrachloride, 950 mg. (4.2 mol. equiv.) of bromine was added, by which reddish orange oil separated out and later crystallized. This mixture was allowed to stand in a sealed vessel at room temperature and the crystal again changed to an oil. After about 3 weeks, the mixture containing oil was dried in a vacuum desiccator over potassium hydroxide and paraffin to get constant weight, and 800 mg. of hexabromo compound (III) was obtained as yellowish orange syrup, which was submitted to elemental analyses and ultraviolet and infrared spectral measurements.

Anal. Found: C, 14.95; H, 1.25. Calcd. for $C_7H_6OBr_6$: C, 14.36; H, 1.02%. I. R. Spectrum: $\tilde{\nu}$(C=O) 1735, 1706 cm^{-1}, (C=C) very weak band (without solvent).

b) *In acetic acid solution.*—A mixture of 100 mg. of tropone dissolved in 1.5 cc. of acetic acid and 950 mg. (6.3 mol. equiv.) of bromine was allowed to stand for 10 days at room temperature and treated as in a), from which 600 mg. of yellowish orange oil was obtained. The analytical values of this oil did not agree with those for the hexabromo compound (Found: C, 17.74; H, 1.83) but its decomposition with sodium acetate afforded 2, 4, 7-tribromotropone and thermal decomposition gave 2, 7-dibromotropone, exactly as in the case of III (q. v.).

c) *Bromination in the presence of sodium acetate under heating.*—A mixture of 30 mg. of tropone, 230 mg. of bromine (5 mol. equiv.) and 70 mg. of sodium acetate in 1.5 cc. of acetic acid was heated for 3 hours on a water bath. At the end of this period, some bromine still remained. Acetic acid was removed and residual crystals were washed with ethanol and water, affording 60 mg. of pale greenish yellow crystals, m. p. 145~160°C. Recrystallization from ethanol-benzene mixture gave 40 mg. of crystals melting at 167~169°C, undepressed on admixture with 2, 7-dibromotropone, m. p. 170°C.

Bromination of 2-Bromotropone.—*a*) *In acetic acid solution.*—To a solution of 150 mg. of 2-bromotropone dissolved in 2 cc. of acetic acid, 640 mg. (5 mol. equiv.) of bromine was added and the mixture was allowed to stand in a sealed vessel for one month at room temperature. Crystals began to separate out from the tenth day. The crystals were collected by filtration to give 320 mg. of colorless crystals, m. p. 115°C (decomp. with efferv.). Recrystallization from ethanol gave colorless needles IV, m. p. 135°C (decomp. with efferv.).

Anal. Found: C, 15.92; H, 1.09. Calcd. for $C_7H_5OBr_5$: C, 16.61; H, 1.00%. U.V. Spectrum: $\lambda_{\max}^{\text{cyclohexane}}$ mμ (log ε): 280(4.35). I. R. Spectrum: $\tilde{\nu}$(C=O, C=C) 1736, 1704, 1607 cm^{-1} (in KBr disk).

b) *Bromination in the presence of sodium acetate under heating.*—A mixture of 50 mg. of 2-bromotropone and 80 mg. of sodium acetate in 2 cc. of acetic acid containing 170 mg. (4 mol. equiv.) of bromine was heated on a water bath for 3 hours. Acetic acid was removed, and the residue was washed with water. Filtration afforded 70 mg. of pale brown crystals, m. p. 130~150°C. Washing with ethanol gave 40 mg. of crystals melting at 162~166°C, and recrystallization from ethanol-benzene mixture gave pale yellow plates, m. p. 169~170°C. This was found to be 2, 7-dibromotropone by mixed fusion.

