Cotton effect, positive; Δ^2-cholestene (III), plain positive; osmate IIIA, Cotton effect negative), considerable information on the location of the double bond can be secured.

(4) The reaction can be conducted on a micro scale,[8] the osmate ester can be isolated and in fact can be chromatographed on silicic acid.

The rotatory dispersion curves of osmate esters of a variety of steroid olefins will be recorded in our detailed paper, together with structural and stereochemical correlations. Experiments are currently underway to expand this approach to *vic*-glycols, since these react[7] with osmium trioxide (in the form of the di-pyridine adduct) to give osmate esters.

(9) National Institutes of Health Postdoctorate Research Fellow, 1959–1960.

DEPARTMENT OF CHEMISTRY
STANFORD UNIVERSITY
STANFORD, CALIFORNIA
E. BUNNENBERG[9]
CARL DJERASSI

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THE IDENTIFICATION OF RADICAL PRODUCTS FROM THE OXIDATION OF DIPHENYLAMINE

Sir:

The mechanism of oxidation inhibition by aromatic amines has been the subject of extensive investigation. Harle and Thomas[1] reported the detection of a relatively stable radical derived from phenyl-α-naphthylamine when this compound was used to inhibit the autoxidation of 1-octadecene at 170°. *Via* kinetic arguments, the concentration *versus* time relationship of this intermediate radical was interpreted in terms of the reversible complex mechanism proposed by Hammond, Boozer, *et al.*,[2] in preference to alternatively proposed schemes of inhibition.

This note reports the identification of the stable radical, diphenyl nitric oxide, as an intermediate product when diphenylamine is used as an oxidation inhibitor. The radical, whose electron paramagnetic resonance spectra is shown in Fig. 1, is detected readily when diphenylamine is present in a hydrocarbon solution undergoing azo-bis-isobutyronitrile (ABN) catalyzed oxidation at 68.5°. The electron paramagnetic resonance spectrum, shown in Fig. 1, is identical with that of diphenyl nitric oxide prepared by the method of Wieland and Offenbäcker,[3] Hoskins[4] observed a similar spectrum when an alkaline solution of diphenylamine was oxidized with air and suggested that the radical responsible was diphenyl nitric oxide.

Azo-bis-isobutyronitrile catalyzed oxidation of solutions containing phenyl-α-naphthylamine, aniline, N-methylaniline, and phenothiazine has also been observed to yield relatively high concentrations of moderately stable radicals. By analogy, it is believed that these radicals are also nitric oxide derivatives. Their electron paramagnetic resonance spectra, which will be published and discussed elsewhere, are consistent with this interpretation. No stable radical products have been observed from very weakly inhibiting tertiary amines, such as N-dimethylaniline.

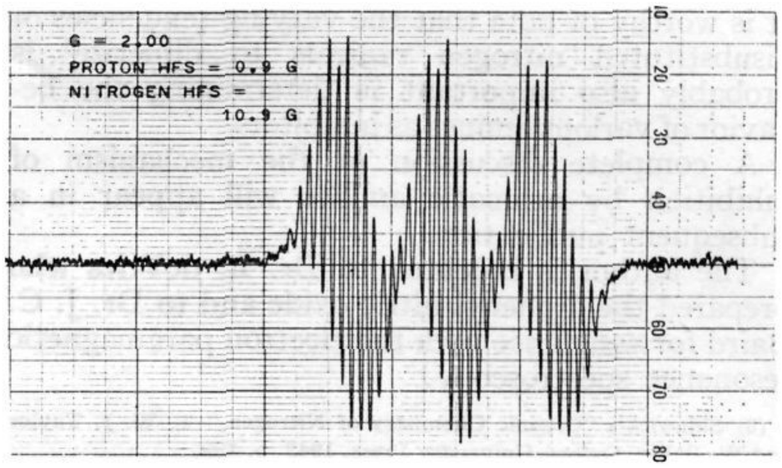

Fig. 1.

Diphenyl nitric oxide is produced when dilute solutions of tetraphenylhydrazine are subjected to ABN catalyzed oxidation. Table I shows the steady state radical concentration to be first order with respect to tetraphenylhydrazine concentration.

