over. This latter process reduced the disulfide formed during the oxidation stage. The haloarylthiol was extracted from the steam distillate with ether. The ether layer was dried over anhydrous sodium sulfate and the haloarylthiol recovered by evaporation of the ether and distillation. Table IV lists the haloarylthiols prepared by this method.

**Haloaryl Disulfides.**—The haloarylthiols obtained in the above process were all converted to their disulfides by the method described by Ritter and Sharpe.[14] When the oxidative acid-catalyzed cleavage of the haloarylmercaptoacetic acids was carried out without using the steam distillation process the haloarylthiols produced were oxidized to their disulfides. Very high yields of haloaryl disulfides were obtained in all cases. Table V summarizes our results.

**Acknowledgment.**— We wish to thank the Directors of Dominion Tar and Chemical Company, Montreal, Canada, for permission to publish this work.

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# Reduction of Mercuric Salts by Dioxenes

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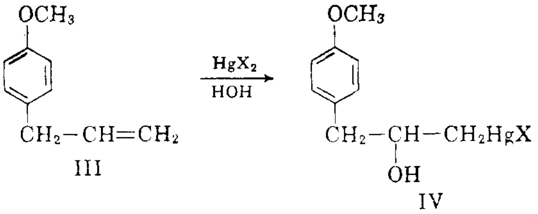
Mercuric salts in aqueous solutions are reduced rapidly and quantitatively by dioxene at room temperature. Isolation of glyoxal as a major product indicates that the double bond of dioxene is a faster reducing agent towards $Hg^{+2}$ than is the aldehyde group of glyoxal. *m*-Propenylanisole does not reduce mercuric salts under conditions that give extensive reduction by its *ortho* or *para* isomer. 2-Methyl-*p*-dioxene is a fast reducing agent; its isomer, *exo*-methylene-*p*-dioxane, is very slow. Easy ionization of the mercury from an intermediate addition compound to form a stable carbonium ion is postulated to account for the fast and strong reducing action towards mercuric salts of dioxene and related compounds.

*p*-Dioxadiene appears to undergo substitution[2] with mercuric salts, but no other chemical reactions usually associated with aromaticity have been observed.[3] It therefore seemed interesting to determine whether *p*-dioxene, the related compound possessing a single double bond, would also be mercurated, or whether it would form the addition compounds typical of an olefin. When dioxene was treated with aqueous mercuric acetate, neither substitution nor addition products were isolated; but oxidation–reduction took place, nearly quantitative yields of free mercury, glyoxal, and ethylene glycol being obtained. The double bond of the dioxene must be a considerably faster reducing agent toward mercuric salts than the aldehyde groups of glyoxal, since, if the reverse had been true, little glyoxal would have been isolated.

When two moles of mercuric acetate were used, the reduction product was mercurous acetate, rather than free mercury. The same fast reduction takes place in methanol, but substitution of anhydrous benzene or an excess of dry dioxene for water as a solvent slowed the reducing action markedly, and the only isolated product was *p*-dioxane-2,3-diol diacetate.

Although most olefins react with mercuric salts to form addition compounds,[4] reducing action has also been observed and occasionally studied.[5] The previous work most closely related to our own is that of Balbiano and Paolini,[6] who found that aqueous mercuric acetate was reduced to free mercury by anethol (I), the latter undergoing oxidation to a mixture of isomers of 1-*p*-anisyl-1,2-propanediols (II) (see Chart B). In contrast, methylchavicol (III) forms stable mercury addition compounds such as IV. A number of related



compounds were studied. In summary, those compounds containing a double bond adjacent to the ring and *ortho* or *para* to an ether group reduced mercuric salts, whereas the isomeric compounds containing an allyl type of unsaturation formed stable addition compounds. A simple example of a compound with the double bond adjacent to the ring but *meta* to the methoxyl group was not studied. The reducing action, or lack of it, of the double bond of the substituted anisoles has been used by Lauer and Leeckley[7] as evidence of the location of the double bond in this general type of compound; those containing a double bond adjacent to the benzene ring reduced mercuric salts.

