# Preparation of Trialkyltriazenes. A Comparison of the N–N Bond Rotation in Trialkyltriazenes and Aryldialkyltriazenes by Variable Temperature $^{13}C$ NMR

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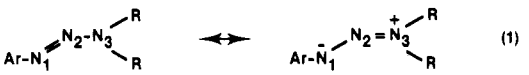
**Abstract:** The synthesis of several trialkyltriazenes in 85–95% yield starting from either benzyl azide or *n*-butyl azide is reported. The starting azide was added to a Grignard reagent or an alkyllithium reagent and the resulting dialkyltriazene, after removal of the nitrogen proton by potassium *tert*-butoxide in *tert*-butyl alcohol, was alkylated with methyl iodide. Alkylation occurred at both N(1) and N(3), the isomers being separated by column chromatography on alumina. The barrier to rotation about the N(2)–N(3) bond, indicative of the contribution of the 1,3-dipolar resonance form, was calculated by the line-width method from variable temperature $^{13}C$ NMR data. The barrier to rotation for these trialkyltriazenes was found to be about 10.5–11 kcal/mol, approximately 3 kcal/mol lower than that of most aryldialkyltriazenes.

## Introduction

Aryldialkyltriazenes have both carcinogenic and tumor-inhibiting properties; consequently, their biological activity has been studied extensively by several groups.[1]

Aryldialkyltriazenes contain an extended $\pi$ system in which there is considerable delocalization of charge density as shown in eq 1. An observable effect of this resonance is an increase



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A B

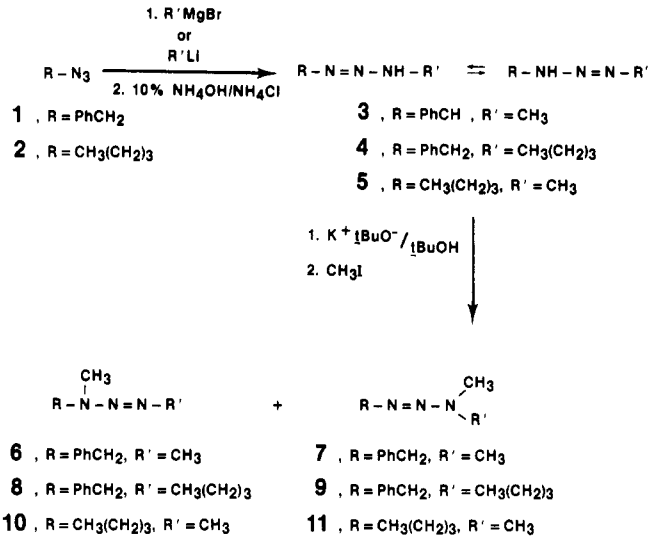
in the effective barrier to rotation about the N(2)–N(3) bond, the magnitude of which has been determined by variable temperature NMR techniques.[2-5] Amine derivatives such as amides,[6] *N*-nitrosamines,[7] enamines,[8] hydrazones,[8] and amidines[9] also exhibit similar characteristics. In aryldialkyltriazenes, the developing negative charge at N(1) is stabilized by the aromatic ring. This stabilization ought to be absent in trialkyltriazenes.

No generally useful synthesis of trialkyltriazenes has been reported. Gale and co-workers[10] reported the trapping of bis(trifluoromethyl)diazomethane by piperidine at −78 °C to afford the trialkyltriazene in modest yields. Paralleling this synthetic procedure was the report of Atherton et al.[11] in which 2,2,2-trifluorodiazoethane was trapped by dimethylamine to give the corresponding trialkyltriazene in 85% yield. Makarov et al.[12] reported the synthesis of 3,3-dimethyl-1-trifluoromethyltriazene in 76% yield by the reaction of nitrosyltrifluoromethane and 1,1-dimethylhydrazine at −50 °C in methanol–ether. More recently, the trapping of the cyclopropyldiazonium ion by dialkylamines was attempted by Kirmse,[13] and Kirmse and Seipp[14] with limited success. They managed to isolate 3,3-dimethyl-1-cyclopropyltriazene in 5% yield, although no triazene was isolated with the higher homologues of dimethylamine. These procedures have very limited general synthetic utility. We report here a facile, high-yield preparation of these compounds. We also report the determination of the N–N bond rotation barriers in these substances, together with similarly determined barriers in aryldialkyltriazenes.

## Results and Discussion

**Synthesis of Trialkyltriazenes.** Several trialkyltriazenes (**6–11**) were prepared from benzyl azide (**1**) or *n*-butyl azide (**2**), which were chosen because of their ease of preparation and handling and stability. The synthetic route is shown in Scheme

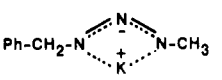
Scheme I




I. In all cases, the isolated overall yields were in the 85–95% range (Table I).

The preparation of dialkyltriazenes was described many years ago by Dimroth.[15] The appropriate alkyl azide was added to the Grignard reagent in diethyl ether solution. When alkyllithiums were used, the reaction had to be carried out in pentane rather than diethyl ether. Thus, when **1** was treated with *n*-butyllithium in pentane, **4** was isolated in quantitative yield. In ether, the azide was recovered unchanged.