TABLE I

STEADY STATE CONCENTRATION OF DIPHENYL NITRIC OXIDE FROM TETRAPHENYLHYDRAZINE AT 68.5°

0.93 *M* cumene in chlorobenzene; 10^{-3} *M* ABN, 1 atmosphere of O_2

$(C_6H_5)_2N\cdot \times 10^4\ M$	2.5	5	10
$(C_6H_5)_2NO\cdot \times 10^5\ M$	3.2	7	13.5

Tetraphenylhydrazine is a weak oxidation inhibitor as shown by the data in Table II, while diphenyl nitric oxide and diphenylamine are strong oxidation inhibitors. From induction period measurements by the method of Boozer and Hammond,[5] we find that diphenyl nitric oxide terminates one half as many oxidation chains as diphenylamine. The rate of oxidation during the inhibition period due to tetraphenylhydrazine is about that to be expected from the observed steady state concentration of diphenyl nitric oxide.

TABLE II

INITIAL OXIDATION RATES AT 68.5°

0.93 *M* cumene in chlorobenzene, 10^{-3} *M* ABN, 1 atmosphere of O_2

Inhibitor	Rate, cc. O_2 l.$^{-1}$ min.$^{-1}$
None	0.62
$10^{-4}\ M\ (C_6H_5)_2NH$	.10
$10^{-4}\ M\ (C_6H_5)_2NO\cdot$	.10
$5 \times 10^{-4}\ M\ (C_6H_5)_2N\cdot$	.20

In the absence of oxygen, diphenyl nitric oxide reacts rapidly with the radicals produced from ABN decomposition; it appears to react considerably more slowly with RO_2 radicals.

These observations suggest that diphenyl nitric oxide is produced by reactions (1) and (2). They also suggest that disubstituted nitrogen radicals

$$(C_6H_5)_2NH + RO_2\cdot \longrightarrow (C_6H_5)_2N\cdot + RO_2H \quad (1)$$

$$(C_6H_5)_2N\cdot + RO_2\cdot \longrightarrow (C_6H_5)_2NO\cdot + RO\cdot \quad (2)$$

and the corresponding nitrogen oxide radicals derivable from amines play an important role in the action of aromatic amines as oxidation inhibitors.

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(1) O. L. Harle and J. R. Thomas, *J. Am. Chem. Soc.*, **79**, 2973 (1957).

(2) G. S. Hammond, C. E. Boozer, C. E. Hamilton and J. N. Sen, *ibid.*, **77**, 3238 (1955).

(3) H. Wieland and M. Offenbäcker, *Ber.*, **47**, 2111 (1914).

(4) R. H. Hoskins, *J. Chem. Phys.*, **25**, 788 (1956).

(5) C. E. Boozer, G. S. Hammond, C. E. Hamilton and J. N. Sen, *J. Am. Chem. Soc.*, **77**, 3233 (1955).

It is worthy of note that the varying tendencies of disubstituted nitrogen radicals to dimerize[6] is probably also important in determining the behavior of various amines as inhibitors.

A complete discussion of the mechanism of inhibition by aromatic amines will appear in a subsequent publication.

The author is indebted to Dr. L. deVries who prepared the diphenyl nitric oxide and to Dr. J. C. Baird for assistance with the electron paramagnetic resonance spectroscopy.

[6] Sidgwick's "Organic Chemistry of Nitrogen," T. W. J. Taylor and W. Baker, Oxford University Press, 1942, p. 389.

RICHMOND LABORATORY
CALIFORNIA RESEARCH CORP.
RICHMOND, CALIF.
J. R. THOMAS

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REARRANGEMENT OF ALLYLIC AZIDES

Sir:

In using azide ion as a trap for cationic intermediates in solvolysis of allylic halides[1] we have observed that allylic azides equilibrate very rapidly. In the present communication we call attention to this behavior of the pentenyl and butenyl azides.

A mixture of α,α-dimethylallyl and γ,γ-dimethylallyl azides may be obtained from treatment of γ,γ-dimethylallyl chloride with a solution of sodium azide in aqueous acetone. This mixture, b.p. 26–39° (40 mm.), has the correct C,H-analysis and displays an infrared band at 2140 cm.$^{-1}$, characteristic of azides.[2] A mixture of α- and γ-methylallyl azides, b.p. 64–72° (300 mm.), with the correct C,H-analysis is obtained analogously from *trans*-crotyl chloride. By low temperature fractionation relatively pure specimens of the four allylic azides can be obtained, and these can be stored at −80° for relatively long periods without serious rearrangement. The physical properties of the four azides are summarized in Table I, the identity of the members of each pair of allylic azides being clear from the b.p., $n^{25}\text{D}$ and the position of olefinic absorption in the infrared spectrum.