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(1) Present address: Canadian Service College, Royal Roads, British Columbia, Canada.

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Our dioxene can be considered as closely related to Balbiano's reducing compounds by vinylogy,[8] since each of his *ortho* or *para* compounds is the vinylogue of a vinyl ether. The *meta* isomer would be related to an allyl rather than to a vinyl ether, and would not be expected to possess the same reducing properties,[7] but would be expected to form an addition compound. We therefore prepared *m*-propenylanisol (V) and tested it. It was found not to reduce mercuric acetate to mercury but to form mercury containing compounds. This experiment defines more precisely the interpretation to be given to the results of a mercuric salt reduction test for location of a double bond in substituted phenol derivatives. Failure to reduce is not necessarily an indication of allyl rather than a vinyl type of compound.

The reduction of mercuric salts is not a general reaction for vinyl ethers. When tested under the condition that gave quantitative reduction for dioxene, neither vinyl ether nor butyl butenyl ether was oxidized, but formed instead gummy addition compounds. Similar addition compounds have been found useful as intermediates in synthesis.[9]

The pronounced reducing properties of dioxene can be explained by a mechanism (see Chart A) similar to that proposed by Barton and Rosenfelder[5e] to account for the oxidation of isodehydrocholesteryl *p*-nitrobenzoate by mercuric acetate. In their case, the carbonium ion was of a particularly stable allyl type. In the dioxene case, the carbonium ion is stabilized by the adjacent oxygen. Recent studies of Jensen and Ouellette[5f] indicate that the critical reaction may be $RHg^+ \rightarrow R^+ + Hg^\circ$ rather than $RHgX \rightarrow R^+ + HgX^-$. Their studies involve the use of strong acids, and their carbonium ions would be much less stable than ours. In the absence of contrary evidence, we have incorporated the Jensen and Ouellette idea into the Barton and Rosenfelder type of mechanism as an alternative; however, when X is an acetate in an almost neutral solution, and a carbonium ion as stable as VI is formed, the principal path of the reaction may be (1) rather than (2).

The unusual stability of the carbonium ion in VI has been discussed by Salomaa,[10] who used it to explain the rate data in the hydrolysis of 2,3-dichloro-*p*-dioxane. Pronounced stability of VI would promote the dissociation of the Hg° in reaction 2 or of the $HgX^-$ in reaction 1. In the presence of an excess of $Hg^{+2}$ cations, the $Hg_2^{+2}$ ion would be formed, and mercurous salts, if of limited solubility as in the case of the acetate, would precipitate rather than mercury.

When the reaction was carried out in the absence of water, but with an excess of dioxene as solvent, it was much slower, as would be expected of an ionic reaction. The only isolated product was 2,3-dioxanediol diacetate in small yield. In the absence of a participating solvent, the only groups available to combine with the carbonium ions are the acetate anions.

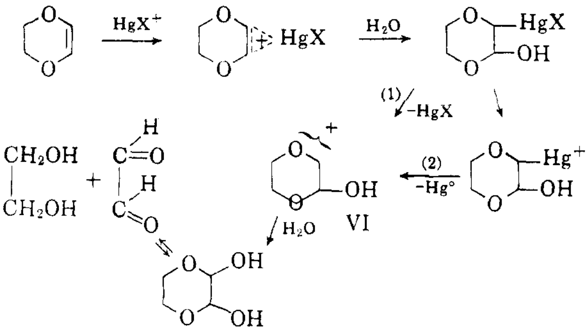

Chart A

This type of theory can also explain Balbiano's results (Chart B). Formation of mercury addition compounds usually follows Markownikoff's rule,[11] but it has been demonstrated by Pearson, Sigal, and Krug[12] that although the predicted isomer is the chief product, lesser amounts of the other isomer may also be detected in some cases. An anti-Markownikoff addition type of intermediate has also been hypothesized by Watanabe, Conlon, and Hwa[13] to explain the catalytic activity of mercuric salts in interchange reactions of allyl ether with alcohols. Thus one would expect the original addition to I to produce both VIII and IX. Furthermore, such addition reactions would be reversible.[14]