The alkylation of the dialkyltriazenes proved to be difficult. Direct reaction with alkylating agents such as methyl iodide or dimethyl sulfate gave no reaction. Methyl fluorosulfonate gave mainly resinous products. Phase-transfer methodology was likewise, unsuccessful. Reaction of the triazenes with potassium *tert*-butoxide in *tert*-butyl alcohol resulted in the formation of the potassium salt of the triazene. This salt proved to be an excellent nucleophile. For example, **12** reacted with methyl iodide to form a 60:40 mixture of 1-benzyl-1,3-dimethyltriazene and 1-benzyl-3,3-dimethyltriazene, respectively, in virtually quantitative yield. Methylation of the salt of **5** resulted in the quantitative formation of **10** and **11** as a



**12**

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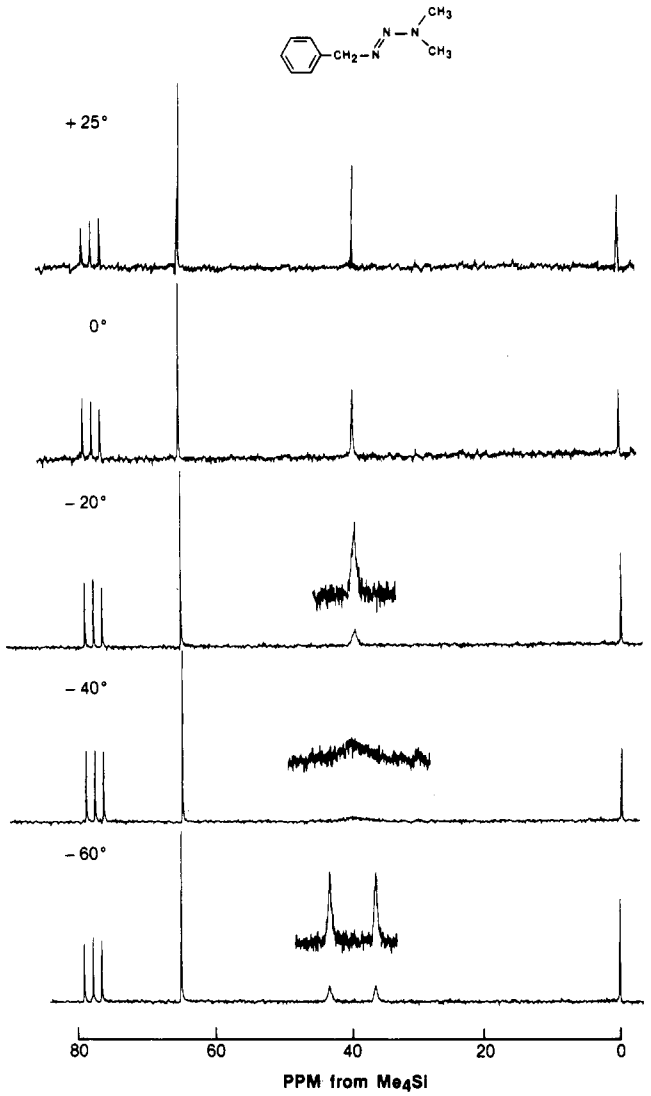



**Figure 1.** Temperature-dependent $^{13}C$ NMR spectra of 1-benzyl-3,3-dimethyltriazene.

50:50 mixture. The isomers were readily separated by column chromatography on alumina.

The trialkyltriazenes (**6–11**) studied are all extremely acid sensitive, decomposing rapidly with the evolution of nitrogen. Their lack of reactivity toward alkylating agents such as methyl iodide, dimethyl sulfate, and methyl fluorosulfonate is similar to 1-phenyl-3,3-dimethyltriazene.[16] Both **7** and 1-phenyl-3,3-dimethyltriazene (**17**) gave *N*,*N*-dimethylacetamide when reacted with acetyl chloride. They are surprisingly stable compounds which can be stored at room temperature in an oxygen atmosphere for several weeks without appreciable decomposition. This similarity in chemical behavior extends to the barrier to rotation about the N(2)–N(3) bond.

**Barriers to Rotation about the N(2)–N(3) Bond.** As a test for the validity of our experimental technique, the temperature-dependent $^{13}C$ spectra of **13** were determined. As can be seen from Table II, the signals for all the aliphatic carbons eventually broadened and emerged as two distinct signals as the temperature was lowered. Because of prior documentation by several groups,[2-4] cis–trans isomerization was ruled out as a cause of this temperature-dependent phenomenon. Also, the chemical shifts for all the carbon atoms were unaffected by changes in concentration.[17] The temperature dependence was measured by the line-width method above and below the coalescence temperature.[18] A plot of log $k$ vs. $1/T$ (correlation coefficient = 0.999) provided an accurate determination of $T_c$.

