THE UNUSUAL STABILITY OF THE N'-TOSYLOXYDIIMIDE-N-OXIDES

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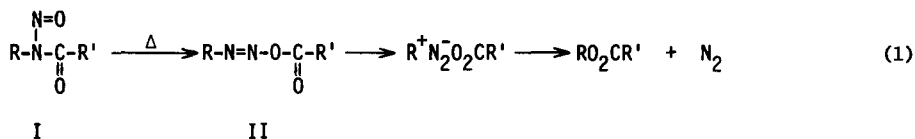
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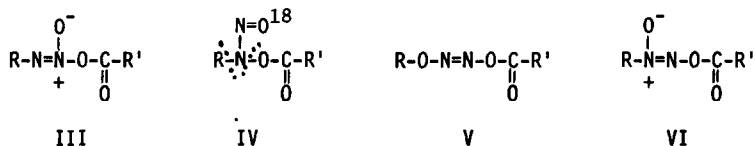California Institute of Technology, Pasadena, California 91109

Intermediates with part structures $-N=N-O$, $-N=N-O-$, $-\overset{\overset{\textstyle O}{\|}}{N}-N=O$, are involved in several deamination reactions (1). It is now apparent that the stabilities and modes of decomposition of these intermediates are strongly dependent on the manner of attachment of the organic groups to the N_2 and N_2O fragments.
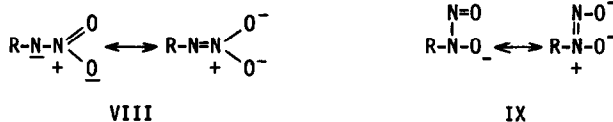
N-Nitrosoamides (I) decompose to yield esters and nitrogen *via* the diazoester intermediate II, which is unstable and not observable directly. Three analogs (III-V) can be prepared, which yield

$$R-\overset{\overset{\textstyle N=O}{|}}{\underset{\underset{\textstyle O}{\|}}{N}}-C-R' \xrightarrow{\Delta} R-N=N-O-\overset{O}{\overset{\|}{C}}-R' \longrightarrow R^+N_2^-O_2CR' \longrightarrow RO_2CR' + N_2 \qquad (1)$$

$$\text{I} \qquad\qquad\qquad \text{II}$$

nitrous oxide and the corresponding esters. Species III is formed in the thermal decomposition of

$$\underset{\text{III}}{R-\overset{\overset{\textstyle O^-}{|}}{N}\overset{+}{=}N-O-\overset{O}{\overset{\|}{C}}-R'} \qquad \underset{\text{IV}}{R-\overset{\overset{\textstyle N=O^{18}}{|}}{N}-O-\overset{O}{\overset{\|}{C}}-R'} \qquad \underset{\text{V}}{R-O-N=N-O-\overset{O}{\overset{\|}{C}}-R'} \qquad \underset{\text{VI}}{R-\overset{\overset{\textstyle O^-}{|}}{N}\overset{+}{=}N-O-\overset{O}{\overset{\|}{C}}-R'}$$
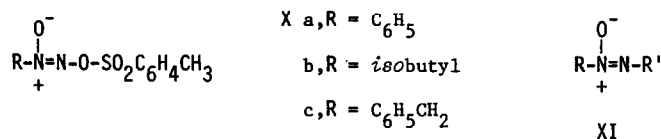
the N-nitroamides (VII; nitro analogs of I) (1d) and also in the acylation of salts of the N-nitroamines (VIII) (1c). Species IV is prepared by the nitrosation of $RNHOCOR'$, and V is formed on rearrangement of $RON(NO)COR'$ (2).

$$R-\underline{N}-N\overset{O}{\underset{\underset{+}{O}}{<}} \longleftrightarrow R-N=N\overset{O^-}{\underset{\underset{+}{O^-}}{<}}$$

VIII

$$R-N-O\overset{N=O}{\underset{-}{}} \longleftrightarrow R-N-O^-\overset{N-O^-}{\underset{+}{}}$$

IX

Intermediate III (R-1-norbornyl) was found to have a half-life of less than a few minutes at -65° (3), and we now report the same instability for IV at -50° (4,5). Species V was given a half-life of *ca.* 100 min at 32° (2). Species VI could, in principal, be formed from the acylation of salts of nitrosohydroxylamines (IX), but the acylation yields as the only isolable compounds, nitrous oxide and the corresponding ester (*via* either IV or VI).

