

premise that a methyl group is only lost from one of the terminal positions (6 or 6a in I), an assumption which seems reasonable for a compound containing an isopropyl group. The spectrum of the C-2 labeled compound has been corrected for undeuterated contaminant by subtracting the spectrum of the unlabeled parent I.

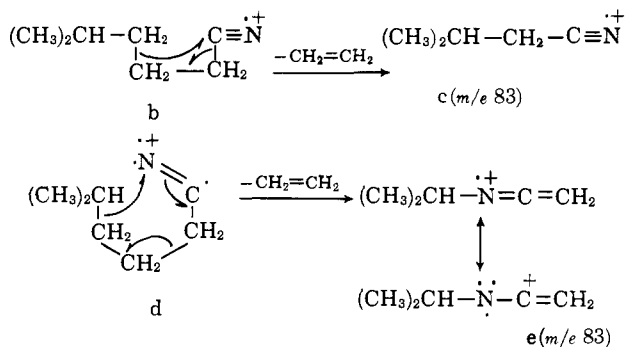
The peak at m/e 83 ($M - 28$) in the spectrum (Fig. 1) of I is essentially all (99%) made up of nitrogen-containing fragments. In Table II the masses observed for isohexyl cyanide and its labeled analogs are collected for the relevant region, the most abundant peak of the group always being given the arbitrary value of 100. The values given in this and subsequent tables are not corrected for under-deuterated contaminants (see Table I) since this would necessitate additional assumptions.

TABLE II
MASS SHIFTS IN THE $M - 28$ REGION

| Compound | m/e | | | | |
|----------------|-------|-----|-----|-----|----|
| | 82 | 83 | 84 | 85 | 86 |
| d_0 -I | 14 | 100 | 8 | 6 | 0 |
| 2- d_2 -I | 21 | 45 | 100 | 62 | 4 |
| 3- d_2 -I | 7 | 100 | 13 | 3 | 0 |
| 5- d_1 -I | 4 | 6 | 100 | 9 | 0 |
| 6,6a- d_2 -I | 2 | 3 | 11 | 100 | 7 |

From Table II it can be seen that the label from C-3 is completely lost, while the deuterium at C-5 and C-6 is retained. Since the expelled 28 mass units must correspond to the elements of ethylene (C_2H_4), two hydrogen atoms have been accounted for. The spectrum of the C-2 labeled analog indicates that about 22% of the remaining hydrogen comes from this source and therefore the rest has to be lost from C-4, where no labeled derivative was available.

Production of ethylene from C-2 and C-3 can be rationalized through a four-membered transition state (see arrows⁶ in b) to yield c, while the dominant process—incorporation of C-3 and C-4—may proceed through a six-membered transition state (d) to give the ion e. The spatial requirements of such an intermediate make it necessary that the molecular ion exist in a mesomeric form (such as d) if this process is to operate among nitriles.



The peak at m/e 69 in the spectrum of I (Fig. 1) is made up of C_4H_7N and C_5H_9 ions in the ratio of 2.04:1. The relevant mass shifts in this region are compiled in Table III, where it can be seen that during the forma-

(6) A full arrow (\curvearrowright) will be used to indicate a two-electron shift, while a "fishhook" (\curvearrowleft) represents a one-electron transfer; see H. Budzikiewicz, C. Djerassi, and D. H. Williams, "Interpretation of Mass Spectra of Organic Compounds," Holden-Day, Inc., San Francisco, Calif., 1964, pp. xi-xiii.

