

1,3,3-Trimethyl-4-vinylcyclopentene 1,2-Oxide (2).—To a cold stirred solution of 4 g (0.029 mol) of the diene from above there was added in a dropwise manner 55.2 ml of a solution of monopero-phthalic acid in ether (0.029 mol). After an additional 3 hr of reaction at room temperature the mixture was worked up in the usual way⁸ to yield 3.2 g of oxide 2 which eluted as a single substance on Carbowax 20M and Apiezon L glpc columns: n^{25}_D 1.4502; ir (neat) 3050, 1635, 998, 910, and 838 cm^{-1} ; nmr (CCl_4) δ 0.72 (s, 3), 0.99 (s, 3), 1.35 (s, 3), 1.80 (m, 3), 2.71 (s, 1), 4.73 (m, 1), 4.97 (m, 1), 5.41 (m, 1).

Anal. Calcd for $\text{C}_{10}\text{H}_{16}\text{O}$: C, 78.89; H, 10.60. Found: C, 79.12; H, 10.55.

Reaction of Epoxide 2 with Stannic Chloride.—Stannic chloride (0.20 ml) was added to a solution of 2 (1.0 g, 0.0065 mol) in 25 ml of benzene and the mixture stirred for 10 hr at room temperature. The reddish reaction mixture was then poured into ice water, shaken vigorously, and extracted with ether. Removal of the solvent after drying over sodium sulfate afforded 0.8 g of material which showed only a single glpc peak on Apiezon L and Carbowax 20M columns. Purification by preparative glpc yielded 6: n^{25}_D 1.4522; ir (CCl_4) 3050, 1730, 1683, and 920 cm^{-1} ; nmr (CCl_4) δ 0.83 (s, 3), 0.98 (s, 3), 1.12 (d, 3, $J = 7$ Hz), 2.22 (m, 4), 4.88 (m, 1), 5.11 (m, 1), 5.58 (m, 1).

Anal. Calcd for $\text{C}_{10}\text{H}_{16}\text{O}$: C, 78.89; H, 10.60. Found: C, 78.93; H, 10.56.

2,3,3-Trimethyl-4-allylcyclopentene.— α -Campholenealdehyde (10.0 g, 0.065 mol) in 50 ml of ether was added rapidly to 225 ml of a solution of methylene triphenylphosphorane (prepared from 16.6 g, 0.049 mol of triphenylmethyl phosphonium bromide and 35 ml, approx 0.05 mol, of *n*-butyllithium) maintained at 0–5°. After 10 min 150 ml of water was added to the creamy suspension. Removal of the solvent after extraction of the aqueous layer with ether and drying afforded 8.6 g of crude product. Distillation through an 18-in. spinning-band column yielded 3.6 g (36%) of pure diene: bp 68–71 (21 mm); n^{25}_D 1.4581; ir (neat) 3050, 3000, 1640, 1355, 911, and 800 cm^{-1} ; nmr (CCl_4) δ 0.77 (s, 3), 0.97 (s, 3), 1.57 (m, 3), 4.88 (m, 1), 5.00 (m, 1), 5.12 (m, 2), 5.52 (m, 1).

Anal. Calcd for $\text{C}_{11}\text{H}_{18}$: C, 87.92; H, 12.07. Found: C, 87.99; H, 12.16.

2,2,2-Trimethyl-4-allylcyclopentene 1,2-Oxide (3).—The epoxidation of the allylcyclopentene from above was carried out as described for 2 to yield 3 (97%): n^{25}_D 1.4556; ir (neat) 3050, 1635, 1358, 910, and 846 cm^{-1} ; nmr (CCl_4) δ 0.72 (s, 3), 0.95 (s, 3), 1.22 (s, 3), 3.02 (m, 1), 4.73 (m, 1), 4.96 (m, 1), 5.42 (m, 1).

Anal. Calcd for $\text{C}_{11}\text{H}_{18}\text{O}$: C, 79.46; H, 10.91. Found: C, 79.73; H, 11.01.

Reaction of 3 with Stannic Chloride.—Treatment of 3 (1.0 g) with stannic chloride in benzene in the manner described above for 2 afforded 0.95 g of dark oil. Analytical glpc on Apiezon L at 160° showed two major components and one minor one with retention times of 8.5, 11.0, and 9.5 min, and in the proportions 54%, 42%, and 4% respectively. The minor component could not be isolated.

Preparative glpc on Apiezon L afforded the 54% component, 2,3,3-trimethyl-4-allylcyclopentanone, 8, as an oil: n^{25}_D 1.4651; ir (CCl_4) 3080, 1740, 1638, and 920 cm^{-1} ; nmr (CCl_4) δ 0.70 (s, 3), 0.95 (s, 3), 0.96 (d, 3), 4.87 (m, 1), 5.10 (m, 1), 5.65 (m, 1).