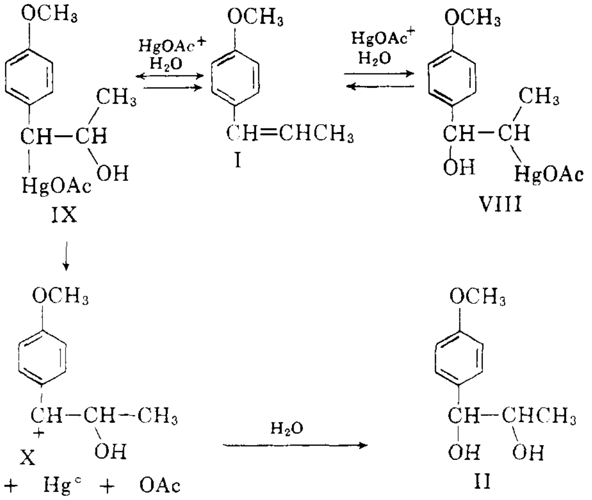

Chart B

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[13] W. H. Watanabe, L. E. Conlon, and J. C. H. Hwa, *J. Org. Chem.*, **23**, 1666 (1958).

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As far as oxidation is concerned, VIII is probably inert, but IX could ionize to the stabilized carbonium ion (X), which would solvate to the observed product II. VIII would serve as a reservoir to replenish IX by way of I as the fruitful reaction proceeds. Eventually, all of the olefin would be oxidized to glycol.

It has been observed that compounds which exist in an enolic form reduce salts of mercury.[15] The possibility needs to be considered that the reducing action of dioxene might be due to a product of hydrolysis that was capable of enolization, such as XIa in Chart C, which could exist as the enol XII.

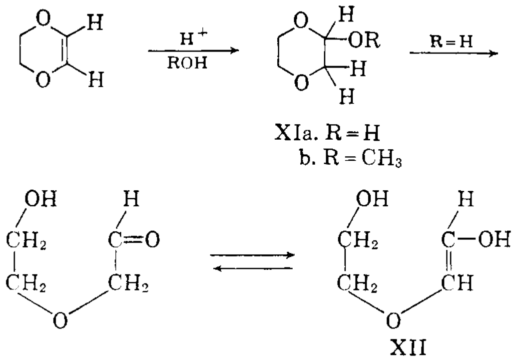

Chart C

Such a mechanism fails to explain the reducing action of dioxene in a methanol solution. When $R = CH_3$, XIb is a stable acetal incapable of existing in an enolic form. Also, we have prepared a pair of isomeric ethers, *exo*-methylene-*p*-dioxane (XIII) and 2-methyl-*p*-dioxene (XIV), both of which would be hydrolyzed rapidly to the same product (Chart D). If the hydrolysis product is the intermediate that reduces mercuric salts, the reducing action of the two should be quite similar. Experimentally, XIV readily reduces aqueous mercuric salts, but XIII does not.