**Table I.** Overall Yields[a] and Isomeric Distribution for the Synthesis of Trialkyltriazenes from Alkyl Azides

| triazene (isomeric pair) | overall yield, % | % alkylation[b] N(1) | % alkylation[b] N(3) |
|---|---|---|---|
| **(6, 7)** | 95 | 40[c] | 60[c] |
| **(8, 9)** | 91 | 39[c] | 61[c] |
| **(10, 11)** | 85 | 50[d] | 50[d] |

[a] Isolated yields. [b] Average of three determinations. [c] Obtained from an LC analysis (see Experimental Section) with the assumption that the response of both isomers to the detector is identical. [d] Obtained from GLC analysis (see Experimental Section) with the assumption that the response of both isomers to the detector is identical.

From $T_c$ = 299 K and $\delta\nu$ = 209.32 Hz,[19] $\Delta G^{\ddagger}$ was calculated to be 13.8 kcal/mol. This compares favorably with a value of 13.7 kcal/mol determined for 1-phenyl-3,3-dimethyltriazene by Akhtar et al.[3] by $^1H$ NMR. Similarly, $\Delta G^{\ddagger}$ was calculated for 1-phenyl-3,3-dimethyl-, 3,3-diethyl- and 3,3-diisopropyltriazene by Lunazzi and co-workers,[5] the values for which were 13.8, 13.8, and 14.4 kcal/mol, respectively.

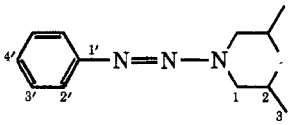
Substitution at the para position of the aromatic moiety of **13** ($p$-$NO_2$, **14**; $p$-Cl, **15**; $p$-$OCH_3$, **16**) provided a set of $\Delta G^{\ddagger}$ values which could be correlated by the Hammett equation.[20] The negative sign and the magnitude of $\rho$ suggest that the observed restricted rotation is due to $\pi$ overlap between the values which could be correlated by the Hammett equation.[20] The negative sign and the magnitude of $\rho$ suggest that the observed restricted rotation is due to $\Pi$ overlap between the amino and azo nitrogens which is lost when the dialkylamino group is rotated 90° out of the Ar—N=N plane. The observed change in rate is thus attributed to the extent by which the substituents influence the difference in $\pi$ delocalization energy between the ground and transition states.[21]

By substitution of an alkyl group for the aromatic moiety in aryldialkyltriazenes, we expected to lessen the stabilization of the developing negative charge at N(1) and, thus, lower the effective barrier to rotation about the N(2)–N(3) bond. This was in fact observed; the effect, however, was much less pronounced than anticipated. A representative sample of the exchange process as a function of temperature using $^{13}C$ NMR is shown in Figure 1 for 1-benzyl-3,3-dimethyltriazene (**7**). Table III shows the exact chemical shifts for **7** and for 1-*n*-butyl-3,3-dimethyltriazene (**11**) as a function of temperature. In a manner similar to that found for the aryldialkyltriazenes, the signals for the *N*-methyls broaden and eventually split into two signals at a reduced temperature. For both structures **7** and **11**, the *N*-methyl which resonates at higher magnetic field is assigned to the position in the 1,3-dipolar form cis to the N atom bearing the negative charge.[22]

The barriers to rotation about the N(2)–N(3) bond for **7** and **11** were calculated by the line-width method[18] and the results were tabulated in Table IV. Both **7** and **11** show an effective barrier to rotation about 3kcal/mol lower than that for **1** and **2**.

Trialkyltriazenes (**6, 8–10**), which are unsymmetrical with respect to the amino portion of the molecule, also show the temperature-dependent phenomenon (Table V), but the calculation of $\Delta G^{\ddagger}$ proved to be quite inexact. As shown in Table V, the appropriate carbons broaden at reduced temperature and sharpen again at even lower temperatures at a different chemical shift. The analytical method of Abraham and Loftus[18] cannot be applied in these cases without some modification. Since the alkyl substituents on the amino nitrogen are not the same, the $\alpha$ carbons will not coalesce. The "coalescence" temperature can be redefined as that temperature at which the signal possesses maximum broadening and minimum height. Obviously, only a visual estimation of $T_c$ can be ex-

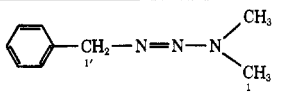
**Table II.** $^{13}C$ Chemical Shifts[a] of 1-Phenyl-3,3-diisobutyltriazene (**13**) as a Function of Temperature

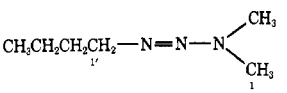


| $t$, °C[b] | C(1′) | C(2′) | C(3′) | C(4′) | C(1) | C(2) | C(3) |
|---|---|---|---|---|---|---|---|
| 60 | 151.23 | 120.54 | 128.46 | 124.90 | 58.94[c] | 27.13 | 20.42 |
| 40 | 151.11 | 120.45 | 128.44 | 124.85 | 59.00[c] | 27.02 | 20.39 |
| 20 | 150.99 | 120.39 | 128.44 | 124.81 | 59.00[d] | 26.93 | 20.34 |
| −5 | 150.82 | 120.27 | 128.44 | 124.76 | 62.51[c] | 27.85[c] | 20.29[c] |
| | | | | | 54.57[c] | 25.75[c] | |
| −20 | 150.72 | 120.20 | 128.44 | 124.73 | 62.59 | 27.85 | 20.47 |
| | | | | | 54.42 | 25.51 | 20.01 |
| −40 | 150.60 | 120.11 | 128.46 | 124.71 | 62.54 | 27.78 | 20.44 |
| | | | | | 54.31 | 25.32 | 19.94 |
| −60 | 150.50 | 120.04 | 128.51 | 124.69 | 62.51 | 27.73 | 20.39 |
| | | | | | 54.21 | 25.14 | 19.91 |

