

ON THE TAUTOMERISM OF 3-ALKYL-1-ARYLTRIAZENES

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(Received in Japan 20 May 1976; received in UK for publication 15 June 1976)

The tautomeric structure of triazenes is the subject of long-standing debate.¹⁾ Alkylaryltriazenes prepared by Dimroth were assigned to structure B, because an aniline, nitrogen and a chloro-alkane were obtained by treatment with dilute HCl.²⁾ Recently Isaacs and Rannala found that the ¹H nmr spectrum of 3-methyl-1-p-tolyltriene 1 shows a doublet for the N-methyl and a quartet for the NH protons, and interpreted this resonance pattern as indicating the presence of the single 3-alkyl-1-aryl tautomeric form A as the more stable one (at -65° C in dichloromethane).³⁾ While the conclusion seems to be reasonable with respect to resonance interaction between the aryl and diazenyl chromophores in A, we found that most of the thermal decomposition of the triene was initiated from the other tautomeric form B, the driving force of the reaction being the stability of the p-tolylaminyl as compared to the methylaminyl radicals.⁴⁾

We now report that the ¹³C nmr spectra of 1 taken at temperatures ranging from -40 to +100° C reveal the presence of ca. 18% B in CDCl₃ at these temperatures. As shown in Fig. 1a and Table 1, the six main peaks at δ 21.2, 31.2, 120.0, 129.4, 135.5 and 147.9 ppm in the ¹³C spectra at lower temperatures are

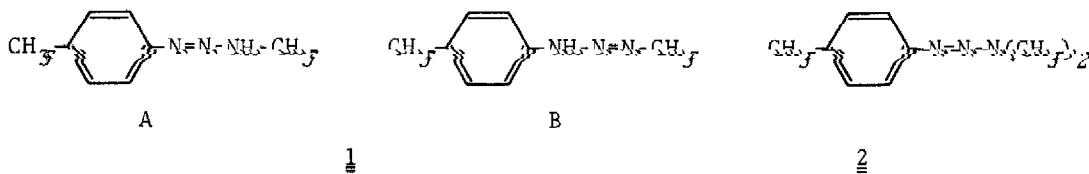


Table 1. ^{13}C nmr shifts^a of triazenes in CDCl_3 at -40 to -50°C .⁵⁾

No	C-1	C-2	C-3	C-4	C-CH ₃	N-CH ₃
<u>1A</u>	147.9	120.0	129.4	135.5	21.2	31.2
<u>1B</u>	b	115.6	129.4	b	21.2	54.0
<u>2</u>	148.2	119.9	129.5	134.9	21.1	35.9
						43.2

^a Accuracies of δ_{C} (in ppm downfield from internal TMS) are about ± 0.05 ppm.

^b Not observable under the S/N of the experimental conditions.

consistent with structure A. This is supported by comparison with the ^{13}C chemical shifts of 3,3-dimethyl-1-p-tolyl-triazene 2 with the fixed structure A (Table 1). For 1 we note two additional peaks at δ 54.0 and 115.6, the latter being still broad. At higher temperatures, the signals except those due to the

