

INTERACTION BETWEEN REMOTE BRIDGEHEAD SUBSTITUENTS
IN 1,6-BIS-(1-CYANO-1-METHYLETHYL)TRIPTYCENES
UNDER ELECTRON IMPACT

Hiizu Iwamura

Department of Chemistry, Faculty of Science, The University of Tokyo,
7-3-1 Hongo, Bunkyo-ku, Tokyo, 113 Japan

(Received in Japan 12 September 1973; received in UK for publication 5 October 1973)

Numerous recent studies¹ suggest that electron impact induced elimination reactions involving the loss of small molecules, such as water, hydrogen halides and acetic acid, are influenced by intramolecular interactions of the atoms concerned which are brought to within approximately normal bonding distances in molecular ions (proximity effects).

We wish to report on the stereospecificity of the elimination of the bridgehead 1-cyano-1-methylethyl groups which are held far apart and rigidly on the triptycene structure. The mass spectra² of atropisomeric 1,6-bis-(1-cyano-1-methylethyl)trptycenes 1a and 1b³ are almost superimposable to each other with three prominent peaks at m/e 388, 320 and 252 which are assigned to the parent M^{\ddagger} , $(M - CMe_2CN)^{\ddagger}$ and $(M - 2 CMe_2CN)^{\ddagger}$ ions, respectively. We note, however, that the relative intensities of the three peaks are reproducibly different between 1a and 1b. The stereochemical dependence of the intensities at several ionization voltages is given in Table I. Notice that, although the proportion of the fragment ions relative to the parent decreases sharply below 20 eV, the ratios 1a/1b of the relative ion intensities are kept constant at values 0.78 and 1.79.

The kinetic relationships for the fragmentation given in Scheme 1 are supported by the observation of metastable ion peaks at m/e 263.9 and 198.5 corresponding to the stepwise loss of stable 1-cyano-1-methylethyl radicals. In the mass spectrometry we may equate the ratios of two ion intensities

Scheme 1

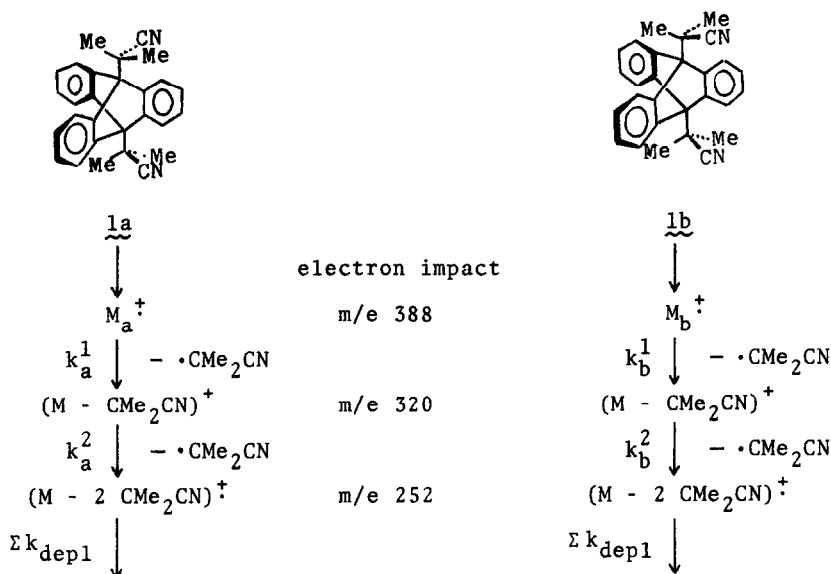


Table I. Relative Ion Intensities

		Nominal Ionizing Potential (eV)				
		70	40	20	17	15
<u>1a</u>	$M^{\ddagger}/(M - 2 \text{ CMe}_2\text{CN})^{\ddagger}$	5.5	5.1	18.6	45.5	92.4
	$(M - \text{CMe}_2\text{CN})^{\ddagger}/(M - 2 \text{ CMe}_2\text{CN})^{\ddagger}$	7.7	7.9	23.2	40.9	67.7
<u>1b</u>	$M^{\ddagger}/(M - 2 \text{ CMe}_2\text{CN})^{\ddagger}$	6.9	6.5	24.5	55.5	125.2
	$(M - \text{CMe}_2\text{CN})^{\ddagger}/(M - 2 \text{ CMe}_2\text{CN})^{\ddagger}$	4.4	4.4	12.5	23.5	37.5
<u>1a/1b</u>	$M^{\ddagger}/(M - 2 \text{ CMe}_2\text{CN})^{\ddagger}$	0.80	0.79	0.76	0.82	0.74
	$(M - \text{CMe}_2\text{CN})^{\ddagger}/(M - 2 \text{ CMe}_2\text{CN})^{\ddagger}$	1.75	1.79	1.85	1.74	1.80

The data are the average of five runs and the deviations are ca. $\pm 4\%$.

