

Alkaline Decomposition of Nitrosohydroxylamine Derivatives<sup>1</sup>

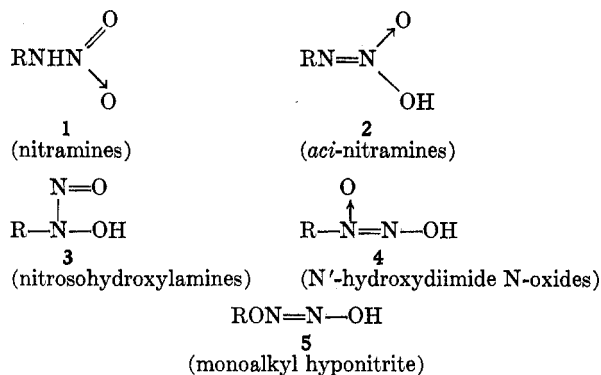
JEREMIAH P. FREEMAN AND LAWRENCE D. LILLWITZ

Department of Chemistry, University of Notre Dame, Notre Dame, Indiana 46556

Received February 10, 1970

Nitrosohydroxylamine tosylates,  $R_2CHN(O)NOSO_2C_7H_7$ , are decomposed by potassium *t*-butoxide to the corresponding aldehyde or ketone. They also decompose thermally to olefins. Attempts to prepare analogous acyl derivatives resulted in cleavage to the corresponding esters,  $R_2CHOC(O)R'$ , and nitrous oxide. Esters also were obtained from nitrosation of *O*-acyl- or *O*-sulfonylhydroxylamines.

There are five constitutional isomers of compounds with the molecular formula  $RN_2O_2H$ .

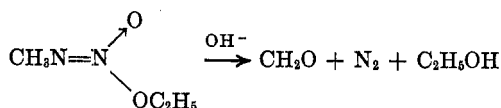


Alkyl derivatives of all these isomers are also known.<sup>2</sup> The highlights of the chemistry of nitramines and their *aci* derivatives have been reviewed,<sup>3</sup> but considerably less is known about nitrosohydroxylamines and their tautomers.

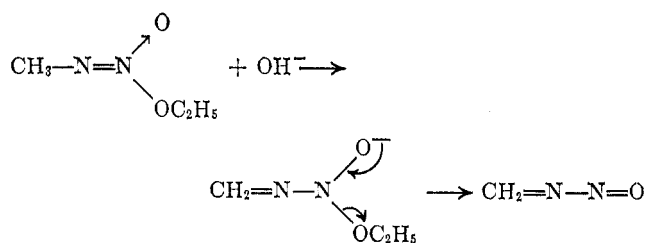
Recently it was found that nitrosohydroxylamines could be converted to the tosyl derivatives of 4.<sup>4</sup> The decomposition of *N*-alkyl-*N'*-tosyloxydiimide *N*-oxides (6) by Grignard reagents<sup>4</sup> prompted an investigation of the action of bases on these compounds and also the *N'*-alkoxy derivatives 7.



For comparison with the present results it should be recalled that alkyl derivatives of 1, secondary nitramines, undergo elimination of nitrous acid when treated with base to yield imines which are hydrolyzed to a mixture of primary amine and aldehyde or ketone.<sup>5</sup> Alkyl "esters" of *aci*-nitramines (2) undergo an elimination reaction in base to produce aldehydes, nitrogen, and alcohol.<sup>6</sup> A mechanism for this somewhat unusual



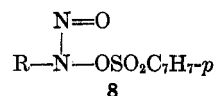
reaction<sup>7</sup> was not postulated, but it seems reasonable that nitrosimines, compounds known<sup>10</sup> to decompose to aldehydes and nitrogen, are involved.



The elimination of the elements of carboxylic acid from a postulated *O*-acyl derivative of 2 to form a nitrosimine has been suggested,<sup>11</sup> although that intermediate was postulated to yield esters in one case<sup>11a</sup> and carbonyl compounds in another.<sup>11b</sup> Some differences between the chemistry of postulated nitramine derivatives and that observed in this investigation will be pointed out in the discussion.

**Structure of Starting Materials.**—The structure of the alkylation products of nitrosohydroxylamines has been a subject of some controversy, but it is assumed in this investigation that structure 7 has been established by recent nmr<sup>12</sup> and chemical<sup>13</sup> studies.

