There is increasing evidence that aromatic hydrocarbons, such as benzene, as well as many other types of compounds may degrade excitation energy *via* decay to an unstable (ground state) isomer which decays rapidly back to the starting material.[41] While evidence regarding this as a general route for internal conversion is rather limited, such isomers have been identified in several cases where energy balances could not be obtained.[42] This mechanism is attractive since it satisfies several existing theories regarding radiationless decay. Studies with pyrazine suggest that isomerization may be important in nitrogen compounds. Pyrazine and substituted pyrazines rearrange to the corresponding pyrimidines, presumably *via* benzvalene or prismane valence tautomers.[43] To date we have been unable to detect valence tautomers as intermediates or products in the photochemistry of the stilbazoles or bispyridylethylenes. We are currently pursuing experiments to test the possibility that enhanced radiationless decay proceeds *via* isomer formation.

Acknowledgments. We thank the Research Corporation and the U. S. Public Health Service (Grant No. GM 15,238-01,2) for support of this work. We are grateful to Professors H. H. Dearman and L. G. Pedersen for valuable discussion.

(41) For a review on this subject see ref 34.

(42) L. Kaplan and K. E. Wilzbach, *J. Am. Chem. Soc.*, **89**, 1030 (1967); K. E. Wilzbach and L. Kaplan, *ibid.*, **89**, 1031 (1967).

(43) F. Lahmani, N. Ivanoff, and M. Magat, *Compt. Rend.*, **263**, 1005 (1966); F. Lahmani and N. Ivanoff, *Tetrahedron Letters*, 3913 (1967).

Radicals from the Acid–Catalyzed Decomposition of 2-Tetrazenes

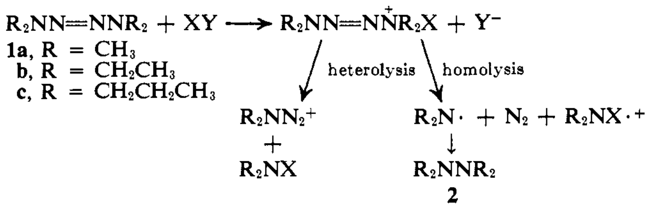
Stephen F. Nelsen, Richard B. Metzler, and Michiko Iwamura

Contribution from the Department of Chemistry, University of Wisconsin, Madison, Wisconsin 53706.

Received March 21, 1969

Abstract: The radical products of acid- or anhydride-catalyzed tetramethyl-2-tetrazene (**1a**) decomposition are **1a**$\cdot^+$ and tetramethylhydrazine radical cation, observed by esr. In solvents which give polyhalomethyl radicals upon halogen abstraction, a transient radical is formed in **1** decompositions; esr splittings show it contains the "CH_2NCH_3" fragment and the solvent radical. In only those solvents which give the transient radical, CIDNP nmr emission in the N-methyl region is observed. It is suggested that the emissing species is solvent radical–dimethylamino radical combination product, and that the transient radical is that derived by hydrogen abstraction from this material.

Wieland[1] showed in 1912 that the decomposition of tetraethyl-2-tetrazene (**1b**) with aqueous hydrochloric acid gave nitrogen, acetaldehyde, ethylamine, and diethylamine. He interpreted the reaction as proceeding by heterolytic cleavage of the protonated tetrazene to diethylamino diazonium ion, which decomposed by loss of a proton and nitrogen to give acetaldehyde ethylimine. The discovery that tetramethyl-2-tetrazene (**1a**) gives tetramethylhydrazine (**2**) radical cation upon treatment with acetic anhydride[2] suggested that homolytic cleavage of acylated tetrazene (cation) was possible. Methylation of **1a** also gave **2**,[3] presumably by a similar route.



$$R_2NN{=}NNR_2 + XY \longrightarrow R_2NN{=}\overset{+}{N}R_2X + Y^-$$

1a, R = CH_3
b, R = CH_2CH_3
c, R = $CH_2CH_2CH_3$

$$\text{heterolysis: } R_2NN_2^+ + R_2NX \qquad \text{homolysis: } R_2N\cdot + N_2 + R_2NX\cdot^+ \longrightarrow R_2NNR_2\ (\mathbf{2})$$

