was evaporated and the residue crystallized from ether: 380 mg (79%); mp 239–241°. The identity of this material with that prepared by the nitrous acid procedure was shown by mixture melting point and ultraviolet, infrared, and pmr spectral comparisons.

Anal. Found: C, 64.29; H, 6.55.

Registry No.—1, 13509-81-4; 2, 13509-82-5; 3, 13509-83-6; nitrous acid, 7782-77-6.

Acknowledgment.—Spectral and rotational data were furnished by Mr. W. Fulmor and his associates. Microanalyses were determined by Mr. L. Brancone and his group and partition chromatography was carried out by Mr. C. Pidacks and his staff.

Synthesis and Proof of Structure of Benzodiiodoxole[1a–c]

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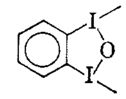
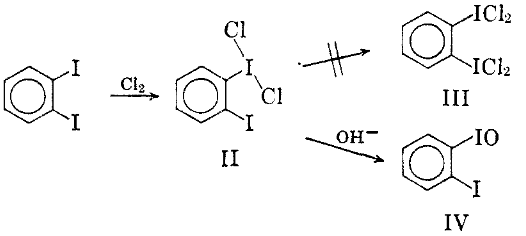
The synthesis, in our laboratories[2] and in others,[3] of a number of ring systems containing iodine as a heteroatom has been extended to the synthesis of a ring containing more than one annular iodine atom. We wish to report here the synthesis and proof of the structure of compounds containing the 1,3,2-benzodiiodoxole (I) ring as an example of such a system.



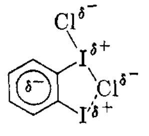
I

In a first attempt, we proceeded to oxidize 1,2-diiodobenzene with chlorine, obtaining 1-iodosodichloro-2-iodobenzene (II) as the sole product (eq 1). This compound has not been prepared previously and is the first polyvalent iodine compound synthesized that is derived from 1,2-diiodobenzene.[4,5] 1-Iodosodichloro-2-iodobenzene is resistant, under the conditions used, to further chlorine addition on the second iodine atom, thus failing to give the desired 1,2-bis(iodosodichloro)benzene (III).

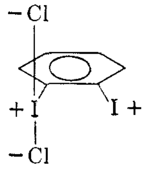


(1)

This is unexpected, since both 1,3-diodobenzene and 1,4-diodobenzene can be readily chlorinated to the corresponding bis(iodosodichloro)benzene derivatives.[6,7] The failure to obtain III indicates that the presence of an iodosodichloro function *ortho* to an iodine atom prevents the addition of a second chlorine molecule. The structure of the iodosodichloro group, as shown by X-ray crystallography,[8] is such that the two chlorine atoms are above and below the plane of the ring, thus precluding steric hindrance to chlorine addition. The easy addition of chlorine to both iodine atoms in *p*-diiodobenzene suggests that the resistance of II to chlorination is not due to a simple electron-withdrawing effect. Thus, if an iodosodichloro group would decrease the electron density on the second iodine to such an extent that chlorine addition would be hindered, it should be similarly operative both for the *ortho* and *para* positions. However, if this effect involved only nonbonding electrons of iodine and chlorine that cannot overlap with the π electrons of the benzene rings, then hindrance would only occur in the *ortho* and not the *para* positions (*i.e.*, A). Another possible explanation is the unfavorable dipole situation, which could also hinder chlorine addition to the second iodine atom (*i.e.*, B). Such a decrease in electron density at the second iodine would prevent an electrophilic chlorine (Cl$^+$) addition. It is of interest that Keefer and Andrews observed similar *ortho* effects on the reaction of the iodosodichloro function[9] and that Maciel[10] has interpreted the ^{19}F nmr spectra of the *m*- and *p*-fluoroiodobenzene dichlorides as indicating a negligible resonance interaction of the –ICl$_2$ function with the benzene ring.[11] Thus, all available evidence strongly favors a field effect (*e.g.*, B).



A



B

1-Iodosodichloro-2-iodobenzene (II) could be readily hydrolyzed to 2-iodoso-2-iodobenzene (IV) and again this compound revealed itself unable to accept a further chlorine atom on the second iodine. The absence of data concerning chlorination (on iodine) of other iodosobenzenes does not allow us to interpret these results at this moment. The only Hammett σ values

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[1] (a) Publication No. 6 of the series Chemistry and Biochemistry of Polyvalent Iodine Compounds. Publication No. 5, *J. Pharm. Sci.*, **55**, 68 (1966). (b) I wish to acknowledge helpful discussion of this work with Drs. Harold Zaugg and L. J. Andrews. (c) This work was supported inp art by NSF-URP Grant GE-6377 and in part by Grant GM-10721 of the National Institutes of Health. (d) National Science Foundation Undergraduate Research Participant, 1964–1965.