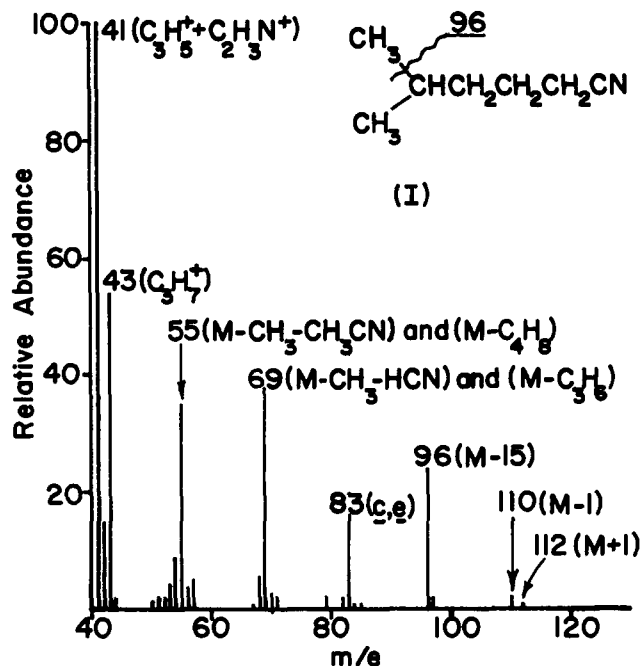


Fig. 1.—Mass spectrum of isohexyl cyanide (I).

tion of both species the labels at C-2 and C-3 are retained. The genesis of the nitrogen-containing fragment(s) must involve the loss of C_3H_6 . Since C-2 and C-3 are not involved, the most plausible explanation is the expulsion of the terminal isopropyl group with back transfer of one hydrogen atom. Rearrangement from C-5 would imply fission of two bonds at the same carbon atom, a less likely process, and therefore the origin of the back-transferred hydrogen can be assumed to be C-6. A possible representation would be f, which is reminiscent of olefin elimination in hydrocarbons.

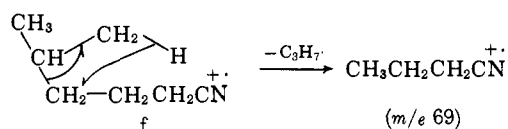


TABLE III
MASS SHIFTS IN THE m/e 69 REGION

| Compound | m/e | | | | |
|----------------|-------|-----|-----|-----|----|
| | 68 | 69 | 70 | 71 | 72 |
| d_0 -I | 17 | 100 | 9 | 5 | 0 |
| 2- d_2 -I | 16 | 25 | 100 | 70 | 6 |
| 3- d_2 -I | 13 | 12 | 19 | 100 | 9 |
| 5- d_1 -I | 9 | 100 | 42 | 4 | 5 |
| 6,6a- d_2 -I | 19 | 100 | 84 | 17 | 2 |

For this process alone, 67% of the label from C-5 as well as 45% d_2 and 22% d_1 from both C-6 and C-6a should be lost (no isotope effect assumed to be operative).

For the formation of the hydrocarbon component of m/e 69, a process analogous to the one observed for isohexyl bromide,⁷ viz., the loss of the terminal methyl group together with hydrogen cyanide, can be invoked. Ignoring first the hydrogen eliminated as hydrogen cyanide, no deuterium loss should be observed from C-5 for this process and 33% of d_1 from C-6 and C-6a; the net result for both fragments C_4H_7N and C_5H_9 would

(7) D. H. Williams, C. Beard, H. Budzikiewicz, and C. Djerassi, *J. Am. Chem. Soc.*, **86**, 877 (1964); see also Chapter 7 in ref. 6.

then be 67% d_1 from C-5, and 45% d_2 and 55% d_1 from C-6 and C-6a. Inspection of Table III indicates that the combined d_2 -loss from C-6 and C-6a and the d_1 -loss from C-5 is higher than calculated, the difference (together with the unknown loss from C-4) accounting for the hydrogen eliminated as hydrogen cyanide. The deuterium labeling data are therefore in agreement with the proposed modes of fragmentation. It remains only to mention that the loss of hydrogen cyanide in this process is much more specific than the loss of hydrogen bromide (together with methyl) from isohexyl bromide,⁷ presumably because of the different spatial requirements of the cyanide and bromide substituents.

The peak at m/e 55 is again made up of two species, C_4H_7 and C_3H_5N , in a ratio of 2.94:1. Table IV shows the relevant mass shifts upon deuteration.