[a] Chemical shifts are relative to $Me_4Si$ and are accurate to ∓0.05 ppm. Data are for $CDCl_3$ solutions. [b] Accurate to ∓0.5 °C. [c] Signal is broadened. [d] Signal is extremely broad.

**Table III.** $^{13}C$ Chemical Shifts[a] of 1-Benzyl-3,3-dimethyltriazene (**7**) and 1-*n*-Butyl-3,3-dimethyltriazene (**11**) as a Function of Temperature[b]





| $t$, °C | C(1) | C(1′) | $t$, °C | C(1) | C(1′) |
|---|---|---|---|---|---|
| 25 | 38.80 | 64.13 | 25 | 38.78 | 60.36 |
| 0 | 38.84 | 64.08 | 0 | 38.80 | 60.38 |
| −20 | 38.8[c] | 64.04 | −40 | 39.0[d] | 60.41 |
| −40 | 39.0[d] | 64.00 | −90[e] | 42.46 | 60.62 |
| −60 | 42.29[c] | 63.98 | | 35.89 | |
| | 35.61[c] | | | | |

[a] Chemical shifts are relative to $Me_4Si$ and accurate to ∓0.05 ppm. [b] Accurate to ∓0.5 °C. [c] Signal is broadened. [d] Signal is extremely broad. [e] Data are for $CD_2Cl_2$ solutions for this temperature only; the remainder are for $CDCl_3$.

**Table IV.** Rotational Data for Selected Triazenes

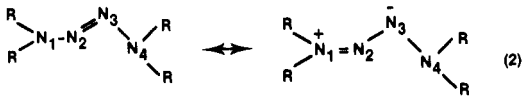
| comp | $T_c$, °C | $\delta\nu$, Hz | $\Delta G$, kcal/mol[a] |
|---|---|---|---|
| **13** | 25 | 189.09 | 13.8[b] |
| **17** | 26 | 209.32 | 13.8 |
| **7** | −42 | 169.05[c,d] | 10.7 |
| **11** | −45 | 165.57[c] | 10.5 |

[a] Accurate to within ∓0.2 kcal/mol. [b] Reference 5. [c] Determined accurately in $CD_2Cl_2$ at −90 °C. [d] $\delta\nu$ = 168.39 Hz at −60 °C in $CDCl_3$; however, the signals were still broadened.

tracted from the spectra. For example, in 1-benzyl-1,3-dimethyltriazene (**6**), if $T_c \approx 40$ °C and $\delta\nu \approx 40$ Hz,[23] the barrier to rotation would be around 11 kcal/mol (∓0.5 kcal/mol).[24] Similarly, if the same approximations are used for triazenes **8–10**, a range of 10.5–11.5 kcal/mol is found for the barriers to rotation.

Examination of Table V also yields an interesting conclusion regarding the orientation of the alkyl groups in the 1,3-dipolar structure. In all examples, the amino methyl is shifted upfield toward $Me_4Si$ at reduced temperature. This requires that the methyl group be cis to the nitrogen atom bearing the negative charge. Consonant with this, the remaining amino alkyl group is shifted downfield away from $Me_4Si$ (most pronounced effect on the $\alpha$ carbon). Thus, the orientation of the alkyl groups on the amino nitrogen depends on the steric requirement of those groups; i.e., the more sterically demanding substituent will orient itself trans to the nitrogen atom bearing the negative charge.

In summary, trialkyltriazenes exhibit a decrease in the effective barrier to rotation of approximately 3 kcal/mol when compared to aryldialkyltriazenes. This suggests that the effect of the aryl ring in stabilizing the 1,3-dipolar contribution is only worth roughly one-quarter of the total barrier. Our initial hypothesis was that the trialkyltriazenes would be more akin to the tetraalkyl-2-tetrazenes, where N–N single bonds rotate freely even at −120 °C,[25] than to aryldialkyltriazenes or nitrosamines. A sufficient condition for restricted rotation seems to be a double bond conjugated with a lone pair on a heteroatom. In tetrazenes, the symmetrical arrangement of two heteroatoms about a double bond probably destabilizes the 1,3-dipolar contribution by simple Coulombic repulsion be-



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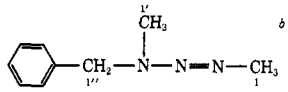
tween the negative charge on atom 3 and the filled nonbonding orbital on atom 4 (eq 2).