The structure of the tosylates 6 had not been established rigorously but was inferred from the structure of the azoxy compounds obtained from their reaction with Grignard reagents.<sup>4</sup> The ultraviolet spectra of the *N*-phenyl ( $\lambda_{\text{max}}$  222 m $\mu$ ,  $\epsilon_{\text{max}}$  32,200;  $\lambda_{\text{max}}$  251 m $\mu$ ,  $\epsilon_{\text{max}}$  20,100) and the *N*-*p*-chlorophenyl ( $\lambda_{\text{max}}$  223 m $\mu$ ,  $\epsilon_{\text{max}}$  25,900;  $\lambda_{\text{max}}$  262 m $\mu$ ,  $\epsilon_{\text{max}}$  17,400) derivatives are compatible with structure 6. The alternative structure 8 (tosyl derivative of 3) would not be expected to show the long-wavelength band. In addition an attempt to prepare 8, R = CH<sub>3</sub>, by the nitrosation of *O*-tosyl-*N*-



(1) This research was supported under Grant No. 5256 from the National Science Foundation and is based upon the Ph.D. Thesis of L. D. Lillwitz.

(2) Hyponitrous acid derivatives, 5, are not of interest in this investigation and will not be discussed further. For leading references to their chemistry, see T. Koenig and M. Deniger, *J. Amer. Chem. Soc.*, **90**, 7014 (1968).

(3) (a) A. Lamberton, *Quart. Rev. Chem. Soc.*, **5**, 75 (1951); (b) P. A. S. Smith, "Open-Chain Nitrogen Compounds," Vol. II, W. A. Benjamin, New York, N. Y., 1966, p 490.

(4) T. E. Stevens, *J. Org. Chem.*, **29**, 311 (1964).

(5) W. H. Jones, *Science*, **118**, 387 (1953).

(6) A. H. Lamberton and G. Newton, *J. Chem. Soc.*, 1791 (1961).

(7) It might have been anticipated that the aldehyde would be derived from the *O*-alkyl group in analogy with similar eliminations of nitrate esters<sup>8</sup> to aldehyde and nitrite ion and nitronate esters<sup>9</sup> to aldehyde and oxime.

(8) J. W. Baker and D. M. Easty, *J. Chem. Soc.*, 1208 (1952).

(9) N. Kornblum and R. A. Brown, *J. Amer. Chem. Soc.*, **86**, 2681 (1964).

(10) C. J. Thoman and I. M. Hunsberger, *J. Org. Chem.*, **33**, 2852 (1968).

(11) (a) E. H. White and C. A. Aufdermarsh, *J. Amer. Chem. Soc.*, **83**, 1174 (1961); (b) E. H. White and R. J. Baumgarten, *J. Org. Chem.*, **29**, 3636 (1964).

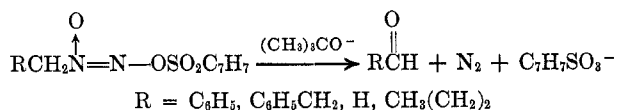
A major product of reaction, ethyl pyruvate, is said to originate from the nitrosimine [Me(CO<sub>2</sub>Et)C=N=N=O].

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

(13) R. B. Woodward and C. E. Wintner, *Tetrahedron Lett.*, 2689 (1969).

methylhydroxylamine yielded only methyl tosylate and nitrous oxide.<sup>14</sup>

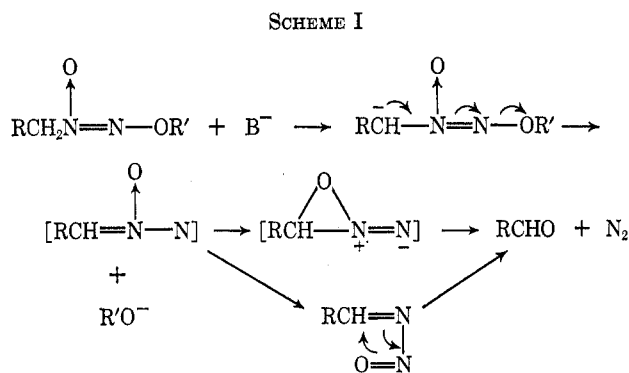
**Alkaline Decomposition.**—Treatment of a series of primary alkyl derivatives of **6** with potassium *t*-butoxide in *t*-butyl alcohol produced the corresponding aldehyde, nitrogen, and tosylate ion.



The corresponding O-alkyl derivatives **7** also decomposed but much more slowly and only when the  $\alpha$ -methylene group was suitably activated. For example, N-benzyl-N'-methoxydiimide N-oxide (**7**, R = C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>; R' = CH<sub>3</sub>) decomposed during a 6-day period to benzaldehyde and nitrogen. However, N-methyl-N'-ethoxydiimide N-oxide was reported recently<sup>15</sup> to be stable to base. It is of some interest that the presence of two N'-methoxydiimide N-oxide (methoxazonyl)<sup>13</sup> groups so stabilizes the resultant carbanion that no decomposition occurs.<sup>13</sup> The limits of groups that activate  $\alpha$ -hydrogen abstraction but do not sufficiently stabilize the resultant carbanion have not been established.