[2] (a) W. Wolf and L. Steinberg, *Chem. Commun.*, 449 (1965); (b) E. Shefter and W. Wolf, *J. Pharm. Sci.*, **54**, 104 (1965); (c) W. Wolf and L. L. J. Hsu, Abstracts of Papers 54C, 146th National Meeting of the American Chemical Society, Denver, Colo., Jan 1964.

[3] (a) G. F. Baker, *et al.*, *J. Chem. Soc.*, 3721 (1965); (b) W. C. Agosta, *Tetrahedron Letters*, (31) 3681 (1965).

[4] C. Willgerodt, "Die Organischen Verbindungen mit Mehrwertigem Jod," F. Encke, Stuttgart, 1914, p 265.

[5] (a) F. M. Beringer and R. M. Grindler, *Iodine Abstr. Rev.*, **3**, 15 (1956); (b) after this work was completed, we became aware that J. Böeseken and Ch. Schneider (*Koninkl. Ned. Akad. Wetenschap. Proc. Ser. B*, **35**, 1140 (1932)) had synthesized a compound, by peracetic acid oxidation of 1,2-diiodobenzene, to which they attributed structure V. No experimental details or properties of the compound were described.

[6] C. Willgerodt and A. Desaga, *Ber.*, **37**, 1301 (1904).

[7] C. Willgerodt, *ibid.*, **27**, 590 (1894).

[8] E. Archer, *Acta Cryst.*, **6**, 88 (1953).

[9] R. M. Keefer and L. J. Andrews, *J. Am. Chem. Soc.*, **81**, 2374 5329 (1959).

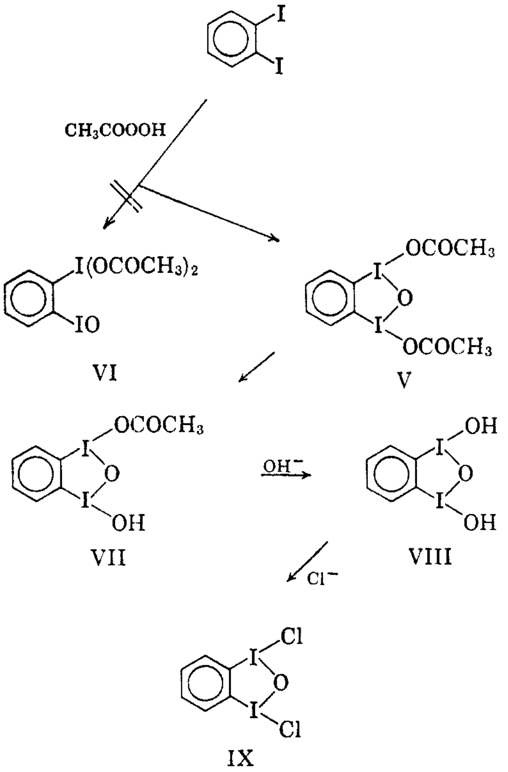
[10] G. E. Maciel, *ibid.*, **86**, 1269 (1964).

[11] Since this paper was written, a proton nmr study of iodonium salts has been reported; F. M. Beringer and J. Galton, *J. Org. Chem.*, **31**, 1648 (1966). These authors suggest a strong resonance interaction between iodonium function and the benzene rings. It is of interest to note this apparent difference between the effects of the two types of trivalent iodine.

that have been estimated so far are for the iodosodichloro function[10] and they suggest a very strong inductive effect of electron withdrawal. No such data have been measured for the iodoso function itself.