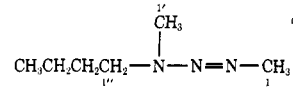
## Experimental Section

Unless otherwise specified, all materials were reagent grade and used without further purification. Aniline (Aldrich) was distilled over Zn dust and stored over 4Å molecular sieves in a light-resistant container. Diisobutylamine and *tert*-butyl alcohol were distilled over BaO and stored over 4Å molecular sieves. Benzyl azide and *n*-butyl azide were prepared and purified by the procedure of Boyer and Hamer.[26] Hexane, pentane, and diethyl ether were dried over sodium shavings before use. The yields reported are isolated yields. Mass spectra were obtained on a Finnigan 3300 mass spectrometer equipped with a Finnigan 6000 data system. The relative intensities have an estimated error of ∓3%. Gas chromatography (GLC) was performed on a Perkin-Elmer Sigma II Series gas chromatograph equipped with a 2 m × 2 mm i.d. column packed with 20% Carbowax 20M on Chromosorb WHP and a nitrogen/phosphorus detector. High-pressure liquid chromatography (LC) was performed on a Laboratory Data Control Constametric II liquid chromatograph equipped with a UV Monitor Model 1203 using a 40 cm × 2 mm i.d. column packed with 18–30 $\mu$ basic alumina. Both gas and liquid chromatographs were interfaced to a Hewlett-Packard Model 3354 computer through a Hewlett-Packard 18652A A/D converter. The area slice method of peak integration was used. NMR spectra were obtained on a Varian XL-100 spectrometer with a Nicolet TT-100 Fourier transform accessory at an rf frequency of 100 MHz for $^1H$ and 25.2 MHz for $^{13}C$. Quadrature phase detection was used for $^{13}C$ spectra along with 10 W of decoupler power with square wave modulation at 70 Hz. The Varian variable temperature controller was calibrated using the proton chemical shift of methanol and has an estimated error of 0.5 °C. Carbon-13 chemical shifts were measured digitally and have an estimated uncertainty of 0.05 ppm. All NMR spectra were obtained

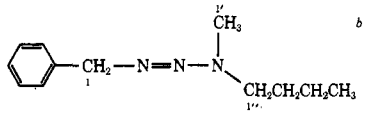
Table V. $^{13}C$ Chemical Shifts[a] of Some Trialkyltriazenes (6, 8, 9, and 10)



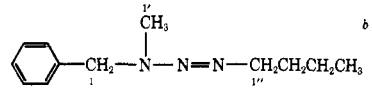
| t, °C | C(1) | C(1′) | C(1″) |
|---|---|---|---|
| 25 | 47.49 | 34.34 | 57.42 |
| −20 | 47.54 | 34.11[d] | 57.64[d] |
| −40 | 47.59 | ~34[e] | ~58[e] |
| −60 | 47.64 | ~33.8[d] | ~58.5[d] |



| t, °C | C(1) | C(1′) | C(1″) |
|---|---|---|---|
| 25 | 47.50 | 34.59 | 53.82 |
| 0 | 47.53 | 34.50 | 53.90 |
| −40 | 47.59 | ~34.3[d] | ~54.2[d] |
| −90 | 47.74 | 33.96 | 54.25 |



| t, °C | C(1) | C(1′) | C(1″) |
|---|---|---|---|
| 25 | 64.02 | 34.64 | 53.75 |
| −20 | 63.91 | ~34.3[d] | ~54.3[d] |
| −60 | 63.89 | 33.97 | 54.86 |



| t, °C | C(1) | C(1′) | C(1″) |
|---|---|---|---|
| 25 | 57.40 | 34.44 | 60.06 |
| −20 | 57.65 | 34.24[d] | 60.08 |
| −60 | ~57.9[e] | 33.98 | 60.16 |

[a] Chemical shifts are relative to $Me_4Si$ and accurate to ±0.05 ppm. [b] Data are for $CDCl_3$ solutions. [c] Data are for $CD_2Cl_2$ solutions. [d] Signal is broadened. [e] Signal is extremely broad.

using tetramethylsilane as an internal standard and $CD_2Cl_2$ or $CDCl_3$ as the solvent.

**Preparation of Aryldialkyltriazenes (13–17).** 1-Phenyl-3,3-dimethyltriazene (**17**), 1-phenyl-3,3-diisobutyltriazene (**13**), 1-(4-nitrophenyl)-3,3-diisobutyltriazene (**14**), 1-(4-chlorophenyl)-3,3-diisobutyltriazene (**15**), and 1-(4-methoxyphenyl)-3,3-diisobutyltriazene (**16**) were prepared by the method of Rondestvedt and Davis.[27] In a typical synthesis, aniline or the appropriately substituted aniline was dissolved in 3 N HCl and diazotized at 0 °C with $NaNO_2$. To this was added the appropriate amine and the resulting solution was made basic with excess $K_2CO_3$. The crude triazenes were purified on an alumina column with pentane as the eluent (**14** required 5% benzene in pentane owing to solubility problems). The physical and spectral properties of **17** were identical with the reported data. Isolated yields were in the 60–75% range.