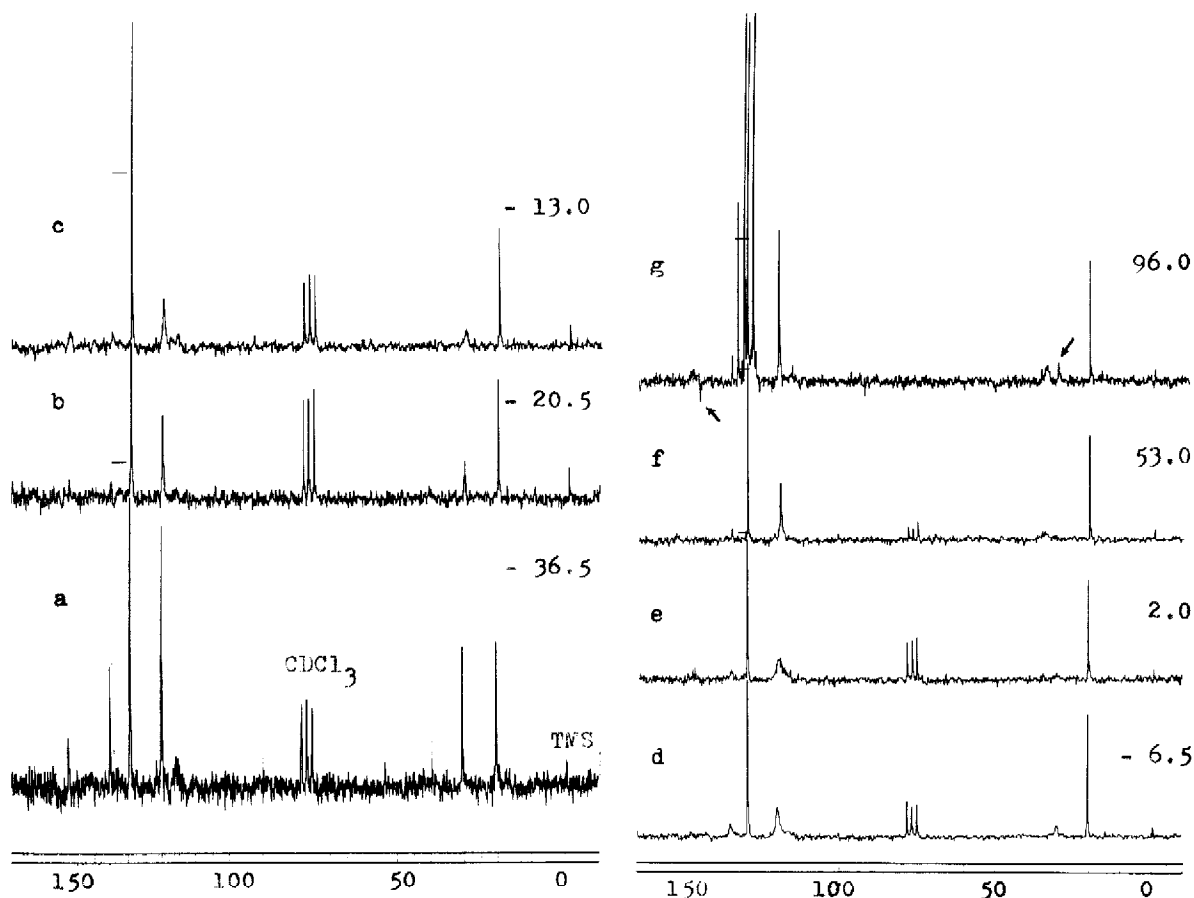
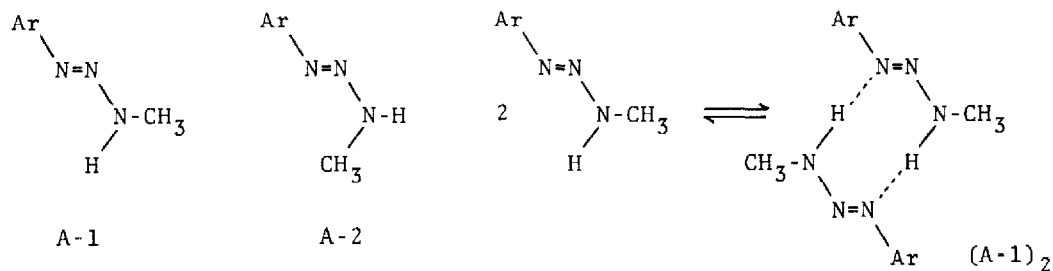


Fig. 1. ^{13}C nmr spectra (20.1 MHz) of 1 at various temperatures: (a) \sim (f) 0.1M in CDCl_3 and (g) in $o\text{-C}_6\text{H}_4\text{Cl}_2$ (The arrowed signals are due to CIDNP).⁴⁾

metacarbons of the ring and the aromatic methyl broaden and start to coalesce. The coalescence temperatures are ca. 0° C for the ortho-carbons and 30° C for the N-methyl carbon. At enough high temperature, we note a single resonance each for the ortho-carbons at δ 119.1 and the N-methyl at 35.1.