A thorough investigation of other alkyl groups was not made but the secondary derivatives examined, RCH<sub>2</sub> = isopropyl and cyclohexyl, behaved in a similar manner yielding the corresponding ketones. The reactions were more sluggish and the yields lower indicating the incursion of side reactions which were not investigated.

A reasonable path for these decompositions is shown in Scheme I. In an effort to determine if the first step



was reversible or possibly concerted with loss of the anion, exchange studies in methanol-*O-d* were carried out with **7** (R = C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>, R' = CH<sub>3</sub>) and in *t*-butyl alcohol-*O-d* with **6** (R = C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub> and (CH<sub>3</sub>)<sub>2</sub>CH). In the former case complete exchange of the benzylic protons was achieved in the presence of sodium methoxide without decomposition. In the latter, using potassium *t*-butoxide, decomposition was apparently faster than exchange as no deuterated material could be recovered.

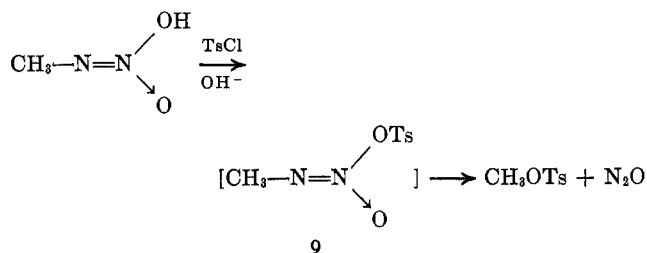
(14) (a) This decomposition is reminiscent of the decomposition of N-nitro amides to esters and nitrous oxide [E. H. White and D. G. Grisley, Jr., *J. Amer. Chem. Soc.*, **83**, 1191 (1961)], and (b) of the decomposition of O,N-dibenzoylhydroxylamines upon nitrosation to benzoic anhydride and nitrous oxide [T. Koenig, T. Fithian, M. Toleda, S. Markwell, and D. Rogers, *J. Org. Chem.*, **34**, 952 (1969)].

(15) A. H. Lamberton and H. M. Yusuf, *J. Chem. Soc.*, 397 (1969).

The oxygen-transfer step is completely speculative, but it appears to be intramolecular since aldehyde formation is not dependent upon a hydrolysis step. Two possible modes of transfer are envisioned. The first is through oxaziridine formation, a common isomerization process for nitrones,<sup>16</sup> followed by nitrogen elimination from a type of intermediate expected to easily lose nitrogen. The second involves isomerization to a nitrosimine, compounds known to decompose readily to aldehydes and nitrogen.<sup>10</sup> The latter intermediate may well be involved since the intense color associated with nitrosimines was observed in several of these reactions. Oxygen transfer from one nitrogen to another has been proposed to account for the formation of N-nitrosimines in the nitrosation of many oximes.<sup>17</sup>

In none of the reactions of the tosyloxydiimide N-oxides was there any indication of the solvolysis reactions reported for the corresponding acyloxydiimide N'-oxides.<sup>14a</sup> In the absence of base no decomposition occurred until temperatures of 180° were reached, whereupon thermal elimination of nitrous oxide and toluenesulfonic acid led to the corresponding olefin (when a  $\beta$ -hydrogen was present). Similar thermal decompositions of analogous azoxy compounds have been noted previously.<sup>18,20</sup>

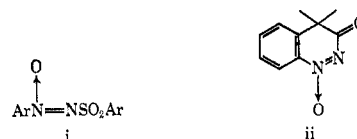
In an attempted synthesis of the tosyl derivative of **2**, **9**, to determine if it were a possible intermediate in the decomposition of the alkyl-N'-tosyloxydiimide N-oxides, only the alkyl tosylate was isolated as expected on the basis of the previous studies of analogous acyl derivatives.<sup>14a</sup> The azoxy tosylates **6** also decomposed



photochemically to yield alkyl tosylate and nitrous oxide. It is tempting to speculate that photochemical isomerization to compounds like **9** is involved in this decomposition. One is tempted to generalize that acyl derivatives of **2** undergo ready solvolysis *via* an oxydiazonium ion while derivatives of the type **6** cannot ionize in this way. The difference is probably associated with the position of the leaving group with respect to the nitrogen atom having the unshared pair of electrons.<sup>21</sup>

(16) G. R. Delpierre and M. Lamchen, *Quart. Rev. Chem. Soc.*, **19**, 329 (1965).