TABLE IV
MASS SHIFTS IN THE m/e 55 REGION

| Compound | m/e | | | | |
|----------------|-------|-----|-----|-----|----|
| | 54 | 55 | 56 | 57 | 58 |
| d_0 -I | 24 | 100 | 12 | 14 | 1 |
| 2- d_2 -I | 24 | 100 | 41 | 36 | 3 |
| 3- d_2 -I | 31 | 32 | 47 | 100 | 24 |
| 5- d_1 -I | 19 | 44 | 100 | 12 | 7 |
| 6,6a- d_2 -I | 31 | 32 | 100 | 16 | 7 |

One mode of formation of the hydrocarbon portion, namely, genesis from the terminal groups by cleavage of the 3,4-bond (yielding C_4H_9) and further loss of two hydrogen atoms, can be eliminated immediately from the data collected in Table IV. This follows, since whatever processes for the abstraction of the two hydrogen atoms might be operative, the two deuterium labels at C-6 and C-6a should be retained to an appreciable extent, which is certainly not the case. Loss of one terminal methyl group and of methyl cyanide (process g analogous to the formation of the hydrocarbon ion m/e 69) is another possibility. Such a proposal (see g) is supported strongly by the predominant loss of one deuterium atom from the 6,6a- d_2 derivative as well as the predominant expulsion of both deuterium atoms from C-2. Again, ignoring the source of the additional hydrogen atom lost in methyl cyanide, the theoretical deuterium losses for the $C_4H_7^+$ component of the m/e 55 peak are compiled in Table V.

The formation of the C_3H_5N species could be visualized by two processes, either through cleavage of the 3,4-bond with transfer of one hydrogen atom (h) to form $CH_3CH_2CN^+$, or cleavage of the 2,3-bond and transfer of the terminal methyl group (i) to give formally the same species. The former process (h) would involve retention of the C-3 label, while the latter (i) postulates retention of one of the C-6 labels. The theoretical deuterium losses for the formation of the ions h and i are summarized in Table V. The over-all effect which should be observed in the spectrum is then available in the "total" entries and may be compared with the experimental results collected in Table IV. Such a comparison indicates that an unambiguous differentiation between processes h and i is not possible and that both may be operative.

Two other intense peaks in the spectrum (Fig. 1) of I merit comment. The major contributor (89%) to the m/e 43 peak is $C_3H_7^+$ and the shifts observed (see Table VI) indicate that it is mainly derived from the

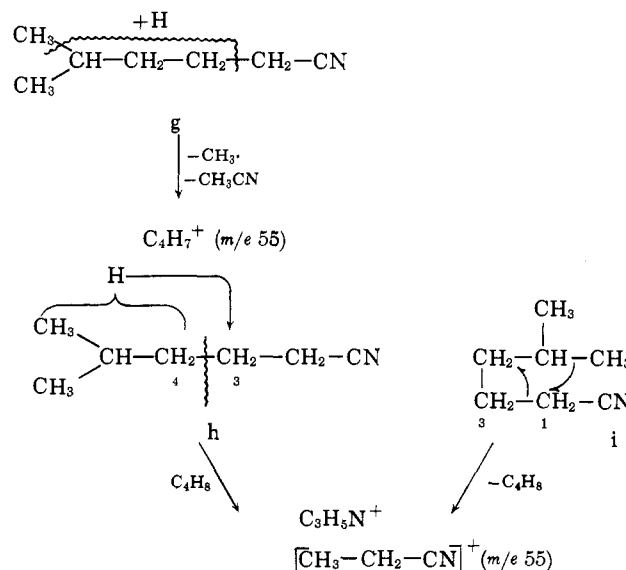


TABLE V
CALCULATED DEUTERIUM LOSSES FOR THE FORMATION OF m/e 55
IN ISOHEXYL CYANIDE

| Compound | Fragment ion ^a | Deuterium lost, % | | |
|----------------|---------------------------|-------------------|-------|-------|
| | | d_2 | d_1 | d_0 |
| 2- d_2 -I | C_4H_7 | 75 | 0 | 0 |
| | C_3H_5N (h or i) | 0 | 0 | 25 |
| | Total | 75 | 0 | 25 |
| 3- d_2 -I | C_4H_7 | 0 | 0 | 75 |
| | C_3H_5N (i) | 25 | 0 | 0 |
| | (h) | 0 | 0 | 25 |
| | Total (i) | 25 | 0 | 75 |
| 5- d_1 -I | (h) | 0 | 0 | 100 |
| | C_4H_7 | 0 | 0 | 75 |
| | C_3H_5N (h or i) | 0 | 25 | 0 |
| 6,6a- d_2 -I | Total | 0 | 25 | 75 |
| | C_4H_7 | 0 | 75 | 0 |
| | C_3H_5N (i) | 0 | 25 | 0 |
| | (h) | 25 | 0 | 0 |
| | Total (i) | 0 | 100 | 0 |
| | (h) | 25 | 75 | 0 |