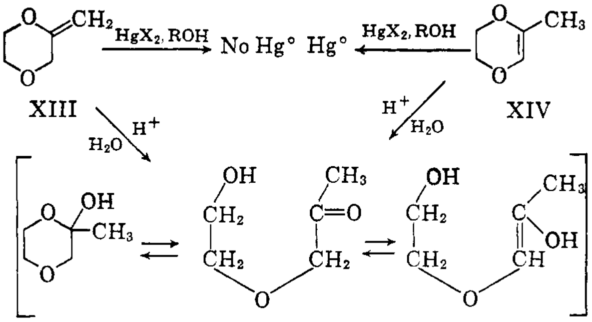

Chart D

The preparation of XIII was similar to that of 2,5-bis(*exo*-methylene)-*p*-dioxane (XV)[16] involving treatment of the iodomethyl compound with strong base. The particular strong base of choice in this case was sodium amide in liquid ammonia. A matter of added interest was that XIII absorbs with a doublet in the infrared at 6.03 $\mu$ and 6.06 $\mu$. Although a similar doublet had been observed for XV, the possibility of an isomeric structure for that compound containing two different types of double bonds has not been eliminated. While XIII does isomerize to XIV, each compound has been isolated, and each has its own spectrum. The double bond in XIV absorbs sharply at 5.93 $\mu$, as compared with 6.1 for dioxene. This confirms Miller's generalization[17] that alkyl substitution in dioxenes causes a shift in the C=C absorption to shorter wave lengths. The structure of XIV was proved by the hydrolysis of the halogen addition product to methylglyoxal and ethylene glycol. The n.m.r. spectra of XIII and XIV were evaluated by Professor A. Louis Allred as consistent with the assigned structures.[18]

## Experimental

**Reaction of Dioxene with Mercuric Acetate. A. In Water.**—To the dioxene[19] (1.73 g., 0.02 mole) was added a solution of mercuric acetate (7.02 g., 0.02 mole, in 50 ml. of water). A gray-black precipitate began forming immediately. The mixture was shaken at room temperature for 0.5 hr., and the precipitated solid (mercury) removed by filtration through a Gooch crucible. After being washed with water, alcohol, and ether, the crucible was dried over calcium chloride and weighed. The mercury, 3.86 g., corresponded to 96% of theoretical. The filtrate was diluted to 100 ml. and aliquot portions used for analysis.

To 25 ml. of the solution was added 1.5 ml. of phenylhydrazine in 15 ml. of dilute acetic acid. The solution was warmed slightly, allowed to stand for 30 min., and then was cooled in an ice bath. The glyoxal osazone was filtered, recrystallized from ethanol–water, filtered, and dried. Weight of recrystallized material was 1.15 g. (96.4%), m.p. 167–168°, lit. 169–170°.[20] Another aliquot portion was used to prepare the semicarbazone, m.p. 269–270°, lit. 270°.[21] On a third aliquot portion, a standard Schotten–Baumann reaction[22] with benzoyl chloride yielded 1.18 g. (87%) of the dibenzoate of ethylene glycol, m.p. 72.5–73°, lit. 73°.[23]

In another experiment the mole ratio was varied, 0.0175 mole of dioxene being added to 0.035 mole of mercuric acetate in 50 ml. of water. Heat was evolved and a lustrous white precipitate of mercurous acetate began to form at once. After being washed with water, alcohol, and ether and then dried, it weighed 8.89 g. (0.034 mole, 98%). Following precipitation of traces of mercurous salts with hydrogen sulfide the osazone of glyoxal (98.8% yield) was prepared as described above.

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(18) After this work was finished, we learned that XIII and XIV had been prepared by Dr. N. D. Dawson (private communication), using an independent method. He proved their skeletal structures by catalytic hydrogenation to the known methyl-*p*-dioxane.

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(21) R. L. Shriner and R. C. Fuson, "The Systematic Identification of Organic Compounds," John Wiley & Sons, Inc., New York, N. Y., 1948, p. 229.

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B. **In Methanol.**—To dioxene (3.3 g., 0.038 mole) in 100 ml. of absolute methanol was added mercuric acetate 25 g., 0.078 mole). A white precipitate of mercurous acetate began forming immediately. Filtered, washed, and dried, it weighed 19.6 g., or 96%. In a second experiment, 0.056 mole of mercuric acetate suspended in 100 ml. of absolute methanol was added in small portions to 0.056 mole of dioxene in 10 ml. of methanol. The precipitate which formed was gray-black, turning to black. It was filtered after 0.5 hr. and allowed to coagulate overnight. The resulting globule of mercury weighed 10.4 g. (92%).

C. **In Benzene.**—Equal molar quantities of mercuric acetate and dioxene in benzene were shaken for 2 days without evidence of reaction. On refluxing for 2 days, some gray precipitate formed. No organic product was identified.