(17) J. P. Freeman, *J. Org. Chem.*, **26**, 4190 (1961). Oxygen transfer must also be involved in the formation of diazotate ions from azoxy sulfones<sup>18</sup> (i) and azoxycarbonyl derivatives<sup>19</sup> (e.g., ii).



(18) W. V. Farrar and J. Masson Gulland, *J. Chem. Soc.*, 368 (1944).

(19) R. J. Sundberg and D. E. Blackburn, *J. Org. Chem.*, **34**, 2799 (1969).

(20) T. E. Stevens and J. P. Freeman, *ibid.*, **29**, 2280 (1964).

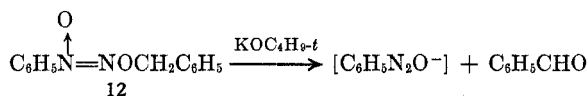
(21) This generalization suggests that the unstable product obtained by the treatment of isobutyl nitrosohydroxylamine with 3,5-dinitrobenzoyl chloride was not the derivative of **4** claimed<sup>14a</sup> but rather a derivative of **3** similar to **8**. This point is under investigation.

In connection with this investigation it was of interest to examine the reactivity in base of derivatives of 7 in which the group R did not bear a hydrogen on the N-oxide carbon.<sup>22</sup> Previously it has been reported that N-phenyl-N'-methoxydiimide N-oxide (10) (7, R = C<sub>6</sub>H<sub>5</sub>; R' = CH<sub>3</sub>) possessed active hydrogen in the Zerewitinoff determination.<sup>23</sup> This result led to an erroneous structure assignment.

Wintner<sup>24</sup> later challenged the validity of this result and attributed the active hydrogen to N-phenyl-N'-methyl-diimide N-oxide (11), a possibility explicitly excluded by the previous workers. It was suggested by Stevens<sup>4</sup> that base-catalyzed elimination of diazotic



acid to yield an aldehyde might be involved. It has now been found that treatment of N-phenyl-N'-benzyloxydiimide N-oxide (12) with potassium *t*-butoxide indeed produces benzaldehyde. The corresponding methoxy compound 10 was inert to potassium *t*-butoxide, how-



ever. These compounds thus bear some similarity to nitronate esters and nitrate esters in their behavior toward bases although they are much more resistant.

Efforts to prepare derivatives of 6 in which R was a tertiary alkyl group were frustrated by the instability of both the nitrosohydroxylamines themselves and of their tosylates. In the case of the *t*-octyl derivative, for example, attempts to recrystallize the solid tosylate led to spontaneous evolution of gas and toluenesulfonic acid. Apparently in this case solvolysis is possible. *t*-Octylnitrosohydroxylamine was very labile and gradually decomposed to *t*-nitrosooctane.

### Experimental Section

**N-Benzyl-N'-tosyloxydiimide N-Oxide.**—A stream of nitrogen-diluted nitric oxide was bubbled through the solution of the benzyl Grignard reagent prepared from 11.7 g of magnesium and 57.7 ml (63.8 g) of benzyl chloride in 11 of dry ether for 50 min. The solution was hydrolyzed with 400 ml of 2 *N* HCl and the ether layer was extracted with 1.5 *N* NaOH. These basic extracts were acidified, reextracted with ether, dried (MgSO<sub>4</sub>), and concentrated. The crude residue (*ca.* 13.0 g) was dissolved in a solution of 8.4 g of *p*-toluenesulfonyl chloride in 100 ml of acetone. At ice-bath temperature 25 ml of 1.5 *N* NaOH was added over a period of 45 min with stirring. The solution was stirred for an additional 30 min; water was added and the product oiled out. Upon cooling 6.6 g (4.5%, based on benzyl chloride) of N-benzyl-N'-tosyloxydiimide N-oxide crystallized. Recrystallization was effected from chloroform-hexane: mp 90–92° (lit.<sup>4</sup> mp 92°); ir (KBr) 1300 and 1510 (O←N=N), 1185 and 1200 cm<sup>-1</sup> (SO<sub>2</sub>).

**N-Phenethyl-N'-tosyloxydiimide N-Oxide.**—The procedure used was the same as that for N-benzyl-N'-tosyloxydiimide N-oxide;<sup>4</sup> yield 7.3 g (8.5%): mp 121.5–122°; ir (Nujol) 1305 and 1520 (O←N=N), 1190 and 1205 cm<sup>-1</sup> (SO<sub>2</sub>); nmr (CDCl<sub>3</sub>) δ 2.45 (s, 3, C<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>), 3.14 (t, 2, *J* = 7 Hz, C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>CH<sub>2</sub>), 4.29 (t, 2, *J* = 7 Hz, C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>CH<sub>2</sub>), 7.48 (m, 9, C<sub>6</sub>H<sub>5</sub>, C<sub>6</sub>H<sub>4</sub>). *Anal.* Calcd for C<sub>15</sub>H<sub>19</sub>N<sub>2</sub>O<sub>4</sub>S: C, 56.2; H, 5.0;

(22) The corresponding derivatives of 2, *e.g.*, R = aryl, were found to be essentially inert to base.<sup>8</sup>

(23) M. V. George, R. W. Kierstead, and G. F. Wright, *Can. J. Chem.*, **37**, 679 (1959).