Replacement of the acyl groups of I and VII by the toluenesulfonyl group led to an analogous rapid formation of sulfonate esters. Further, the reaction of toluenesulfonyl chloride with salt VIII similarly yielded only the esters (6), and the analogous reaction with benzenediazotate salts led to the ionic compound, benzene diazonium toluenesulfonate.

In view of the instabilities of the intermediates in the reactions just discussed, it was surprising that the reaction of IX with toluenesulfonyl chloride was reported to give high yields of stable, crystalline compounds with structure X (R=alkyl or aryl) (7). The proof of structure rested principally on the *nmr* spectra (7,8) and on the reaction with Grignard reagents (R=aryl groups) to give azoxy compounds of structure XI (7). In view of possible ambiguities in the nmr

$$R-\overset{O^-}{\underset{+}{N}}=N-O-SO_2C_6H_4CH_3$$

X a,R = C_6H_5

b,R = *iso*butyl

c,R = $C_6H_5CH_2$

$$R-\overset{O^-}{\underset{+}{N}}=N-R'$$

XI

shifts (9) and the possibility of forming XI from isomers of X, the structure of X_a was determined by X-ray diffraction techniques. The structure of Stevens (X) was found, in fact, to be correct (*vide infra*). The determination showed, further, that the oxygens attached to nitrogen were *cis* oriented. We have prepared aliphatic analogs X_b and X_c (7), and by a comparison of the infrared, ultraviolet, and *nmr* spectra with those of X_a and with model compounds, feel that structures X_b and X_c are correct for the aliphatic analogs.
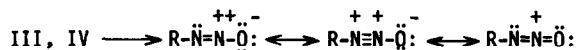
An interesting question is thus posed: why is X_c, with the potential formation of a tosylate leaving group and a benzyl carbonium ion, so stable (half-life of 27 hours at 61° in chloroform) - relative to III (R=1-norbornyl) which decomposes at -65° with the formation of a strained

bridgehead carbonium ion and a carboxylate leaving group? One factor which may account for this stability is the resonance stabilization of reaction intermediates; ionization of X leads to a cation for which no resonance contributor can be drawn with a full octet about each atom:
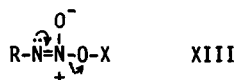
$$X \longrightarrow R-\ddot{N}=\ddot{N} \longleftrightarrow R-\overset{..}{N}-\ddot{N}:$$
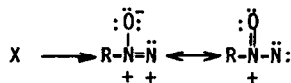
XII

-no such difficulty occurs with related ions from II, III, IV, and V:

$$III, IV \longrightarrow R-\overset{++}{\ddot{N}}=N-\overset{-}{\underset{..}{O}}: \longleftrightarrow R-\overset{++}{N}\equiv N-\overset{-}{\underset{..}{O}}: \longleftrightarrow R-\overset{+}{\ddot{N}}=N=\ddot{O}:$$

XIII

An alternative view is that an electron pair on the nitrogen *beta* to the departing group of III and IV, etc. (but not of X) is available for participation in the ionization. A similar argument

$$R-\overset{O^-}{\underset{+}{\overset{|}{N}=N-O-X}} \qquad XIII$$

is often used to account for the high S_N1 reactivity of α-haloethers (10).

