= 16 Hz), 5.56 (dd, J = 16, 7 Hz). Its mass spectrum displayed no parent M^+ but showed fragments $M^+ - Cl$ 361/363/365/367, ratio 40:99:100:28 (theory for Cl_2Br_2 above); $M^+ - Br$ 317/319/321/323, ratio 48:100:68:16 (theory for Cl_3Br 51:100:65:18); 229/231/233; 193/195/197; 167/169/171; and 131/133.

The dibromotrichlorodimethyloctadiene 8 was obtained impure in HPLC fractions 12–13 (17 mg). It was tentatively identified by its GC/MS peak and its mass spectrum, which was identical with that above for 7.

Oregonene A (9) was obtained as a clear oil in HPLC fractions 14–15 (50 mg). Its ^1H NMR ($CDCl_3$) is described in the text and in benzene-d_6 the H_5 and H_6 multiplet was simplified to a doublet (J = 16 Hz) and a doubled doublet (J = 16, 6 Hz). Its mass spectrum showed no parent M^+ but displayed fragments: $M^+ - Cl$ 395/397/399/401/403, ratio 33:87:100:41 (theory for Cl_3Br_2 32:92:100:50); $M^+ - Br$ 351/353/355/357, ratio 39:100:90:34 (theory for Cl_4Br 44:100:83:33), 315/317/319; 228/230/232; 167/169/171; 131/133.

Several attempts were made to dehalogenate the C_7 and C_8 positions. The reaction conditions ($NaCNBH_3$, HMPT, 70 °C, 2 h)[8] that successfully didebrominated 1,2-dibromo-1-methylstyrene in 83% yield in our hands gave no reaction with oregonene A (9). More forcing conditions caused decomposition.

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Registry No.—**5**, 57766-75-3; **6**, 57766-76-4; **7**, 62447-48-7; **8**, 62447-49-8; **9**, 62416-32-4.

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(5) For *trans*-2-butenyl chloride, $-CH_2Cl$ 45.5 ppm, and for *trans*-2-butenyl bromine, $-CH_2Br$ 33.3 ppm.
(6) For a discussion of the γ effect by halogens in acyclic systems see (a) P. Crews and E. Kho-Wiseman, *J. Org. Chem.*, in press; see also (b) G. C. Levy and G. R. Nelson, "Carbon-13 Magnetic Resonance for Organic Chemists", Wiley-Interscience, New York, N.Y., 1972, Chapter 3.
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Deoxygenation of *N*-Nitrosodibenzylamine with Aryl Azides

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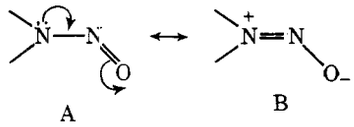
Recently a great deal of attention has been focused on *N*-nitrosamines because of their synthetic utility[1] as well as their carcinogenic[2,3] and carcinostatic[3] properties. The large contribution of dipolar form B to the structure of *N*-nitrosamines, clearly indicated by spectral data,[4] helps explain some of the chemistry of this class of compounds; thus, structure B suggests that *N*-nitrosamines may formally be regarded as *N*-oxides of *N*-nitrenes. These considerations coupled with our interest in novel methods to generate *N*-nitrenes,[5] led us

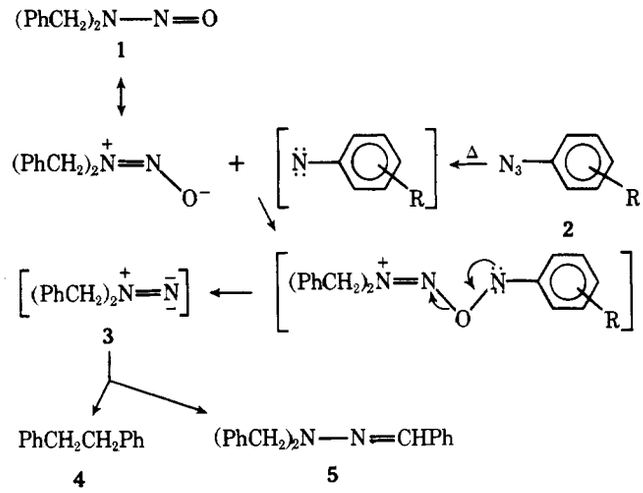


A B

to consider the "deoxygenation" of *N*-nitrosamines as a route to these reactive intermediates.

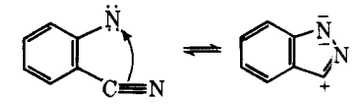
It was reported earlier[6] that the reaction of *N*-nitrosodibenzylamine (1) with iron pentacarbonyl resulted in the formation of products traceable to *N*-dibenzylaminonitrene (3). It was felt that electron-deficient species such as *C*-nitrenes should react with *N*-nitrosamines to yield *N*-nitrenes. This communication describes our results.

