

A mixture of 2.0 g (0.05 mol) of  $\text{NaBH}_4$  in 10 ml of THF (method A-1) or DMF (method B-1) was stirred and cooled in an ice bath while 0.05 mol of anhydride in 40 ml of THF (DMF) was added in 5 min. The ice bath was removed and stirring was continued for 1 hr. (Method A-1 and B-1) 6 *N* HCl (20 ml) was added cautiously and the mixture was concentrated. Water (100 ml) was added and the mixture was extracted with 50 ml of  $\text{Et}_2\text{O}$ . The  $\text{Et}_2\text{O}$  extract was dried ( $\text{Na}_2\text{SO}_4$ ), concentrated, and distilled giving the desired lactone. (Method A-2 and B-2) Ethanolic 10 *N* HCl (10 ml) was added and the resulting mixture was heated on a steam bath 1 hr, filtered, concentrated, and distilled giving the desired lactone.

**Reduction of *cis*-1-Methylcyclohexane-1,2-dicarboxylic Acid Anhydride with  $\text{NaBH}(\text{OMe})_3$ .**—Method A-1 was used; only the 0.05 mol of  $\text{NaBH}_4$  was replaced by 0.10 mol of  $\text{NaBH}(\text{OMe})_3$ . The yield was 78% of *cis*-2-methyl-2-hydroxymethylcyclohexane carboxylic acid  $\gamma$ -lactone (II).

**Reduction of *cis*-1-Methylcyclohexane-1,2-dicarboxylic Acid Anhydride with Na and EtOH.**—The procedure reported by Linstead and Millidge<sup>7</sup> was used. The yield of II was 35%.

**Registry No.**— $\text{NaBH}_4$ , 16940-66-2.

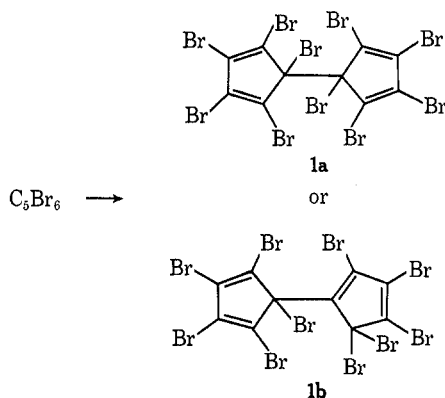
### Decabromo-3,3'-dihydrofulvalene

S. D. MCGREGOR AND C. W. ROBERTS<sup>1</sup>

*Hydrocarbons and Monomers Research  
Laboratory, The Dow Chemical Company,  
Midland, Michigan 48640*

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West and Kwitowski<sup>2</sup> recently reported the isolation of  $\text{C}_{10}\text{Br}_{10}$  (1), mp 139–140°, from the reactions of hexabromocyclopentadiene ( $\text{C}_5\text{Br}_6$ ) with copper(I) bromide or various metals. Possible structures for this dihydrodecabromofulvalene were noted as 1a or 1b.



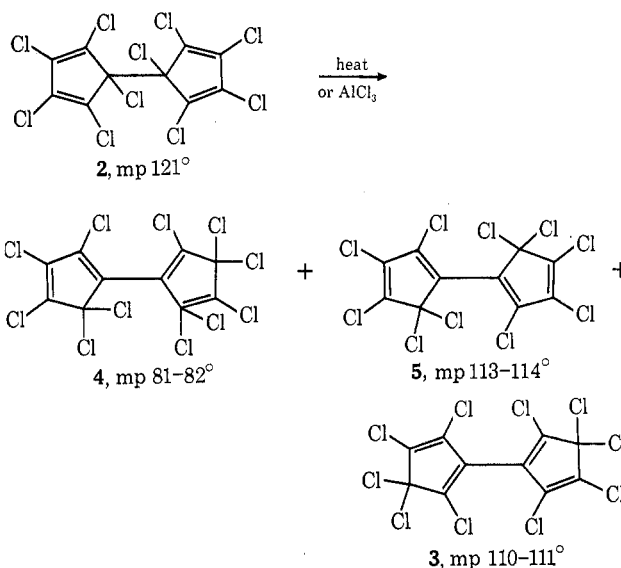
In a more recent report Smith and West<sup>3</sup> describe the isomerization of the chlorine compound  $\text{C}_{10}\text{Cl}_{10}$ , mp 121° (2), to three new isomers which were assigned the structures 3, 4, and 5 by nqr analysis.