(24) C. Wintner, Ph.D. Thesis, Harvard University, 1963.

N, 8.8; S, 10.0. Found: C, 56.27; H, 5.05; N, 9.30; S, 10.01.

**N-Methyl-N'-tosyloxydiimide N-Oxide.**—A stream of nitrogen-diluted nitric oxide was bubbled through the solution of the methyl Grignard reagent prepared from 4.22 g of magnesium and 25 g methyl iodide in 400 ml of dry ether for 45 min. The solution was hydrolyzed with 2 *N* HCl and the ether layer was extracted with 1.5 *N* NaOH. To the basic extracts was added 12.0 g of *p*-toluenesulfonyl chloride in one portion and the mixture was stirred for 4 hr. The solution was then filtered to yield a white solid which was recrystallized from chloroform-hexane to give 3 g (7.5%): mp 83–84° (lit.<sup>4</sup> mp 86°); ir (Nujol) 1320 and 1495 (O←N=N), 1185 and 1195 cm<sup>-1</sup> (SO<sub>2</sub>).

**N-*n*-Butyl-N'-tosyloxydiimide N-Oxide.**—The procedure used was the same as that for N-benzyl-N'-tosyloxydiimide N-oxide.<sup>4</sup> After tosylation, the solution was stirred for an additional 1.5 hr, extracted with methylene chloride, and dried (CaCl<sub>2</sub>). The oil obtained was chromatographed on silica gel. The hexane eluate contained only tosyl chloride. Methylene chloride was used to elute N-*n*-butyl-N'-tosyloxydiimide N-oxide as a light yellow oil: nmr (CDCl<sub>3</sub>) δ 7.70 (q, 4, C<sub>6</sub>H<sub>4</sub>), 4.12 (t, 2, CH<sub>2</sub>N=N), 2.45 (s, 3, C<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>), 2.3–0.5 (m, 7, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>); ir (neat) 1310 and 1510 (O←N=N), 1185 and 1200 cm<sup>-1</sup> (SO<sub>2</sub>). *Anal.* Calcd for C<sub>11</sub>H<sub>16</sub>N<sub>2</sub>O<sub>4</sub>S: C, 48.51; H, 5.92; N, 10.29. Found: C, 48.71; H, 5.98; N, 11.11.

**N-Cyclohexyl-N'-tosyloxydiimide N-Oxide.**—The procedure used was the same as that for N-benzyl-N'-tosyloxydiimide N-oxide;<sup>4</sup> yield 9.0 g (20%); mp 93–94.5° (lit.<sup>26</sup> mp 93–94.5°); ir (Nujol) 1310 and 1510 (O←N=N), 1185 and 1200 cm<sup>-1</sup> (SO<sub>2</sub>); nmr (CDCl<sub>3</sub>) δ 0.8–2.2 (broad m, 10, C<sub>6</sub>H<sub>10</sub>), 3.9–4.6 (broad m, 1, CHN(→O)=N). *Anal.* Calcd for C<sub>13</sub>H<sub>18</sub>N<sub>2</sub>O<sub>4</sub>S: C, 52.33; H, 6.08; N, 9.39. Found: C, 51.91; H, 6.18; N, 9.61.

**N-Benzyl-N'-methoxydiimide N-Oxide.**—This compound was prepared by Wright's procedure<sup>25</sup> using the sodium salt of N-benzyl-N-nitrosohydroxylamine: mp 28–29°; bp 104° (0.2 mm); ir (neat) 1295 and 1500 cm<sup>-1</sup> (O←N=N); nmr (CDCl<sub>3</sub>) δ 4.06 (s, 3, CH<sub>3</sub>), 5.12 (s, 2, CH<sub>2</sub>), 7.43 (s, 5, C<sub>6</sub>H<sub>5</sub>). *Anal.* Calcd for C<sub>9</sub>H<sub>10</sub>N<sub>2</sub>O<sub>2</sub>: C, 57.8; H, 6.1; N, 16.9. Found: C, 59.28; H, 6.09; N, 16.43.