Direct oxidation of 1,2-diodobenzene with peracetic acid, according to the method of Sharefkin,[12] gave a compound $C_{10}H_{10}I_2O_5$ in 26% yield. Iodometric titration indicated an equivalent weight of 115.2, corresponding to a molecular weight of 460.8 for a compound with two polyvalent iodine functions. Two structures are possible for this product: 1,3-diacetoxy-1,3-dihydro-1,3,2-benzodiiodoxole (V) or its isomer, 1-(iodosodiacetate)-2-iodosobenzene (VI) (Scheme I). The method of synthesis used makes the latter, unsymmetrical structure most unlikely. Infrared absorption in the NaCl region shows a carbonyl band at 1632 cm^{-1}. This low carbonyl absorption strongly suggests that a considerable interaction occurs between the carbonyl and the polyvalent iodine functions. Such effects had been noted previously[2a,2c,3a,13,14] and appear in good agreement with the field effect suggested for 1-iodosodichloro-2-iodobenzene (II).

SCHEME I



Studies in the far-infrared, where characteristic iodine bands normally occur, show a very complex pattern in the 225–500 cm^{-1} region. The bands appearing in this region have not yet been definitively assigned, but their presence appears to be associated with compounds of polyvalent iodine; they are absent in compounds of monovalent iodine.

In order to decide if this compound had the symmetrical structure V or the unsymmetrical structure VI, we studied the nmr spectra of these compounds to decide these alternatives. The results show characteristic A_2B_2 patterns,[15] also called AA'BB' patterns.[16] In the spectra obtained, only 12 lines were observed, which presumably correspond to the unresolved 24 lines characteristic of spectra of disubstituted benzene derivatives. The chemical shifts are 8.00 and 7.64 ppm, as compared with 6.92 and 7.83 ppm for 1,2-diiodobenzene.[15] The upfield shifts correspond to the protons in positions 4 and 5, whereas the downfield shifts correspond to the proton in positions 3 and 6. Their coupling constants are listed in Table I. These results conclusively prove that the compound obtained by peracetic oxidation of 1,2-diiodobenzene is indeed the benzodiiodoxole derivative (V).

TABLE I

NMR STUDIES OF COMPOUNDS VII AND IX

	ν_A, ppm	ν_B, ppm	J	J'	J_A	J_B
1,2-Diiodobenzene (12 lines)	6.92	7.83	7.9	1.5	0.3	7.3
VII	7.64	8.00	9.66	0.34	0	3.61[a]
IX	7.63	7.85	9.19	0.41	0	3.88[a]

[a] Based on an assumed $J_A = 0$.

When the diacetoxy compound, after recrystallization from 4 N acetic acid, was washed with water, we obtained another compound that analyzes for the 1-acetoxy-3-hydroxy-1,3-dihydro-1,3,2-benzodiiodoxole (VII). This compound shows a carbonyl band at 1607 cm^{-1} and characteristic far-infrared bands. Hydrolysis of either compound VI or VII, by dilute sodium hydroxide, at room temperature, leads to a clear, slightly yellow solution. This solution presumably contains the 1,3-dihydroxy compound VIII, which has not yet been isolated. Addition of hydrochloric acid gave a light yellow precipitate, which had the composition of 1,3-dichloro-1,3-dihydro-1,3,2-benzodiiodoxole (IX). It shows no carbonyl absorption band and its nmr shows again a similar A_2B_2 pattern, comparable to that of the diacetoxy compound. Only a small chemical shift was observed for the 3,6 protons compared to 1,2-diodobenzene, 7.85 ppm as compared to 7.83 ppm, but a noticeable shift was observed for the 4,5 protons, 7.63 ppm as compared to 6.92 ppm. The coupling constants of the aromatic protons are very similar to those of the diacetoxy compounds V (Table I).

Experimental Section

The nmr spectra were taken on Varian A-60 instruments; we wish to thank Dr. F. J. Petracek and Mr. R. K. Crossland for their assistance in taking them. The infrared measurements were recorded on a Perkin-Elmer Infracord, a Perkin-Elmer 221, and a Beckman IR 7, in the NaCl and CsI regions.

1-Iodosodichloro-2-iodobenzene (II).—Dry chlorine gas was passed, with stirring, through a solution of 0.4 ml of *o*-diiodobenzene in 30 ml of chloroform at room temperature. Precipitation of yellow needlelike crystals began after about 4 min and the reaction was continued for 15 min. The crystals were filtered and washed with chloroform and dried to give 0.58 g (70% yield), mp 112–113°. The product is insoluble in cold water, base, acetic acid, and chloroform.

Anal. Calcd for $C_6H_4Cl_2I_2$: C, 17.95; H, 0.99; mol wt (iodometric), 401. Found: C, 18.00; H, 1.05; mol wt, 412.