Work in our laboratories on the chemistry of hexabromocyclopentadiene has led us to the isolation of  $\text{C}_{10}\text{Br}_{10}$ , mp 140.5–142°, from two reaction sequences and prompts us to report its occurrence and to assign it a structure.

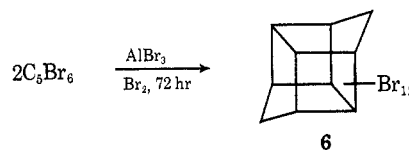
(1) To whom inquiries should be addressed.

(2) R. West and P. T. Kwitowski, *J. Amer. Chem. Soc.*, **90**, 4697 (1968).

(3) R. M. Smith and R. West, *J. Org. Chem.*, **35**, 2681 (1970); see also V. Mark and E. O'Neil, *ibid.*, in press. We thank Dr. West for a pre-publication copy of his manuscript. Cf. R. M. Smith and R. West, Abstracts, 157th National Meeting of the American Chemical Society, Minneapolis, Minn., April 1969, ORGN 60.

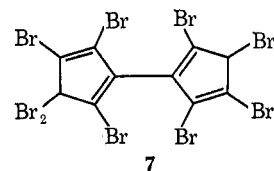


The reaction of  $\text{C}_5\text{Br}_6$  with metallic copper in 95% ethanol at 45° results in a mixture of  $\text{C}_{10}\text{Br}_{10}$  and  $\text{C}_5\text{Br}_6$  separable on a silica column to give an 85% yield of  $\text{C}_{10}\text{Br}_{10}$  (1), mp 140.5–142°. In a preparation of  $\text{C}_{10}\text{Br}_{12}$  (6), mp 340–350° dec, from  $\text{C}_5\text{Br}_6$ <sup>4</sup> the reaction



was stopped at the end of 45 hr. The “recovered”  $\text{C}_5\text{Br}_6$  possessed a melting point range of 111–115° and was separable into  $\text{C}_5\text{Br}_6$  and pure  $\text{C}_{10}\text{Br}_{10}$  (1). This eutectic “recovered  $\text{C}_5\text{Br}_6$ ” appears to be the same as West's 1:1 complex of  $\text{C}_5\text{Br}_6$  and  $\text{C}_{10}\text{Br}_{10}$ , mp 108–109°.<sup>2</sup>

Compound 1 has three bands in the carbon–carbon double bond region in the infrared (1626, 1579, 1550  $\text{cm}^{-1}$ ). Examination of the ir spectra of the various  $\text{C}_{10}\text{Cl}_{10}$  isomers<sup>5</sup> reveals that only one of these, 3, shows this three peak pattern. Not only are the carbon–carbon double bond regions for 1 and 3 virtually identical, there is a gross similarity of the entire infrared spectra for these compounds which is not noted with the other  $\text{C}_{10}\text{Cl}_{10}$  isomers. This suggests that the skeletal structures and double bond locations for 1 and 3 are the same; *i.e.*, structure 7 is proposed as the structure of



$\text{C}_{10}\text{Br}_{10}$ , mp 140.5–142°. This structure also appears chemically to be the most logical choice, since, of all the possible dicyclopentadienyl structures, this stands out as being the least sterically crowded molecule and, therefore, most certainly the most thermodynamically stable. This point gains credence by the fact that all

