BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 43 1778—1782 (1970)

3,4-Benzotropolone and Related Compounds. VIII.[1] Azo, Nitro and Amino Derivatives of 6-Hydroxy-2,3-benzotropone

Masamatsu Hoshino and Seiji Ebine

Department of Chemistry, Saitama University, Urawa, Saitama

(Received September 29, 1969)

On diazo coupling and nitration, 6-hydroxy-2,3-benzotropone (I) and its 5-bromo derivative (II) gave their 7-azo (V and VI) and 7-nitro substitution products (VII and VIII), respectively. In the same reactions, 7-bromo-6-hydroxy- (III) and 5,7-dibromo-6-hydroxy-2,3-benzotropones (IV) replaced their 7-bromo substituent to give the same 7-azo and 7-nitro substitution products as above. On nitration of III and IV, 2,2-dibromo- (IX) and 2,2,7-tribromo-4,5-benzocyclohepta-4,6-diene-1,3-diones (X) were also formed. Hydrogenation of V, VI, VII and VIII gave 7-amino-6-hydroxy-2,3-benzotropone (XI), diazotization of which gave 2-diazo-4,5-benzocyclohepta-4,6-diene-1,3-dione (XII). 7-Chloro-6-hydroxy-2,3-benzotropone (XV) was brominated to 2-bromo-2-chloro-4,5-benzocyclohepta-4,6-diene-1,3-dione (XVII) at room temperature, to 5-bromo-7-chloro-2,3-benzotropone (XVI) at 100°C, and to 2-chloro-2,7-dibromo-4,5-benzocyclohepta-4,6-diene-1,3-dione (XVIII) with excess bromine at 100°C. XVII and XVIII were easily debrominated to XV and XVI, respectively, on heating with hydrochloric or hydrobromic acid. XV changed into a mixture of I and II on heating with hydrobromic acid.

Nitration, azo coupling and related reactions of 6-hydroxy-2,3-benzotropone (I)[2],*1 have been investigated as a series of benzotroponoid studies.[1-3]

I and its 5-bromo derivative (II),[2] like tropolone[4,5] and its benzologs,[6-8] underwent coupling with diazotized *p*-toluidine in a pyridine solution to give the corresponding 7-*p*-tolylazo derivatives (V and VI). 7-Bromo (III)[3] and 5,7-dibromo (IV)[3] derivatives of I also reacted with diazotized *p*-toluidine, expelling their 7-bromo substituent, to give the same products (V and VI) as above.

Nitration of I and II, like that of tropolone[5] and its benzologs,[7,9] was not successful in concentrated sulfuric acid but successful in acetic acid solution to give 6-hydroxy-7-nitro-2,3-benzotropone (VII) and its 5-bromo derivative (VIII), respectively, in good yields. On nitration of III, the 7-bromo substituent was replaced with a nitro group to give VII and the liberated bromo cation attacked an unreacted III to give 2,2-dibromo-4,5-benzocyclohepta-4,6-diene-1,3-dione (IX) (infrared absorption spectrum in KBr disk: 1690 and 1653 cm^{-1} for two carbonyls). Intermediate formation of the bromo cation, however, has no experimental evidence. A similar nitration of IV gave a tribromo diketone (X),[3] a possible product (VIII) not being isolated. X was also obtained by bromination of IV and IX.

7-Amino-6-hydroxy-2,3-benzotropone (XI) was produced by hydrogenation of azo compounds (V and VI) or nitro compounds (VII and VIII). Treatment of XI with nitrous acid at 0—5°C resulted in the formation of 2-diazo-4,5-benzocyclohepta-4,6-diene-1,3-dione (XII), which would be produced *via* an intermediate diazonium salt. The structure of XII was confirmed by intense infrared absorption at 2178 cm^{-1} characteristic to diazoketone[10] and by Wolff rearrangement reaction to 1-hydroxy-2-naphthoic acid along with a small amount of α-naphthol on heating in aqueous solution, and to

1) Part VII. M. C. Woods, S. Ebine, M. Hoshino, K. Takahashi and I. Miura, *Tetrahedron Lett.*, **1969**, 2879.

2) S. Ebine, M. Hoshino and K. Takahashi, This Bulletin, **41**, 2942 (1968).

*1 6-Hydroxy-2,3-benzotropone is tautomeric with 3-hydroxy-4,5-benzotropone. Since it is not clear which form predominates in the tautomeric mixture, the former form is tentatively employed in this paper.

