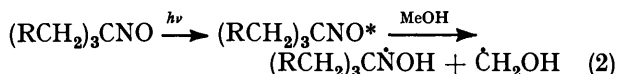
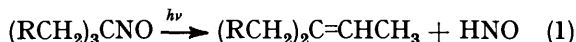


## The Photolysis of C-Nitroso-compounds. Part 8.<sup>1</sup> The Solution Photolysis of Some Tertiary C-Nitroso-compounds

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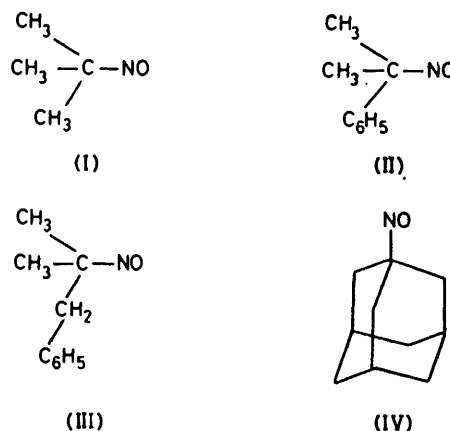
The photolysis of the nitrosoalkanes 2-methyl-2-nitrosopropane (I), 2-nitroso-2-phenylpropane (II), 2-benzyl-2-nitrosopropane (III), and 1-nitrosoadamantane (IV) with visible light ( $\lambda > 540$  nm) yielded trialkylhydroxylamines and, with the exception of (IV), alkenes as main products. In methanol the alcohols, alkyl nitrites, and methyl nitrite were obtained additionally. These products are rationalised on the basis of a homolytic dissociation into a free radical and nitric oxide in the primary step. The reaction of nitric oxide with the substrate rather than a direct photoelimination of HNO is identified as the major source of alkenes.

TERTIARY C-nitrosoalkanes, in particular 2-methyl-2-nitrosopropane, have been widely used for trapping short-lived free radicals as stable nitroxide radicals and e.s.r. spectroscopy has been used in the study of these nitroxides.<sup>2,3</sup> The free radicals can be generated by the photolysis of the nitrosoalkane followed by subsequent self-scavenging by the substrate and thus identified as the symmetrical di-t-alkyl nitroxide.<sup>4</sup> Relatively few studies of the photolyses have been reported. The gas-phase visible light photolysis<sup>5</sup> of 2-methyl-2-nitrosopropane involves the participation of di-t-butyl nitroxide. We have shown elsewhere<sup>6</sup> that the HNO elimination mechanism invoked by Hammick *et al.*<sup>7</sup> is incorrect in geminally substituted systems and it is apparent that the photolysis of 2,5-dimethyl-2-nitrosohexane in benzene reported by him can only be regarded as a preliminary study. The other reported photolyses are concerned with aprotic solvents, *i.e.* 2-methyl-2-nitrosopropane in benzene<sup>4,8</sup> and 1-ethyl-1-nitrosocyclohexane in ether.<sup>9</sup> We have established<sup>6</sup> that solvent participation by alcohols is an important feature in the photolyses of other nitroso-compounds in alcoholic solution and a preliminary study<sup>10</sup> showed that methyl nitrite is formed in the photolysis of 2-methyl-2-nitrosopropane in methanol. Our previous studies<sup>6</sup> of the photochemistry of methanolic solutions of nitroso-compounds have been concerned with geminally substituted compounds of the type  $R_2CXNO$  where  $X = Cl, NO_2,$  and  $CN$ . It was thought advisable to study the photolysis of a number of tertiary C-nitroso-compounds in methanol in order more fully to understand the photochemistry of the  $\text{>C-NO}$  function and in particular to establish whether there is any convincing evidence for the participation of such primary photochemical processes as (1) and (2) which have been proposed by others.<sup>7,11</sup>



Consequently we selected four different nitroso-compounds, 2-methyl-2-nitrosopropane (I), this being the simplest tertiary nitrosoalkane, 2-nitroso-2-phenylpropane (II), for studying the influence of a phenyl group, 2-benzyl-2-nitrosopropane (III), which offers the

possibility of forming two different alkenes as photo-products, and 1-nitrosoadamantane (IV), where Bredt's rule<sup>12</sup> would suggest the unlikelihood of the formation of adamantene.