Anal. Calcd for $\text{C}_{11}\text{H}_{18}\text{O}$: C, 79.46; H, 10.91. Found: C, 79.29; H, 10.85.

Isolation of the 42% component by preparative glpc afforded 2,3,3-trimethyl-1-allylcyclopenten-4-ol, 7: n^{25}_D 1.4816; ir (CCl_4) 3600, 3050, 1630, 1057, 992, and 915 cm^{-1} ; nmr (CCl_4) δ 0.90 (s, 3), 0.96 (s, 3), 1.52 (m, 3), 3.72 (m, 1), 4.78 (m, 1), 4.97 (m, 1), 5.50 (m, 1).

Anal. Calcd for $\text{C}_{11}\text{H}_{18}\text{O}$: C, 79.46; H, 10.91. Found: C, 79.63; H, 10.69.

1,3,3-Trimethyl-4-allylcyclopentene.—Application of the previously described procedure for addition of methylene triphenylphosphorane to campholenealdehyde to 5 afforded the title compound: bp 60–61° (17 mm); n^{25}_D 1.4521; ir (neat) 3050, 1635, 1645, 995, 911, and 825 cm^{-1} ; nmr (CCl_4) 0.80 (s, 3), 1.0 (s, 3), 1.62 (m, 3), 4.78 (m, 1), 5.02 (m, 1), 5.45 (m, 1).

Anal. Calcd for $\text{C}_{11}\text{H}_{18}$: C, 87.92; H, 12.07. Found: C, 87.94; H, 12.11.

1,3,3-Trimethyl-4-allylcyclopentene 1,2-Oxide (4).—Epoxidation of the diene from above by the previously described procedure⁸ afforded 4, purified by preparative glpc: n^{25}_D 1.4500; ir (neat) 3030, 1635, 1359, 996, 913, and 840 cm^{-1} ; nmr (CCl_4)

δ 0.72 (s, 3), 0.98 (s, 3), 1.30 (s, 3), 4.72 (m, 1), 4.97 (m, 1), 5.42 (m, 1).

Anal. Calcd for $\text{C}_{11}\text{H}_{18}\text{O}$: C, 79.46; H, 10.91. Found: C, 79.43; H, 11.01.

Reaction of 6 with Stannic Chloride.—Treatment of 4 (0.5 g) with stannic chloride in benzene by the previously described procedure afforded 0.45 g of 9. The material was purified by preparative glpc on Apiezon L at 160°: n^{25}_D 1.4536; ir (CCl_4) 3050, 1725, 1635, 1242, 920, and 865 cm^{-1} ; nmr (CCl_4) δ 0.80 (s, 3), 0.96 (s, 3), 1.06 (d, 3, $J = 7$ Hz), 4.87 (m, 1), 5.10 (m, 1), 5.60 (m, 1).

Anal. Calcd for $\text{C}_{11}\text{H}_{18}\text{O}$: C, 79.46; H, 10.91. Found: C, 79.35; H, 10.68.

Registry No.—1,3,3-Trimethyl-4-(2'-hydroxyethyl)-cyclopentene, 4605-50-9; 1,3,3-trimethyl-4-(2'-acetoxyethyl)cyclopentene, 25527-89-3; 1,3,3-trimethyl-4-vinylcyclopentene, 25527-90-6; 2, 25515-35-9; 3, 25515-36-0; 4, 25515-37-1; 1,3,3-trimethyl-4-allylcyclopentene, 25527-91-7; 6, 25527-92-8; 2,3,3-trimethyl-4-allylcyclopentene, 25527-93-9; 7, 25527-94-0; 8, 25527-95-1; 9, 25527-96-2.

Reduction of Cyclic Anhydrides with NaBH_4 . Versatile Lactone Synthesis

DENIS M. BAILEY AND ROBERT E. JOHNSON

*Sterling-Winthrop Research Institute,
Rensselaer, New York 12144*

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Over 20 years ago Chaikin and Brown¹ reported that, with NaBH_4 , acid anhydrides show only slight reduction on prolonged heating. Since then, only two isolated examples of the NaBH_4 reduction of cyclic anhydrides have appeared in the literature.^{2,3} More recently, the NaBH_4 reduction of mixed carboxylic-carbonic anhydrides⁴ and thiophthalic anhydride⁵ have been recorded. We have examined the reduction of a number of cyclic anhydrides with this reagent and have found that δ and γ lactones can be isolated in good to excellent yields (51–97%). This procedure is more convenient and more versatile than the previously reported methods using LiAlH_4 ⁶ or $\text{LiAlH}(\text{O}-t\text{-Bu})_3$.^{6a} The steric course of the NaBH_4 reduction of 5-membered unsymmetrical cyclic anhydrides is identical with that observed with LiAlH_4 ^{6a} or $\text{Na}-\text{EtOH}$.⁷ In most instances hydride attack takes place principally at the carbonyl group adjacent to the more highly substituted carbon atom. Thus, the reduction of *cis*-1-methylcyclohexane-1,2-dicarboxylic acid anhydride (I) to