Results and Discussion

As previously reported,[2] treatment of **1a** with acetic, trifluoracetic, benzoic, maleic, succinic, phthalic, or dichloromaleic[4] anhydrides in DMF or acetonitrile results in nitrogen evolution and the formation of **2**$\cdot^+$. When a study of the rate of nitrogen evolution from the reaction with acetic anhydride was attempted, it became obvious that a complicated reaction was taking place. In cumene at 50°, the rate of nitrogen evolution increased almost as rapidly as the square of initial anhydride concentration (at 0.19 *M* **1a**, 1.57 *M* Ac_2O gave a rate constant of 2.5×10^{-4} sec^{-1}; 2.25 *M*, 4.9×10^{-4}; 3.26 *M*, 9.4×10^{-4}); only 69–74% of the theoretical N_2 was evolved, and there was an induction period corresponding to about one half-life of the final rate constant observed. The reaction was strongly catalyzed by added acetic acid (1 *M* in Ac_2O, 1 *M* in HOAc gave a rate of about 6×10^{-3} sec^{-1}) and the nitrogen yield increased to over 95% of theoretical. Studies were also carried out at 30° in carbon tetrachloride, this solvent giving substantially greater rates than cumene. With just acetic acid, long induction periods were observed. The length of the induction period was shorter and final rate observed larger if nitrogen was not bubbled through the solution before introduction of **1a** to start the reaction; neither was very reproducible, probably due to difficulties in complete removal of oxygen.

Titration of **1a** with hydrochloric acid in water showed that pK_a of (H-**1a**)$^+$ is about 3.9 ± 0.1; **1a** did not become detectably diprotonated even in 0.5 *M* hydrochloric acid. Thus a significant fraction of **1a** should become protonated upon mixing with acetic

(1) H. Wieland, *Ann.*, **392**, 133 (1912).

(2) S. F. Nelsen, *J. Am. Chem. Soc.*, **88**, 5666 (1966).

(3) W. H. Bruning, C. J. Michejda, and D. Romans, *Chem. Commun*, 11 (1967).

(4) High concentrations give a different radical.[2]

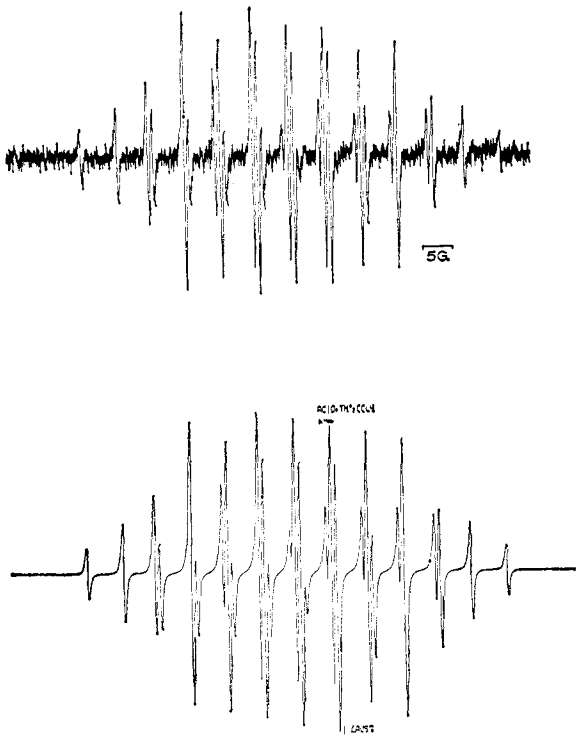


Figure 1. Esr spectrum of the transient radical (A) from decomposition of tetramethyl-2-tetrazene (**1a**) with acetic acid in carbon tetrachloride.

acid, but diprotonation is not feasible. Quite possibly protonated (H-**1a**)$^+$ decomposes in a way similar to acylated material (Ac-**1a**)$^+$. Observed rates were within an order of magnitude of each other for using acetic anhydride and acetic acid at the same concentration.