3) M. Hoshino and S. Ebine, *ibid.*, **41**, 2949 (1968).

4) T. Nozoe, E. Sebe and S. Ebine, *Proc. Japan Acad.*, **26** (8), 24 (1950).

5) W. von E. Doering and L. H. Knox, *J. Amer. Chem. Soc.*, **73**, 828 (1951); J. W. Cook, J. D. Loudon and D. K. V. Steel, *J. Chem. Soc.*, **1954**, 530.

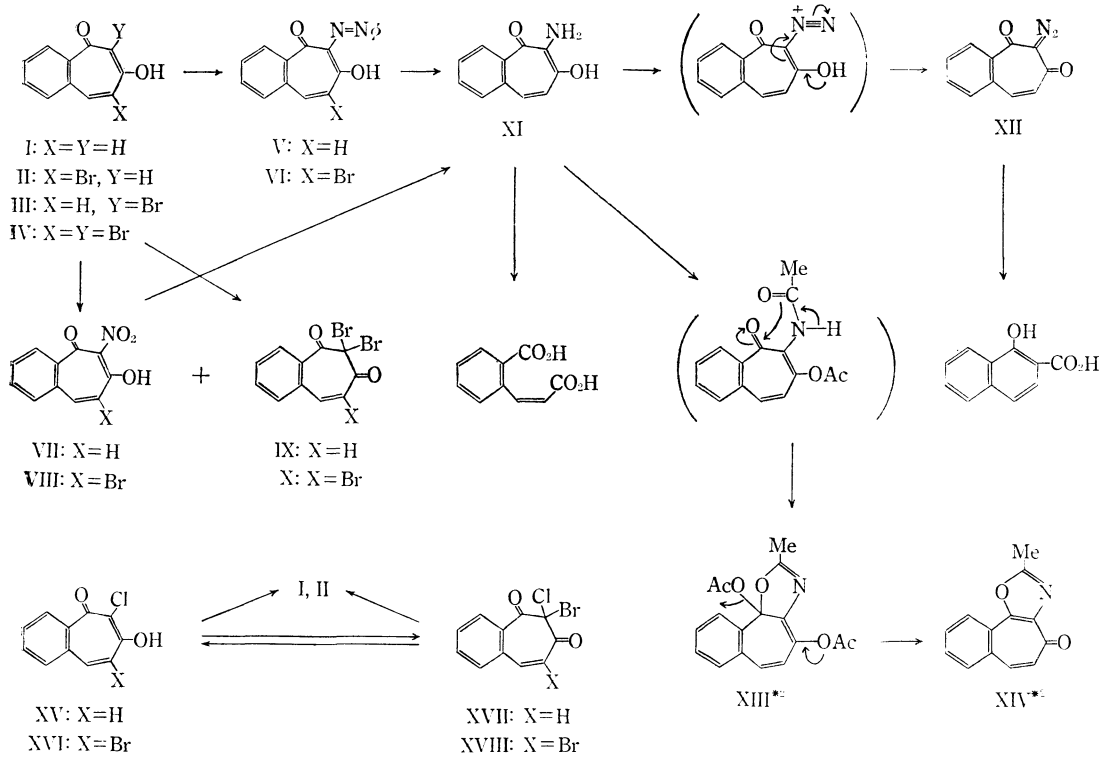
6) D. S. Tarbell and J. C. Bill, *J. Amer. Chem. Soc.*, **74**, 1234 (1952).

7) G. A. Nicholls and D. S. Tarbell, *ibid.*, **74**, 4935 (1952).

8) S. Ebine, This Bulletin, **38**, 2029 (1965).

9) S. Ebine, *ibid.*, **35**, 122 (1962).

10) M. P. Cava, R. L. Litle and D. R. Napier, *J. Amer. Chem. Soc.*, **80**, 2258 (1958).