The results are interpreted in terms of rapid equilibrium between forms A and B of the triazene 1, with the two additional peaks at the lower temperature assigned to form B. The shift data of the ortho-carbons, δ 120.0 and 115.6 for A and B, respectively, are considered reasonable in reference to the corresponding values δ 122.7 and 112.5 of p-azotoluene and p-hydrazotoluene, respectively. The proportion of B is estimated from the relative intensities of these clearly discerned signals at the lower temperature to be ca. 18 % (17 % by the relative peak heights of the two N-CH₃'s and 19 % by the peak height of the ortho-carbons due to A relative to that of the meta-carbons due to A + B). If it is assumed that the location $\langle\delta\rangle$ of the coalesced single peak is related to the proportion p_B of tautomer B in the equilibrium by conventional relationship, $p_B = \frac{\delta_A - \langle\delta\rangle}{\delta_A - \delta_B}$, we get 18 % and 17 % from the ortho-carbons and N-methyl carbon, respectively, as the proportion of B at the higher temperature.

It might be argued that the temperature dependent ¹³C nmr spectra obtained here might be originating from other exchange processes. The first of these may be restricted rotation around the N²-N³ bond. It is well established by the dynamic ¹H nmr studies that in 2 the N¹ = N² bond is fixed trans and there is a barrier to rotation (ΔG_c) of 12.1^{6a)} (13.0^{6b)}) Kcal/mole for the N²-N³ single bond. From the coalescence of the ¹³C signals of the N(CH₃)₂ group of 2, we obtain $\Delta G_c = 13.2$ Kcal/mole. These results would allow us to assume hindered rotation (A-1 \rightleftharpoons A-2) in triazene 1. The barrier to the process observed in this study is estimated to be 13[~]13.5 Kcal/mole by assuming the coalescence of C-2 and N-methyl signals with $\Delta\nu = 4.4$ and 22.9 ppm at 0° C and 30° C, respectively.⁷⁾ The values are thus quite close to that of rotation. However, it is not highly likely that the chemical shifts of the N-methyl carbons differ by 23 ppm between A-1 and A-2, since in 2 this difference is only 7.3 ppm. Moreover, the shift data of the ring carbons are consistent with the presence of two kinds of substituents of considerably different electronic effect; the ortho-carbon shifts of A and B correspond nicely to the azo and hydrazo type chromophores,



respectively. In other words, it is considered as a remote possibility that a mere conformational change will produce large shifts of the ortho-, para- and ipso-carbons in the N-substituted phenyl ring.

Secondly, a monomer-dimer equilibrium, e.g., $2(A-1) \rightleftharpoons (A-1)_2$, could be responsible for the exchange process.⁸⁾ The possibility is ruled out in the present case by the vapor phase osmometric determination of the effective molecular weight of 1 as 145 ± 5 .⁹⁾

Thus the temperature dependent ^{13}C nmr spectra of 1 are best explained in terms of tautomerism $A \rightleftharpoons B$ in which form A predominates but form B is still present in ca. 18 %. The conclusion is in harmony with the ir study by Hadži and Jan,¹⁰⁾ a CCl_4 solution of the triazene 1 shows a weak absorption (0.09 in unit of $10^4 \text{ mol}^{-1} \times 1 \text{ x cm}^{-2}$) due presumably to form B at 3337 cm^{-1} in addition to the main band at 3468 cm^{-1} (0.56) which is attributed to the $\text{CH}_2\text{N-H}$ stretching of form A. The failure to detect the ^1H nmr signals due to form B³⁾ may be ascribed to low intensities of these signals which could be still broad owing to appreciable rate of the site-exchange which is not frozen out by the time scale of ^1H nmr. The separation of chemical shifts between the exchanging species is smaller in ^1H than in ^{13}C nmr.

References and Notes

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