1-Iodoso-2-iodobenzene (IV).—1-Iodosodichloro-2-iodobenzene (2.03 g) was stirred into 70 ml of 0.1 N sodium hydroxide for 3 days at room temperature. The pH was adjusted to approxi-

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[12] J. G. Sharefkin and H. Saltzman, *Anal. Chem.*, **35**, 1428 (1963).

[13] J. E. Leffler, R. D. Faulkner, and C. C. Petropoulos, *J. Am. Chem. Soc.*, **80**, 5435 (1958).

[14] R. Bell and K. J. Morgan, *ibid.*, 1209 (1960).

[15] J. Martin and B. P. Dailey, *J. Chem. Phys.*, **37**, 2594 (1962).

[16] R. Whitman, *J. Mol. Spectry.*, **10**, 250 (1963); *J. Chem. Phys.*, **36**, 2085 (1962).

mately 8 by $NaHCO_3$ addition. The insoluble product was washed with water, ether, and absolute alcohol and dried to give 1.4 g (81% yield), mp 187° dec.

Anal. Calcd for $C_6H_4I_2O$: C, 20.83; H, 1.17; mol wt (iodometric), 346. Found: C, 20.94; H, 1.25; mol wt, 352.

1,3-Diacetoxy-1,3-dihydro-1,3,2-benzodiiodoxole (V).—*o*-Diiodobenzene (1 ml, 2.5 g) was dissolved in 5 ml of glacial acetic acid, warmed to 30°, and treated with 5 ml of 40% peracetic acid, dropwise and with good stirring. After all the peracetic acid had been added, the mixture was stirred for another 20 min; 100 ml of water was then added to yield a thick white crystalline precipitate. The precipitate was filtered and washed with ether, recrystallized from 4 *N* acetic acid, and dried to yield a fine, glass woollike product (0.9 g, 0.26%), mp 226–229°.

Anal. Calcd for $C_{10}H_{10}I_2O_5$: C, 25.86; H, 2.16; mol wt, 464. Found: C, 25.21, 25.25; H, 2.39, 1.98; mol wt (iodometric), 460.8.

1-Acetoxy-3-hydroxy-1,3-dihydro-1,3,2-benzodiiodoxole (VII).—1,3-Diacetoxy-1,3-dihydro-1,3,2-benzodiiodoxole (1 g) was triturated with distilled water to yield a fine yellow granular powder, washed with water, and dried to give 0.9 g, mp 214°.

Anal. Calcd for $C_8H_8I_2O_4$: C, 22.74; H, 1.89; mol wt, 422. Found: C, 23.20; H, 1.88; mol wt, 418.5.

1,3-Dichloro-1,3-dihydro-1,3,2-benzodiiodoxole (IX).—1-Acetoxy-3-hydroxy-1,3-dihydro-1,3,2-benzodiiodoxole (1 g) was suspended in 300 cc of 1 *N* NaOH and stirred until all the yellow powder was completely dissolved. The mixture was stirred for several hours and showed a clear yellow-green color. Slow addition of concentrated HCl resulted in the precipitation of a fluocculent light yellow powder. The product was recrystallized from dilute base: yield, 0.8 g (80%); mp 167–170°.

Anal. Calcd for $C_6H_4Cl_2I_2O$: C, 17.26; H, 0.96; I, 60.9; Cl, 17.39; O, 3.89; mol wt, 417. Found: C, 17.81, 17.73; H, 1.00, 1.10; I, 60.2; Cl, 17.02, 16.52; O, 4.76; mol wt, (iodometric) 415.6.

Registry No.—II, 13509-76-7; IV, 13509-77-8; V, 13509-78-9; VII, 13509-79-0; IX, 13509-80-3.

Azetidines. I. The Wittig Rearrangement of a 1-Benzylazetidine[1,2]

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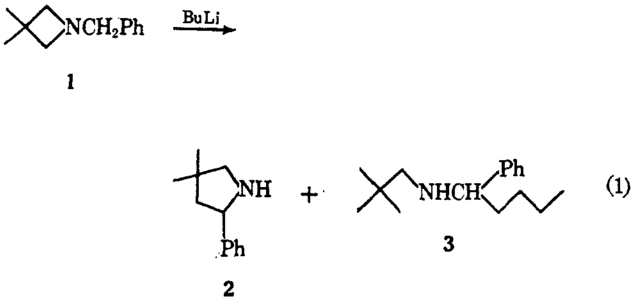
Received April 27, 1967