Since bibenzyl (4) and benzylidenedibenzylhydrazine (5) are known transformation products of *N*-dibenzylaminonitrene (3),[7] *N*-nitrosodibenzylamine (1) was selected as the substrate for our investigation. A solution of 1 in chlorobenzene was heated to reflux with a twofold excess of phenyl azide until nitrogen evolution ceased. Work-up of the reaction mixture gave 81.5% of recovered 1 along with trace amounts



of bibenzyl (4); thin-layer chromatography showed the presence of azoxybenzene.[8] Since the anticipated course of the reaction was predicated on the electron-deficient nature of the *C*-nitrenes, the reaction of 1 was carried out with aryl azides containing groups which should enhance the electron-deficient nature of the *C*-nitrenes derived from them.[9] 4-Nitrophenyl azide gave a 46% yield of bibenzyl (4), while only 48% of 1 was recovered. Similarly, 4-cyanophenyl azide afforded a 48% yield of 4, although a much larger amount (93.7%) of 1 was recovered. Unexpectedly, *p*-chlorophenyl azide gave *no* bibenzyl, while 79.5% of 1 was unreacted. The anomalous effect of the chlorine was further confirmed by the reaction of 2-chloro-4-nitrophenyl azide with 1 in which only 14% of 4 (compared with 4-nitrophenyl azide) was obtained and 1 was recovered in 63% yield. 2,3-Dichlorophenyl azide gave 4 and 5, albeit in low yield.[10]

With substituents in the 2 position, such as *o*-benzoyl and *o*-nitro, capable of reacting with the nitrene[11] to give stable compounds, little or no bibenzyl was obtained (see Table I, entries 8 and 9); 3-phenylanthranil and benzofuroxan were the major products, respectively. 2-Cyanophenyl azide provided a surprising contrast to the aforementioned azides; bibenzyl was isolated in as good a yield (47%) as those obtained from 4-nitro- and 4-cyanophenyl azides. This may be rationalized by the fact that the cyano group, being located ortho to the nitrene, may interact with and in a sense "store" the nitrene without forming a stable compound in contrast to the nitro and benzoyl groups (vide supra[11]). These data led to the



expectation that the synergistic effect of a cyano group in the 2 position coupled with that of a nitro group in the 4 position should result in providing us with a most efficient azide for

Table I. Reaction of *N*-Nitrosodibenzylamine (1) with Azides[a]

Registry no.	Azide	Recovered 1, %	$PhCH_2$-CH_2Ph, %	Other products
622-37-7	(1) Phenyl azide	81.5	Traces	*b*
1516-60-5	(2) 4-Nitrophenyl azide	48.5	46	
18523-41-6	(3) 4-Cyanophenyl azide	93.7	48	
31656-77-6	(4) 2-Cyanophenyl azide	66.5	47	
3296-05-7	(5) 4-Chlorophenyl azide	79.5	0	*c*
62416-01-7	(6) 2-Chloro-4-nitrophenyl azide	63	14	*d*
62416-02-8	(7) 2,3-Dichlorophenyl azide	0	1	*c, d*
16714-27-5	(8) 2-Benzoylphenyl azide	90	Traces	*e*
1516-58-1	(9) 2-Nitrophenyl azide	80	0	*f*
62460-41-7	(10) 2-Cyano-4-nitrophenyl azide	9.7	69.5	*d*
941-55-9	(11) Tosyl azide	>99	Traces	
1070-19-5	(12) *tert*-Butyl azidoformate	89	0	

[a] All reactions were carried out in enough chlorobenzene to give a homogeneous solution using 5 mmol of *N*-nitrosodibenzylamine and 10 mmol of the azides. The yields of bibenzyl are based on the amount of unrecovered nitrosamine. Other products such as the azo compounds and biphenyls were formed. [b] In this reaction, azoxybenzene was sought (see ref 8) and detected by thin-layer chromatography. [c] Trace amounts of benzylidenedibenzylhydrazine (5) were detected. [d] Benzaldehyde was identified as a by-product. [e] 3-Phenylanthranil was isolated in nearly quantitative yield. [f] Benzofuroxan was isolated in 32% yield.

the deoxygenation of 1. That this expectation was fully warranted was shown by the fact that a 70% yield of bibenzyl was obtained with less than 10% of recovered *N*-nitrosamine. Our results indicated that aryl azides may be useful for the removal of semiionic oxygen in compounds such as *N*-oxides, azoxy compounds, and nitrones.

Experimental Section

Materials. *N*-Nitrosodibenzylamine was prepared according to the literature procedure.[12] The azides were obtained from the corresponding amines.[13] Three new azides were prepared by the same method.