### RESULTS

The tertiary C-nitroso-compounds are prepared as crystalline solids in the *trans*-dimeric form. Methanolic solutions of (I)—(III) were left in the dark at room temperature for 2 h to allow the establishment of the monomer-dimer equilibrium. Compound (IV) required refluxing in the dark to promote dissolution of the dimer, followed by

TABLE 1

Visible absorption of compounds (I)—(IV) in methanol

Compound	$10^2$ Concentration (M) <sup>a</sup>	$\lambda_{max.}/nm$	$\epsilon^b / 1 \text{ mol}^{-1} \text{ cm}^{-1}$
(I)	2.60	679	17.5
(II)	1.60	678	4.5
(III)	1.38	679	21.4
(IV)	2.00	680	25.4

<sup>a</sup> This is the hypothetical concentration assuming 100% monomer formation. <sup>b</sup> Calculated from optical density at  $\lambda_{max.}$  based upon 100% monomer formation.

TABLE 2

$a_N$  Splitting of the symmetrical nitroxides obtained on photolysis

Compound	$a_N$ (G)
(I)	16.0
(II)	15.3
(III)	16.0
(IV)	16.1

TABLE 3

Compound Solvent 10% Concentration (M) Products	Percentage yields of photolytic products from the photolyses of compounds (I)—(IV)					
	(I) MeOH 2.0	(I) * C <sub>6</sub> H <sub>6</sub>	(II) MeOH 0.8	(III) MeOH 1.4	(III) C <sub>6</sub> H <sub>6</sub> 1.4	(IV) MeOH 2.0
R <sub>2</sub> NOR	11	15	+	+	+	4
(R <sub>2</sub> NORH)+NO <sub>2</sub> <sup>-</sup>	5	—	—	—	—	—
Alkene	16	32	17	20, <sup>a</sup> 10 <sup>b</sup>	56, <sup>a</sup> 11 <sup>b</sup>	—
RH	<1	—	<1	<1	—	<1
MeONO	18	—	8	14	—	5
ROME	20	—	40	13	—	9
ROH	9	—	9	11	—	4
Ketone <sup>d</sup>	3	—	10	—	—	—
RNO <sub>2</sub>	<1	11	5	<1	11	20 <sup>c</sup>
RONO	—	7	—	—	8	—
RONO <sub>2</sub>	—	3	—	—	—	+

\* Results from refs. 4 and 8. +, Detected by mass spectrometry; —, not detected.

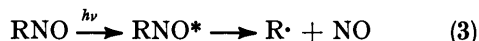
<sup>a</sup> 2-Benzylpropene. <sup>b</sup> 2-Methyl-1-phenylpropene. <sup>c</sup> Mixture of RNO<sub>2</sub> and RONO<sub>2</sub>. <sup>d</sup> Acetone, from (I), and acetophenone, from (II).

overnight equilibration in the dark. The visible spectra were measured at 22° and the results are summarised in Table 1. Table 2 presents the  $a_N$  splitting values of the nitroxides obtained on photolysis of the methanolic solutions within the cavity of an e.s.r. spectrometer. Table 3 summarises the percentage yields of product for photolysis of solutions of (I)—(IV) and compares the analogous values for (I) due to Maassen<sup>4</sup> and McGregor.<sup>8</sup>

#### DISCUSSION

The solutions of the nitroso-compounds employed contain varying proportions of the monomer. It seems probable that (IV) is present predominantly as monomer and that the dimer content increases on passing from (III) to (I) to (II) as evidenced by the apparent molar extinction coefficient. This may be correlated with the bulkiness of the tertiary alkyl group. The presence of the dimer of (I) in methanol solution can also be shown from the fact that irradiation of the solution for 5 min was sufficient to give complete bleaching of the solution. On ceasing photolysis the blue colour of the monomer reappears as further dissociation of the dimer occurred. The same phenomenon was observed in the dark reaction of (I) with nitric oxide if the solution was flushed with nitrogen to remove any excess of nitric oxide after the initial reaction of nitric oxide with (I).

