XX was chromatographed on alumina to give XVI in a almost quantitative amount. Hydrolyses of XX with 20% HCl resulted in the formation of the starting materials, XV and XVI.

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Summary

Reaction of diketene with three of aminopyridine and their N-oxides was examined. 2-Aminopyridine (I) afforded its acetoacetate (II) and 2-methyl-4*H*-pyrido[1,2-*a*]pyrimidin-4-one (III) as a by-product. N-oxide of I (V) afforded its acetoacetate (VI) and 2-[(6-acetoacetamido-2-pyridyl)methyl]-6-methyl-4*H*-pyran-4-one (VII). 3-Amino isomers (VIII and IX) underwent their acetoacetates (XII and XVIII) respectively. Although 4-aminopyridine 1-oxide (XIV) did not react with diketene, 4-aminopyridine (XVI) afforded 1-(4-pyridyl)-3-acetyl-6-methyl-2,4-(1*H*,3*H*)-pyridinedione (XVII).

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129. Yoshio Kitahara and Tadahiro Kato : Heptafulvenes. IV.*1 Mass Spectra of 8,8-Dicyanoheptafulvene Derivatives.

(Chemical Research Institute of Non-Aqueous Solutions, Tohoku University*2)

8,8-Dicyanoheptafulvene and a number of its derivatives (I) have been synthesized recently. The ionic structure (Ib) makes a major contribution to the structure of these of derivatives which are considered*1,1,2) to belong to a stable type of aromatic compound possessing a 6 π -electron structure.

X = H, alkyl, phenyl, OCH₃

Rapid progress has been made³⁾ in the investigation of the structure of organic compounds and their fragment ions through analysis of the cation mass spectra obtained by electron impact of these compounds.

In this paper, we discuss the mass spectra of the twelve heptafulvene derivatives*3 and two other compounds

shown below;

8,8-dicyanoheptafulvene (II), dicyanostyrene (III), phenylpropiolonitrile (IV), 1-methyl-8,8-dicyanoheptafulvene (V), 1-isopropyl-8,8-dicyanoheptafulvene (VI), 2-methyl-8,8-dicyanoheptafulvene (VII), 2-isopropyl-8,8-dicyanoheptafulvene (VIII), 3-methyl-8,8-dicyano-

*1 part III. Y. Kitahara, K. Doi, T. Kato : Bull. Chem. Soc. Japan, to be published.

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*3 The measured 8,8-dicyanoheptafulvene derivatives were all synthesized in the author's laboratory.

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heptafulvene (K), 3-isopropyl-8,8-dicyanoheptafulvene (X), 1-phenyl-8,8-dicyanoheptafulvene (XI), 3-phenyl-8,8-dicyanoheptafulvene (XII), 1-methoxy-8,8-dicyanoheptafulvene (XIII), 3-methoxy-5-isopropyl-8,8-dicyanoheptafulvene (XIV), 3-methoxy-4-isopropyl-8,8-dicyanoheptafulvene (XV).

The measurements were carried out with a Hitachi model RMU-6A mass spectrometer. The conditions for measurement which varied slightly according to the sample, were as follows, Sub-oven temperature: $150\sim 210^{\circ}$; Main-oven temperature: $150\sim 210^{\circ}$; Inlet-pipe temperature: $150\sim 210^{\circ}$; Total emission: $80\mu\text{A}$; Ionizing potential: 75 eV ; Ion accelerator potential: 2 kV ; Vacuum: $3\times 10^{-6}\text{ mm. Hg}$.

At the temperature of measurements, the heptafulvene derivatives were found not to undergo isomerization and decomposition reactions.

Fig. 1. Mass Spectrum of 8,8-Dicyanoheptafulvene (II)

Fig. 2. Mass Spectrum of 8,8-Dicyanostyrene (III)

Fig. 3. Mass Spectrum of Phenylpropionitrile (IV).

Fig. 4. Mass Spectrum of 1-Methyl-8,8-dicyanoheptafulvene (V)

Fig. 5. Mass Spectrum of 1-Isopropyl-8,8-dicyanoheptafulvene (VI)

Fig. 6. Mass Spectrum of 1-Phenyl-8,8-dicyanoheptafulvene (XI)

Fig. 7. Mass Spectrum of 3-Phenyl-8,8-dicyanoheptafulvene (XII)

Fig. 8. Mass Spectrum of 1-Methoxy-8,8-dicyanoheptafulvene (XIII)

Fig. 9. Mass Spectrum of 3-Methoxy-5-isopropyl-8,8-dicyanoheptafulvene (XIV)

Fig. 10. Mass Spectrum of 3-Methoxy-4-isopropyl-8,8-dicyanoheptafulvene (XV)

The mass spectrum (Fig. 1) of 8,8-dicyanoheptafulvene (II) showed a very strong parent peak. This is attributed to the high degree of aromaticity of compound (II) and is probably due to the existence of a stable tropylium cation (IIb) formed during the electron impact.