**Decomposition of N-Benzyl-N'-tosyloxydiimide N-Oxide.**—Into a three-necked 250-ml pear-shaped flask, equipped with thermometer, equilibrating addition funnel, and magnetic stirrer and attached to a vacuum rack, was placed 1.22 g (4.0 mm) of N-benzyl-N'-tosyloxydiimide N-oxide dissolved in 45 ml of *t*-butyl alcohol.

In the addition funnel was placed 0.46 g (4.0 mm) of potassium *t*-butoxide. The N-benzyl-N'-tosyloxydiimide N-oxide solution was frozen out with liquid N<sub>2</sub>, and the potassium *t*-butoxide solution dripped onto the frozen solution. The pressure was reduced to 0.001 mm and the frozen mixture warmed to 50° with vigorous stirring. The gas collected proved to be N<sub>2</sub> by mass spectral analysis and the amount indicated 70% decomposition of the starting material. A 2,4-DNP derivative of the remaining (filtered to remove potassium tosylate) neutralized *t*-butyl alcohol solution yielded the benzaldehyde derivative: mp 239–240° (lit.<sup>26</sup> mp 237°).

**Decomposition of N-Primary Alkyl-N'-tosyloxydiimide N-Oxides with Potassium *t*-Butoxide.**—The following general procedure was used for the decomposition of the N-alkyl-N'-tosyloxydiimide N-oxides. The diimide N-oxide was dissolved in the least amount of *t*-butyl alcohol and an equimolar amount of potassium *t*-butoxide in *t*-butyl alcohol was added slowly with stirring. After 1 hr the reaction mixture (a slurry in some cases) was filtered to remove potassium tosylate and neutralized with HCl if necessary. In all cases a strong odor of the aldehyde appeared except in the case of formaldehyde; these were isolated as the 2,4-DNP derivatives from the neutral solution. Phenylacetaldehyde was identified by comparison of its glpc retention time on a silicone column at 135° with that of authentic material. The yields (%) of aldehyde (based upon 2,4-DNP's isolated) were as follows: C<sub>6</sub>H<sub>5</sub>CHO (61), C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>CHO (47), CH<sub>3</sub>O (54), and C<sub>2</sub>H<sub>5</sub>CHO (52).

**Decomposition of N-Benzyl-N'-methoxydiimide N-Oxide with Potassium *t*-Butoxide.**—The procedure was the same as that for

(25) These analyses were obtained by T. E. Stevens, Rohm and Haas Co., Huntsville, Ala.

(26) R. L. Shriner, R. C. Fuson, and D. Y. Curtin, "The Systematic Identification of Organic Compounds," 5th ed, Wiley, New York, N. Y., 1964, p 320.

N-alkyl-N'-tosyloxydiimides N-oxides. The solution was stirred for 6 days until the reaction was complete (no more precipitate formed and solution was neutral to litmus). The 2,4-DNP derivative of benzaldehyde, mp 237–239° (lit.<sup>26</sup> mp 237°), was isolated; yield (calcd as C<sub>6</sub>H<sub>5</sub>CHO), 57%.

**Decomposition of N-Phenyl-N'-benzyloxydiimide N-Oxide with Potassium *t*-Butoxide.**—The diimide N-oxide<sup>23</sup> (1.0 g) and potassium *t*-butoxide (0.5 g) were dissolved in *t*-butyl alcohol (10 ml) and the mixture was refluxed for 3 hr. The reaction mixture was cooled and filtered. The 2,4-DNP derivative of benzaldehyde was isolated from the solution; yield (calcd as C<sub>6</sub>H<sub>5</sub>CHO), 42%.

**Deuterium Exchange of N-Benzyl-N'-methoxydiimide N-Oxide.**—To a solution of 0.02 g of sodium in 5 ml of CH<sub>3</sub>OD (99%) was added 0.3 g of N-benzyl-N'-methoxydiimide N-oxide, and the mixture was stirred for 3 hr. The CH<sub>3</sub>OD was evaporated, deuterium oxide added, and the solution extracted with chloroform. Nmr analysis showed 95% exchange of the methylene protons at  $\delta$  5.12. Medium intensity C–D stretching at 4.44  $\mu$  was detected in the infrared spectrum of this material.

**Decomposition of N-Cyclohexyl-N'-tosyloxydiimide N-Oxide.** (a) **Potassium *t*-Butoxide.**—The procedure used was the same as that for the decomposition of the primary alkyldiimide N-oxide derivatives except ether was employed as the solvent. During the rapid addition of base the solution turned deep raspberry in color. After the precipitate was filtered, the ether evaporated, and the residue taken up in ethanol, a 2,4-DNP derivative of cyclohexanone, mp 160–161° (lit.<sup>28</sup> mp 162°), was obtained in 45% yield by the usual procedure. Nitrogen, by mass spectral analysis, proved to be the only gas collected when the decomposition was carried out by the procedure used for the potassium *t*-butoxide decomposition of 6, R = C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>.