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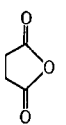

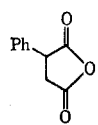
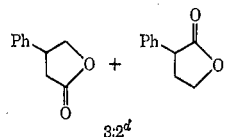

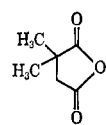
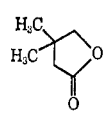
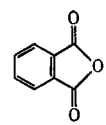
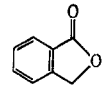
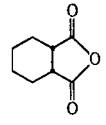
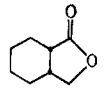
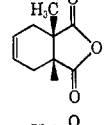
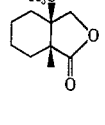
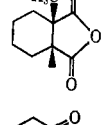
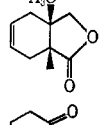


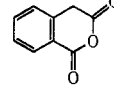
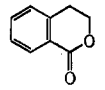
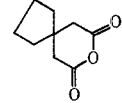
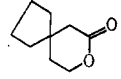
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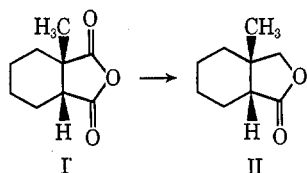
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TABLE I
 LACTONES PRODUCED FROM THE NaBH₄ REDUCTION OF CYCLIC ANHYDRIDES

Starting anhydride	Registry no.	Product ^a	Method ^b	% yield	Mp or bp (mm), °C	Lit. mp or bp (mm), °C
	108-30-5		B-2	51	184-194 (760)	202-203 (760) ^c
	1181-15-3	 +  3:2 ^d	A-1	67	171-173 (13)	113-122 (0.1) ^e
	17347-61-4		A-2	74	79-82 (13)	207-208 (760) ^c
	85-44-9		B-1	97	71-73	72-73 ^f
	13149-00-3		A-1	76	123-125 (13)	72-77 (0.5) ^e
	25357-31-7		A-1	65	127-131 (13)	68-72 (0.1) ^e
	14679-27-7		A-1	80	120-123 (13)	51-61 (0.07) ^e
	108-55-4		A-2	67	110-113 (13)	102-104 (7) ^g
	703-59-3		A-2	55	177-178 (13)	176 (20) ^h
	5662-95-3		A-2	68	138-147 (13)	<i>i</i>

^a Ir and nmr spectra were consistent with the structures assigned. ^b See Experimental Section. ^c A. Windaus and F. Klanhart, *Ber.*, **54** [B], 58 (1921). ^d The 3:2 ratio of lactones was identical with that found by Bloomfield and Lee⁶ in their LiAlH₄ reduction experiments. ^e Reference 6. ^f J. H. Gardner and C. A. Naylor Jr., *Org. Syn.*, **16**, 71 (1936). ^g S. F. Friess, *J. Amer. Chem. Soc.*, **71**, 2571 (1949). ^h J. Colonge and P. Boisse, *C. R. Acad. Sci.*, **239**, 1047 (1954). ⁱ No mp recorded: N. A. Klitgaard, *Dan. Tidsskr. Farm.*, **42**, 84 (1968); *Chem. Abstr.*, **71**, 3021j (1969).

lactone II was accomplished with either NaBH₄, LiAlH₄,^{6a} NaBH(OMe)₃, or Na-EtOH.⁷



In only one case was exclusive reduction at the carbonyl adjacent to the less sterically crowded carbon atom of a 5-membered cyclic anhydride observed. This exception was the report by Vaughan, *et al.*,³ that

camphoric anhydride was reduced to α -campholide by NaBH₄. We repeated this work, and nmr analysis of the reduction product confirmed the structure assignment. The results of our NaBH₄ reduction experiments are compiled in Table I. Yields are of distilled product.

Experimental Section

General Procedures for the NaBH₄ Reduction of Cyclic Anhydrides to Lactones.—Unless otherwise stated in Table I, all lactones were shown to be one pure isomer by glpc using a Hewlett-Packard research chromatograph, Model 5751B, equipped with glass columns packed with 3% OV 17 on 100-120 mesh Gas-Chrom Q.