The spectrum of 8,8-dicyanoheptafulvene (II) showed a peak corresponding to a fragment ion (m/e 127) which is 27 mass units less than the molecular ion (m/e 154) and corresponds to the elimination of hydrogen cyanide. Rearrangement of the ring from a seven-membered to a six-membered one was assumed to have occurred during elimination of the hydrogen cyanide and this is supported by the fact that low-mass region (less than m/e 127) of the spectrum of II was similar to that (Fig. 3) of phenyl propionitrile (IV).⁴⁾ It is known that, under the influence of bases, certain heptafulvene

4) Synthesized according to V. Grignard, V. Courtot : Bull. Soc. chim. France, [IV], 17, 228 (1915).

derivatives easily rearrange to dicyanostyrene (III) derivatives.*^{1,1)} Similarly, it could be assumed that the 8,8-dicyanoheptafulvene ion formed by electron impact would first rearrange to the six-membered ring analogue, the dicyanostyrene ion.

The mass spectrum (Fig. 2) of dicyanostyrene (III) is similar to that of II, particularly in that both showed a metastable ion at 105 mass units corresponding to a fragment m/e 127; II and III are therefore assumed to have a similar ionic structure after electron impact. Comparison of Figs. 1 and 3 showed a relatively strong $(M-51)^+$ peak at m/e 103 in the latter spectrum. This peak probably arises through formation of the fragment (III_d) from III as shown in the following scheme.

As can be seen in the structure (III), one of the cyano group is close to the benzene ring and it could be assumed that ring closure would occur between the cyano group and the ion (III_b), formed by electron impact, to form III_c and removal of the cyanoacetylene moiety in III_c would lead to the fragment (III_d).

8,8-dicyanoheptafulvene derivatives, with either a methyl or an isopropyl group at the 1-, 2-, or 3-position, gave in each case a series of quite similar spectra. Since the position of the alkyl substituent made no significant difference in the spectra, we will confine our discussion to 1-isopropyl- and 1-methyl-8,8-dicyanoheptafulvene. In the

spectra of the isopropyl-8,8-dicyanoheptafulvenes, the parent ion peak was not the strongest peak; the characteristic base peak was in each case identical with that corresponding to the ion of 8,8-dicyanoheptafulvene (II). This indicates that the 8,8-dicyanoheptafulvene ion is more stable than the branched-chained derivatives (parent ion). It is therefore expected that removal of a methyl group ($M-15$)⁺ from the parent ion (m/e 196) to give the fragment ions, m/e 181 followed by the elimination of an ethylene group, would lead finally to the strong m/e 154 peak. The fragmentation to the 8,8-dicyanoheptafulvene ion (II) occurs through removals of an isopropyl group and a methyl and an ethylene group, is supported by appearance of the metastable ions (abbreviated as M.S.) of m/e 121, 131, and 145.

Comparison of the spectra (Fig. 4) of the methyldicyanoheptafulvene derivatives with that of the parent 8,8-dicyanoheptafulvene (Fig. 1), revealed a strong ($M-27$)⁺ peak in the case of the parent compound, whereas the spectra of the methyl heptafulvene derivatives exhibited a strong characteristic ($M-28$)⁺ peak besides the ($M-27$)⁺ peak. This was explained by assuming that during elimination of hydrogen cyanide, rearrangement to a fragment ion ($M-27$)⁺ containing a six-membered ring had occurred, and that this fragment through loss of a hydrogen radical afforded a ($M-28$)⁺ fragment which rearranges with formation of a seven-membered ring and leads to a stable tropylium cation.

It is of interest that the spectrum (Fig. 6) of 1-phenyldicyanoheptafulvene (XI) showed a ($M-1$)⁺ as its base peak. It apparently arises through some sorts of interaction between the phenyl group and the nearby cyano group, since the spectrum of 3-phenylheptafulvene*⁴ (XII) (Fig. 7) shows a (M)⁺ as its base peak. There are number of possible structures for the ($M-1$)⁺ ion of 1-phenyldicyanoheptafulvene; the following, however, is considered the most likely.