1-Phenyl-3,3-diisobutyltriazene (**13**): $^1H$ NMR ($CDCl_3$) δ 0.89 (d, 12 H), 2.14 (m, 2 H), 3.47 (d, 4 H), 7.30 (m, 5 H); mass spectrum *m/z* (rel intensity) 233 (2.14, M+), 148 (15.84), 105 (21.28, benzenediazonium ion), 77 (100.00, benzene cation). Anal. ($C_{14}H_{23}N_3$) C, H, N.

1-(4-Nitrophenyl)-3,3-diisobutyltriazene (**14**): $^1H$ NMR ($CDCl_3$) δ 0.97 (d, 12 H), 2.22 (m, 2 H), 3.61 (d, 4 H), 7.50 and 8.12 (aa′bb′, 4 H); $^{13}C$ NMR ($CDCl_3$) 25 °C δ 20.06 and 20.54 (C-3), 25.80 and 28.02 (C-2), 55.38 and 63.37 (C-1), 120.26 (C-2′), 124.62 (C-3′); mass spectrum *m/z* (rel intensity) 278 (0.71, $M^+$), 193 (15.44), 150 (24.77, *p*-nitrobenzenediazonium ion), 122 (100.00, *p*-nitrobenzene cation). Anal. ($C_{14}H_{22}N_4O_2$) C, H, N.

1-(4-Chlorophenyl)-3,3-diisobutyltriazene (**15**): $^1H$ NMR ($CDCl_3$) δ 0.93 (d, 12 H), 2.18 (m, 2 H), 3.53 (d, 4 H), 7.33 (m, 4 H); $^{13}C$ NMR ($CDCl_3$) 25 °C δ 20.32 (C-3), ~26.2 (C-2, very broad), ~54.6 and 62.7 (C-1, very broad), 121.42 (C-2′), 128.51 (C-3′), 129.84 (C-4′), 149.56 (C-1′); mass spectrum *m/z* (rel intensity) 267 (1.69, $M^+$), 182 (13.40), 139 (32.36, *p*-chlorobenzenediazonium ion), 111 (100.00, *p*-chlorobenzene cation). Anal. ($C_{14}H_{22}N_3Cl$) C, H, N.

1-(4-Methoxyphenyl)-3,3-diisobutyltriazene (**16**): $^1H$ NMR ($CDCl_3$) δ 0.94 (d, 12 H), 2.16 (m, 2 H), 3.49 (d, 4 H), 3.78 (s, 3 H), 6.87 and 7.38 (aa′bb′, 4 H); $^{13}C$ NMR ($CDCl_3$) 25 °C δ 20.37 (C-3), 26.94 (C-2, broad), 55.30 ($OCH_3$), ~60 (C-1, very broad), 113.80 (C-3′), 121.12 (C-2′), 144.91 (C-1′), 157.12 (C-4′); mass spectrum *m/z* (rel intensity) 263 (3.60, M+), 178 (4.88), 135 (30.84, *p*-methoxybenzenediazonium ion), 107 (100.00, *p*-methoxybenzene cation). Anal. ($C_{15}H_{25}N_3O$) C, H, N.

**Preparation of Trialkyltriazenes.** The syntheses of the precursor dialkyltriazenes were carried out according to the procedure outlined by Dimroth[15] and refined by Lee and Ko.[29] In a typical synthesis, a solution of 1 equiv of the appropriate alkyl azide in diethyl ether under a nitrogen atmosphere was added, over a 30-min period, to an ice-cooled solution of 1.5 equiv of the appropriate Grignard reagent in diethyl ether. The only modification of this synthesis occurs when an alkyllithium reagent is used as the alkylating agent; then pentane must be used as the solvent. After addition was completed, the reaction mixture was allowed to gradually warm to room temperature (2 h). The complex was then decomposed by the slow addition of an excess of 10% $NH_4OH$–10% $NH_4Cl$ solution. The aqueous layer was discarded and the ethereal layer washed with several 100-mL portions of water, dried over $MgSO_4$ and concentrated under reduced pressure. The crude dialkyltriazenes were chromatographed on an alumina column (elution series for 2 g of crude material; 200 mL of hexane, then 200 mL of hexane–ether (4:1) for a 1-m column). The unreacted azide eluted off in the initial fraction and the pure dialkyltriazene appeared after the eluent polarity had been increased.

1-Benzyl-3-methyltriazene (**3**) was isolated in 95% yield: $^1H$ NMR ($CDCl_3$) δ 1.58 (very broad band, 1 H), 3.18 (s, 3 H), 4.70 (s, 2 H), 7.34 (s, 5 H); mass spectrum *m/z* 149 ($M^+$), 91 (100.00, tropylium ion). 1-Benzyl-3-*n*-butyltriazene (**4**) was isolated in 92% yield: $^1H$ NMR ($CDCl_3$) δ 0.94 (t, 3 H), 1.50 (m, 4 H), 3.52 (t, 2 H), 4.66 (s, 2 H), 7.32 (s, 5 H); mass spectrum *m/z* (rel intensity) 191 ($M^+$), 91 (100.00, trophylium ion). 1-*n*-Butyl-3-methyltriazene (**5**) was not isolated.

