Oxides (Ib) and (Ic) were obtained by analogy (see Table 2).

2-Butylnaphtho[2,3-f]isoquinoline-7,12-dione (IIa). A mixture of 0.17 g (Ia) and 0.1 ml PCl_3 in 10 ml dry chloroform was heated at reflux for 20 min, poured into water, and neutralized with aqueous $NaHCO_3$. Product (IIa) was extracted with $CHCl_3$ and purified by chromatography on silica gel with chloroform eluent. The yield of (IIa) was 0.15 g (see Table 2).

Products (Ib) and (Ic) were reduced analogously to give (IIb) and (IIc) (see Table 2).

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SYNTHESIS OF 1-PHENYL-3,3-DIMETHYLTRIAZENE 2-OXIDE AND THE CORRESPONDING TRIAZENE FROM NITRO COMPOUNDS AND N-MAGNESIUM BROMIDES

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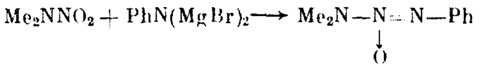
UDC 542.91:547.416:547.551+
546.46'141

The reaction of dimethylnitramine with $Ph{-}N(MgBr)_2$ gives 1-phenyl-3,3-dimethyltriazene 2-oxide, which is the first reported triazene 2-oxide. The reaction of nitrobenzene with $Me_2NNHMgBr$ gives only the corresponding triazene.

Triazene 1-oxides are well-known compounds [1]. However, no information has been available on triazene 2-oxides, in which N^1 is directly bound to a carbon atom. The first representative of this class, 1-phenyl-3,3-dimethyltriazene 2-oxide (III), was obtained according to the following scheme.



$$Me_2NNO_2 + PhN(MgBr)_2 \longrightarrow Me_2N{-}\underset{\displaystyle O}{\underset{\downarrow}{N}}{=}N{-}Ph \qquad (1)$$

(I) (II) (III)

An attempt to obtain 1-phenyl-3,3-dimethyltriazene 1-oxide, which is an isomer of (III), by the action the magnesium derivative of dimethylhydrazine (IV) on nitrobenzene proved unsuccessful. The reaction product does not contain an N-oxide fragment, apparently as a result of the high reductive capacity of (IV).

$$PhNO_2 + \underset{(IV)}{Me_2NNHMgBr} \longrightarrow PhN{=}N{-}NMe_2 \qquad (2)$$

Reductive condensation with formation of only an azo product was also observed in reaction (3).

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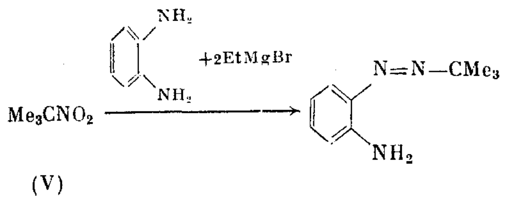

(3)

On the other hand, only an azoxy product is obtained in the reaction of (V) and (II) [2] as in reaction (1).

The reductive action of strong electron-donor magnesium-containing reagents has been observed in the reactions of magnesium derivatives of o-phenylenediamine with aromatic nitro compounds [3].

EXPERIMENTAL

The PMR spectra were obtained on a Bruker AM-300 spectrometer. The ^1H NMR spectra were taken at 300 MHz, while the ^{13}C NMR spectra were taken at 75.5 MHz and the ^{14}N NMR spectra were taken at 21.7 MHz. The mass spectra were taken on a Varian MAT CH-6 mass spectrometer with direct sample inlet into the ion source. Samples of Me_2NNO_2 [4], $PhN(MgBr)_2$ [5], and Me_3CNO_2 [6] were obtained according to reported procedures. All the reactions were carried out in anhydrous solvents in an argon atmosphere.

1-Phenyl-3,3,dimethyltriazene 2-Oxide (III). A sample of (I) in 10 ml abs. THF was added with stirring to a freshly prepared solution of 6.58 g (22 mmoles) (II) in 40 ml abs. THF at 0°C, maintained for 24 h at 20°C, treated with aqueous NH_4Cl, and extracted with ether. The extract was washed with 10% hydrochloric acid and dried over $MgSO_4$. The solvent was removed in vacuum using a water pump. The product was separated by chromatography on silica gel with 1:1 ether—hexane as the yield. The yield of (III) was 0.46 g (25%), bp 64°C (0.25 mm). Found, %: C 58.41; H 6.72; N 25.82. $C_8H_{11}N_3O$. Calculated, %: C 58.18; H 6.67; N 25.46. Mass spectrum (m/z): 165 [M^+]. PMR spectrum in $CDCl_3$ (δ, ppm, TMS): 3.30 s (Me), 7.21 t (p-H), 7.37 t (m-H), 7.65 d (o-H). ^{13}C NMR spectrum in $CDCl_3$ (δ, ppm, TMS): 41.7 (Me), 123.6 ($C^{2,6}$), 126.8 ($C^{3,5}$), 128.5 (C^4), 144.2 (C^1). ^{14}N NMR spectrum in $CDCl_3$ (δ, ppm, $MeNO_2$ as standard): −48.3 ($N \rightarrow O$).