When photolysis was carried out within the e.s.r. spectrometer cavity the only radicals that could be detected were the respective di-*t*-alkyl nitroxides. This implies that the production (and subsequent scavenging) of radicals other than those produced from the direct photodissociation reaction (3) with subsequent reaction (4) is either of little significance or that any unsym-



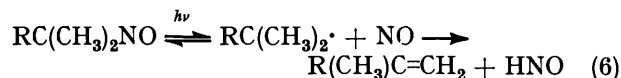
metrical nitroxides formed are of low stability. The e.s.r. signals of the nitroxides derived from (I), (III), and (IV) were observed to remain unchanged on removal of the light source; the signal for the nitroxide derived from (II) decayed rapidly suggesting a decomposition reaction. The tri-*t*-alkylhydroxylamines are major pro-

ducts in the photolysis of (I) and (IV) and although only detected qualitatively for (II) and (III) could well represent a major proportion of the products derived from the free radicals R. We therefore add (5) to the reaction scheme.



In the photolysis of (I)—(III) the alkenes derived from the radicals are significant products whereas the corresponding alkanes are trace products only. It is known<sup>13</sup> that the disproportionation : combination ratios for *t*-butyl and cumyl radicals in benzene are 4.6 and 0.054 respectively. Consequently the absence of alkanes and C-C coupling products demonstrates convincingly that the usual auto-disproportionation-combination of alkyl radicals is unimportant in our systems due to the preponderance of the self-scavenging reaction (4). Clearly, other pathways must be available explaining the high alkene yields.

Alkene production in the  $\lambda$  500—750 nm photolysis of *C*-nitroso-monomers has been observed frequently following Hammick's original, unproven postulate of a single-step photoelimination of HNO.<sup>7,14</sup> Thus, major products either remained unexplained<sup>9,15</sup> or were thought to arise from the alternative bimolecular disproportionation of two alkyl radicals<sup>4</sup> or of an alkyl-nitric oxide radical pair.<sup>8</sup> The quantum yields for the disappearance of nitrosoalkanes known from the earlier work<sup>7,14</sup> are close to one indicating that product formation competes quite successfully with the alkyl radical-nitric oxide recombination. If the well known marked preference for combination as opposed to abstraction in alkyl radical nitric oxide systems is taken into account, it becomes evident that the two-step reaction (6) cannot explain the



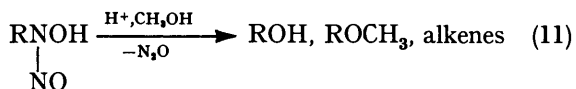
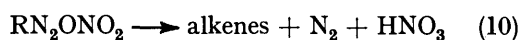
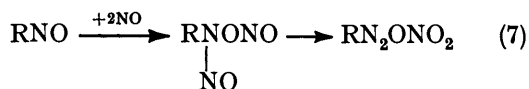
high alkene yields. Homolytic sources for the olefin<sup>5,16</sup> seem, in fact, to be of minor importance altogether because of the considerable influence of the solvent evident from Table 3 as well as the clear deviation of the distribution of alkenes (V) and (VI) in the photolysis of

(III) from the 3 : 1 statistical ratio expected for a homolytic disproportionation.<sup>13</sup>



A statistical ratio of (V) to (VI) perhaps slightly corrected in favour of (VI) because of its greater thermodynamic stability should be observed if the formation of the olefins from (III) proceeded by a single-step *syn*-elimination of HNO from the  $n\text{-}\pi^*$  excited nitroso-compound. We conclude therefore that the olefin isomer distribution in the case of (III) as well as the marked effect of solvent on the alkene yields and the product pattern in general rule out a significant contribution of both homolytic two- (6) and single-step (1) elimination mechanisms. Most of our previous studies of the photolysis of *C*-nitroso-compounds support this conclusion.