The decomposition of X_b in chloroform yields isobutyl toluenesulfonate, N_2O, isobutylene, and toluenesulfonic acid; no isobutane or hexachloroethane are formed suggesting that an ionic reaction analogous to the last steps of equation 1 is occurring. Further, compound X_c decomposes with approximately four times the rate of X_b. Compounds of structure X thus serve as a bridge for the fields of deamination and solvolysis, since on decomposition they yield an inert molecule (N_2O) between the carbonium and negative ions (as in deamination) (1d), and the carbonium ion formation step is amenable to kinetic analysis (as in solvolysis) (10,11).

Structure Determination

Crystals of X_a suitable for X-ray analysis were grown from ethyl acetate by slow evaporation. The resulting large, plate-like crystals were cut to a size of 0.5 x 0.5 x 0.2 mm and surveyed using a precession camera. The survey indicated the crystals were triclinic (no systematic absences) (12). The density, measured by flotation, was 1.40 g/cm^3; the density calculated on the basis of two molecules per unit cell was 1.385 g/cm^3.

Cell dimensions were determined on the General Electric-Datex diffractometer, and the least-squares refined dimensions are as follows:

$$a = 9.193 \pm .002 \text{ Å} \qquad \alpha = 121.82° \pm .07°$$
$$b = 10.472 \pm .002 \text{ Å} \qquad \beta = 115.38° \pm .07°$$
$$c = 9.579 \pm .002 \text{ Å} \qquad \gamma = 83.32° \pm .07°$$

One angstrom intensity data (maximum $\sin\Theta/\lambda = 0.5°$) were collected on a General Electric-Datex diffractometer using nickel filtered copper radiation. A Θ-2Θ scan technique was employed, background was counted for 10 seconds at each end of the scan, and the scan rate was 2° per minute in 2Θ. A single check reflection (102) that was monitored every 30 reflections showed no decay and was well within counter statistics.

The diffractometer output was processed using subprograms of the CRYRM crystallographic computer system (13). The processing included corrections for background and for Lorentz and polarization effects. The data was placed on an absolute scale by means of Wilson (14) statistics.

The crystal was tentatively assigned to space group P $\bar{1}$ on the basis of a Howells, Phillips, Rogers plot (15) and its density measurement. The final structural result confirmed the presence of a center of symmetry.

A trial structure was derived from the collected intensity data and phase information provided by statistical phasing. A set of phases was obtained by a reiterative application of the Sayre's equation (16). This process was conveniently accomplished by the application of a computer program written by R. E. Long (17). Input to the program consisted of 197 reflections with normalized structure factors, $|E|$, greater than or equal to 1.5. A starting set of 7 signs was used to phase the remaining reflections. Among the 16 solutions, the set of signs with the highest internal consistency, other than that with all signs the same, was used in the preparation of an E map. This map clearly revealed the entire trial structure.

Full matrix least-squares refinement of coordinates, anisotropic temperature factors, and scale factor reduced the R-index to 7.9%. A difference Fourier indicated no misplaced or missing major atoms and was used to locate the hydrogen atoms. The addition of the hydrogens to the structure factor calculation (hydrogen parameters were not refined) and added refinement of parameters including secondary extinction factor (18), reduced the R-index to its final value of 5.1%.

The structure obtained was stereographically plotted (Fig. 1) using the ORTEP program of

C. K. Johnson (19). The standard deviations in the coordinates, derived from the residuals and

the diagonal elements of the inverse matrix of the final least-squares cycle, correspond to

positional uncertainties of about .001 Å for the sulfur atom, about .009 Å for the carbon atoms,

and .003 Å for the nitrogen and oxygen atoms. The uncertainties for the S, C, N, O bonds are

about .01 Å. Uncertainties in the bond angles involving the S, C, N, O atoms are approximately

0.5°. Since the hydrogen positions were not refined, no error estimates will be made for

distances and angles involving these atoms.

