Non-equivalence of α-Hydrogens of 3,3-Dialkyl-1-tosyltriazenes

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Summary The n.m.r. spectra of 3,3-dialkyl-1-tosyltriazenes, a novel class of compounds, exhibit two distinct alkyl peaks.

A NOVEL class of compounds, 3,3-dialkyl-1-tosyltriazenes (III) has been isolated from the reaction of 1,1-dialkylhydrazine anions (I) with tosyl azide (II).† The magnetic nonequivalence of the α-hydrogens in dialkyl *N*-nitrosamines was initially reported by Looney, Phillips, and Reilly[1a] and later by Karabatsos and Taller.[1b] A wide variety of compounds of the same type (IV) has been studied subsequently.[2] It now seems well established that this effect is due to the restricted rotation around the N–A bond caused by the substantial contribution of resonance form (IV′) to the structure of these molecules. Since the tosyltriazene group can be considered formally as the aza-analogue of *N*-nitrosamines, it was expected that a similar effect would be observable in our case.

Our expectation was realized. The n.m.r. spectra‡ of (IIIa) and of (IIIb) each exhibited two distinct peaks for the methyl and methylene protons, respectively, at *room temperature*. The methyl groups of (IIIa) appeared as two sharp singlets at τ 6·50 and 6·83 ($\Delta\tau$ 0·33) while the methylene protons of (IIIb) showed two sharp peaks at τ 4·97 and 5·10 ($\Delta\tau$ 0·13). In the case of 3,3-dialkyl-1-aryltriazenes, the single peak for the α-hydrogens did not split into two distinct absorptions until well below room temperature.

The comparison of the $\Delta\tau$ values between the methyl and

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† Satisfactory elemental analyses were obtained for all new compounds.

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benzyl series revealed the same "counterbalancing" effect of the phenyl groups. As in the *N*-nitrosamines,§ $\Delta\tau$ for the two methyl peaks in (IIIa) was much larger than that of the benzylic hydrogens of (IIIb). This may reflect the greater susceptibility of the methyl group to the polarization induced by the electron withdrawing group [B in (IV)].

Restricted rotation caused by the partial double bond between N and A (IV) is evidently a necessary but not a sufficient condition for the different chemical shifts of the α-hydrogens. The origin and the magnitude of the shielding experienced by the hydrogens *cis* to B has been ascribed to the partial negative charge residing on B.[1b] This interesting hypothesis seems even more plausible when the n.m.r. data for compounds of related structures are examined in the present context. Middleton[4] reported that *NN*-dimethylthionitrosamine (V) exhibited two distinct and well separated peaks at τ 5·90 and 6·40 ($\Delta\tau$ 0·50)¶, while the n.m.r. spectrum of *NN*-dimethylsulphinylhydrazine (VI) showed a single peak at τ 6·63. While no quantitative comparison can be made at this time, it can be safely assumed that S=O and N–Tos are both better electron-withdrawing groups than sulphur. Yet (VI) shows a single peak and in (IIIa), $\Delta\tau$ is only 0·33. The presence of negative charge localized on atom B thus assumes an even greater importance since in (III) and (VI) the possibility of further delocalization of charge on adjacent atoms apparently reduces or eliminates the influences of the partial negative charge on the *cis*-hydrogens. If this is true, then it would appear that the contribution of (VI′) [and to a much lesser extent of (III′)] to the ground state is very large indeed.[5]

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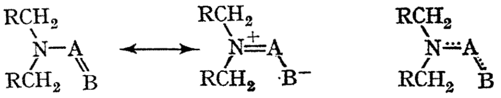
$$\underset{\text{(I)}}{R_2NNH} + \underset{\text{(II)}}{TosN_3} \xrightarrow{\text{low temp.}} \underset{\text{(III)}}{R_2N{\cdot}N{:}N{\cdot}Tos}$$

(a) R=Me, (b)R=PhCH$_2$; Tos=*p*-toluenesulphonyl.

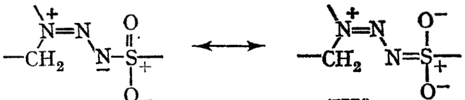


(IV) (IV′) (IV″)

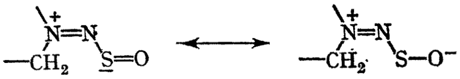
A=—C, N; B= >C, —N, O

$Me_2N{\cdot}N{:}S$ (V)

$Me_2N{\cdot}N{:}S{:}O$ (VI)



(III) (III′)



(VI) (VI′)

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§ The spectrum of *NN*-dibenzylnitrosamine was also determined for comparison and showed two sharp peaks for the benzylic protons at τ 4·86 and 5·39 ($\Delta\tau$ 0·53); these values agree very well with those previously obtained (ref. 1b) for *cis*- and *trans*-benzylic protons.

¶ Dimethylnitrosamine shows two peaks at τ 6·24 and 7·04 ($\Delta\tau$ 0·80) (ref. 1b).

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