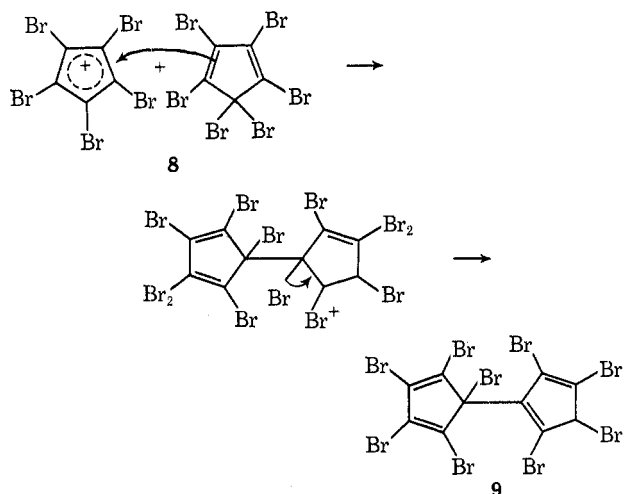
(4) C. W. Roberts and M. B. Chenoweth, U. S. Patent 3,212,973 (Oct 19, 1965).

(5) E. D. Weil, U. S. Patent 3,219,710 (Nov 23, 1965).

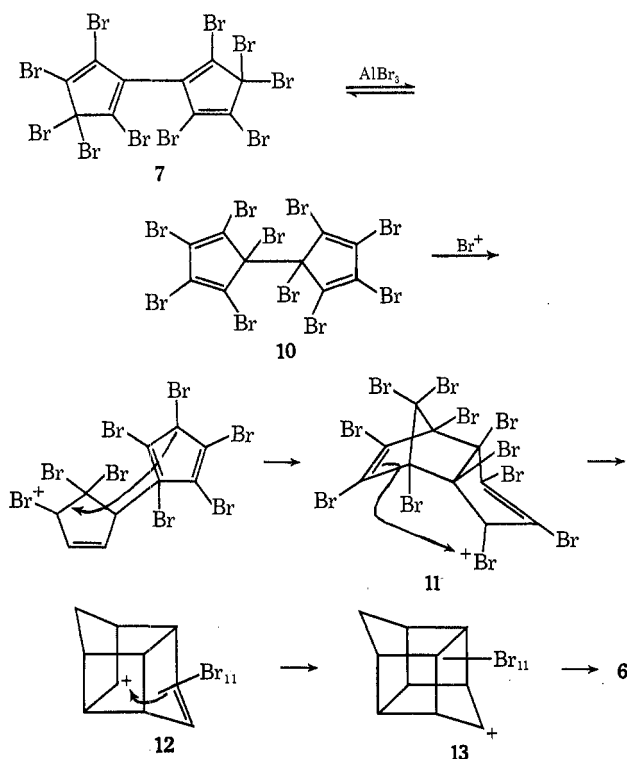
syntheses of **1** have been under conditions where one might expect to obtain the most stable isomer.

Compound **1** reacts in bromine in the presence of aluminum tribromide to give  $C_{10}Br_{12}$  (**6**), mp 340–350° dec, identical with the compound prepared directly from  $C_5Br_6$ .

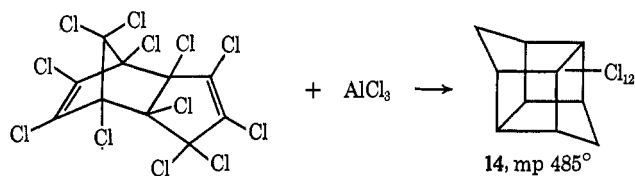
The formation of **1** and its reaction to form **6** may be explained as follows. In the presence of aluminum bromide the pentabromocyclopentadienyl cation (**8**) is undoubtedly formed. Attack on this by a molecule of  $C_5Br_6$  followed by elimination of bromonium ion (assisted by  $AlBr_4^-$  to give  $Br_2$ ) leads either to **9** or a symmetrical structure, **10**, depending on which bromine is



lost. In the presence of aluminum bromide, **9** or **10** may isomerize to the most thermodynamically stable isomer, **7**. The bromines on **7** are free to move from position to position in the presence of aluminum bromide, *i.e.*, all of the possible dicyclopentadienyl structures are in a state of dynamic equilibrium under these conditions. While this equilibrium apparently strongly



favors structure **7**, it is not necessary that a given isomer be present in high concentration for it to be seriously considered as the only one involved in a particular reaction. Thus isomer **10**, though probably present only in very low concentration is used in the proposed mechanism for the formation of **6** because it is the only isomer for which straightforward pathways can easily be envisioned to give **6**.<sup>6</sup> Structure **11** is attractive as an intermediate in the overall reaction both because of the simplicity of the mechanism when it is employed and because of its apparent precedent in the reaction shown below.<sup>7</sup>