In the course of an investigation of the butyllithium-induced rearrangement of 1,1-dibenzyl-3,3-dimethylazetidinium bromide,[3] it was found that appreciable amounts of 1-benzyl-3,3-dimethylazetidine (1) and *n*-pentylbenzene were formed (in addition to rearrangement products) in a nearly equimolar ratio. The yield of 1 was 13% when the reaction was carried out at −2°. When the reaction temperature was 36°, however, the yield of 1 was only 0.7% and three new amines were formed in yields of 4.3, 5.6, and 0.4%. Further examination of this latter aspect of the reaction revealed what is believed to be the first example of a 1,2-rearrangement of a tertiary benzylamine to a secondary amine.

Treatment of an ethereal solution of 1 with a 3 *M* excess of butyllithium at reflux temperature afforded 4,4-dimethyl-2-phenylpyrrolidine (2) (*ca.* 19%) and N-(2′,2′-dimethylpropyl)-1-phenylpentylamine (3) (*ca.* 17% (eq 1). The remaining material was the starting



1 2 3

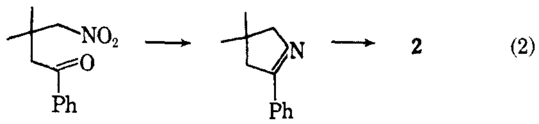
compound (1) and a small quantity (*ca.* 2%) of higher boiling amines.[4] The temporal course of the reaction was followed by the vapor phase chromatographic analysis of aliquots at intervals (Table I). It was noted that the reaction slowed down markedly after a few hours and had essentially stopped after 24 hr even though about 65% of the starting material could still be recovered.

TABLE I

DATA ON REACTION OF 1 WITH BUTYLLITHIUM IN ETHER

Time, hr	Product compn, mole % 1	2	3
0.5	92.1	2.2	5.7
2.5	77.0	8.6	14.4
3.5	73.9	10.1	16.0
10.5	66.3	17.9	15.8
24	64.7	18.6	16.7

The structure of 2 was established by its absorption spectra (infrared and nmr) and analysis and confirmed by comparison with the product from the lithium aluminum hydride reduction of 4,4-dimethyl-2-phenyl-1-pyrroline (5) which was in turn prepared by reduction and cyclization of the known[5] 3,3-dimethyl-4-nitrobutyrophenone (4) (eq 2). The structure of the ring-opened product (3) was revealed by the nmr spectrum and by comparison of this with that of a model compound, N-methyl-1-phenylpentylamine, readily prepared by the reaction of benzylidenemethylamine and butyllithium.



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These results are remarkable in two respects. First, although the Wittig rearrangement[6] has been studied extensively,[7,8] the reaction has heretofore been observed only with ethers (with which good results are obtained

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[1] From the Ph.D. Thesis of Max T. Wills, University of Washington.

[2] Supported in part by State of Washington Initiative 171 Funds for Research in Biology and Medicine. Preliminary report: A. G. Anderson and M. T. Wills, *Angew. Chem.*, **79**, 574 (1967); *Angew. Chem. Intern. Ed. Engl.*, **6**, 557 (1967).

[3] Further results from the study of this and other reactions of strong bases on quaternary azetidinium salts will be reported in succeeding publications in this series.

[4] An attempt to effect this reaction with the weaker base phenyllithium gave only recovered starting material.

[5] L. I. Smith and V. A. Engelhardt, *J. Am. Chem. Soc.*, **71**, 2671 (1949).

[6] G. Wittig and L. Löhmann, *Ann.*, **550**, 260 (1942).

[7] For leading references, see (a) H. E. Zimmerman, "Molecular Rearrangements," P. de Mayo, Ed., Interscience Publishers, Inc., New York, N. Y., 1963, pp 372–377; (b) D. J. Cram, "Fundamentals of Carbanion Chemistry," Academic Press Inc., New York, N. Y., 1965, pp 165, 230–233.

[8] For more recent studies of the Wittig rearrangement with particular reference to the mechanism, see (a) P. T. Lansbury, V. A. Pattison, J. D. Sidler, and J. B. Bieber, *J. Am. Chem. Soc.*, **88**, 78 (1966); (b) U. Schöllkopf and H. Schäfer, *Ann.*, **663**, 22 (1963); (c) Y. Makisumi and S. Notzumoto, *Tetrahedron Letters*, No. 51, 6393 (1966).