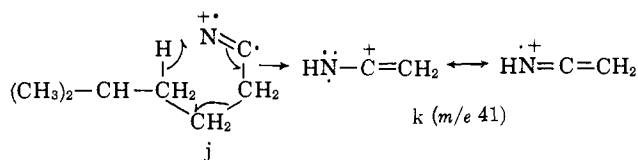
^a The C_4H_7 - C_3H_5N ratio is ca. 3:1 as determined by high resolution mass spectrometry.

terminal isopropyl group. The m/e 41 peak, on the other hand, is made up of two species, *viz.*, $C_3H_5^+$ and $C_2H_3N^+$, in a ratio of 1:1.8. The former is ubiquitous in organic substances with a hydrocarbon chain and in the present case originates largely from the isopropyl group (see shifts to m/e 42 for 5- d_1 and 6,6a- d_2 analogs, Table VI).

TABLE VI
MASS SHIFTS IN THE m/e 41-43 REGION

| Compound | m/e | | | | | | |
|----------------|-------|----|-----|----|-----|----|----|
| | 39 | 40 | 41 | 42 | 43 | 44 | 45 |
| d_0 -I | 19 | 5 | 100 | 13 | 48 | 2 | 0 |
| 2- d_2 -I | 16 | 19 | 78 | 66 | 100 | 54 | 2 |
| 3- d_2 -I | 18 | 6 | 100 | 22 | 59 | 7 | 4 |
| 5- d_1 -I | 15 | 17 | 100 | 32 | 13 | 53 | 2 |
| 6,6a- d_2 -I | 12 | 20 | 100 | 66 | 29 | 16 | 64 |

The formation of the $C_2H_3N^+$ ion k has been rationalized³ by invoking a six-membered transition state j, similar to d, but involving the C-4 hydrogen atom. The observed absence of shifts in any labeled analogs, except at C-2, is in agreement with this formulation although a C-4 labeled derivative was not available to settle this point unambiguously.



Experimental

The isohexyl cyanides were obtained according to the following general procedure: A mixture of 20 mg. of isohexyl bromide was heated under reflux for 24 hr. with a solution of 500 mg. of sodium

cyanide in 1 ml. of water and 1 ml. of methanol. The reaction mixture was then extracted with ether, the ether solution dried, and the solvent removed by fractional distillation. Purification of the oily residue by gas phase chromatography (silicone rubber column operating at 60°) yielded pure compounds which were immediately injected into the mass spectrometer.

The low resolution mass spectra were measured with a CEC 21-103C mass spectrometer equipped with a heated all-glass inlet system, ionizing voltage 70 v., ionizing current 50 μ a. For the measurement of the high resolution spectra we are indebted to Mr. A. P. Gifford of Consolidated Electrodynamics Corp., Pasadena, Calif., where those data were obtained with a CEC 21-110 instrument.

[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS, URBANA, ILL.]

Synthesis, Brominolysis, and Pyrolysis of a "Dewar" Anthracene. A Free Radical Displacement on Carbon

BY DOUGLAS E. APPLEQUIST AND ROGER SEARLE

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A photoadduct of anthracene and 9,10-dichloroanthracene reacts with triphenylmethylsodium to give 9,10-dehydrodianthracene (IV), a locked "Dewar" anthracene structure. This substance undergoes free radical chain addition of bromine to the interbridgehead single bond. Pyrolysis of IV gives anthracene and bianthryl, but no indication of the anticipated dibenzobutalene (VII).