1-hydroxy-2-naphtho-*p*-toluidide on heating with *p*-toluidine in xylene solution. Acetylation of XI gave an unusual product (XIII), hydrolysis of which gave a compound (XIV). XIV is assumed to be an oxazolobenzotropone based on its infrared absorption spectrum (KBr): 1620, 1590, 1548 and 1130 cm^{-1} for C=O, C=N, C=C and C–O–C, no absorption for acetoxyl and acetamide carbonyls. The structure of XIII is also assumed as given in the chart due to infrared absorption at 1770 and 1710 cm^{-1} for two acetyl carbonyls. A similar reaction has been reported in the case of acetylation of 3-amino-4,5-benzotropolone[7] and 3-aminotropolone.[11]

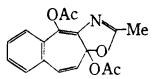
By analogy to the case of III and IV, 7-chloro-6-hydroxy-2,3-benzotropone (XV) was subjected to halogenation and dehalogenation. Bromination of XV at 100°C gave 5-bromo-7-chloro-6-hydroxy-2,3-benzotropone (XVI).[3] Bromination of XV and XVI at room temperature gave the corresponding bromo chloro diones (XVII and XVIII) which, on treatment with alkali or hydrochloric acid, turned back to the original XV and XVI, respectively. Bromination of III at room temperature gave III-bromine adduct[3] instead of IX.

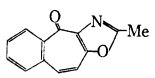
XV remained unchanged on heating with hydrochloric acid but changed to give both I and II on heating with hydrobromic acid. A similar treatment of XVI, XVII and XVIII with hydrobromic acid liberated one of their halogen substituents to afford II in good yield. III and XV also liberated with difficulty their halogen substituent to give I on heating with sulfuric acid. The diones (IX, XVII and XVIII) were dehalogenated under mild condition to the tropones (III, XV and XVI, respectively). Halogenation and dehalogenation of these chloro derivatives are analogous to those of the corresponding bromo derivatives.[3]

Experimental*3

Azo Coupling of 6-Hydroxy-2,3-benzotropone (I)[2] and Its Bromo Derivatives (II[2], III[3] and IV[3]). *6-Hydroxy-7-p-tolylazo-2,3-benzotropone (V).* To a solution of 300 mg of I in 5 m*l* of pyridine was added a diazotized *p*-toluidine solution prepared from 243 mg of *p*-toluidine, 132 mg of sodium nitrite and 3.14 m*l* of 2.4N hydrochloric acid. After standing overnight in an ice-chest, the precipitate formed was filtered and recrystallized from ethanol, giving 480 mg (95%) of V, reddish orange needles, mp 153—154°C, infrared

*2 Alternative structures XIII′ and XIV′ are conceivable. It is not clear which pair of structures are more correct.

XIII′ 

XIV′ 

11) Y. Kitahara, *Sci. Rep. Tohoku Univ., Ser. I*, **40**, 87 (1956).

*3 Thanks are due to the Department of Chemistry, Tohoku University, for the microanalyses.

spectrum above 1500 cm^{-1} (KBr, cm^{-1}): 3406, 1638, 1591, 1556, ultraviolet spectrum (MeOH), mμ (log ε): 229 (4.44), 265 (4.38), 455 (4.46).

Found: C, 74.17; H, 4.77; N, 9.43%. Calcd for $C_{18}H_{14}N_2O_2$: C, 74.47; H, 4.86; N, 9.65%.

Coupling of 200 mg of 7-bromo-6-hydroxy-2,3-benzotropone (III) with diazotized *p*-toluidine gave 30 mg (13%) of the same product (V) as above.

5-Bromo-6-hydroxy-7-p-tolylazo-2,3-benzotropone (VI). Coupling of 200 mg of 5-bromo-6-hydroxy-2,3-benzotropone (II) and 300 mg of 5,7-dibromo-6-hydroxy-2,3-benzotropone (IV) with diazotized *p*-toluidine gave 230 mg (78%) and 130 mg (39%), respectively, of the same VI, orange needles (from ethanol), mp 181—182°C, infrared spectrum above 1500 cm^{-1} (KBr, cm^{-1}): 3420, 1647, 1590, 1565, ultraviolet spectrum (MeOH), mμ (log ε): 257 (4.67), 460 (4.45).

Found: C, 58.36; H, 4.05; N, 7.34%. Calcd for $C_{18}H_{13}N_2O_2Br$: C, 58.55; H, 3.55; N, 7.59%.

4-Bromo-6-hydroxy-7-p-tolylazo-2,3-benzotropone.[2] Coupling of 4-bromo-6-hydroxy-2,3-benzotropone with diazotized *p*-toluidine gave 4-bromo-6-hydroxy-7-*p*-tolylazo-2,3-benzotropone, reddish orange needles, mp 152—153°C, in 70% yield, infrared spectrum above 1500 cm^{-1} (KBr, cm^{-1}): 3420, 1655, 1608, 1588, 1560, ultraviolet spectrum (MeOH), mμ (log ε): 230 (4.28), 265 (4.27), 450 (4.45).