1-Phenyl-3,3-dimethyltriazene. A solution of 0.96 g (16 mmoles) Me_2NNH_2 in 5 ml abs. THF was added with stirring to a freshly prepared solution of EtMgBr obtained from 16.5 mg-equiv. Mg. and 16 moles EtBr in 30 ml abs. THF at 0°C, heated to reflux, maintained for 10 min, and cooled to 0°C. Then, a solution of 1 g (8.1 mmoles) $PhNO_2$ in 5 ml abs. THF was added at the same temperature and heated at reflux for 3 h. The mixture was then treated with aqueous NH_4Cl and extracted with ether. The extract was dried over $MgSO_4$. The product was separated by chromatography on a silica gel column with chloroform eluent. The yield was 0.36 g (30%), bp 70°C (0.35 mm) [7]. PMR spectrum in $CDCl_3$ (δ, ppm, TMS): 3.12 s (Me), 7.07 t (p-H), 7.27 t (m-H), 7.45 d (o-H). ^{13}C NMR spectrum in $CDCl_3$ (δ, ppm, TMS): 38 br (Me), 120.5 ($C^{2,6}$), 125.3 ($C^{3,5}$), 128.75 (C^4), 150.97 (C^1). ^{14}N NMR spectrum in $CDCl_3$ (δ, ppm, $MeNO_2$): +63.5, −27.0, −227.2.

1-(2-Aminophenyl)-2-(1,1-dimethylethyl)diazene. A solution of 15 mmoles o-phenylenediamine in 10 ml THF was added with stirring to a freshly prepared solution of EtMgBr prepared from 35 mg-equiv. Mg and 30 mmoles EtBr in 30 ml abs. THF at 0°C. The mixture was heated at reflux for 10 min and cooled to 0°C. Then, 9.7 mmoles (V) in 5 ml THF was added, heated at reflux for 3 h, treated with aqueous NH_4Cl, and extracted with ether. The extract was dried over $MgSO_4$ and evaporated. The product was separated by chromatography on a silica gel column with chloroform eluent. The yield was 0.79 g (46%). This product was identified relative to the spectra described in our previous work [8].

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N-LITHIUM DERIVATIVES OF ALIPHATIC AMINES IN THE SYNTHESIS OF 1-ALKYL-2-PHENYLDIAZENE 2-OXIDES

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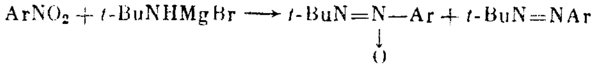
Magnesium derivatives of aliphatic amines containing α-hydrogen atoms, in contrast to t-BuNHMgBr, do not form phenylaliphatic diazene oxides upon reaction with nitrobenzene, but rather reduce it to azobenzene and azoxybenzene. Asymmetric diazene oxides are formed when the magnesium derivatives are replaced by lithium derivatives. The reaction of t-BuNHLi with dimethylnitramine gives 1,3,5-trimethyl-1,3,5-triazacyclohexane.

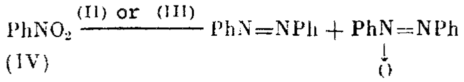
We have shown that aromatic nitro compounds [1], in contrast to their aliphatic analogs [2], react with the magnesium derivative of tert-butylamine (I) to give azoxy derivatives.

 (1)

$$ArNO_2 + \underset{(I)}{t\text{-}BuNHMgBr} \longrightarrow t\text{-}BuN{=}\underset{\substack{\downarrow\\ O}}{N}{-}Ar + t\text{-}BuN{=}NAr \qquad (1)$$

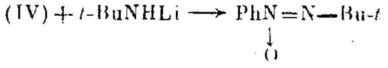
Azo derivatives are also formed as in the reaction of aromatic nitro compounds with aromatic dimagnesylamines [3].

In the present work, we attempted to expand reaction (1) to other amines. Going from t-BuNHMgBr (I) to i-PrNHMgBr (II) and n-BuNHMgBr (III) leads to a sharp increase in the reductive capacity, apparently due to the ready loss of the α-hydrogen atoms. Thus, the action of these reagents on nitrobenzene (IV) under the conditions of reaction (1) leads mainly to the reductive condensation of (IV), namely, azobenzene and azoxybenzene.

 (2)

$$\underset{(IV)}{PhNO_2} \xrightarrow{(II)\text{ or }(III)} PhN{=}NPh + PhN{=}\underset{\substack{\downarrow\\ O}}{N}Ph \qquad (2)$$

In the condensation with (IV), N-lithium derivatives of alkylamines are significantly more active than N-magnesium derivatives. Thus, while the reaction of (IV) with (I) is complete after reflux in THF for 3 h and requires maintenance for many hours at ~20°C [1], the reaction with (V) is complete after only several minutes at −40°C. In this case, the reductive processes are reduced to a minimum and tert-butylphenyldiazene and products of the reductive condensation of (IV) are virtually not formed [see reaction (2)].

 (3)

$$(IV) + \underset{(V)}{t\text{-}BuNHLi} \longrightarrow \underset{(VI)}{PhN{=}\underset{\substack{\downarrow\\ O}}{N}{-}Bu\text{-}t} \qquad (3)$$

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