Bromination of 4-Bromotropone.—*a*) *In acetic acid solution.*—To a solution of 400 mg. of 4-bromotropone dissolved in 10 cc. of acetic acid, 1.73 g. (5 mol. equiv.) of bromine was added and the mixture was allowed to stand in a sealed vessel at room temperature. After about one month, some needle crystals crystallized out but the mixture was allowed to stand for a total of 3 months and the crystals were collected. The first crop of crystals was 450 mg. of pale yellow needles, m. p. 183°C. The mother liquor was allowed to stand over potassium hydroxide in a vacuum desiccator and a second crop of 15 mg. of crystals, m. p. 175~179°C, and a third crop of 15 mg. of crystals, m. p. 173~175°C, were obtained. All these crystals showed no depression of the melting point on admixture with 2, 4, 7-tribromotropone, m. p. 183°C. The final residual oil decomposed on heating, evolving bromine and afforded 90 mg. of 2, 4, 7-tribromotropone, m. p. 177~179°C.

b) *In chloroform solution.*—To a solution of 150 mg. of 4-bromotropone dissolved in 3 cc. of chloroform, 390 mg. (3 mol. equiv.) of bromine was added, and the mixture was allowed to stand in a sealed vessel for one month. This was then dried to constant weight over potassium hydroxide and paraffin in a vacuum desiccator and 410 mg. of reddish orange viscous oil V was obtained. This oil began to crystallize after a few days but showed such a tendency to decompose that the oil itself was submitted to analyses and spectral measurements.

Anal. Found: C, 16.54; H, 1.38. Calcd. for $C_7H_5OBr_3$: C, 16.61; H, 1.00%. I. R. Spectrum: $\tilde{\nu}$(C=O, C=C) 1738, 1675, 1605 cm^{-1} (without solvent).

On washing with benzene, the crystals which melted at ca. 85°C with decomposition were obtained but after standing, they showed m. p. 125~140°C.

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[13] m. p. are uncorrected. The microanalyses were carried out by Mr. Shin-ichi Ohyama to whom the author's sincere acknowledgements are hereby extended.

Bromination of 2, 5-Dibromotropone. — *a*) *In acetic acid solution.*—One gram (3 mol. equiv.) of bromine was added to a solution of 550 mg. of 2, 5-dibromotropone dissolved in 6 cc. of acetic acid and the mixture was allowed to stand in a sealed vessel at room temperature. Needle crystals began to crystallize out after one month and the crystals were collected after a total of two months. The first crop of 100 mg. of pale yellow needle crystals, m. p. 183∼184°C, were collected and the filtrate was dried over potassium hydroxide, affording a second crop of 220 mg. of crystals, m. p. 180∼181°C. Both were identified with 2, 4, 7-tribromotropone by mixed fusion. The final mother liquor also began to crystallize but was dissolved in chloroform and passed through a short column of alumina. Removal of the solvent from the effluent afforded 220 mg. of crystals which melted at 80∼120°C with decomposition. It probably contained some addition products but recrystallization from benzene gave only 50 mg. of 2, 4, 7-tribromotropone, m. p. 178∼180°C, and the residue could not be purified further.

b) *In chloroform solution.*—To a solution of 280 mg. of 2, 5-dibromotropone dissolved in chloroform, 510 mg. (3 mol. equiv.) of bromine was added and the mixture was allowed to stand in a sealed vessel for 2 weeks. This was dried to a constant weight over paraffin and potassium hydroxide in a vacuum desiccator to remove the chloroform and 460 mg. of reddish orange oil VI was obtained. This oil was submitted to analyses and spectral measurements as it had a tendency to undergo decompostition.

Anal. Found: C, 19.97; H, 1.16. Calcd. for $C_7H_4OBr_4$: C, 19.83; H, 0.95%. I. R. Spectrum: $\tilde{\nu}$ (C=O, C=C) 1658, 1613 cm^{-1}.

After about 2 days, the oil crystallized and melted at 60∼65°C with decomposition, but recrystallization from ethanol afforded crystals melting at 165∼173°C, and indicated that the majority had changed to 2, 4, 7-tribromotropone.