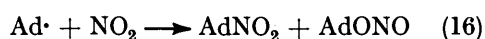
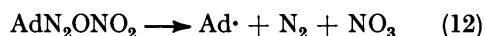
The reaction of nitric oxide with (I) and (III) provides some interesting experimental evidence for the origin of alkene production in the photolyses. This unavoidable dark reaction is necessarily important in the photolyses as well, since the nitric oxide generated in the primary step will be trapped by the substrate. With (I) isobutene, *t*-butyl methyl ether, and methyl nitrite are the main products of this dark reaction. Compound (III) reacted similarly with excess of nitric oxide yielding the alkenes (V) and (VI) in a ratio of *ca.* 8 : 1 and 1-benzyl-1-methylethyl methyl ether and methyl nitrite. It is significant that both the photolyses as well as the dark reactions with nitric oxide give rise to alkenes and methyl ethers resulting undoubtedly from solvolytic reactions of intermediates. These reactions can be rationalised plausibly *via* an *NO*-dinitrosohydroxylamine and diazonitrate intermediate [reactions (7)–(11)].



In benzene (8), (9), and (11) are absent and the formation of alkenes must now be dominated by (10) with a possible contribution from (11). Some of the nitric acid from this sequence of reactions appears in the form of an alkoxydialkylammonium salt. The unusual, but unambiguous preference for the formation of the terminal olefin from (III) indicates that unsolvated, 'hot'

carbonium ions may be of some importance in these systems, an interesting aspect of this work, which was, however, not pursued.

No evidence for the formation of the elusive bridge-head olefin adamantene<sup>17</sup> could be found in the photolysis of (IV). The 9-methoxyadamantane resulting from the photolysis of (IV) in [<sup>2</sup>H<sub>4</sub>]methanol showed only incorporation of the methoxy group from the solvent but no incorporation of deuterium into the skeleton.<sup>18</sup> The product pattern obtained can be adequately understood on the basis of concomitant heterolytic and homolytic decomposition of adamantyl diazonitrate and *N*-nitroso-1-hydroxylaminoadamantane. The homolytic reactions (12)–(16) and the subsequent solvolysis (17) are probable

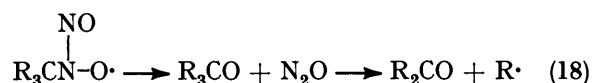


(Ad = 1-adamantyl)

pathways accounting for the formation of 1-nitroadamantane and adamantan-1-ol.

Production of nitro-compounds, alkyl nitrites, and nitrates is particularly evident in aprotic solvents where solvolytic reactions of intermediates and products are absent. The formation of alkyl nitrates, however, is also likely to proceed by heterolytic decomposition of diazonium nitrates and ionic recombination of unsolvated carbonium ions and nitrate counter ions.

The observation of carbonyl compounds among the products of photolysis of (I) and (II) is of interest in that it indicates the intermediacy of alkoxy radicals. The reaction sequence (18) similar to that proposed by Koenig<sup>19</sup> is a probable route.



No evidence has been found for the production of hydroxylamines in any of our photolyses implying that photoreduction based upon hydrogen abstraction by an electronically excited nitroso-compounds (2) is of no importance. The absence of the solvent derived spin adducts supports this conclusion.

Both our e.s.r. experiments as well as our product studies indicate that the *t*-nitrosoalkanes we investigated were unstable towards photolysis with light absorbed by the  $n\text{-}\pi^*$  band ( $\lambda$  *ca.* 530–760 nm) of the nitroso-chromophore. Complications due to this direct photodecomposition can arise in all photochemical e.s.r. experiments with *t*-nitrosoalkanes as spin traps.<sup>20</sup> A low concentration of the scavenger and exclusion of light of wavelengths larger than 500 nm seems advisable, therefore, for such experiments.