When both $(HOAc)_0$ and $(Ac_2O)_0$ were much greater than (**1a**)$_0$, a first-order plot was only linear for the middle portion. During the first "half-life" and after four, the slope was greater. More than one reaction is clearly responsible for nitrogen evolution, and the oxygen sensitivity implies that radical reactions are taking place. Acetic acid is expected to catalyze acylation of **1a**, which we believe to be the first step in the reaction with anhydrides, since nitrogen evolution is much faster with more reactive anhydrides, like trifluoroacetic. One possible chain-carrying reaction, abstraction of hydrogen by trichloromethyl radical, may be ruled out since chloroform is not formed in significant amounts. Nmr studies, using *t*-butylbenzene as internal standard, showed that for each mole of **1a** decomposed, 1 mol of acetic anhydride is consumed, and 1 mol of dimethylacetamide (1.01, 0.96 observed in two runs) and 0.62, 0.64 mol of acetic acid are formed. Products from the other dimethylamino group of **1a** are not soluble in carbon tetrachloride and appear as intractable oils. Using mixtures of acetic acid and anhydride the reaction is faster, but dimethylacetamide is still a major product. Scavenging studies to count radicals are also difficult. Koelsch's radical[5] (bisbiphenylene-β-phenylallyl) was employed, mixing a solution of it with a decomposing solution of excess tetrazene **1a** and acetic anhydride and monitoring both nitrogen evolution and visible absorption at 860 nm.[6] Koelsch radical was shown to be stable to acetic anhydride, acetic acid, and **1a** in acetonitrile. When added to decomposing **1a**–acetic anhydride mixtures (ratio of **1a** to Koelsch radical greater than 100) OD_{860} did decrease, but a plot of OD_{860} *vs.* time did not drop linearly to zero as required for efficient scavenging, but showed much curvature. Although OD_{860} dropped to less than 5% of its initial value, the final solutions were still colored (λ_{max} 880 mμ) and contained radicals. Koelsch radical is not a good scavenger for this system, but about 6% of the **1a** molecules decomposing did result in destruction of it; the radical yield is probably higher.

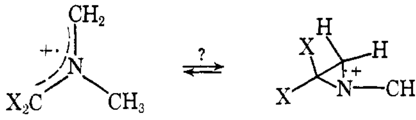
In DMF or acetonitrile, **1a** and acetic anhydride (as well as trifluoroacetic, maleic, and dichloromaleic anhydrides) gave well-resolved esr spectra of tetramethylhydrazine (**2**) radical cation.[2] In less polar solvents, such as chloroform and benzene, the esr spectrum of $\mathbf{2}\cdot^+$ is preceded by an ill-resolved series of multiplets, which have the proper gross splitting and *g* factor to be $\mathbf{1a}\cdot^+$, presumably broadened by exchange with neutral **1a**. Over a period of 2 to 3 hr the broad lines of $\mathbf{1a}\cdot^+$ gradually fade and the resolved spectrum of $\mathbf{2}\cdot^+$ becomes more intense. Behavior of the esr spectra is the same if acetic or formic acid is used to decompose **1a**. In carbon tetrachloride a different radical ("A") is formed rapidly after mixing, persists for 10–20 min at room temperature (using carbon tetrachloride solutions 0.2–1.0 *M* in **1a** and 0.2–2.0 *M* in acid or anhydride), and disappears being replaced by the $\mathbf{1a}\cdot^+$–$\mathbf{2}\cdot^+$ mixture observed in other solvents. Indistinguishable A spectra (see Figure 1) were observed using carbon tetrachloride or bromotrichloromethane, even in mixture with chloroform or benzene (about 1:1), but no A was ever observed without these compounds being present. A consists of a fairly well-resolved 27-line pattern, and is easily analyzed for $a_N = 12.6$ G, $a_{3H} = 11.75$G, $a_{2H} = 6.3$G; the *g* factor (by comparison with Fremy's salt) is 2.0059 ± 0.0002. A was easier to observe if the solutions were not degassed but was also seen with continuous argon purging. When the solvent for **1a**–acetic acid mixtures was 0.84 *M* carbon tetrabromide in benzene, a different radical preceded the observation of the $\mathbf{1a}\cdot^+$–**2** mixture; it consisted of 23 rather broad lines we could not resolve further. If a radical had $2a_{2H} = a_N = a_{3H}$, a 13-line pattern with intensities (outside to middle, rounded off) of 7:14:36:57:79:100:100 would result. If a_{2H} were actually slightly different from one-half the other two, the underlined lines would be broadened, and observed less intense. If $a_N \neq a_{3H}$, all the lines but the outer two on each side would be broadened. The observed spectrum with carbon tetrabromide had intensities of about 11:22:35:73:75:100:88 (a ±5% variation for any of these numbers might be observed in a given scan). We believe the spectrum observed indicates none of the above equalities is exact: the spectrum is consistent with $a_{2H} \cong 6.2 \pm 0.1$ G, $a_N \cong a_{3H} \cong 12.0 \pm 0.2$ G. This species must be quite similar to that from carbon tetrachloride and bromotrichloromethane. With α,α,α-trichlorotoluene as a solvent a very complicated spectrum precedes the $\mathbf{1a}\cdot^+$–$\mathbf{2}\cdot^+$ mixture, which would be reasonable if phenyl splittings were superimposed on the others. These results indicate that A incorporates a dimethylamino group and the radical left behind after abstraction of a