2-Chloro-4-nitrophenyl azide (70% yield): mp 65–66 °C, pale yellow needles from a mixture of acetone–95% ethanol. Anal. Calcd for $C_6H_3ClN_4O_2$: C, 36.29; H, 1.52; N, 28.22. Found: C, 36.23; H, 1.71; N, 28.29.

2,3-Dichlorophenyl azide (76% yield): mp 61–62 °C, pale yellow needles from 95% ethanol. Anal. Calcd for $C_6H_3Cl_2N_3$: C, 38.33; H, 1.61; N, 22.35. Found: C, 38.54; H, 1.90; N, 22.50.

2-Cyano-4-nitrophenyl azide (17% yield): mp 107–108 °C, pale yellow needles from 95% ethanol. Since this azide deteriorates on standing, an elemental analysis was performed on its triphenylphosphine imine adduct, mp 247–248 °C (from benzene). Anal. Calcd for $C_{25}H_{18}N_3O_2P$: C, 70.92; H, 4.25; N, 9.93. Found: C, 71.09; H, 4.35; N, 9.87.

Typical Procedure. A solution of 1.14 g (5 mmol) of *N*-nitrosodibenzylamine and of 2-cyano-4-nitrophenyl azide (1.89 g, 10 mmol) in 40 mL of chlorobenzene was purged with nitrogen for 30 min. The solution was then heated to reflux for 48 h with stirring in a nitrogen atmosphere. After careful evaporation of the solvent, the residue was chromatographed on silica gel (60–200 mesh, 50 g) using hexane, varying mixtures of hexane–benzene, and finally benzene.

All products reported were characterized by direct comparison with an authentic sample by at least one of the following methods: IR, NMR, mixture melting point, and TLC retention time.[14]

Acknowledgment. The support of this work by the National Institutes of Health (GM 13689-10) is acknowledged with gratitude.

Registry No.—1, 5336-53-8; $PhCH_2CH_2Ph$, 103-29-7; 2-cyano-4-nitrophenyl azide triphenylphosphine imine adduct, 55210-55-4.

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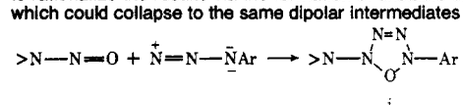
(9) R. A. Abramovitch and E. P. Kyba, "Chemistry of the Azido Group", S. Patai, Ed., Interscience Publishers, New York, N.Y., 1971, p 270. It is also possible to rationalize the results via the formation of unstable oxatetrazolines (i) which could collapse to the same dipolar intermediates (ii). On the basis



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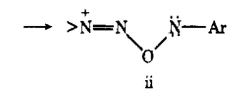
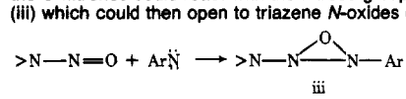
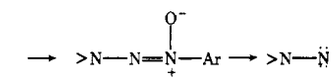


ii

of the present data, we favor the nitrene mechanism. In the same context, the *C*-nitrenes could react with the nitroso group to give oxadiaziridines (iii) which could then open to triazene *N*-oxides (iv) which are known to

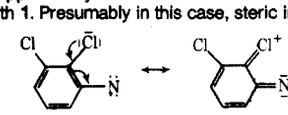


iii



iv

fragment to the *N*-nitrenes (M. Koga and J.-P. Anselme, unpublished results).
(10) While the inductive effect of a chloro substituted at any position would be expected to make the nitrene *more* electron deficient, in the ortho and para positions the chlorine may act as an electron-donating group to render the nitrene *less* electron deficient. Thus, if this putative resonance stabilization and concomitant deactivation of the nitrene by a chloro substituent could be inhibited, then deoxygenation of 1 should be possible. This hypothesis seems to be supported by the results from the reaction of 2,3-dichlorophenyl azide with 1. Presumably in this case, steric inhibition of resonance,



i ii

such as shown, allows the chlorine in the ortho position to exert only its inductive effect. See Y. T. Struckhov and S. L. Solenova-Sidorova, *Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 93 (1960); S. L. Chien and R. Adams, *J. Am. Chem. Soc.*, **56**, 1787 (1934); see also J. March, "Advanced Organic Chemistry", McGraw-Hill, New York, N.Y., 1968, p 123.
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(14) See footnote *a* of Table I.

2-Methyl-3-butyn-2-ol as an Acetylene Precursor in the Mannich Reaction. A New Synthesis of Suicide Inactivators of Monoamine Oxidase[1]

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The propargylamines, *N*-[3-(2,4-dichlorophenoxy)propyl]-*N*-methyl-2-propynylamine (clorgyline, **1a**) and L-