### Experimental Section

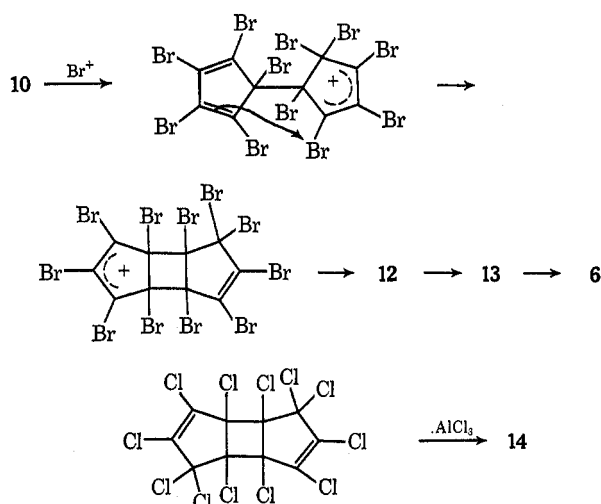
Infrared spectra were obtained with a Beckman IR-9 spectrometer. The mass spectra were obtained on a CEC-21-110B (direct probe) instrument. The isotope peaks observed match the relative abundances calculated for the naturally occurring isotopes.

**Hexabromocyclopentadiene** was prepared both by Straus's method and by a modification of West's procedure,<sup>2</sup> the latter being preferred. Recrystallization from *n*-hexane or methanol yielded yellow crystalline product, mp 86.5–88°, with an infrared spectrum identical with a known pure standard.

**Preparation of  $C_{10}Br_{10}$  (**7**) from Hexabromocyclopentadiene.**—A mixture of 43.2 g (0.08 mol) of  $C_5Br_6$ , 100 ml of absolute ethanol, 50 ml of benzene, and 5 ml of  $H_2O$  was placed in a 500 ml erlenmeyer flask equipped with a magnetic stirring bar, thermometer, and nitrogen purge. The stirred mixture was heated to 45° when it became homogenous. To the solution was added 5.08 g of copper (0.08 g-atom) in the form of copper-bronze (pigment grade) during 5 min; 10 min after addition was complete the copper powder appeared to have reacted. The mixture was stirred at 40–45° for 16 hr and the solvent evaporated under reduced pressure at a bath temperature no higher than 45°. The total residue (48 g) was treated with three 200-ml portions of methylene chloride and the combined solutions extracted with two 100-ml portions of 0.1 *N* sulfuric acid and three 200-ml portions of  $H_2O$ . The organic layer was dried over anhydrous  $MgSO_4$  and the solvent evaporated to give 42 g of crude product.

(6) E. T. McBee, J. D. Idol, and C. W. Roberts, *J. Amer. Chem. Soc.*, **77**, 4375 (1955).

(7) A second attractive mechanistic possibility, pointed out by a referee, and also having precedent in chlorocarbon chemistry is shown below.



(8) F. Straus, L. Kollek, and W. Heyn, *Ber.*, **63B**, 1868 (1930).