D. **In Excess Dioxene.**—To dioxene (8.4 g., 0.097 mole) was added 31.2 g. (0.097 mole) of mercuric acetate. After an induction period of 10 min., heat began to be evolved, and the mercuric acetate began to darken. An additional 10 ml. of dioxene was added and allowed to react for 2 weeks. The gray-black precipitate of mercury and mercurous acetate after washing with ether weighed 20.8 g. The ether washings were concentrated and distilled under reduced pressure. From the distillate, after crystallization from ice water, a small amount of dioxane-2,3-diol diacetate was identified by comparison with an authentic sample.[24]

**Reaction of Propenylanisoles with Aqueous Mercuric Acetate.** A. ***o*-Propenylanisole.**—*o*-Methoxybenzaldehyde was converted to 1-(*o*-anisyl)-1-propanol,[25] which was dehydrated by vacuum distillation in the presence of a trace of iodine, b.p. 115–116°/19 mm., $n^{20}$D 1.5590. Lit., b.p. 222–223°/760; $n^{20}$D 1.5604.[26] To 16.77 g. (0.053 mole) of mercuric acetate in 80 ml. of water was added 7.8 g. (0.053 mole) of *o*-propenylanisole and the mixture was shaken continuously. Formation of much mercury was noted after 2 days. At the end of 2 weeks, the precipitated mercury, contaminated with a little mercurous acetate, weighed 11.74 g., slightly more than theoretical if mercury alone had been formed quantitatively. The ether extract was dried and fractionated to give 3.4 g. of 1-(*o*-anisyl)-1,2-propanediols.

*Anal.* Calcd.: C, 65.9; H, 7.74. Found: C, 65.70; H, 7.82.

B. ***m*-Propenylanisole.**—*m*-Bromoanisole was converted to the Grignard reagent and treated with propionaldehyde to yield 1-(*m*-anisyl)-1-propanol. Dehydration, caused by dropping into sirupy phosphoric acid[27] maintained at 200°, yielded *m*-propenylanisole, b.p. 118–120°/19 mm. $n^{20}$D 1.5530.[28] Mercuric acetate (4.33 g., 0.014 mole) in 21 cc. of water was shaken with *m*-propenylanisole (2.0 g., 0.014 mole) for 2 weeks. No mercury was formed. Addition of sodium chloride caused precipitation of white granular material, some of which did not melt below 250°. Two fractions were separated by alcohol extraction, but neither has been identified. Analysis indicated that they were impure or complex addition compounds. No glycol was found.

C. **Anethole.**—The anethole (6.00 g., 0.04 mole), mercuric acetate (12.9 g., 0.04 mole), and 65 ml. of water were treated as described for *o*-propenylanisole with parallel results. Mercury was formed almost quantitatively, 4.84 g. of the mixed glycols (66% yield) were recovered by ether extraction and distillation. Without mechanical losses, the yield would have been considerably higher.

**Vinyl Ethers.**—Butyl butenyl ether was treated with aqueous mercuric acetate as described for dioxene. A yellow gummy precipitate, but no blackness of mercury, was observed. The mixture was then refluxed for 8 hrs., the precipitate filtered, and the filtrate freed of mercury salts by hydrogen sulfide and tested for hydroxyaldehydes with phenylhydrazine. No osazone formed. Vinyl ether gave similar negative results.

**Iodomethyl-*p*-dioxane.**—β-Allyloxyethanol[29] was treated in succession with mercuric acetate, base, iodide ion, and iodine, substantially as described by Werner and Scholz,[30] to yield over-all *ca.* 55% of iodomethyl-*p*-dioxane.