---

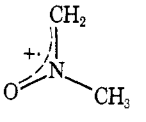
[5] C. F. Koelsch, *J. Am. Chem. Soc.*, **79**, 4439 (1957); **54**, 4744 (1932).

[6] S. F. Nelsen and P. D. Bartlett, *ibid.*, **88**, 143 (1966).

halogen from these materials. The simplest hypothesis would seem to be the radical **3**, which could exist in the cyclic form **4**. It would be difficult to explain the equality of the 6.3 G splitting protons in the open-chain form. The 2H splitting being only half the methyl splitting could also find explanation in the decreased hyperconjunction caused by the aziridine ring. The nitroxide cation **5** is ruled out principally because different though similar species were obtained with $CXCl_3$ and CBr_4, but also because stable nitroxides do not give radical cations with splittings compatible with A.[7]



3 **4**



5

Nmr studies of the **1a**–acid or –anhydride system during the time it was decomposing proved particularly intriguing. A typical series of spectra, successively scanned between about δ 5 and 2 ("250-sec" scan rate), are shown in Figure 2. In this run, sufficient **1a** to make a 1.1 *M* solution was injected into 1.9 *M* acetic anhydride in carbon tetrachloride to initiate the reaction. The first thing to happen was broadening of the **1a** methyl peak until it had virtually disappeared, although the acetic anhydride methyl peak remained relatively sharp (up to the 3-min spectrum). Then from 4′ through the 8.5-min spectrum, a negative peak appears, reaches a maximum, and disappears again. The changes from 12 to 26 min are trivial ones, just due to the cooling of the contents of the tube, which heats up to above 50° during the decomposition, so that the dimethylacetamide responsible for the larger two peaks downfield from acetic anhydride is above its coalescence temperature in the 12-min spectrum, but later cools. The initial broadening of **1a** absorption is quite reasonable, since an oxidizing agent is definitely formed in the reaction, and **1a** is easily oxidized ($E_{1/2}{}^0 \cong 0.42$ *vs.* sce for **1a** in acetonitrile). Electron exchange between **1a** and $\mathbf{1a}\cdot^+$ would give the specific broadening shown; furthermore, $\mathbf{1a}\cdot^+$ could be observed by esr at intermediate times under these conditions (much later than the nmr broadening sets in, however). Nmr emission (and enhanced absorption) in systems containing reacting radicals has been observed previously[8] and termed chemically induced dynamic nuclear polarization (CIDNP).[8] The polarization results from the proton spin polarization of a radical being at least partially maintained in formation of a diamagnetic product. The sign of the polarization is not really understood, and compounds which are not obviously involved in the reaction can alter it.[8b] Our results are qualitatively like those of Bargon, Fischer, and Johnsen,[8a] who observed nmr emission for the benzene singlet in decomposing benzoyl peroxide–cyclohexane mixtures. No peak remains at the position of the negative peak after it disappears, however; it is likely that the emitter is unstable to the reaction conditions. We observe a similar negative peak in all those, and only those, solvents which give the transient esr spectrum (A type). The shifts of these negative peaks are summarized in Table I. The accuracy of measuring δ_{neg} is not better than ±0.5 Hz. Because of the high concentrations of each compound, the four-cycle shift difference for the negative peak between acetic acid and anhydride induced peaks may not mean a different species is emitting. Benzene clearly lowers δ_{neg} appreciably, and no real difference can be observed between the CCl_4, $CBrCl_3$, and CBr_4 peaks; even the emitting species from $PhCCl_3$ might have a quite similar structure. The spreading of the **1a** peak was observed in all solvents studied, but no negative peaks were ever observed in cyclohexane, benzene, chloroform, acetone-d_6, or acetonitrile-d_3. Dimethylacetamide, dimethylamine, and N-chlorodimethylamine were ruled out as the emitter on the basis of chemical shift. Both the negative nmr peak and the esr spectrum of the A type appear early in the reaction. It is not likely that the esr spectrum of a radical precursor of a diamagnetic species showing the CIDNP phenomenon would be observed under our conditions; the reaction leading to destruction of the radical must presumably be very fast to preserve spin polarization. Yet some connection between the negative peak and A is implied. The coupling product of