(b) **Thermal Decomposition.**—The diimide N-oxide was dissolved in *o*-dichlorobenzene and the solution was heated at 180° for 30 min. Vpe analysis on a silicone column at 25° of the solution indicated a nearly quantitative yield of cyclohexene.

(c) **Photolysis.**—The diimide N-oxide (0.90 g) was dissolved in 400 ml of cyclohexane and irradiated with a Hanovia high-pressure submersion lamp with a Pyrex filter for 22 hr while stirring. The brownish residue obtained was chromatographed on silica gel with hexane, yield 0.45 g (50%) of cyclohexyl *p*-toluenesulfonate, identified by comparison with an authentic sample.<sup>27</sup>

**N-*t*-Octyl-N'-tosyloxydiimide N-Oxide.**—Nitrosation<sup>29</sup> of 29 g of *t*-octylhydroxylamine<sup>29</sup> with 13.8 g of sodium nitrite yielded, upon recrystallization from chloroform–pentane, 12.0 g (31%) of the ammonium salt: mp 55–60°; sublimes 55° (0.3 mm); ir 1320 and 1500 (O←N=N), 3300 cm<sup>-1</sup> (NH<sub>4</sub><sup>+</sup>). *Anal.* Calcd for C<sub>8</sub>H<sub>21</sub>N<sub>3</sub>O<sub>2</sub>: C, 50.3; H, 11.0; N, 22.0. Found: C, 50.17; H, 11.05; N, 21.88.

The method of Stevens<sup>4</sup> using 7.5 g of the ammonium salt of *t*-octylnitrosylhydroxylamine and 7.5 g of *p*-toluenesulfonyl chloride yielded 11.0 g (86%) of the tosylate. Decomposition occurred upon attempts to make Nujol mulls for ir and upon attempted recrystallization from chloroform–hexane.

**Decomposition.**—A small amount of the diimide N-oxide was dissolved in chloroform and warmed for a few minutes. The nmr spectrum of the solution showed diisobutylene (by comparison with the spectrum of authentic material) and *p*-toluenesulfonic acid to be present.

**N-*t*-Octyl-N'-methoxydiimide N-Oxide.**—The method of Wright<sup>25</sup> using 1.7 g of the ammonium salt of *t*-octylnitrosylhydroxylamine and 1.7 g of dimethyl sulfate was employed. The crude oil was chromatographed on silica gel and eluted with 1:1 methylene chloride–hexane yielding 0.1 g (7%) of light brown oil; ir (neat) 1360 and 1485 cm<sup>-1</sup> (O←N=N); nmr (neat)  $\delta$  0.95 (s, 9, (CH<sub>3</sub>)<sub>3</sub>C), 1.5 (s, 6, (CH<sub>2</sub>)<sub>3</sub>C), 1.88 (s, 2, CH<sub>2</sub>), 3.90 (s, 8, OCH<sub>3</sub>). *Anal.* Calcd for C<sub>9</sub>H<sub>20</sub>N<sub>2</sub>O<sub>2</sub>: C, 57.4; H, 10.6; N, 15.0. Found: C, 56.44; H, 10.32; N, 15.30.

**Attempted Solvolysis.**—A small amount of the diimide N-oxide was dissolved in 95% ethanol and refluxed on a steam bath for 0.5 hr; it was recovered unchanged.

**Decomposition of N-Phenyl-N'-methoxydiimide N-Oxide with Potassium *t*-Butoxide.**—The diimide N-oxide<sup>23</sup> (3.1 g) and potas-

sium *t*-butoxide (2.25 g) were dissolved in 25 ml of *t*-butyl alcohol and the mixture was refluxed overnight. The precipitate was filtered and identified as the potassium salt of N-phenyl-N-nitrosylhydroxylamine (by ir, nmr, and reaction with dimethyl sulfate to yield starting material). No 2,4-DNP derivative of formaldehyde could be obtained from the solution.

**Preparation of *t*-Butyl N-Methyl-N-hydroxycarbamate.**—The method of Carpino<sup>30</sup> using methylhydroxylamine hydrochloride (15.7 g) was employed. The light yellow oil obtained (19.1 g, 92%) was chromatographed on silica gel with 1:1 chloroform–methylene chloride: ir (neat) 1670 (C=O) and 3300 cm<sup>-1</sup> (OH); nmr (neat)  $\delta$  1.46 (s, 9, C(CH<sub>3</sub>)<sub>3</sub>), 3.11 (s, CH<sub>3</sub>-N). *Anal.* Calcd for C<sub>6</sub>H<sub>13</sub>NO<sub>2</sub>: C, 49.0; H, 8.8; N, 9.5. Found: C, 48.80; H, 8.47; N, 9.55.