Due to limitations of space, further pertinent X-ray data cannot be presented here. F-tables,

atomic coordinates, and bond lengths and angles may be obtained from the author (Bordner) (20).
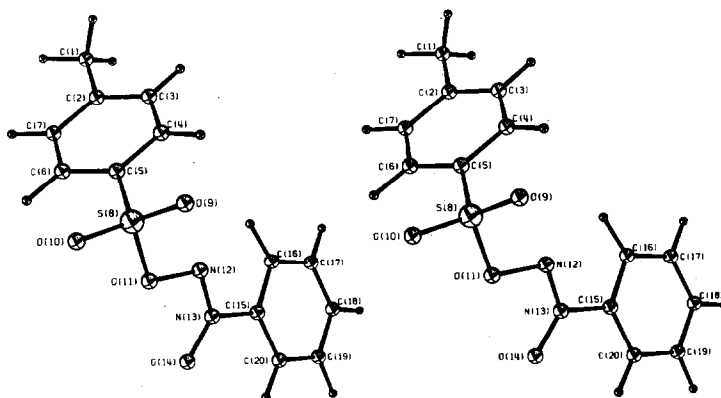

Figure 1

REFERENCES

1. (a) E. H. White, *J. Amer. Chem. Soc.*, 77, 6011 (1955); (b) E. H. White and C. A. Aufdermarsh,
    Jr., *ibid.*, 83, 1179 (1961); (c) E. H. White and D. W. Grisley, Jr., *ibid.*, 83, 1191 (1961);
    (d) E. H. White and D. J. Woodcock, Chapter 8, "The Chemistry of the Amino Group," S. Patai,
    Ed., John Wiley and Sons, Inc., New York, 1968.

2. T. Koenig and M. Deinzer, *J. Amer. Chem. Soc.*, 88, 4518 (1966).

3. E. H. White, H. P. Tiwari, and M. J. Todd, *J. Amer. Chem. Soc.*, 90, 4734 (1968).

4. Isotopic labelling shows that the decomposition occurs as indicated in IV.

5. A similar decomposition of nitrosodibenzoylhydroxylamine has been reported recently by
    Koenig *et al.*, (*J. Org. Chem.*, **34**, 952 (1969)). See also ref. 1c.

6. No detectible X is formed, indicating that oxygen migration from nitrogen to nitrogen is
    not occurring.

7. T. E. Stevens, *J. Org. Chem.*, **29**, 311 (1964); **32**, 1641 (1967); E. A. Dorko and T. E.
    Stevens, *ibid.*, **31**, 871 (1966).

8. J. P. Freeman, *ibid.*, **28**, 2508 (1963).

9. F. D. Greene and S. S. Hecht, *Tetrahedron Letters*, 575 (1969).

10. A. Streitwieser, Jr., "Solvolytic Displacement Reactions," McGraw-Hill Book Company, Inc.,
    New York, 1962; E. R. Thornton, "Solvolysis Mechanisms," The Ronald Press Company, New
    York, 1964.

11. It is possible, however, that the decomposition of X may proceed *via* acylmigration and the
    nitrosohydroxylamine structure (IV).

12. (a) This result was confirmed by a Delaunay (12b) reduction which revealed no higher
    symmetry. The cell dimensions reported are not the reduced cell dimensions but were used
    for convenience. (b) Delaunay, *Zeit. f. Krist.*, **84**, 132 (1933).

13. D. J. Duchamp, Amer. Cryst. Assoc. Meeting, Bozeman, Montana, paper B-14, P. 29 (1964).

14. A. J. C. Wilson, *Nature*, **150**, 152 (1942).

15. E. R. Howells, D. C. Phillips, D. Rogers, *Acta Cryst.*, **3**, 210 (1950).

16. D. Sayre, *Acta Cryst.*, **5**, 60 (1952).

17. R. E. Long, Doctoral Dissertation, University of California, Los Angeles (1965).

18. A. C. Larson, *Acta Cryst.*, **23**, 664 (1967).

19. C. K. Johnson, ORTEP, ORNL-3794, Oak Ridge National Laboratories, Oak Ridge, Tennessee,
    U.S.A. (1965).

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    27607.