In general, the mass spectra of molecules with methoxyl or ketonic substituents are known to show characteristic fragmentations.⁵⁾ Similarly, the spectra of the methoxyheptafulvene derivatives showed fragmentation quite different from that of the parent compound, dicyanoheptafulvene, or of the derivatives with alkyl substituents. Differences were also observed in the fragmentations of the 1-methoxy- and 3-methoxy-

*⁴ The authors are indebted to Dr. H. Horino for a gift of 4-phenyltropone.

5) For an example, see ref. 3a), p. 213.

Of these fragment ions, the $(M-40)^+$, m/e 144 peak is characteristic of compound (XIII) and does not appear in the spectra of the 3-methoxyheptafulvene derivatives (XIV) and (XV). This fragment ion is considered to result from interaction between the methoxyl group at the 1-position and the cyano group at the 8-position. The possible fragmentation processes and the structures of these fragments are considered to be as below.

From an analysis of the fragment ions and metastable ions arising from 3-methoxy-5-isopropyl-8,8-dicyanoheptafulvene (XIV), the relations between these fragments and the possible structures of these fragments are shown in the scheme above.

From a comparison of the spectrum of 3-methoxy-4-isopropyl-8,8-dicyanoheptafulvene (XV) with that of compound (XIV), it was noticed that the (M-15)⁺ peak in the case of XV was much stronger than that in the case of XIV, and that the (M-45)⁺ and (M-47)⁺ peak which were present in the spectrum of XV were absent in that of XIV. The (M-15)⁺ fragment corresponds to the elimination of a methyl group from the parent ion. This methyl group could have been lost from either the isopropyl or methoxyl group, but since, as mentioned before, the (M-15)⁺ peak was absent in the spectrum of the 1-methoxy derivative (XIII), it follows that the (M-15)⁺ peak results from loss of a methyl from the isopropyl group.

The greatly enhanced strength of the (M-15)⁺ fragment, in the case of XV is probably due to the contribution of the conjugated structure (XVb) in which conjugation between the ethyl cation and the non-bonding electrons of the methoxyl group is established through the double bond.

The structures of (M-45)⁺ and (M-47)⁺ are considered to be as follows.

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Summary

The mass spectra of 8,8-dicyanoheptafulvene and its derivatives, which are considered to belong to a non-benzenoid aromatic compound, were measured.

The high degree of aromaticity of 8,8-dicyanoheptafulvenes was made clear by mass spectrometry.

Low mass regions of dicyanoheptafulvene showed the elimination of hydrogen cyanide from parent ion and rearrangement to phenylpropionitrile ion.

The mass spectra of methoxy dicyanoheptafulvenes showed fragmentation quite different from that of 8,8-dicyanoheptafulvenes.

The structures and fragmentation processes of dicyanoheptafulvenes were discussed.

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130. Kazuo Tori, Yoshio Hamashima, and Akira Takamizawa : Nuclear Magnetic Resonance Studies of Bridged Ring Systems. V.*¹ Signals of Methyl Groups in Bornane Derivatives.*²

(Shionogi Research Laboratory, Shionogi & Co., Ltd.*³)

In recent years, many studies dealing with nuclear magnetic resonance (NMR) spectra of compounds having a bicyclo[2.2.1]heptane skeleton have been made in connection with their stereochemistry.^{1~8)} Kumler, *et al.*¹⁾ investigated the spectra of some 3-halogenocamphors and assigned the three methyl signals on the bases of the magnetic anisotropy effects of the carbonyl group and halogen atoms, and the effect of freedom of rotation of the methyl groups which is reflected in sharpness (or the amplitude) of their signals. Wolinsky⁹⁾ also applied the downfield shift of a methyl signal due to the close approach of a bromine atom for structure estimation of α -bromoderivatives of 4,4-dimethylbicyclo[3.2.1]octan-2-one and 4,4-dimethylbicyclo[3.2.1]octan-3-one, inspecting the NMR spectra of several known compounds such as 3,3-dibromocamphor (XXX)

*¹ Part IV. K. Tori, K. Kitahonoki, Y. Takano, H. Tanida, T. Tsuji : Tetrahedron Letters, No. 11, 559 (1964).

*² A part of this paper was delivered at "The 2nd Symposium on Nuclear Magnetic Resonance (Japan)," in Tokyo, November (1962).

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