**Preparation of *t*-Butyl N-Methyl-N-*p*-toluenesulfonylcarbamate.**—The method of Carpino<sup>30</sup> using *t*-butyl N-methyl-N-hydroxycarbamate (4.80 g) was employed. Recrystallization from benzene–petroleum ether yielded 7.2 g (70%), mp 67–68°; ir (Nujol) 1740 (C=O), 1175 and 1185 cm<sup>-1</sup> (SO<sub>2</sub>); nmr (CDCl<sub>3</sub>)  $\delta$  1.24 (s, 9, C(CH<sub>3</sub>)<sub>3</sub>), 2.46 (s, 3, C<sub>6</sub>H<sub>4</sub>-CH<sub>3</sub>), 3.25 (s, 3, CH<sub>3</sub>-N), 7.65 (q, 4, C<sub>6</sub>H<sub>4</sub>). *Anal.* Calcd for C<sub>18</sub>H<sub>19</sub>NO<sub>3</sub>S: C, 51.8; H, 6.3; N, 4.7; S, 10.6. Found: C, 51.83; H, 6.38; N, 4.71; S, 10.82.

**N-Methyl-O-(*p*-toluenesulfonyl)hydroxylamine.**—The method of Carpino<sup>31</sup> using *t*-butyl N-methyl-*p*-toluenesulfonylcarbamate (7.2 g) was employed: yield of crude product, 4.7 g (100%); mp 47–50°; ir (Nujol) 3330 (NH), 1170 and 1185 cm<sup>-1</sup> (SO<sub>2</sub>); nmr (CDCl<sub>3</sub>)  $\delta$  2.55 (s, C<sub>6</sub>H<sub>4</sub>-CH<sub>3</sub>), 2.72 (s, CH<sub>3</sub>-N), 6.45 (broad s, NH), 7.63 (q, C<sub>6</sub>H<sub>4</sub>). Because of the sensitivity of this compound to solvolytic decomposition, it was not further purified. Its spectral properties are consistent with the structure assigned.

**Attempted Preparation of N-Methyl-N-nitroso-O-(*p*-toluenesulfonyl)hydroxylamine.**—Nitrosation by the method of Paskovich and Zimmerman<sup>32</sup> using 4.1 g of N-methyl-O-(*p*-toluenesulfonyl)hydroxylamine was carried out with N<sub>2</sub>O<sub>4</sub> in CCl<sub>4</sub>. The only organic product isolated was methyl *p*-toluenesulfonate: yield 1.70 g (45%); bp 124° (1 mm).

**Attempted Synthesis of N-Methyl-N'-tosyloxydiimide N'-Oxide.**—The silver salt of methylnitramine<sup>33</sup> (6.67 g) was stirred in 50 ml of acetonitrile (cooled to 0°) while tosyl chloride (7.0 g) in 25 ml of acetonitrile was added slowly. The solution was stirred overnight, the silver chloride filtered off, and the acetonitrile evaporated. The residue was chromatographed on silica gel. The column was first eluted with hexane and then methylene chloride. The first fraction contained tosyl chloride (by ir); the second contained methyl tosylate (by ir, nmr, and Sadtler's Index), 2.5 g (37%).

**Registry No.**—N-Phenethyl-N'-tosyloxydiimide N-oxide, 25370-87-0; N-*n*-butyl-N'-tosyloxydiimide N-oxide, 25370-88-1; N-cyclohexyl-N'-tosyloxydiimide N-oxide, 25370-89-2; N-benzyl-N'-methoxydiimide N-oxide, 25370-90-5; N-benzyl-N'-tosyloxydiimide N-oxide, 25370-91-6; N-phenyl-N'-benzyloxydiimide N-oxide, 25370-92-7; *t*-octylnitrosylhydroxylamine ammonium salt, 25370-98-3; N-*t*-octyl-N'-methoxydiimide N-oxide, 25370-93-8; N-phenyl-N-methoxydiimide N-oxide, 25370-94-9; *t*-butyl N-methyl-N-hydroxycarbamate, 19689-97-5; *t*-butyl N-methyl-N-*p*-toluenesulfonylcarbamate, 25370-96-1; N-methyl-O-(*p*-toluenesulfonyl)hydroxylamine, 25370-97-2.

**Acknowledgment.**—We are indebted to the National Science Foundation for a grant in support of this research and for an equipment grant for the purchase of the A-60A nmr instrument used in this investigation.

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