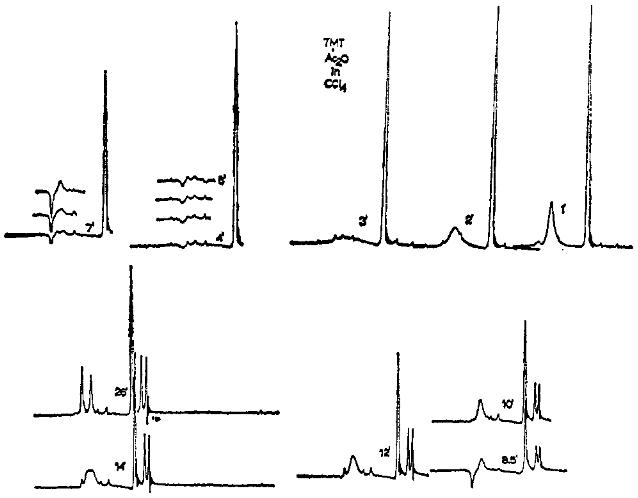


Figure 2. Successive nmr scans of a decomposing mixture of **1a** and acetic anhydride in carbon tetrachloride. The time after mixing is indicated for each scan.

Table I. Chemical Shifts of Negative Nmr Peaks

Initial concn of mixture	[**1a**], *M*	"Acid" (*M*)	δ_{neg},[a] Hz
CCl_4	1.2	HOAc (0.9–1.8)	65
CCl_4	1.1	Ac_2O (0.93–1.9)	69
$CBrCl_3$	0.6	HOAc (1.6)	65
$CBrCl_3$	0.6	Ac_2O (1.0)	69
$PhCCl_3$	1.6	HOAc (1.7)	54–55
0.8 *M* CCl_4 in benzene	1.2	HOAc (1.4)	45–46
4.5 *M* CCl_4 in benzene	1.2	HOAc (1.4)	49–50
1.3 *M* $CBrCl_3$ in benzene	1.2	HOAc (1.4)	44–45
1.3 *M* CBr_4 in benzene	0.6	HOAc (0.6)	44

[a] From AcOH.

---

[7] M. Iwamura, unpublished work form these laboratories.

[8] (a) J. Bargon, H. Fischer, and U. Johnsen, *Z. Naturforschg.*, **22a**, 1551 (1967); (b) H. R. Ward and R. G. Lawler, *J. Am. Chem. Soc.*, **89**, 5518 (1967); **91**, 746 (1969) (with R. A. Cooper); (c) R. A. Lepley, *ibid.*, **90**, 2710 (1968): **91**, 749 (1969); **91**, 748 (1969) (with R. L. Landau).