Bromination of 2, 7-Dibromotropone. — *a*) *In acetic acid solution.*—Three hundred milligrams (3.3 mol. equiv.) of bromine was added to a solution of 150 mg. of 2, 7-dibromotropone dissolved in 15 cc. of acetic acid and the mixture was allowed to stand for one month at room temperature. This mixture was dried over potassium hydroxide in a vacuum desiccator to give 200 mg. of pale yellow crystals, m. p. 155°C (decomp.), which was recrystallized from benzene and afforded pale yellow prisms VII, m. p. 156∼157°C (decomp.).

Anal. Found: C, 20.45; H, 1.61. Calcd. for $C_7H_4OBr_4$: C, 19.83; H, 0.95%. U. V. Spectrum: $\lambda_{\max}^{\text{cyclohexane}}$ mμ (log ε): 230 (3.95), 295 (3.73). I. R. Spectrum: $\tilde{\nu}$ (C=O, C=C) 1656, 1613 cm^{-1}. (in KBr disk).

In another experiment by the same procedure, some crystals other than VII were obtained, which partially melted at 105°C and melted with decomposition at 130°C (Anal. Found: C, 16.55; H, 0.94%).

b) *Bromination under heating.*—A solution of 70 mg. of 2, 7-dibromotropone dissolved in 3 cc. of acetic acid containing 130 mg. (3 mol. equiv.) of bromine was sealed in a tube and heated in a boiling water bath for 6 hours. The mixture was dried over potassium hydroxide in a vacuum desiccator and 70 mg. of pale yellow plates, m. p. 167∼169°C, were obtained. This was the recovered starting material.

c) *Bromination in the presence of sodium acetate under heating.*—A mixture of 50 mg. of 2, 7-dibromotropone and 50 mg. of sodium acetate dissolved in 2 cc. of acetic acid containing 90 mg. (3 mol. equiv.) of bromine was heated for 3 hours. Treatment as above afforded 50 mg. of plae yellow crystals, m. p. 145∼163°C, which on recrystallization from ethanol-benzene mixture gave 30 mg. of crystals melting at 168∼169°C and 5mg. of those melting at 160∼163°C. Both were found to be 2, 7-dibromotropone by admixing.

Reaction of Various Bromine Addition Compounds with Sodium Acetate in Ethanol Solution. — *a*) *2, 3, 4, 5, 6, 7-Hexabromocycloheptanone* (*III*).—A solution of 300 mg. of III and 200 mg. of sodium acetate dissolved in 5 cc. of ethanol was refluxed on a water bath for 30 minutes. The ethanol was evaporated off from the mixture and a small amount of water was added to the residual solution by which 100 mg. of pale yellow needles, m. p. 180∼181°C, was obtained. The mixed melting point proved it to be 2, 4, 7-tribromotropone. This mother liquor, was diluted with water, extracted with chloroform and the extract was passed through a column of alumina. The alumina was eluted with ethanol and evaporation of ethanol from the effluent left 100 mg. of colorless crystals, m. p. 157∼162°C, which showed no depression on admixture with 2, 7-dibromotropone but the mixed melting point was depressed on fusion with 2, 4, 7-tribromotropone. Therefore, this was assumed roughly to be 2, 7-dibromotropone.

b) *2, 4, 5, 6, 7-Pentabromo-2-cyclohepten-1-one* (*IV*).—To a solution of 80 mg. of IV dissolved in 5 cc. of ethanol, 100 mg. of sodium acetate was added and the mixture was heated on a water bath for 50 minutes. Evaporation of ethanol left 30 mg. of pale yellow needles, m. p. 178∼180°C, and the melting point was raised to 180∼181°C on recrystallization from benzene, undepressed on admixture with 2, 4, 7-tribromotropone.

c) *2, 3, 4, 6, 7-Pentabromo-4-cyclohepten-1-one* (*V*).—A mixture of 200 mg. of V and 100 mg. of sodium acetate in 4 cc. of ethanol was refluxed on a water bath for 30 minutes and thereafter treated as in a), from which 90 mg. of crystals, m. p. 110∼155°C (sint. 80°C), was obtained. Recrystallization from ethanol afforded 30 mg. of pale yellow crystals, m. p. 173∼175°C, whose mother liquor will be designated as (A). The melting point of these crystals was raised to 179∼180°C by recrystallization from benzene and admixed melting point test identified them to be 2, 4, 7-tribromotropone.