$M^{\ddagger}/(M - 2 \text{ CMe}_2\text{CN})^{\ddagger}$ and $(M - \text{CMe}_2\text{CN})^{\ddagger}/(M - 2 \text{ CMe}_2\text{CN})^{\ddagger}$ to $\Sigma k_{\text{depl}}/k^1$ and $\Sigma k_{\text{depl}}/k^2$, respectively. Σk_{depl} includes all the rate constants of depletion of $(M - 2 \text{ CMe}_2\text{CN})^{\ddagger}$ ion whether by decomposition or instrumental removal.⁴ Therefore the results in Table I lead directly to $k_b^1/k_a^1 = 0.78$ and $k_b^2/k_a^2 = 1.79$. In other words, the rate of elimination of the first CMe_2CN radical from the parent M^{\ddagger}

ion is faster for 1a, while the subsequent fragmentation is slower for the $(M - CMe_2CN)^+$ ion from 1a. These results appear to have twofold significance. Firstly, we have to consider some kind of intramolecular interaction between two bridgehead 1-cyano-1-methylethyl groups in the parent ions to effect the acceleration of fragmentation in M_a^+ or the retardation in M_b^+ . Secondly, the result that the next steps to give a common $C_{20}H_{12}$ ion⁵ have different rates $(k_a^2 \neq k_b^2)^6$ in 1a and 1b requires that $(M - CMe_2CN)^+$ ions formed from parent ions M_a^+ and M_b^+ are not identical. Since it is apparent that isomerism present in 1a and 1b is structurally lost as soon as one of the CMe_2CN groups is removed, the origin of the discrimination must be sought in the amount of excess electronic energy or uneven distribution of the excess energy.

In order to account for the above two phenomena consistently, a mechanism is needed in which excitation of one end of the molecule results in conformation dependent transfer to the other end in the parent ions. Transfer of electrons or electronic excitation can be a candidate for the mechanism.⁷ The one assumes the role of the triptycene skeleton as a conductor of electronic interaction between the bridgehead substituents. In the parent ion M_b^+ , two benzene rings flanking the cyano groups are especially effective in diffusing the positive charge initially induced under electron impact in the cyano group on one of the CMe_2CN substituent over to the cyano group on the other end of the bridgehead via π -type through-space interaction. There is only one such benzene ring which is oriented gauche to the two cyano groups simultaneously in M_a^+ . Secondly the transmission of electronic excitation can also be conformation-dependent. There is considerable literature on long-range dipole-dipole singlet energy transfer. The transfer efficiency is known to depend on the distance as well as the relative orientation of the transition dipole vectors.⁸ Thus it is apparent from molecular models that excess electronic energy in one of the cyano groups can be transferred over to the other more efficiently in M_b^+ in which two cyano groups are eclipsed (proximity effects). The excess electronic energy is more easily concentrated in one C-C bond β to the cyano group in M_a^+ and elimination of one CMe_2CN group is facilitated in M_a^+ than in M_b^+ . Conversely, the memory of the diffusion of the positive charge and/or excess electronic energy over to

the other end of the molecule in M_b^+ must be kept in daughter ion $(M - CMe_2CN)^+$ and be used in weakening the remaining C-CMe₂CN bond more effectively than in $(M - CMe_2CN)^+$ ion from M_a^+ (memory effects).

REFERENCES

- (1) S. Meyerson and A. W. Weitkamp, Org. Mass Spectrom., 1, 659 (1968); M. M. Green, J. M. Moldowan, D. J. Hart, and J. M. Krakower, J. Amer. Chem. Soc., 92, 3491 (1970); C. C. Fenselau and C. H. Robinson, ibid., 93, 3070 (1971); D. R. Dimmel and J. M. Seipenbusch, ibid., 94, 6211 (1972); J. K. McLeod and R. J. Wells, ibid., 95, 2387 (1973).
- (2) Measured on a Hitachi RMU-6 instrument using the direct inlet system at source temperatures between 150 and 170° at which temperatures the thermal isomerization between 1a and 1b is negligible.³ The authors are indebted to Dr. T. Nishihama for the spectral measurement.
- (3) H. Iwamura, Chem. Commun., 232 (1973).
- (4) For the kinetic approach to the mass spectrometry within the framework of the quasi-equilibrium theory, see M. M. Bursey and F. W. McLafferty, J. Amer. Chem. Soc., 88, 529 (1966); ibid., 89, 1 (1967); R. G. Cooks, I. Howe, and D. H. Williams, Org. Mass Spectrom., 2, 137 (1969).
- (5) M. I. Bruce, Chem. Commun., 593 (1967).
- (6) All attempts to detect any metastable ion peak at m/e 163.7 due to the concerted loss of two CMe₂CN groups from the parent ions were unsuccessful.
- (7) Both singlet and triplet energy transfer between bridgehead chromophors across the bicyclo[2.2.2]octane structure has been shown to be efficient (H. E. Zimmerman and R. D. McKelvey, J. Amer. Chem. Soc., 93, 3638 (1971)).
- (8) Th. Förster, Discuss. Faraday Soc., 27, 7 (1959).