Thin layer chromatography (silica–heptane) indicated a mixture of  $C_5Br_8$  and  $C_{10}Br_{10}$ . The 42 g was dissolved in 400 ml of *n*-heptane (400 ml) and run through a silica (Davison 922 grade, 200–325 mesh) gel column. The first fraction gave 5.0 g of recovered  $C_5Br_8$ , while the main fraction gave 27.4 g of  $C_{10}Br_{10}$ , mp 140.5–142°, an 85% yield based on recovered  $C_5Br_8$ : ir (Nujol) 1626, 1579, 1550, 1287, 1183, 1148, 1099, 1000, and 692  $cm^{-1}$ ; uv  $\lambda_{max}^{hexane}$  333 nm (log  $\epsilon$  3.28); mass spectrum showed a molecular ion peak at  $m/e$  910 (calcd for  $C_{10}Br_{10}$ ,  $m/e$  910). The mass spectrum itself is interesting in that it shows only ions resulting from the consecutive loss of bromine all the way from  $C_{10}Br_{10}^+$  to  $C_{10}^+$ ; each of these ions also had a doubly charged partner, which in most cases was the more intense.

*Anal.* Calcd for  $C_{10}Br_{10}$ : C, 13.07; Br, 86.93. Found: C, 13.20; Br, 86.80.

**Isolation of  $C_{10}Br_{10}$  (7) from the Preparation of Dodecabromopentacyclo[5.3.0.0<sup>2,6</sup>.0<sup>3,9</sup>.0<sup>4,8</sup>]decane (6).**—Hexabromocyclopentadiene (473 g, 0.875 mol) was placed in a 3-l., three-necked, round-bottomed flask equipped with a nitrogen inlet, a reflux condenser connected successively to a calcium chloride drying tube and a water scrubber, and a stirrer. Bromine (800 ml) was added and to the resulting solution was added 105 g of aluminum bromide. After refluxing for 45 hr water was added dropwise to destroy the aluminum bromide and the bromine was removed by steam distillation. The dark brown viscous oil remaining after removal of the bromine was treated with hot hexane leaving a dark brown solid. Recrystallization of the solid from THF–hexane gave about 120 g of pure  $C_{10}Br_{12}$ , mp 340–350° dec. The hexane washings proved to be a mixture of  $C_5Br_8$ , another similar compound (later identified as  $C_{10}Br_{10}$ , 7) and an intractable tar. This last component was effectively removed by running the entire solution through a column of silica gel. After three recrystallizations of a sample of this material from 95:5 hexane–benzene a material was obtained having the physical appearance of  $C_5Br_8$  but melting at 111–115°. Mass spectrographic analysis of this material showed that it was a mixture of  $C_5Br_8$  and a second component that was identified as  $C_{10}Br_{10}$ . The  $C_{10}Br_{10}$  was obtained in pure form by removal of the  $C_5Br_8$  by sublimation at 105° and 0.1 mm for 15 hr followed by recrystallization of the residue from 1:1 benzene–hexane. The material thus obtained was homogeneous to mass spectroscopy ( $C_{10}Br_{10}$ ), was shown by ir to be free of  $C_5Br_8$  and melted at 140–142°. Infrared and uv spectra were identical with those of 7 above.

**Preparation of 6 from 7.**—Compound 7 (5 g) was dissolved in bromine (20 ml) and 3 g of aluminum bromide was added. The mixture was stirred under reflux for 72 hr, cooled, water slowly added, and the bromine removed by steam distillation. Filtration of the residue gave a red solid that was added to 50 ml of benzene; after stirring for about 10 min the white solid (5.1 g) was collected by filtration. The solid thus obtained was shown by infrared analysis to be  $C_{10}Br_{12}$  (6), yield 87%, mp 340–350° dec.

**Registry No.**—7, 25568-68-7.

**Acknowledgment.**—The authors are grateful to R. Nyquist for determining infrared spectra, L. Shadoff for the mass spectral data, and L. Swim for elemental analyses.