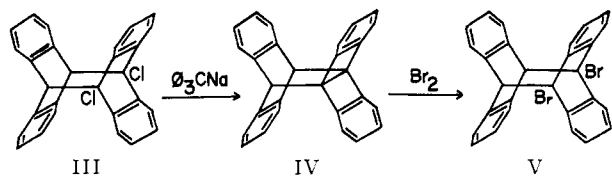
A synthetic goal of considerable current interest is the so-called "Dewar benzene" system (I).¹ A technique for the stabilization of systems of type I which



does not seem to be in the literature is the introduction of a paracyclophane bridge (as in II) which is too short to permit "valence tautomerization" to the normal benzenoid structure. An example of such a stabilized "Dewar" aromatic compound is here reported.

A benzene solution of equimolar amounts of anthracene and 9,10-dichloroanthracene, upon irradiation for a few days, gives variable yields, up to 61%, of the photoadduct 9,10-dichlorodianthracene (III). The structure of III is assigned in part from the numerous analogous reactions,² and in part from the reactions which follow.

A slurry of III in benzene-ether reacted with triphenylmethylsodium at reflux temperature to give

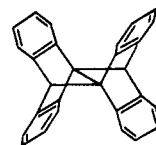


9,10-dehydrodianthracene (IV) in crude yields as high as 26%. The reaction is similar to the previously reported transannular debromination with phenyllithium of the photodimer of 9-bromoanthracene to give 9,10'-dehydrodianthracene (VI).^{2b} Compound IV is a

(1) (a) E. E. van Tamelen and S. P. Pappas, *J. Am. Chem. Soc.*, **84**, 3789 (1962); (b) E. E. van Tamelen, Abstracts of the Eighteenth National Organic Chemistry Symposium, Columbus, Ohio, June 16-20, 1963, p. 71.

(2) (a) F. D. Greene, S. L. Misrock, and J. R. Wolfe, Jr., *J. Am. Chem. Soc.*, **77**, 3852 (1955); (b) D. E. Applequist, R. L. Little, E. C. Friedrich, and R. E. Wall, *ibid.*, **81**, 452 (1959); (c) D. E. Applequist, E. C. Friedrich, and M. T. Rogers, *ibid.*, **81**, 457 (1959); (d) D. E. Applequist, T. L. Brown, J. P. Kleiman, and S. T. Young, *Chem. Ind. (London)*, 850 (1959); (d) R. Calas, P. Mauret, and R. Lalonde, *Compt. rend.*, **247**, 2146 (1958).

"Dewar" form of anthracene in the same sense that II is a "Dewar" form of benzene. Compound IV is a colorless solid, m.p. 338-342° dec.; gives satisfactory analyses for carbon, hydrogen and molecular weight; and has a satisfactory ultraviolet spectrum for such a structure^{2b}: λ_{\max} 269.3 m μ (ϵ 4170), 275.1 (ϵ 4060), and 283.7 (ϵ 3020) (solvent, methylene chloride). Chemical confirmation of structure IV is obtained from its surprisingly facile reaction with bromine in refluxing carbon tetrachloride to give 9,10-dibromodianthracene (V), which was found to give a 1:1 mixture of anthracene and 9,10-dibromoanthracene upon melting. An attempted synthesis of V by irradiation of such a mixture failed to give isolable amounts.



VI

It was found that the brominolysis of IV is promoted by free radical initiators and inhibited by free radical traps. Thus, a sample of IV in refluxing carbon tetrachloride with a threefold excess of bromine was converted to V to the extent of less than 10% (as determined by v.p.c. analysis for IV, anthracene, and 9,10-dibromoanthracene) in 4.6 min. in the dark, whereas with 1 equivalent of trichloroacetyl peroxide added, the reaction was about 89% complete in this time. Photoinitiation was also found, though it was less pronounced. Whereas a refluxing control in the dark, again containing a threefold excess of bromine, was about 44% complete in 30 min. (v.p.c. analysis), an irradiated mixture with only the theoretical amount of bromine present gave an 82% isolated yield of V after 25 min. When about one-tenth of an equivalent of isoamyl nitrite, a known inhibitor of radical brominations,³ was added to a dark reaction (threefold bromine

(3) M. S. Kharasch, P. C. White, and F. R. Mayo, *J. Org. Chem.*, **3**, 33 (1938).