Ethanol was evaporated off from the mother liquor (A), the residue was dissolved in chloroform, and the solution was passed through a short alumina column. Evaporation of chloroform from the effluent gave 50 mg. of crystals melting at 70∼80°C. The crystals were dissolved in carbon tetrachloride and again passed through a short alumina column. Crystals obtained from the effluent were recrystallized from ethanol and afforded 30 mg. of colorless plates, m. p. 83∼84°C. (*Anal.* Found: C, 33.59; H, 2.53%.)

d) *2,5,6,7-Tetrabromo-2,4-cycloheptadien-1-one* (*VI*).—A solution of 130 mg. of oily VI and 70 mg. of sodium acetate dissolved in 2.5 cc. of ethanol was heated on a water bath for 30 minutes, water was added to the mixture, and crystals that separated out were collected by filtration to give 90 mg. of yellowish needles, m. p. 179∼180°C, undepressed on admixing with 2, 4, 7-tribromotropone.

e) *2,4,5,7-Tetrabromo-2,6-cycloheptadien-1-one* (*VII*).—A mixture of 100 mg. of VII and 100 mg. of sodium acetate in 2.5 cc. of ethanol was refluxed on a water bath for 30 minutes, ethanol was evaporated, and water was added to the residue by which 70 mg. of pale yellow silky crystals, m. p. 155∼170°C, were obtained. Recrystallization from benzene first afforded 30 mg. of crystals melting at 182∼183°C, identified by admixture with 2, 4, 7-tribromotropone. Concentration of this recrystallization mother liquor gave another crop of crystals, m. p. 160∼173°C, which were dissolved in chloroform and passed through an alumina column. Elution with ethanol afforded 20 mg. of crystals, m. p. 169∼170°C, showing no depression on admixture with 2, 7-dibromotropone.

Thermal Decomposition of Various Bromine Addition Compounds in Acetic Acid Solution. — *a*) *2, 3, 4, 5, 6, 7-Hexabromocycloheptanone* (*III*).—A solution of 120 mg. of III dissolved in 2 cc. of acetic acid was refluxed in an oil bath for 3 hours, during which the evolution of hydrogen bromide (blue coloration of Congo-red paper) and bromine (blue coloration of iodine-starch paper) was observed. Acetic acid was then evaporated from the solution, and the residue was washed with ethanol, affording 40 mg. of pale yellow crystals, m. p. 150∼161°C. The crystals were dissolved in chloroform and the solution was passed through a short alumina column. Evaporation of chloroform from the effluent left crystals melting at 160∼165°C, which were recrystallized from ethanol-benzene mixture, giving 25 mg. of pale yellow plates, m. p. 170∼171°C, identified as 2, 7-dibromotropone by mixed fusion.

b) *2, 4, 5, 6, 7-Pentabromo-2-cyclohepten-1-one* (*IV*).—A solution of 80 mg. of IV dissolved in 2 cc. of acetic acid was refluxed on a water bath for 3 hours, acetic acid was evaporated, and the crystalline residue was washed with ethanol, affording 30 mg. of colorless plates, m. p. 169∼170°C, undepressed on admixture with 2, 7-dibromotropone.

c) *2, 3, 4, 6, 7-Pentabromo-4-cyclohepten-1-one* (*V*).—A solution of 80 mg. of V dissolved in 2cc. of acetic acid was refluxed for 3 hours and thereafter treated as in b), affording 45 mg. of crystals melting at 125∼140°C. Recrystallization from ethanol gave 20 mg. of pale yellow needles, m. p. 178∼180°C, identified as 2, 4, 7-tribromotropone by mixed fusion.