Found: C, 58.50; H, 3.45; N, 7.56%. Calcd for $C_{18}H_{13}N_2O_2Br$: C, 58.55; H, 3.55; N, 7.59%.

Nitration of I, II, III and IV. *6-Hydroxy-7-nitro-2,3-benzotropone (VII).* To a stirred suspension of 400 mg of I in 10 m*l* of glacial acetic acid was dropped at 10—15°C 0.174 m*l* of concentrated nitric acid (sp. gr. 1.38), diluted with an equal volume of glacial acetic acid in the course of one and a half hours. The mixture was stirred for further 4 hr and then allowed to stand at room temperature overnight. A precipitate formed was collected and recrystallized from ethanol to give 440 mg (87%) of pale yellow, granular crystals, mp 203°C (dec), infrared spectrum above 1500 cm^{-1} (KBr, cm^{-1}): *ca.* 3388, 3026, 1640, 1600, 1560, 1515, ultraviolet spectrum (MeOH), mμ (log ε): 258 (4.63), 335 (3.89).

Found: C, 60.77; H, 3.20; N, 6.14%. Calcd for $C_{11}H_7NO_4$: C, 60.83; H, 3.25; N, 6.45%.

5-Bromo-6-hydroxy-7-nitro-2,3-benzotropone (VIII). A similar nitration of 300 mg of 5-bromo-6-hydroxy-2,3-benzotropone (II) gave 280 mg (79%) of VIII, pale yellow, granular crystals, mp 103—105°C (dec), infrared spectrum above 1500 cm^{-1} (KBr, cm^{-1}): *ca.* 3440, 3026 (shoulder), 1605, 1573, 1548, ultraviolet spectrum (MeOH), mμ (log ε): 273 (4.66).

Found: C, 44.86; H, 2.04; N, 4.31%. Calcd for $C_{11}H_6NO_4Br$: C, 44.62; H, 2.04; N, 4.73%.

2,2-Dibromo-4,5-benzocyclohepta-4,6-diene-1,3-dione (IX). III (300 mg) was nitrated in the same way as above and the crude product was fractionally recrystallized from dilute methanol to give 46 mg (18%) of VII and 127 mg (32%) of IX, intensely yellow, granular crystals, mp 110—111°C, infrared spectrum (KBr, cm^{-1}): 1690 and 1653 for two carbonyls, ultraviolet spectrum (MeOH), mμ (log ε): 243 (3.89).

Found: C, 40.10; H, 1.94%. Calcd for $C_{11}H_6O_2Br_2$: C, 40.03; H, 1.83%.

2,2,7-Tribromo-4,5-benzocyclohepta-4,6-diene-1,3-dione (X).[3] a) Nitration of 300 mg of IV in acetic acid or acetic anhydride solution gave 105 mg (28%) of X, mp 131—132°C. (Found: C, 32.91; H, 1.38%. Calcd for $C_{11}H_5O_2Br_3$: C, 32.81; H, 1.23%).

b) A solution of 30 mg of bromine in 0.2 m*l* of acetic acid was added to a solution of 50 mg of IV in 3 m*l* of acetic acid, and the resulting solution was allowed to stand at room temperature for 2 hr. The solvent was removed *in vacuo* and the residue was extracted with warm petroleum ether. After standing in an ice-chest, the precipitate formed was collected and recrystallized from ethanol to give 17 mg (27%) of X, mp 132—133°C.

The products obtained in the above two ways were identified by mixture mp determination and infrared comparison with an authentic sample.[3]

7-Amino-6-hydroxy-2,3-benzotropone (XI) and Its Derivatives. *7-Amino-6-hydroxy-2,3-benzotropone (XI).* A solution of 300 mg of V or 400 mg of VII in 50—100 m*l* of ethanol was hydrogenated with a theoretical amount of hydrogen in the presence of 100 mg of 5% palladium chloride-charcoal catalyst. After completion of the reaction, the catalyst was filtered, the solution was evaporated and the product was recrystallized from ethanol giving 160 mg (83%) or 255 mg (74%) of XI, yellow needles, mp 192—193°C (dec). A similar hydrogenation of 400 mg of VI, VIII or 4-bromo-6-hydroxy-7-*p*-tolylazo-2,3-benzotropone in ethanol in the presence of 100 mg of 5% palladium chloride-charcoal and 400 mg of fused sodium acetate gave XI in around 80% yield. Infrared spectrum above 1500 cm^{-1} (KBr, cm^{-1}): *ca.* 3386, 3046, 1638, 1573, 1538, ultraviolet spectrum (MeOH), mμ (log ε): 254 (4.51), 410 (4.05).