The alkylation of the dialkyltriazenes was carried out by the reaction of methyl iodide with the dialkyltriazene anion–potassium cation complex. In a typical synthesis, using **3** as the example, 1.49 g (0.01 mol) of **3** in 25 mL of *tert*-butyl alcohol was added dropwise under a nitrogen atmosphere to a stirred solution of 1.35 g (0.012 mol) of potassium *tert*-butoxide in 50 mL of *tert*-butyl alcohol. After the addition was completed, 2.82 g (0.02 mol) of methyl iodide in 10 mL of *tert*-butyl alcohol was added dropwise over a 15-min period and the resulting mixture was allowed to stir overnight at ambient temperature. The excess *tert*-butyl alcohol was removed on a steam bath at reduced pressure and 100 mL of ether was added immediately after removal from the steam bath. The resulting heterogeneous mixture was filtered to remove excess KI, dried over $MgSO_4$, refiltered, and concentrated at reduced pressure. The crude liquid was purified on an alumina column (eluent hexane–ether, 20:1), unreacted starting material eluting off with hexane–ether (4:1). High-pressure liquid chromatography using a basic alumina column (solvent hexane–ether, 20:1) afforded base line separation of the two positional isomers; 1-benzyl-1,3-dimethylriazene (**6**), retention time 4.48 min, 40%) and 1-benzyl-3,3-dimethyltriazene (**7**, 5.86 min, 60%); both colorless liquids, overall yield 95%.

1-Benzyl-1,3-dimethyltriazene (**6**): $^1H$ NMR ($CDCl_3$) δ 2.86 (s, 3 H), 3.46 (s, 3 H), 4.74 (s, 2 H), 7.30 (m, 5 H); mass spectrum *m/z* (rel intensity) 163 (0.79, M+), 134 (10.06, 120 (49.01), 105 (5.46), 91 (100.00, tropylium ion). Anal. ($C_9H_{13}N_3$) C, H, N.

1-Benzyl-3,3-dimethyltriazene (**7**): $^1H$ NMR ($CDCl_3$) δ 3.13 (s, 6 H), 4.76 (s, 2 H), 7.32 (s, 5 H); mass spectrum *m/z* (rel intensity) 163 (0.23, $M^+$), 134 (2.99), 120 (0.62), 105 (0.79), 91 (100.00, tropylium ion). Anal. ($C_9H_{13}N_3$) C, H, N.

**Alkylation of 1-Benzyl-3-*n*-butyltriazene (4).** **4** was alkylated according to established procedures using 1.91 g (0.01 mol) with 1.35 g (0.012 mol) of potassium *tert*-butoxide and 2.82 g (0.02 mol) of methyl iodide. Workup, followed by purification on an alumina col-

umn (eluent hexane–ether, 20:1), afforded a mixture of two positional isomers in 91% yield. Separation by LC on a basic alumina column (solvent hexane–ether, 20:1) afforded the two isomers (colorless liquids): 1-benzyl-1-methyl-3-*n*-butyltriazene (**8**, retention time 3.28 min, 39%) and 1-benzyl-3-methyl-3-*n*-butyltriazene (**9**, 5.65 min, 60%).

1-Benzyl-1-methyl-3-*n*-butyltriazene (**8**): $^1$H NMR ($CDCl_3$) $\delta$ 0.95 (t, 3 H), 1.1–1.8 (m, 4 H), 2.88 (s, 3 H), 3.63 (t, 2 H), 4.75 (s, 2 H), 7.30 (m, 5 H); mass spectrum *m/z* (rel intensity) 205 ($M^+$), 91 (100.00, tropylium ion). Anal. ($C_{12}H_{19}N_3$) C, H, N.

1-Benzyl-3-methyl-3-*n*-butyltriazene (**9**): $^1$H NMR ($CDCl_3$) $\delta$ 0.95 (t, 3 H), 1.1–1.8 (m, 4 H), 2.98 (s, 3 H), 3.59 (t, 2 H), 4.75 (s, 2 H), 7.30 (s, 5 H); mass spectrum *m/z* (rel intensity) 205 (M+), 91 (100.00, tropylium ion). Anal. ($C_{12}H_{19}N_3$) C, H, N.

**Alkylation of 1-*n*-Butyl-3-methyltriazene (5).** Immediately after workup of the reaction sequence leading to **5**, the product was dissolved in *tert*-butyl alcohol. Assuming quantitative conversion to **5** from *n*-butyl azide and methylmagnesium bromide, this compound was alkylated according to established procedures with 1.2 equiv of potassium *tert*-butoxide and 2 equiv of methyl iodide. Workup and purification on an alumina column (eluent hexane–ether, 20:1) afforded a colorless liquid with a 50:50 mixture of positional isomers in 85% yield. GLC with a 20% Carbowax 20M on Chromosorb WHP column (column temperature 50 °C) afforded base line separation of the two isomers: 1-*n*-butyl-1,3-dimethyltriazene (**10**, retention time 10.2 min, 50%); 1-*n*-butyl-3,3-dimethyltriazene (**11**, 14.6 min, 50%).