Ethanol was evaporated from the recrystallization mother liquor, the residue was dissolved in chloroform, and passed through an alumina column. This effluent gave 10 mg. of pale yellow crystals, m. p. 120∼135°C, which were not identified.

d) *2, 5, 6, 7-Tetrabromo-2, 4-cycloheptadien-1-one* (*VI*).—A solution of 90 mg. of VI dissolved in 2 cc. of acetic acid was refluxed for 3 hours and thereafter treated as in b), affording 30 mg. of dark brownish crystals, m. p. 165∼175°C. The crystals were dissolved in benzene and passed through an alumina column, and evaporation of the solvent left yellow needles, m. p. 172∼176°C, undepressed on admixing with 2,4,7-tribromotropone.

e) *2,4,5,7-Tetrabromo-2,6-cycloheptadien-1-one* (*VII*).—A solution of 60 mg. of VII dissolved in 2 cc. of acetic acid was refluxed in an oil bath for 3 hours and thereafter treated as in b), affording 40 mg. of pale yellow plates, m. p. 169∼170°C, identified with 2, 7-dibromotropone by mixed fusion.

Thermal Decomposition of Various Bromine Addition Compound.—*a*) *2,3,4,5,6,7-Hexabromocycloheptanone* (*III*). — One hundred milligrams of III was placed in a small test tube and dipped in an oil bath at 145∼150°C by which the compound melted and decomposed, with evolution of hydrogen bromide and bromine. The contents were heated at this temperature for 20 minutes, cooled, and the crystalline residue was washed out with ethanol, affording 40 mg. of dark brown crystals, m. p. 140∼150°C. The crystals were dissolved in benzene, passed through a column of alumina, and the column was eluted with chloroform. The benzene eluate gave a few mg. of crystals, m. p. 140∼150°C, and the chloroform effluent gave 25 mg. of colorless crystals, m. p. 169∼170°C. Mixed fusion proved the latter to be 2, 7-dibromotropone.

b) *2, 4, 5, 6, 7-Pentabromo-2-cyclohepten-1-one* (*IV*).—One hundred milligrams of IV was heated and decomposed in a small test tube as in a) and 50 mg. of colorless crystals, m. p. 145∼150°C, were obtained. Recrystallization from ethanol afforded colorless plates, m.p. 150∼157°C. These crystals were dissolved in chloroform, passed through an alumina column, and eluted with ethanol. Chloroform effluent afforded a few mg. of colorless crystals, m. p. 170∼172°C, and ethanol eluate afforded 30 mg. of colorless plates, m. p. 167∼169°C. By mixed fusion, the former was identified with 2, 4, 7-tribromotropone and the latter with 2, 7-dibromotropone.

c) *2, 3, 4, 6, 7-Pentabromo-4-cyclohepten-1-one* (*V*).—Thermal decomposition of 120 mg. of V in a small test tube as in a) afforded 60 mg. of pale brown crystals, m. p. 177∼179°C, which were recrystallized from ethanol to pale yellow needles, m. p. 182∼183°C and identified with 2, 4, 7-tribromotropone by admixture with an authentic sample.

d) *2, 5, 6, 7-Tetrabromo-2, 4-cycloheptadien-1-one (VI)*.—Thermal decomposition of 120 mg. of VI in a small test tube as in a) afforded 70 mg. of pale yellow crystals, m. p. 179∼181°C, which showed no depression on admixing with 2, 4, 7-tribromotropone.

e) *2, 4, 5, 7-Tetrabromo-2, 6-cycloheptadien-1-one (VII)*.—Thirty milligrams of VII was placed in a small test tube and heated for 20 minutes in an oil bath at 160°C. After cooling, the crystalline residue was sublimed at 5 mm. Hg in a bath at 140°C and afforded 15 mg. of crystals melting at 163∼166°C. Recrystallization from benzene raised the melting point to 167∼169°C, undepressed on admixing with 2, 7-dibromotropone.

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