Found: C, 70.71; H, 5.05; N, 7.16%. Calcd for $C_{11}H_9NO_2$: C, 70.58; H, 4.85; N, 7.48%.

Hydrochloride. Colorless needles, mp 223—225°C (dec).

Found: C, 59.15; H, 4.46; N, 6.00%. Calcd for $C_{11}H_{10}O_2NCl$: C, 59.07; H, 4.51; N, 6.26%.

Sulfate. Pale yellow crystals, mp 208—210°C (dec).

Found: C, 46.23; H, 4.14; N, 4.64%. Calcd for $C_{11}H_{11}O_6NS$: C, 46.31; H, 3.89; N, 4.91%.

Picrate. Yellow needles, mp 172°C (dec).

Found: C, 55.73; H, 3.59; N, 11.16%. Calcd for $C_{28}H_{21}O_{11}N_5$: C, 55.72; H, 3.51; N, 11.61%.

Reaction of XI with Acetic Anhydride. A mixture of 400 mg of XI, 400 mg of fused sodium acetate and 12 m*l* of acetic anhydride was heated at 100°C for 30 min. After cooling the mixture was poured on ice and the precipitate which separated was collected by filtration. The precipitate (A) and the filtrate (B) were worked up as follows. Recrystallization of A from ethanol gave 304 mg (45%) of a compound (XIII), colorless prisms, mp 146°C, infrared spectrum (KBr, cm^{-1}): 1770, 1710, 1635 (shoulder), 1623, 1593, 1580, *etc.*, ultraviolet spectrum (MeOH), mμ (log ε): 236 (4.45), 325 (3.91).

Found: C, 65.14; H, 4.83; N, 4.43%. Calcd for $C_{17}H_{15}NO_5$: C, 65.17; H, 4.82; N, 4.47%.

Extraction of B with ethyl acetate, evaporation of the solvent from the organic layer and recrystallization of the residue from ethanol gave 87 mg (19%) of oxazole derivative (XIV), colorless needles, mp 192—193°C (dec), infrared spectrum (KBr, cm^{-1}): 1628 (shoulder), 1620, 1590, 1548, *etc.*, ultraviolet spectrum (MeOH), mμ (log ε): 237 (4.31), 270 (4.71).

Found: C, 73.70; H, 4.13; N, 6.14%. Calcd for

$C_{13}H_9NO_2$: C, 73.92; H, 4.30; N, 6.63%.

Heating of XIII with concentrated hydrochloric acid at 100°C for 20 min gave XIV in 83% yield.

Oxidation of XI to o-Carboxycinnamic Acid. To a solution of 200 mg of XI in 20 m*l* of 0.5N sodium hydroxide was added 5 m*l* of 35% hydrogen peroxide. After standing for 2 hr at room temperature, the solution was acidified with 6N hydrochloric acid to give 70 mg (34%) of *o*-carboxycinnamic acid, mp and mixed mp 186—188°C.

2-Diazo-4,5-benzocyclohepta-4,6-diene-1,3-dione (XII) and Its Wolff Rearrangement. *Diazoketone (XII).* To a stirred suspension of 500 mg of XI in 12.5 m*l* of 42% borofluoric acid (HBF_4) was dropped a solution of 204 mg of sodium nitrite in 1 m*l* of water and the reaction mixture was set aside for 1 hr at 0—5°C. The precipitate (A) was collected by filtration. The filtrate was set aside for several days, giving a precipitate (B) of unknown compound (mp>240°C, 149 mg). The precipitate (A) was recrystallized from methanol to afford 314 mg (59%) of XII, yellow needles, mp 118—119°C, infrared spectrum (KBr, cm^{-1}): *ca.* 2178, 1636, 1579(shoulder), 1578, 1560, *etc.*, ultraviolet spectrum (MeOH), mμ (log ε): 255 (4.61), 330 (3.90), NMR spectrum ($CDCl_3$, ppm): 8.84 (an aromatic H), 7.64 (multiplet, three aromatic H), 7.21 and 6.45 (AB pattern, 6-H and 7-H, J=13.1 Hz).