A mixture of 2.0 g (0.05 mol) of 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 Et_2O . The Et_2O extract was dried (Na_2SO_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 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 γ -lactone (II).

Reduction of *cis*-1-Methylcyclohexane-1,2-dicarboxylic Acid Anhydride with Na and EtOH.—The procedure reported by Linstead and Millidge⁷ was used. The yield of II was 35%.

Registry No.— NaBH_4 , 16940-66-2.

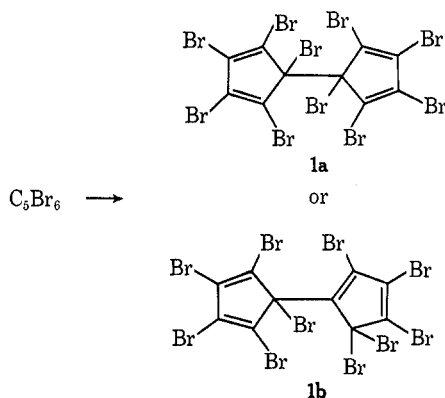
Decabromo-3,3'-dihydrofulvalene

S. D. MCGREGOR AND C. W. ROBERTS¹

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

Received December 29, 1969

West and Kwitowski² recently reported the isolation of $\text{C}_{10}\text{Br}_{10}$ (1), mp 139–140°, from the reactions of hexabromocyclopentadiene (C_5Br_6) with copper(I) bromide or various metals. Possible structures for this dihydrodecabromofulvalene were noted as 1a or 1b.



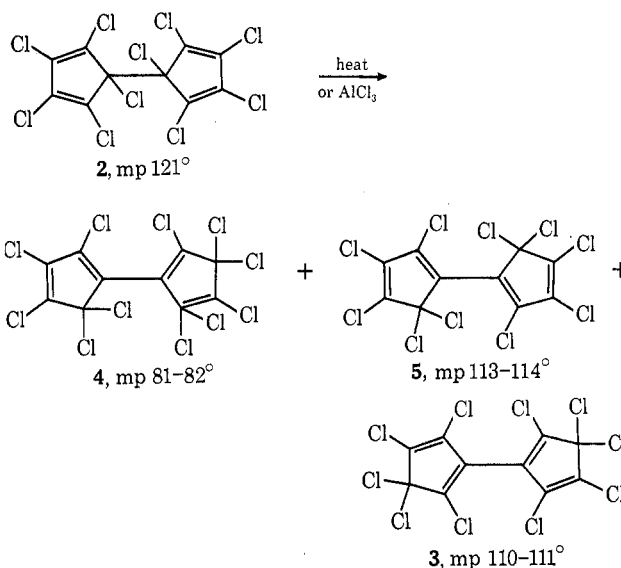
In a more recent report Smith and West³ describe the isomerization of the chlorine compound $\text{C}_{10}\text{Cl}_{10}$, mp 121° (2), to three new isomers which were assigned the structures 3, 4, and 5 by nqr analysis.

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.

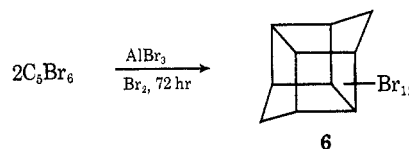
(1) To whom inquiries should be addressed.

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

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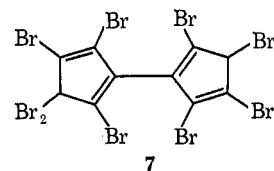


The reaction of C_5Br_6 with metallic copper in 95% ethanol at 45° results in a mixture of $\text{C}_{10}\text{Br}_{10}$ and C_5Br_6 separable on a silica column to give an 85% yield of $\text{C}_{10}\text{Br}_{10}$ (1), mp 140.5–142°. In a preparation of $\text{C}_{10}\text{Br}_{12}$ (6), mp 340–350° dec, from C_5Br_6 ⁴ the reaction



was stopped at the end of 45 hr. The "recovered" C_5Br_6 possessed a melting point range of 111–115° and was separable into C_5Br_6 and pure $\text{C}_{10}\text{Br}_{10}$ (1). This eutectic "recovered C_5Br_6 " appears to be the same as West's 1:1 complex of C_5Br_6 and $\text{C}_{10}\text{Br}_{10}$, mp 108–109°.²

Compound 1 has three bands in the carbon-carbon double bond region in the infrared (1626, 1579, 1550 cm^{-1}). Examination of the ir spectra of the various $\text{C}_{10}\text{Cl}_{10}$ isomers⁵ 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).