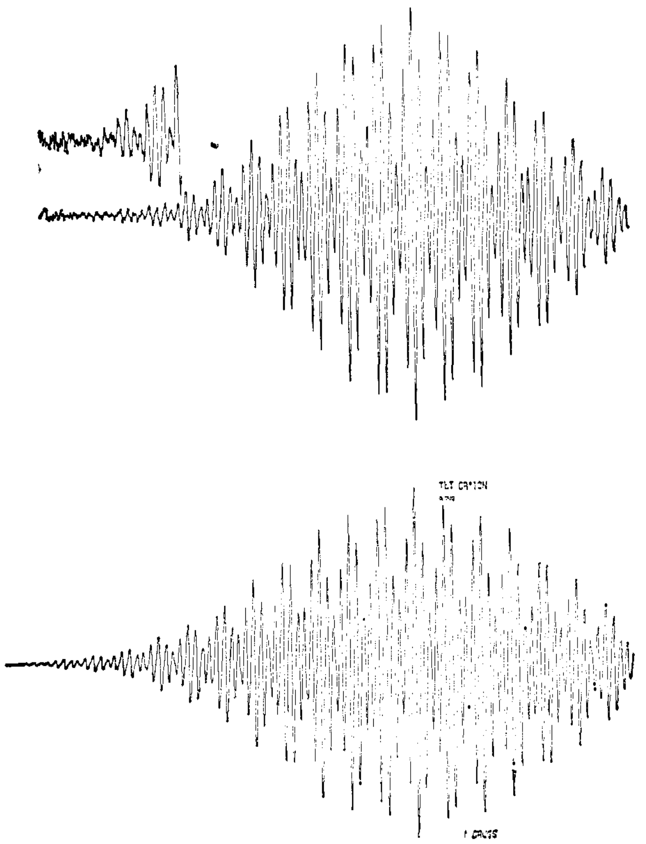


Figure 3. Esr spectrum of electrolytically generated **1b**$\cdot^+$ The lower spectrum is calculated using the splittings quoted in the text and a line width of 350 mG.

$CCl_3\cdot$ and $Me_2N\cdot$ exists in ionic form, as dichloromethylenedimethylammonium chloride (**6**), and as

$$(CH_3)_2\overset{+}{N}{=}CCl_2\overset{-}{Cl}$$

6

such is virtually insoluble in our solvents. A saturated chloroform solution shows the N-methyl nmr peak about 65 Hz downfield from added acetic acid (which reacts slowly with the salt). This is certainly less than conclusive evidence for **6** being the emitter, but it is our best candidate. Furthermore, hydrogen abstraction from **6** leads to **3** (or **4**), a structure compatable with the esr spectrum observed for A.

It would clearly be valuable to know how the spectra for A and δ_{neg} change with differing substitution. Unfortunately, our attempts in this direction have been frustrated by the fact that no radical corresponding to A and no negative nmr peaks have ever been observed from homologs of **1a** with anhydrides and acids. Using either acid or anhydride alone, little reaction takes place. At about 2 *M* initial concentration of each, the **1b** peaks broaden, and heat and nitrogen are evolved. Similarly, the esr behavior was quite different with **1b** than **1a**. With either 2 *M* acetic anhydride or 2 *M* acetic acid in a variety of solvents no radicals were observed, although intense color (purple to brown) developed slowly. The intense color was not observed with **1a**, but has been found with all higher homologs studied. A strong spectrum did result from mixing **1b** with acetic anhydride and acetic acid (1 *M* or more in each), or with dichloromaleic anhydride or trifluoroacetic anhydride; the spectrum was similar in DMF, carbon tetrachloride, bromotrichloromethane, and benzene. At elevated temperature the radical was much less stable, but the resolution was better. The same radical was obtained by electrolytic oxidation of **1b** at room temperature in acetonitrile, but the resolution is comparable to that of the 55° spectrum generated using trifluoroacetic anhydride in DMF. The spectrum is of tetraethyltetrazene cation, and shows $a_{4H} = 15.25$, $a_{2N} = 10.60$, $a_{4H} = 4.68$, $a_{2N} = 1.25$ G (Figure 3). The much greater inequality of methylene splittings of **1b**$\cdot^+$ compared to **1a**$\cdot^{+9}$ is a striking example of conformational selectivity. Inspection of a model will show that the ethyl groups *syn* to the N=N bond sterically should not have their methyls in the nitrogen plane, which makes $a_{CH_2}(syn)$ small. The best conformation for the *anti* ethyl groups is with their methyls in the plane, causing the methylene protons to be more nearly aligned with the p orbitals than the free rotation value, and give $a_{CH_2}(anti)$ a larger value than a_{CH_3} of **1a**$\cdot^+$. If the rotation was slow on the esr time scale, there would be four instead of only two kinds of methylene protons. At low temperatures the methylene splittings broaden more rapidly than the nitrogen splittings, but we could not get low enough temperature to give a resolved "frozen" spectrum (at −90° in $(CF_3CO)_2O$–DMF broad peaks due to the nitrogen splittings and almost complete loss of observable methylene peaks were seen). With **1c** only very broadened spectra of **1c**$\cdot^+$ were observed upon treatment with acids or anhydrides, or electrolytic oxidation.