**Exomethylene-*p*-dioxane (XIII).**—The procedure was modeled after one of Puterbaugh and Newman[31] for hydrogen bromide elimination in a difficult case. In a 1-l. round bottom flask cooled with Dry Ice and fitted with stirrer, dropping funnel and Dry Ice condenser, was placed 300 ml. of liquid ammonia. A trace of ferric nitrate was added, followed by 6.0 g. (0.30 g.-atom) of sodium in small portions. Iodomethyl-*p*-dioxane (68.4 g., 0.30 mole) dissolved in 250 ml. of anhydrous ether was added dropwise over a period of 0.5 hr. The ammonia was allowed to evaporate (6 hr.) and the reaction mixture was heated to ether reflux for 30 min. To the cooled mixture, moist ether, then water and additional ether were added. The water layer was saturated with sodium chloride and the ether layer separated, water-washed, and dried with sodium sulfate. After ether removal with a Vigreux column, the residue on fractionation under nitrogen in a Holzman column yielded 10.6 g. (53%) of a liquid, b.p. 123–124°; $n^{25}$D 1.4477. The analytical sample was obtained in a similar run.

*Anal.* Calcd. for $C_5H_8O_2$: C, 59.98; H, 8.06. Found: C, 59.86; H, 7.96.

**2-Methyl-*p*-dioxene (XIV).**—In one experiment almost identical with the one above, the ether solution was allowed to stand for 4 days in contact with sodium sulfate. On distillation, a yield of 13.6 g. (45.4%) of the isomeric methyl-*p*-dioxene (XIV), b.p. 115–116°, $n^{25}$D 1.4386, was obtained. Attempts to prepare XIII by treatment of iodomethyl-*p*-dioxane with water–diethylene glycol solutions of sodium hydroxide[32] resulted in yields of *ca.* 35% of material that boiled from 112–115°, and was later shown to be almost pure 2-methyl-*p*-dioxene. One such carefully distilled sample, b.p. 112°, $n^{25}$D 1.4393, was analyzed.

*Anal.* Calcd. for $C_5H_8O_2$: C, 59.98; H, 8.06. Found: C, 59.81; H, 8.01.

In other sodium hydroxide experiments using carbitol (technical grade, E. K. P. 2413) and water as solvent, the boiling point of the dried product varied from 110–120°.

**Catalytic Conversion of XIII to XIV.**—In a 5-ml. round-bottom flask was placed 0.1 g. of 10% palladium-on-charcoal, 0.2 g. of hydroquinone, 1.0 g. of biphenyl and 2.53 g. of XIII. The apparatus was flushed with nitrogen and the contents refluxed for 24 hr. Distillation through a Holzman column under nitrogen gave 1.85 g., b.p. 114–114.5°, of XIV for a 73% yield. $n^{25}$D 1.4381. Infrared indicated pure XIV. In a similar experiment, XIII was heated under nitrogen with activated silica. After 3 hr., infrared spectra still indicated absence of XIV. The purest sample of XIII was obtained by displacement chromatography over dried alumina, using pentane as precursor and methanol as chaser. The boiling point of the purified sample was 122–124°, $n^{25}$D 1.4479–1.4484. A similarly purified sample of XIV had a boiling point of 115.5–116°, $n^{25}$D 1.4375–1.4382. The criterion of purity was the absence of absorption due to the isomeric substance in the infrared spectra.

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[24] J. Boeseken, F. Tellegen, and P. C. Henriques, *J. Am. Chem. Soc.*, **55**, 1284 (1933).

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[29] C. D. Hurd and M. Pollack, *J. Am. Chem. Soc.*, **60**, 1905 (1938).

[30] L. H. Werner and C. R. Scholz, *ibid.*, **76**, 2701 (1954). This compound was first prepared in our laboratories by Hal Waite, Senior thesis, June, 1954. Part of the material used in this work was that prepared by Waite.

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**Structure of 2-Methyl-p-dioxene (XIV).**—A pentane solution of bromine was added to 0.29 g. of XIV dissolved in 10 ml. of pentane until the color of bromine barely faded. The pentane was expelled by nitrogen at room temperature, the resulting oil dissolved in dilute hydrochloric acid, and the mixture warmed on the steam bath for 0.5 hr. To half of this solution was added 1 ml. of phenylhydrazine and enough acetic acid to give a clear solution. A flocculent yellow precipitate of osazone formed immediately, m.p. 144.5–146°; lit. 145°, yield 69%.[33] The dibenzoate of ethylene glycol was isolated from the other half of the hydrolysate by procedures described above; yield, 18%.

