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THE CHEMICAL STUDY OF PSEUDOAROMATIC COMPOUNDS. II*

NOVEL FORMATION OF 8,8-DICYANOHEPTAFULVENE FROM THE REACTION OF TROPOTHIONE WITH TETRACYANOETHYLENE

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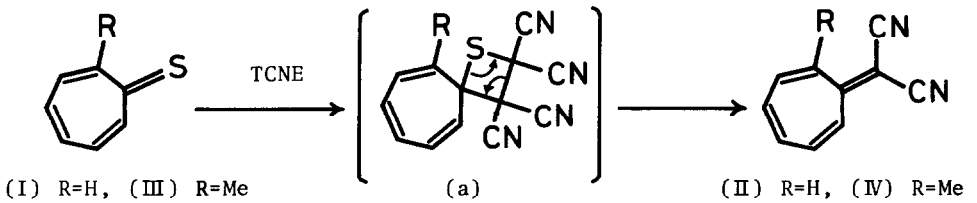
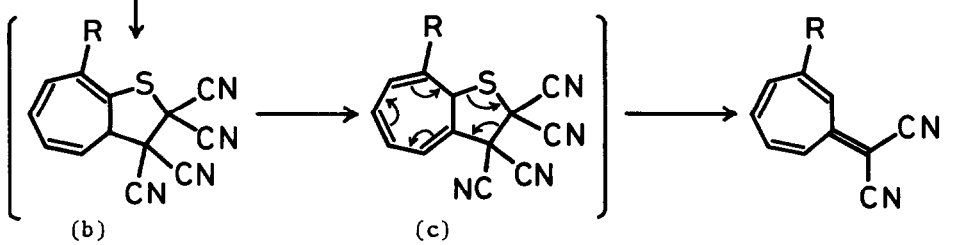
In our previous paper,[1] we reported that the cycloaddition reaction of tropothione (cycloheptatrienethione) (I) with some dienophiles gave a 1,8-cycloadduct or its unusual rearrangement product by the rare $[_{\pi}8_s+_{\pi}2_s]$ type of reaction, in contrast with tropones, as well known, formed normally 1,4-cycloadduct with dienophiles by the $[_{\pi}4_s+_{\pi}2_s]$ type of reaction.[2] We wish to report, different from the previous findings, that the reaction of (I) with tetracyano-



[1]



[2]

* For Part I see reference 1).

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ethylene (TCNE) gave unexpectedly a heptafulvene (II) with extrusion of $(CN)_2C=S$.

To a freshly prepared solution of 1.41 g of (I) in 200 ml of CH_2Cl_2 or benzene, was added dropwise at 0° or 10°C a solution of 1.0 g of TCNE in 5 ml of tetrahydrofuran. Then a deep red color of (I) immediately disappeared, and the reaction mixture was evaporated under reduced pressure below 20°C to give a pale brownish residue which partially crystallized. Purification over silicagel column eluted from $CHCl_3$ gave 288 mg of 8,8-dicyanoheptafulvene (II) as red needles, m.p. and mixed m.p. 200-201°C[3] in 24% yield.

As regards this novel formation of (II), two reaction paths are to be considered; [1] *via* intermediate (a) by the cycloaddition of $[_\pi2_s+_\pi2_a]$ manner, [2] *via* intermediate (b) of the $[_\pi8_s+_\pi2_s]$ type of cycloadduct which was isomerized to (c), as shown in the scheme. For our mechanistic interpretation of the formation of (II) from (I), 2-methyltropothione (III)[4] instead of (I) was subjected to the reaction with TCNE so as to persure the reaction path, giving the product of (IV)[5] as red needles.

From this evidence, The formation of (II) seems to proceed *via* path [1].

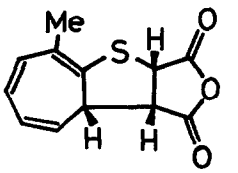
REFERENCES AND NOTES

1) T. Machiguchi, M. Hoshino, S. Ebine, and Y. Kitahara, J. Chem. Soc. (Chem. Commun.), in the press.

2) Cf. T. Nozoe, in "Nonbenzenoid Aromatic Compounds," ed. D. Ginsburg, Interscience, New York, p. 396 (1959); T. Nozoe, in "The Chemistry of Nonbenzenoid Aromatic Compounds," ed. M. Oki, Butterworths, London, p. 250 (1971).

3) All of the ir, uv, nmr, and mass spectrum were completely accorded with an authentic sample prepared by the reaction of tropone with malononitrile in a acetic anhydride by the method descrived in the literature.[6]

4) Compound (III) was synthesized starting with 2-methyltropone,[7] and the structural confirmation was done by its maleic anhydride adduct (i).



(i)

5) 1-Methyl-8,8-dicyanoheptafulvene: Y. Kitahara, and T. Kato, Chem. Pharm. Bull., 12, 916 (1964).

6) Y. Kitahara and K. Doi, presented at the Tohoku Local Meetings of the Chemical Chemical Society of Japan, Yamagata, June,1959; T. Nozoe, T. Mukai, T. Osaka, and N. Shishido, Bull. Chem. Soc. Japan, 34, 1384 (1961).

7) T. Mukai, Nippon Kagaku Zasshi, 79, 1547 (1958).