1-*n*-Butyl-1,3-dimethyltriazene (**10**): $^1$H NMR ($CDCl_3$) $\delta$ 0.93 (t, 3 H), 1.1–1.8 (m, 4 H), 2.93 (s, 3 H), 3.14 (s, 3 H), 3.50 (t, 2 H); mass spectrum *m/z* 129 ($M^+$). Anal. ($C_6H_{15}N_3$) C, H, N.

1-*n*-Butyl-3,3-dimethyltriazene (**11**): $^1$H NMR ($CDCl_3$) $\delta$ 0.95 (t, 3 H), 1.1–1.8 (m, 4 H), 3.05 (s, 6 H), 3.54 (t, 2 H); mass spectrum *m/z* 129 ($M^+$). Anal ($C_6H_{15}N_3$) C, H, N.

**Separation of Isomers.** The separation of the three pairs of isomers (**6, 7**), (**8, 9**), and (**10, 11**) was effected by column chromatography with hexane as the eluent. Approximately 250 mg of the isomeric mixture was placed on a 2-m alumina column and the flow rate adjusted to 5 mL/min. The progress of separation was monitored by LC (18–30 $\mu$ $Al_2O_3$ basic, solvent hexane–ether (20:1), flow rate 2.0 mL/min) and/or GLC (20% Carbowax 20M on Chromosorb WHP, carrier gas helium, 20 mL/min, nitrogen–phosphorus detector at 260 °C, injector *t* 125 °C, column *t* 175 °C). For the isomeric mixture (**10, 11**) the column temperature was lowered to 50 °C. Samples (5 $\mu$L) were injected directly from the aliquots (25 mL), the collection of which commenced after the first isomer had been detected.

**6** (80 mg, GLC retention time 6.60 min) and **7** (90 mg, GLC 9.45 min) were isolated along with 70 mg of a mixture of isomers. **8** (75 mg, GLC 13.92 min), **9** (92 mg, GLC 18.96 min), and 62 mg of the isomeric mixture were isolated by the above separation techniques. In both separations, isomeric purity was cross-checked by LC. Column separation of **10** and **11** was somewhat poorer; **10** (20 mg, GLC 9.20 min at 50 °C), **11** (15 mg, GLC 13.12 min), and 90 mg of the isomeric mixture. The lower recovery was probably due to the higher volatility of these compounds.

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(17) A dilution study was carried out at three temperatures (60, −5, and −60 °C) and at three concentrations (0.572, 0.286, and 0.143 M) for each temperature with no effect on chemical shift noted.
(18) The rate of the exchange process was estimated above the coalescence temperature using the equation

$$k = (\pi/2)\delta\nu[(\delta\nu/h)^2 - (h/\delta\nu)^2 + 2]^{1/2}$$

where *h* is the total line width at half height in Hz (corrected for natural line width by subtracting from it the line width of the $Me_4Si$ signal at the same temperature) and $\delta\nu$ is the separation of signals in the absence of exchange. This equation is valid to the coalescence point. The broadening of the separate signals under slow exchange can be directly related to the exchange rate by the equation

$$k = \pi(h - h_0)$$

where $h_0$ is the line width in the absence of exchange. Once again the observed exchange broadening was corrected for natural line width. This equation is only valid when the signals are separate. At the coalescence temperature $h = h_0$, $k = 1/\tau$, and the first equation condenses to

$$\tau = 2/\pi\delta\nu$$

If this interchange is treated as a typical rate process, the temperature dependence of the rate constant *k* for the interchange may be expressed by

$$k = RT/Nh \exp(-\Delta G^{\ddagger}/RT)$$

The rate constant at coalescence is given by $k = 1/\tau$ and after rearrangement of terms the above equation condenses to

$$\Delta G^{\ddagger}/RT = 22.96 + \ln(T_c/\delta\nu)$$

where $R = 1.9872 \times 10^{-3}$ kcal/mol, $T_c$ is the coalescence temperature in degrees Kelvin, and $\delta\nu$ is the separation of signals in Hz. Abraham, R. J.; Loftus, P. "Proton and Carbon-13 NMR Spectroscopy"; Heyden and Son: London, 1978; pp 165–168.
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(20) This excellent linear relationship was observed when log $k_x/k_H$ was plotted against the Hammett $\sigma$ values ($\rho = -2.04$). This is in excellent agreement with the results of Akhtar (ref 3, $\rho = -2.09$) and Marullo (ref 2, $\rho = -2.01$) for para-substituted 1-phenyl-3,3-dimethyltriazenes. The earlier studies used $^1$H NMR.
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$$\delta D = 2|D_{25°C} - D_{90°C}|$$

These chemical shifts are for the *N*-methyl carbon.
(24) Using the chemical shift data for the *N*-benzyl $\alpha$ carbon which gives $T_c \approx -35$ °C and $\delta\nu = 55.2$ Hz, the $\Delta G^{\ddagger}$ is again calculated to be about 11 kcal/mol.
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