## EXPERIMENTAL

G.c. separations were carried out on a Perkin-Elmer model F11 FID gas chromatograph and a Hewlett-Packard (F and M 720) instrument equipped with a thermal conductivity detector. Mass spectra were run on an A.E.I. MS30 instrument at 70 eV coupled to a Pye series 104 gas chromatograph. The spectra of solids were obtained with an all glass heated inlet system in addition to the direct inlet. Pye-Unicam SP 1800, Perkin-Elmer 457 and R-60, and JEOL MH-100 and JES-PE spectrometers were available to record electronic, i.r., n.m.r., and e.s.r. spectra respectively. The solvents used in photolyses were purified as described previously.<sup>6</sup>

**Starting Materials.**—2-Methyl-2-nitrosopropane was prepared by a known method.<sup>21</sup> 1-Nitrosoadamantane,<sup>22</sup> 2-nitroso-2-phenylpropane,<sup>23</sup> and 2-benzyl-2-nitrosopropane<sup>24</sup> were obtained by reduction of their nitro-analogues and subsequent dichromate oxidation of the resulting crude hydroxylamines. Recrystallisation from methanol-water afforded the crystalline dimers, m.p. 75–76° (lit.,<sup>23</sup> 67–72°) for (II) and 79° (lit.,<sup>24</sup> 74°) for (III).

**Reference Compounds.**—Acetone, isobutene, isobutane, t-butyl alcohol, and t-butyl methyl ether, acetophenone,  $\alpha$ -methylstyrene, and adamantan-1-ol were commercially available. 2-Nitro-2-phenylpropane was obtained as described in the literature.<sup>25</sup> The nitro analogues of (I), (III), and (IV) were prepared by the oxidation of the amines.<sup>21</sup> A sample of 2-phenylpropan-2-ol was obtained by the action of phenylmagnesium bromide on acetone. The alcohol and the corresponding methyl ether<sup>26</sup> were purified by preparative g.l.c. The isomeric alkenes (V) and (VI), obtained in the ratio 1 : 3 by phosphoric acid dehydration of crude 2-benzylpropan-2-ol and 2-benzyl-2-methoxypropane from the acid catalysed addition of methanol to the crude olefin mixture were purified in small quantities by preparative g.l.c. and structurally distinguished by n.m.r. and i.r. spectra.

**Analytical.**—All product analyses were carried out by g.l.c. unless stated otherwise. Product identity was established by g.l.c. retention times and the comparison with authentic samples on columns of widely differing polarity, by coupled g.l.c.–m.s. and in doubtful cases by condensation of g.l.c. fractions and separate i.r. or n.m.r. spectroscopic investigation. Methyl nitrite in methanol was determined by u.v. spectrophotometry ( $\epsilon$  75 at  $\lambda_{\max}$  351 nm). Quantitative g.l.c. analyses were carried out using the internal standard method. Relative f.i.d. and t.c.d. response factors were determined with mixtures of known composition.

**Photolyses.**—Unless otherwise stated the solutions were degassed by at least three freeze-pump-thaw cycles on a vacuum line at  $10^{-4}$  Torr, sealed under vacuum in silica cells equipped with graded seals and photolysed by exposure to the light of a tubular 400 W high pressure sodium lamp as described previously.<sup>10</sup> A saturated aqueous potassium dichromate solution was used to cut off light of wavelengths below 540 nm permitting selective irradiation of the monomeric form of the substrate. Exposure times required for complete photolysis varied from 35 min to 3 h depending on the initial substrate concentration, the rate of dimer dissociation and the dissociation equilibrium.