### Novel "Meisenheimer" Complexes.

#### Alkyl-2,4,6-trinitrocyclohexadienate Anions

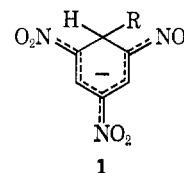
R. P. TAYLOR<sup>1</sup>

*Frick Chemical Laboratory, Princeton University,  
Princeton, New Jersey 08540*

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1,3,5-Trinitrobenzene (TNB) reacts with a variety of anionic bases to yield brightly colored solutions of species known as "Meisenheimer" compounds ( $\sigma$  com-

plexes, 1, where R =  $-OH$ ,  $-OCH_3$ ,  $-CH_2COCH_3$ ,  $-CH_2NO_2$ ,  $-CN$ ).<sup>2–5</sup> Such structures have been postulated as intermediates in nucleophilic aromatic substitution reactions, and, in a few instances, stable adducts have been isolated.<sup>2–5</sup> We report here the preparation, isolation, and initial investigation of salts of new complexes of this type in which alkyl groups are coordinated to the ring (1, R =  $CH_3$  or  $n-C_4H_9$ ).



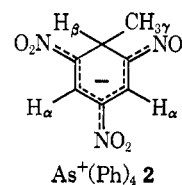
Alkyl-2,4,6-trinitrocyclohexadienate anions (1, R =  $CH_3$  or  $n-C_4H_9$ ) are readily prepared by adding TNB to solutions of the appropriate tetraalkylboron salts (see Experimental Section below). The visible spectra of these compounds are typical of TNB anion complexes (Table I).<sup>3</sup> The positions and intensities of the bands are very similar in a variety of polar and non-polar solvents.

TABLE I  
ABSORPTION MAXIMA FOR ACETONITRILE  
SOLUTIONS OF COMPLEXES OF STRUCTURE 1

R	Cation	$\lambda_1$ , $m\mu$	$\epsilon_1^a$ , l. $mol^{-1} cm^{-1}$	$\lambda_2$ , $m\mu$	$\epsilon_2^a$ , l. $mol^{-1} cm^{-1}$
$CH_3$	$As^+(Ph)_4$	470	31,600	572	14,900
$n-C_4H_9$	$N^+(Me)_4$	474	31,800	568	14,800
$n-C_4H_9$	$As^+(Ph)_4$	474	31,500	568	14,700

<sup>a</sup> Spectra obtained immediately after mixing; estimated errors <5% (see Experimental Section).

#### Nmr Spectra. A. Tetraphenylarsonium Methyl-2,4,6-trinitrocyclohexadienate (2).



of an acetonitrile- $d_3$  solution of the compound obtained from the reaction of tetraphenylarsonium tetramethylboride and TNB is consistent with structure 2 (see Table II).<sup>6</sup> The resonance frequencies and splitting

TABLE II  
NMR CHEMICALS SHIFTS ( $-\delta$ ) AND COUPLING CONSTANTS (cps)  
FOR COMPOUNDS 2<sup>a</sup> AND 3<sup>a</sup>

Compd	$H_\alpha$	$H_\beta$	$H_\gamma$	$J_{H_\alpha-H_\beta}$	$J_{H_\beta-H_\gamma}$	Cation protons
2	8.24	4.64	1.14	$0.75 \pm 0.05$	$6.2 \pm 0.1$	7.75 <sup>b</sup>
3	8.39	4.84	...	$0.75 \pm 0.05$	$4.2 \pm 0.1$	3.08 <sup>b</sup>

<sup>a</sup> Salts are  $\sim 0.1 M$  in acetonitrile- $d_3$ . A small impurity peak which was shown to be water was detected at 2.1 ppm. <sup>b</sup> Multiplet. <sup>c</sup> Butyl protons appear as a broad multiplet extending from  $\sim 0.8$  to 1.9 ppm.

- (1) National Science Foundation Predoctoral Fellow, 1969–1970.
- (2) M. R. Crampton, *Advan. Phys. Org. Chem.*, **7**, 211 (1969).
- (3) E. Bunce, A. R. Norris, and K. E. Russell, *Quart. Rev. Chem. Soc.*, **22**, 123 (1968).
- (4) R. Foster and C. A. Fyfe, *Rev. Pure Appl. Chem.*, **16**, 61 (1966).
- (5) C. A. Fyfe, *Can. J. Chem.*, **46**, 3047 (1968).
- (6) Integrated intensities of the resonance absorptions agree with the proposed peak assignments.