Found: C, 66.70; H, 3.30; N, 14.35%. Calcd for $C_{11}H_6N_2O_2$: C, 66.66; H, 3.05; N, 14.14%.

XII (147 mg, 69%) as well as a trace (4 mg, 2%) of 1-hydroxy-2-naphthoic acid were formed when a solution of 82 mg of sodium nitrite in 2 m*l* of water was added to a suspension of 200 mg of XI in 10 m*l* of 6N sulfuric acid, and the resulting mixture was allowed to stand at 0—5°C for 1 hr and then refluxed for 5 min.

Wolff Rearrangement of XII. a) A suspension of 100 mg of XII in 40 m*l* of water was refluxed for 4.5 hr, during which time the suspended mixture became homogeneous. After cooling, the solution was extracted with ethyl acetate and then the organic layer was shaken with aqueous sodium bicarbonate. The organic layer was evaporated and the residue was recrystallized from petroleum ether to give 12 mg (14%) of α-naphthol, mp and mixed mp 91—93°C. The aqueous sodium bicarbonate layer was acidified with dilute hydrochloric acid and then extracted with ethyl acetate. The extract was evaporated and the residue was recrystallized from benzene to give 55 mg (59%) of 1-hydroxy-2-naphthoic acid, mp and mixed mp 188.5—190.5°C, which was identified by infrared comparison with an authentic sample.

A solution of 200 mg of 1-hydroxy-2-naphthoic acid in 50 m*l* of water was refluxed for 2.5 hr to give 150 mg of α-naphthol, proving that a part of 1-hydroxy-2-naphthoic acid was decarboxylated to α-naphthol during the above Wolff rearrangement.

b) A solution of 120 mg of XII and 500 mg of *p*-toluidine in 15 m*l* of xylene was refluxed for 3 hr. The solution was washed with dilute hydrochloric acid to remove excess *p*-toluidine and the organic layer was evaporated. Recrystallization of the residue from cyclohexane gave 125 mg (74%) of 1-hydroxy-2-naphtho-*p*-toluidide, mp and mixed mp 149—151°C (Found: C, 78.17; H, 5.47; N, 5.06%. Calcd for $C_{18}H_{15}NO_2$: C, 77.96; H, 5.45; N, 5.05%).

Derivatives of 7-Bromo-6-hydroxy-2,3-benzotropone (III)[3] and 7-Chloro-6-hydroxy-2,3-benzotropone (XV)[3]. *Acetate of III.* Colorless granular crystals (from ether-petroleum ether), mp 139—140°C.

Found: C, 53.18; H, 3.30%. Calcd for $C_{13}H_9O_3Br$: C, 53.27; H, 3.09%.

Methyl Ether of III. Colorless prisms (from methanol), mp 138—139°C.

Found: C, 54.48; H, 3.58%. Calcd for $C_{12}H_9O_2Br$: C, 54.36; H, 3.42%.

Acetate of XV. Colorless plates (from methanol), mp 141—142°C.

Found: C, 62.37; H, 3.70%. Calcd for $C_{13}H_9O_3Cl$: C, 62.79; H, 3.65%.

Methyl Ether of XV. Colorless needles (from methanol), mp 137—137.5°C.

Found: C, 64.88; H, 4.15%. Calcd for $C_{12}H_9O_2Cl$: C, 65.32; H, 4.11%.

Bromination of XV.[3] *5-Bromo-7-chloro-6-hydroxy-2,3-benzotropone (XVI).* A solution of 52.5 mg of bromine in 2 m*l* of acetic acid was added to a solution of 50 mg of XV[9] in 2 m*l* of acetic acid and the resulting solution was heated at 100°C for 1 hr. On evaporation of the solvent *in vacuo*, recrystallization of the residue from ethanol gave 53.5 mg (77%) of XVI, yellow needles, mp and mixed mp 213—214°C (dec), whose infrared spectrum coincided with that of a sample prepared by a different method.[3]

2-Bromo-2-chloro-4,5-benzocyclohepta-4,6-diene-1,3-dione (XVII). Bromination of 100 mg of XV with 80 mg of bromine and 60 mg of fused sodium acetate in 10 m*l* of acetic acid at room temperature (18°C) gave 135 mg (98%) of XVII, yellow plates (from methanol), mp 121—122°C (dec), infrared spectrum (KBr, cm^{-1}): 1698 and 1663 for two carbonyls, ultraviolet spectrum (MeOH), mμ (log ε): 247 (4.10), 334 (3.65).