**Photolysis of (I) in CH<sub>3</sub>OH and CD<sub>3</sub>OD.**—Acetone, t-butyl alcohol, isobutane, isobutene, t-butyl methyl ether, methyl nitrite, tri-t-butylhydroxylamine, and 2-methyl-2-nitrosopropane, were identified as products using a combination of

chromatographic and spectroscopic techniques. Larger scale photolyses (100–500 ml of  $5 \times 10^{-3}$ M solutions) provided in addition an involatile solid, m.p. 98° (decomp.), after removal of the solvent and of volatile products. The solid had a strong, broad i.r. absorption at  $1395 \text{ cm}^{-1}$ . It was identified as t-butoxydi-t-butylammonium nitrate, the free hydroxylamine being liberated on addition of sodium hydroxide solution. A yellow involatile oil was also recovered in ca. 1% yield by preparative g.l.c.,  $\lambda_{\max}$  (methanol) 373 nm;  $\nu_{\max}$  (neat)  $1450 \text{ cm}^{-1}$  (s), and identified tentatively as N-nitroso-NO-di-t-butylhydroxylamine. A search for t-butylhydroxylamine by g.l.c. and for formaldehyde by the chromatropic acid test was unsuccessful, whilst g.s.c. on a 12 ft  $\times$   $\frac{1}{4}$  in Phasepak P column using the t.c.d. gas chromatograph revealed N<sub>2</sub>O as a product.

Quantitative photolyses were carried out with portions (4 ml) of  $2 \times 10^{-3}$ M-solutions and analysed by f.i.d.–g.l.c. for t-butyl alcohol, 2-methyl-2-nitrosopropane, and tri-t-butylhydroxylamine on a 2 m  $\times$   $\frac{1}{8}$  in 15% LAC on 80–100 Chromosorb P column with toluene as internal standard. Isobutane, isobutene, and t-butyl methyl ether were analysed on a 4 m  $\times$   $\frac{1}{8}$  in 15% squalane on 80–100 Chromosorb P column with toluene as internal standard. The yield of acetone was determined relative to that of t-butyl methyl ether on a 6 ft  $\times$   $\frac{1}{8}$  in, Porapak Q column.

Preparative g.l.c. (6 ft  $\times$   $\frac{1}{4}$  in, 5% Carbowax 20M/TPA on 60–80 Chromosorb W) of the photolysate obtained in [<sup>2</sup>H<sub>4</sub>]methanol provided a t-butyl methyl ether with a mass spectral base peak at  $m/e$  76 as compared to  $m/e$  73 for the base peak of the undeuterated ether indicating the incorporation of an OCD<sub>3</sub> group.

**Photolysis of (II) in CH<sub>3</sub>OH.**—Acetophenone,  $\alpha$ -methylstyrene, 2-phenylpropan-2-ol, cumene, 2-nitro-2-phenylpropane, and 1-phenyl-1-methylethyl methyl ether were identified as products by g.l.c.–m.s. studies and g.l.c. peak enhancement with authentic samples. Tris-(1-phenyl-1-methylethyl)hydroxylamine was tentatively identified in the involatile photolysis residue on the basis of a strong peak in the mass spectrum at  $m/e$  372 corresponding to the  $M^+ - 15$  fragment. The quantitative studies were carried out with  $8.0 \times 10^{-3}$ M solutions requiring 3 h for completion of the photolysis. Product yields were determined by g.l.c. (2 m  $\times$   $\frac{1}{8}$  in 15% LAC on 80–100 Chromosorb P) with 1-bromonaphthalene as internal standard after removal of the bulk of solvent in vacuo at ambient temperature.

**Photolysis of (III) in CH<sub>3</sub>OH and C<sub>6</sub>H<sub>6</sub>.**—Product identities were established by micropreparative g.l.c. separation on the  $\frac{1}{4}$  in Carbowax column described already followed by i.r. and m.s. examination of the condensed fractions and comparisons with the authentic materials. The products identified were (V), (VI), 2-benzylpropan-2-ol, 1-benzyl-1-methylethyl methyl ether, and 2-benzyl-2-nitrosopropane. An m.s. peak at  $m/e$  206 of the involatile photolysate residue was assigned to a C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>C(CH<sub>3</sub>)<sub>2</sub>NOH-[C(CH<sub>3</sub>)<sub>2</sub>]<sup>+</sup> fragment and is believed to originate from the fragmentation of the trialkylhydroxylamine. The quantitative experiments were carried out using the same column and internal standard as described for (II).