We find the large difference in reactivity toward acids and anhydrides of **1a** from its higher homologs surprising, but presume it is mainly caused by steric effects. The question of the origin of the dimethylamino radicals is still unanswered; all of our data is compatible with either initial homolytic cleavage, or heterolytic bond cleavage followed by electron transfer. That dimethylamino radicals are formed is, we feel, amply demonstrated by observation of radicals derived both from its dimerization product and from combination with solvent-derived radicals.

Experimental Section

Materials. The tetrazenes **1a, 1b,** and **1c** were prepared by mercuric oxide oxidation[10] of the 1,1-dialkylhydrazine.[11] Commercial solvents and reagents were employed. N-Chlorodimethylamine[12] was prepared by treatment of dimethylamine with N-chlorosuccinimide in ether;[13] dichloromethylenedimethylimmonium chloride was commercial material (Aldrich).

Esr experiments were performed on a Varian E.3 spectrometer. Spectra were synthesized on a CDC 3600 computer to check the splittings assigned. The *g* factor of A was estimated using a capillary tube of Fremy's salt in aqueous sodium bicarbonate as reference compound inserted inside a 1-mm thick flat cell containing the sample. The concentrations reported in the text were only determined by syringing in the various components and are not good to better than 10%.

Nmr experiments employed a Varian A-60A instrument.

---

(9) $a_{6H} = 11.72$, $a_{6H} = 10.45$, $a_{2N} = 10.93$, $a_{2N} = 1.07$ G: W. M. Tolles, D. W. Moore, and W. E. Thun, *J. Am. Chem. Soc.*, **88**, 3476 (1966).

(10) W. E. Bull, J. A. Seaton, and L. F. Avdrieth, *ibid.*, **80**, 2516 (1958).

(11) B. Ioffe, *J. Gen. Chem. USSR*, **28**, 1354 (1958).

(12) G. H. Coleman, *J. Am. Chem. Soc.*, **55**, 3001 (1933).

(13) M. F. Grunden and B. E. Reynolds, *J. Chem. Soc.*, 2445 (1964).

Nitrogen evolution was measured by displacement of *n*-butyl phthalate in a 100-ml gas buret. In the abortive Koelsch radical work, a pressure transducer was used,[14] and a Beckman DU was used to measure the optical density. A Radiometer Model 26 pH meter was employed; measurements were in water using 1.000 *M* hydrochloric acid; back-titration with base gave the same shaped curve. A Sargent 15 polarograph with ir compensator and rotating platinum electrode was used to measure the oxidation potential of **1a**.

Acknowledgment. We wish to thank the National Science Foundation and the Wisconsin Alumni Research Foundation for generous support of this work. S. F. N. thanks the Sloan Foundation for general support. We thank Mr. M. Micke for measuring some of the nitrogen evolution kinetics runs.

---

(14) The apparatus was a simplified version of that of L. R. Mahoney, R. W. Beyma, A. Warnicle, and C. H. Rust, *Anal. Chem.*, **36**, 2516 (1964).

Carbethoxynitrene. The Stereochemistry of the Intermolecular Singlet Carbon–Hydrogen Insertion

Joseph M. Simson[1] and Walter Lwowski[2]

Contribution from the Research Center, New Mexico State University,
Las Cruces, New Mexico 88001, and the Department of Chemistry,
Yale University, New Haven, Connecticut 06520. *Received March 10, 1969*

Abstract: Carbethoxynitrene inserts into the C–H bonds of 3-methylhexane with a selectivity that does not change over a concentration range from 100 to 1.2 mol % of the hydrocarbon. The selectivity is also unaffected by the presence of a triplet nitrene trap, α-methylstyrene, and by using a heavy atom solvent, dibromomethane, instead of dichloromethane. The insertion into the tertiary C–H bond of optically active 3-methylhexane proceeds with 100% retention of configuration, under all reaction conditions, and irrespective of the path by which the nitrene is generated. It is concluded that only the singlet state of carbethoxynitrene participates to a measurable extent in the insertion reaction.