Found: C, 46.06; H, 2.17%. Calcd for $C_{11}H_6O_2BrCl$: C, 46.27; H, 2.12%.

2-Chloro-2,7-dibromo-4,5-benzocyclohepta-4,6-diene-1,3-dione (XVIII). a) Bromination of 100 mg of XV with 184 mg of bromine and 105 mg of fused sodium acetate in 10 m*l* of acetic acid at 60—70°C gave 119 mg (67%) of XVIII, yellow prisms (from methanol), mp 140—141°C (dec), infrared spectrum (KBr, cm^{-1}): 1706 and 1691 for two carbonyls, ultraviolet spectrum (MeOH), mμ (log ε): 270 (3.86), 277 (3.86).

Found: C, 36.39; H, 1.51%. Calcd for $C_{11}H_5O_2Br_2Cl$: C, 36.25; H, 1.38%.

b) A similar treatment of 200 mg of XVI with 150 mg of bromine and 150 mg of fused sodium acetate in 70 m*l* of acetic acid gave 230 mg (90%) of XVIII.

Dehalogenation of Halo-6-hydroxy-2,3-benzotropones (III[3], XV[3], XVI[3]) and Halo-4,5-benzocyclohepta-4,6-diene-1,3-diones (IX, XVII, XVIII). *From III and XV to I (and II).* a) A solution of 150 mg of XV in 20 m*l* of acetic acid and 20 m*l* of 47% hydrobromic acid was refluxed for 2 hr. Evaporation of the solvent and fractional recrystallization of the residue from dilute alcohol gave 44 mg (35%) of I, 208°C (dec) and 72 mg (40%) of II, mp 234°C (dec).

XV remained unchanged on heating with hydrochloric acid.

b) A solution of 100 mg of III in 15 m*l* of acetic acid and 10 m*l* of 6N sulfuric acid was refluxed for 2 hr. Concentration of the reaction mixture and dilution with 50 m*l* of water gave 76.2 mg of a precipitate of unchanged III. After filtration the filtrate was extracted

with ethyl acetate and the extract was evaporated to give 13 mg (19%) of I, mp 208°C (dec).

Heating of III with hydrobromic acid gave I (4%) and II (29%).[9]

c) A similar treatment of 100 mg of XV with 6N sulfuric acid gave 4.2 mg (5%) of I, a greater part of XV remained unreacted.

From XVI, XVII, and XVIII to II. A 50-mg sample of XVI, XVII or XVIII, dissolved in 5 m*l* of acetic acid and 5 m*l* of 47% of hydrobromic acid, was heated for 2 hr. Evaporation of the solvent and recrystallization of the residue from methanol gave II, mp 234°C (dec), in over 90% yield.

From IX, XVII and XVIII to III, XV and XVI, respectively. a) A solution of 50 mg of IX in 6 m*l* of N sodium hydroxide was set aside at room temperature for 1 hr. The solution was acidified with dilute hydrochloric acid and the precipitate which separated was recrystallized from ethanol to give 20 mg (52%) of III, mp 173.5°C (dec).

b) XVII (50 mg), 5 m*l* of 6N hydrochloric acid and 8 m*l* of acetic acid were heated under reflux for 1 hr. The solution was evaporated and the residue was recrystallized from methanol to give 24 mg (66%) of XV, mp 173°C.

c) XVIII (50 mg), 5 m*l* of 47% hydrobromic acid and 8 m*l* of acetic acid were set aside at room temperature for 2 days. Concentration of the solution gave 31 mg (79%) of XVI, mp 214°C (dec).

XVIII (50 mg), 5 m*l* of 6N hydrochloric acid and 8 m*l* of acetic acid were refluxed for 1 hr, yielding 20 mg (52%) of XVI.

XVIII (100 mg) and 20 drops of 2N potassium hydroxide in 20 m*l* of methanol were allowed to stand at room temperature for 1 hr. Removal of methanol, acidification with dilute hydrochloric acid, extraction with chloroform, and evaporation of the solvent from the extract gave 21 mg (27%) of XVI.

The above products I, II, III, XV and XVI were identified by elemental analyses, mixture mp determinations and infrared comparisons with authentic samples.[3]

The present work has been supported in part by a Grant for Scientific Research from the Ministry of Education.