**Treatment of XIII and XIV with Mercuric Acetate.**—A sample of XIV (0.0023 mole) was treated in water solution with mercuric acetate (0.0023 mole) at room temperature. There was an immediate grayish precipitate which soon turned black. A sample of XIII under similar treatment gave only traces of very light gray precipitate. In another experiment, XIII was tested with methanolic suspension of mercuric acetate. There was no immediate reduction to mercury. After standing 24 hr., a trace of black mercury developed. Under similar conditions, XIV gave an immediate black precipitate of mercury.

**N.m.r. Spectra of XIII and XIV (by Dr. A. Louis Allred).**—The n.m.r. spectrum of XIV consisted of three peaks with the areas in the ratio 1:4:3. The most intense peak is in the methylene absorption region and is relatively broad. The peak of intensity 1 in the olefin absorption region and the peak of intensity 3 in the methyl absorption region are split slightly, because of weak spin–spin coupling. The n.m.r. spectrum of XIII consisted of three peaks, with partially resolved fine structure, in the absorption region of methylene groups and terminal olefins. Two small peaks with appropriate intensities, chemical shifts, and fine structure indicated that about 5% of the sample consisted of compound XIV. The n.m.r. spectra were obtained with a Varian Associates high-resolution spectrometer at 40 Mc. and room temperature.

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# A Product of the Chemical Reduction of o-Benzenediacetonitrile

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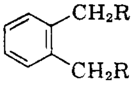
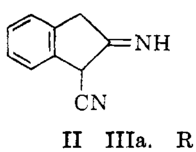
The sodium reduction product of o-benzenediacetonitrile (Ia) which was assigned the structure 2-methyl-2-indanamine (IIIa) by von Braun is shown to be 2-indanamine (IIIc). An authentic synthesis of the former substance is described. Some indanylhydrazines and related substances with monoamine oxidase activity were prepared. The acid-catalyzed degradation of benzyl-type hydrazines to the amine and olefin is reported, in some cases (X), the reaction being surprisingly facile. Mechanisms for the unusual loss of a carbon atom during the reduction of Ia and for the new elimination reaction of benzylhydrazines are suggested.

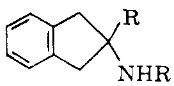
In 1892 Zanetti[4] discovered that the reduction of o-benzenediacetonitrile (Ia) with sodium and alcohol yielded two products, one a diamine to which he assigned structure Ib and the second a monoamine of $C_{10}H_{13}N$ composition. A reinvestigation of this reaction by von Braun twenty-four years later[5] led to the same results. While accepting the Zanetti structure Ib for the diamine, von Braun devoted his attention to the monoamine. Its oxidation to phthalic acid, its inertness to catalytic or chemical reduction and its formation also from the sodium–alcohol reduction of 1-cyano-2-iminoindane (II), a compound readily obtained by a sodium ethoxide-induced cyclization of o-benzenediacetonitrile (Ia),[6] convinced him that he was dealing with an indanamine. He further observed that exhaustive methylation of the amine, Hofmann elimination of the quaternary ammonium salt and formation of an anisal derivative of the resulting indene afforded a crystalline product which proved to be different from the anisylidene derivative of the then known 1-methylindene. Hence von Braun considered it to be the derivative of 2-methylindene and was led to conclude that the monoamine is 2-methyl-2-indanamine (IIIa).



Ia. $R = CN$
b. $R = CH_2NH_2$
c. $R = CH_2CONH_2$



II



IIIa. $R = CH_3, R' = H$
b. $R = H, R' = COC_6H_5$
c. $R = R' = H$
d. $R = H, R' = NH_2$

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