Carbethoxynitrene,[3] EtOOCN, inserts into C–H bonds to form N-substituted carbamates, EtOOCNHR. The order of reactivities of various types of C–H bonds has been studied,[4–8] and it has been found that the C–H bonds of saturated, unstrained hydrocarbons are reactive in the order tertiary > secondary > primary. With 2-methylbutane, for example, the relative reactivities for tertiary, secondary, and primary C–H bonds are about 30:10:1, respectively. Bridgehead C–H bonds react readily.[9,10]

It has been shown that carbethoxynitrene can exist, in solution, in both the singlet and the triplet states, and that both these species can undergo a number of intermolecular reactions.[11–16] For example, both the singlet and the triplet nitrene give aziridines with C=C double bonds, albeit with different stereochemistry,[11–13] but only the singlet carbethoxynitrene expands the benzene ring to give N-carbethoxyazepine.[17] The rate with which singlet carbethoxynitrene decays to the triplet (ground) state is comparable to the rate of intermolecular reactions of the singlet.[11–13] Generating the singlet, one can thus adjust the fraction of triplet in the nitrene population by adjusting the concentration of the reactant. Alternatively, one can reduce this fraction by using triplet carbethoxynitrene traps, such as α-methylstyrene.[12,13]

The reaction of carbethoxynitrene with cyclohexene gives more insertion products (into the C–H bonds in the 3 and 4 positions) as more of the nitrene is in the singlet state. This is true both for the absolute yields of insertion products and for the fraction of insertion products in the product mixture (of aziridine and insertion products).[18] Thus, it appears that singlet carbethoxynitrene inserts much more efficiently than the triplet. A question remains: Are the rates of C–H insertion (into unactivated C–H bonds) for singlet and triplet carbethoxynitrene different by just an order of magnitude, or is the triplet slower by a large factor, perhaps

---

(1) National Institutes of Health Predoctoral Fellow, 1963–1966.

(2) To whom correspondence should be addressed: Chemistry Department, New Mexico State University, Box 3-C, Las Cruces, N. M. 88001. Part of this work was presented at the 153rd National Meeting of the American Chemical Society, Miami Beach, Fla., April 1967, Abstract O-163.

(3) W. Lwowski and T. W. Mattingly, Jr., *Tetrahedron Lett.*, 277 (1962); W. Lwowski, T. J. Maricich, and T. W. Mattingly, Jr., *J. Amer. Chem. Soc.*, **85**, 1200 (1963).

(4) W. Lwowski and T. J. Maricich, *ibid.*, **86**, 3164 (1964).

(5) M. F. Sloan, T. J. Prosser, N. R. Newburg, and D. S. Breslow, *Tetrahedron Lett.*, 2945 (1964).

(6) W. Lwowski and T. W. Mattingly, *J. Amer. Chem. Soc.*, **87**, 1947 (1965).

(7) W. Lwowski and T. J. Maricich, *ibid.*, **87**, 3630 (1965).

(8) D. S. Breslow, T. J. Prosser, A. F. Marcantonio, and C. A. Genge, *ibid.*, **89**, 2384 (1967).

(9) J. Meinwald and D. H. Aue, *Tetrahedron Lett.*, 2317 (1967).

(10) D. S. Breslow, E. I. Edwards, R. Leone, and P. von R. Schleyer, *J. Amer. Chem. Soc.*, **90**, 7097 (1968).

(11) W. Lwowski and J. S. McConaghy, *ibid.*, **87**, 5490 (1965).

(12) J. S. McConaghy and W. Lwowski, *ibid.*, **89**, 2357 (1967).

(13) J. S. McConaghy and W. Lwowski, *ibid.*, **89**, 4450 (1967).

(14) A. Mishra, S. N. Rice, and W. Lwowski, *J. Org. Chem.* **33**, 481 (1968).

(15) A. L. J. Beckwith and J. W. Redmond, *Aust. J. Chem.* **19**, 1859 (1966).

(16) A. L. J. Beckwith and J. W. Redmond, *Chem. Commun.*, 165 (1967).

(17) W. Lwowski and R. L. Johnson, *Tetrahedron Lett.*, 891 (1967).

(18) W. Lwowski and F. P. Woerner, *J. Amer. Chem. Soc.*, **87**, 5491 (1965).