TABLE I

PROPERTIES OF PENTENYL AND BUTENYL AZIDES

Allyl azide	B.p. °C.	B.p. Mm.	$n^{25}\text{D}$	Infrared abs., cm.$^{-1}$	Purity, %
α,α-Me$_2$	10.5–11.5	10	1.4260	1635	99.0
γ,γ-Me$_2$	11.0–11.5	3.0	1.4520	1665	98.5
α-Me	7.0– 8.0	25	1.4200	1635	97.8
γ-Me	12.0–12.5	10	1.4410	1667	96.7

Mixtures of the isomeric azides can be analyzed vapor phase chromatographically with a Silicone on Celite column at 25°, and this makes it possible to follow the rearrangement of the pure materials into equilibrium mixtures of the two isomers. As illustrated in Table II, the percentage of primary isomer (100 F_P) at equilibrium at 25° is *ca.* 75% for the pentenyl system and *ca.* 64% for the butenyl analog in a variety of solvents.

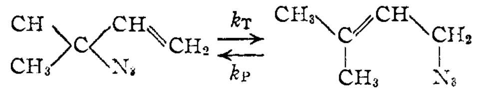
TABLE II

EQUILIBRATION OF ALLYLIC AZIDES AT 25.0°

System Solvent	Pentenyl 100 F_P[a]	Pentenyl $10^5(k_P + k_T)$[b] sec.$^{-1}$	Butenyl 100 F_P[a]	Butenyl $10^5(k_P + k_S)$[b] sec.$^{-1}$
n-C_5H_{12}	70.0	4.93	62.1	1.88
Et_2O	73.0	11.1	63.6	4.28
Me_2CO	77.0	31.0	65.2	11.0
EtOH	74.4	24.1	63.4	7.18
AcOH	76.7	36.4		
80% EtOH	74.4	62.1		
70% Me_2CO	77.0	90.6	65.6	24.9

[a] ±0.2. [b] Average mean deviation, ±2%.

The equilibrations of the azides in various solvents obey closely the expected kinetics for first order forward and back reactions according to the scheme



In Table II are illustrated the observed ($k_P + k_T$) values for the pentenyl azides and the analogous ($k_P + k_S$) values for the butenyl analogs. From these and the observed equilibrium constants, the separate k_P and k_T or k_S values are thus available. In the pentenyl series, (k_T/k_P) is *ca.* 3, while (k_S/k_P) is nearly 2 for the butenyl compounds.

The rates of the allylic azide rearrangements are remarkably insensitive to methyl substitution in the substrate azide or to solvent change. Thus, the tertiary:secondary (k_T/k_S) ratios are *ca.* 3–4, while the γ,γ-dimethylallyl:γ-methylallyl rate ratios are only *ca.* 2. The solvent change from pentane to 70% aqueous acetone increases rates of equilibration by a factor of approximately one power of ten. The small sensitivity of rate of azide isomerization to structure and solvent is in marked contrast with the high sensitivity observed with the corresponding chlorides.[1,3] With α,α-dimethylallyl chloride, for example, rates of acid production or isomerization increase by many powers of ten over the pentane → 70% acetone solvent spectrum. Thus, while rate of isomerization of α,α-dimethylallyl azide is roughly equal to that of α,α-dimethylallyl chloride in 70% acetone, it is powers of ten faster in pentane.[3]

The azide isomerization is an instructive example in the whole spectrum of merging ion pair and non-ionic cyclic rearrangement mechanisms of allylic rearrangements.[4,5] It is clear that the change from ground state to transition state in azide isomerization involves very little increase in polar character. It is also interesting that no detectable solvolysis competes with azide isomerization, even in 70% aqueous acetone.

There is considerable resemblance between the allylic azide rearrangement, here reported, and the isomerization of allylic thiocyanates to isothio-

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[1] C. Wilcox, unpublished work.

[2] E. Lieber, C. N. R. Rao, T. S. Chao and C. W. W. Hoffman, *Anal. Chem.*, **29**, 916 (1957).

[3] A. Gagneux, unpublished work.

[4] (a) Discussion, "Symposium on Molecular Rearrangements," Queen Mary College, University of London, April 6, 1954; see *Chem. Eng. News*, **32**, 1898 (1954); *Nature*, **173**, 898 (1954); (b) S. Winstein and G. C. Robinson, THIS JOURNAL, **80**, 169 (1958).

[5] (a) W. G. Young, S. Winstein and H. L. Goering, *ibid.*, **73**, 1958 (1951); (b) F. F. Caserio, G. E. Dennis, R. H. De Wolfe and W. G. Young, *ibid.*, **77**, 4182 (1955); (c) S. H. Sharman, F. F. Caserio, R. F. Nystrom, J. C. Leak and W. G. Young, *ibid.*, **80**, 5965 (1958); (d) K. L. Olivier and W. G. Young, *ibid.*, **81**, 5811 (1959).