In experiments with benzene as solvent an unknown (ca. 5%) and 1-benzyl-1-methylethyl nitrite were formed additionally. The latter hydrolysed during g.l.c. and was analysed as the alcohol.

**Photolysis of (IV) in CH<sub>3</sub>OH and CD<sub>3</sub>OD.**—Product identification rested on i.r. and m.s. evidence only. 1-Adamantyl nitrate ( $1620 \text{ cm}^{-1}$ ), 1-nitroadamantane ( $1522 \text{ cm}^{-1}$ ),

adamantan-1-ol,  $\nu_{\max}$  3 350 and 1 460  $\text{cm}^{-1}$ ,  $m/e$  152 ( $M^+$ ), adamantyl methyl ether,  $m/e$  166 ( $M^+$ ), and tri-(1-adamantyl)hydroxylamine,  $m/e$  435 ( $M^+$ ) were identified. The characteristic peaks for 1,1-biadamantyl,  $m/e$  270 ( $M^+$ ), and adamantene dimer,<sup>17</sup>  $m/e$  268 ( $M^+$ ), were absent. An unidentified carbonyl compound (1 730  $\text{cm}^{-1}$ ) was also present. The absence of adamantane was established by g.l.c.

The quantitative photolysis was carried out with 25  $\text{cm}^3$  of a  $2 \times 10^{-2}\text{M}$  solution requiring 1 h for complete photolysis. The trisubstituted hydroxylamine precipitated during the photolysis as a solid, m.p. 190° (decomp.). The filtered photolysate was worked up by preparative layer chromatography with chloroform as eluant and five fractions were isolated, weighed, and characterised. An unstable major product present in the crude photolysate decomposed during chromatography and could not be isolated. Characteristic i.r. bands of the crude photolysate at 3 060 and 1 585  $\text{cm}^{-1}$  and the decomposition to nitrous gases<sup>15</sup> and products including nitrosoadamantane permit a tentative identification as *N*-nitroso-1-adamantylhydroxylamine.

A small scale experiment with  $\text{CD}_3\text{OD}$  as solvent followed by m.s. and i.r. examination of the photolysis residue after removal of the solvent provided clear evidence against deuterium incorporation into the adamantane skeleton and for incorporation of three deuterium atoms into the methoxy group of the methyl ether,  $m/e$  169 ( $M^+$ ).

**Dark Reactions of NO with (I) and (III).**—Purified NO was passed into a degassed  $2 \times 10^{-2}\text{M}$  solution of (I) in methanol resulting in the rapid disappearance of the blue colour of the monomer. Isobutene (74%), *t*-butyl methyl ether (14%), and methyl nitrite were identified as the main products. Under the same conditions a methanolic solution of (III) provided 1-benzyl-1-methylethyl methyl ether as well as (V) and (VI) in the ratio 8.5:1 as main products. In benzene as solvent the methyl ether was absent and the ratio of (V) to (VI) was 7.3.

**Preparation and Methanolysis of Alkyl-*N*-nitrosohydroxylamines.**<sup>16</sup>—The crude hydroxylamino analogues of (I), (III), and (IV) obtained by zinc dust reduction of the nitroalkanes were nitrosated in 1M aqueous hydrochloric acid solution by the dropwise addition of one equivalent of aqueous sodium nitrite at 0 °C. The resulting solutions were diluted with methanol (100 ml) and left at ambient temperature for several hours and then examined by g.l.c. Isobutene and *t*-butyl alcohol were the major and *t*-butyl methyl ether an insignificant minor product for the *t*-butyl derivative; 2-benzylpropan-2-ol and the methyl ether were the chief

and the alkenes (V) and (VI) trace products for the 1-benzyl-1-methylethyl derivative. The products obtained in the same way from the nitrosated methanolic-aqueous solution of 1-adamantylhydroxylamine were extracted with dichloromethane and identified as a mixture of adamantan-1-ol and its methyl ether by m.s. and i.r. studies of the crude involatile residue obtained after appropriate work-up.

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