Synthesis of Some 8, 8-Disubstituted Heptafulvene Derivatives[1]

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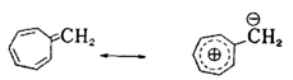
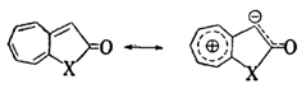
Heptafulvene (methylenecycloheptatriene) (A) can be regarded as a methylene analog of tropone and is also one of the typical non-alternant hydrocarbones with a cyclic conjugated double bond system. Its structure suggests more or less the contribution of a 6-π



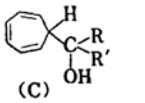
(A)



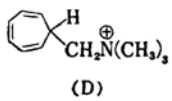
(B)

electron system as tropylium ion. Consequently, it seems of interest to examine the aromaticity and reactivity of this type of compounds comparing with those of azulenes and azulane-2-one type of compounds (B: X=O or NH)[2]. Theoretical interests on the unique ring system attracted also much attention of physical chemists as well as organic chemists and calculation by molecular orbital method has been carried out by Berthier and Pullman[3], Bergman et al.[4] and Julg and Pullman[5,6].

Attempts have already been made for synthesis of heptafulvene derivatives. In 1953, Grundmann, Ottman and Gollner[7], and van Aardt[8] in 1954, attempted the elimination of water from tropyl carbinols (C) but a facile formation of a polymer or styrenes as a rearrangement product was observed and the desired compound could not be obtained. In 1954, Doering and Wiley[9] succeeded in obtaining heptafulvene by the Hofmann elimination of



(C)



(D)

the quaternary ammonium salt (D), obtained from norcaradienecarboxamide, under special conditions. Recently details of this work have been published[10]. According to Doering and Wiley, heptafulvene is a very unstable compound and easily undergoes polymerization but its structure has been proved from the formation of methylcycloheptane by hydrogenation and of dimethyl azulene 1, 2-dicarboxylate by addition with dimethyl acetylene dicarboxylate followed by oxidation. Matteson, Drysdale and Sharkey[11] also obtained heptafulvene, though in a minute amount, by pyrolytic decomposition of methylenecycloheptadienes.

The reason for the larger lability of heptafulvene compared with tropone is considered to be due to the difference in the electron-withdrawing power of the carbonyl and methylene

1) A part of this work was presented at the Local Meeting of Tohoku District of the Chemical Society of Japan, Yamagata, June, 1959.

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2) T. Nozoe, S. Seto, S. Matsumura and T. Terasawa, *Chem. & Ind.*, 1954, 1356.

3) G. Berthier and B. Pullman, *Trans. Faraday Soc.*, 45, 484 (1949).

4) E. D. Bergman, E. Fischer, D. Ginsburg, Y. Hirshberg, D. Lavie, M. Mayot, A. Pullman and B. Pullman, *Bull. soc. chim. France*, V18, 684 (1951).

5) A. Julg, *J. Chem. Phys.*, 52, 50 (1955).

6) A. Julg and B. Pullman, ibid., 52, 481 (1955).

7) C. Grundmann, G. Ottman and G. Gollner, *Ann.*, 582, 178 (1953).

8) Van Aardt, *J. Chem. Soc.*, 1954, 2965.

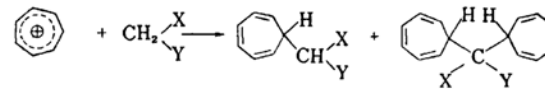
9) Abstract of papers presented at The 126th Meeting of the American Chemical Society, New York, N. Y., September, 1954, p. 10.

10) W. von E. Doering and D. W. Wiley, *Tetrahedron*, 11, 183 (1960).

11) D. S. Matteson, J. J. Drysdale and W. H. Sharkey, *J. Am. Chem. Soc.*, 82, 2853 (1960).

group, that is, the difference in the contribution of the tropylium-type structure. If this is the case, it may be anticipated that a more stable heptafulvene derivative would be obtained by the introduction of an electron-withdrawing group, such as cyano or ethoxycarbonyl, into the 8-position of heptafulvene. The present series of work was undertaken on such assumption.

Condensation of tropylium ion and active methylene compound has been reported by Vol'pin, Ahrem and Kursanov[12], and by Conrow[13]. Similar to their method, reaction of tropylium ion and malononitrile gave tropylmalononitrile (I) and ditropylmalononitrile (II). Further reaction of I with tropylium ion also afforded II. Such a fact and the ultraviolet and infrared spectra in Table I supported the structures of I and II to be correct.



X=Y=CN or CO_2Et (I) X=Y=CN (II) X=Y=CN

(III) X=CN, Y=CO_2Et (IV) X=CN, Y=CO_2Et

(V) X=Y=CO_2Et

Condensation of tropylium ion and ethyl cyanoacetate proceeded in the same way by which ethyl tropylcyanoacetate[12] (III) and ethyl ditropylcyanoacetate (IV) were obtained. IV was also obtained by the reaction of III with tropylium ion. The structures of III and IV were supported by their ultraviolet and infrared spectroscopic data given in the Table.

It is already known that diethyl tropylmalonate (V) is obtained by the reaction of tropylium ion and diethylmalonate[12,13], but the reaction of V with tropylium ion failed to afford diethyl ditropylmalonate. This is probably rather attributed to the smaller electron-withdrawing power of the ethoxycarbonyl group than that of the cyano group or to the steric hindrance of the bulky ethoxycarbonyl group.

As was expected, application of a dehydrogenation agent to the tropilidene derivatives, I, III and V, successfully afforded the desired 8,8-disubstituted heptafulvenes. Application of one mole of bromine to I in chloroform, and subsequent heating of the bromide thereby obtained, resulted in the formation of reddish crystals (VI), $C_{10}H_6N_2$, m.p. 200°C, in 50% yield, with liberation of hydrogen bromide. Oxidation of I with *N*-bromosuccinimide in *tert*-butanol containing pyridine and water also gave VI, in 70% yield, accompanying a small amount of rearrangement product, benzalmalononitrile (VII)[14]. VI could be obtained by refluxing I with chloranil in xylene. The infrared absorption of the cyano group in VI shifted to a smaller wave number by 55 cm^{-1} than in I (cf. Table) and shows there is a fair degree of conjugation of the cyano group with the unsaturated system. The ultraviolet spectrum of VI is similar to that of 1-oxaazulan-2-one derivatives (Fig. 1). These facts

TABLE I. ULTRAVIOLET AND INFRARED SPECTRUM

Compd.	UV in MeOH mμ (log ε)	IR, cm^{-1}
I	260(3.71)	2900, 2260(CN), 1406, 1340, 1330, 1289, 1184, 1064, 930, 900, 813, 764, 695 (a)
II	255(3.81)	3010, 2870, 2260(CN), 1615, 1530, 1445, 1440, 1275, 1210, 1196, 772, 735, 695 (a)
III	256(3.46)	2980, 2260(CN), 1740(CO), 1468, 1448, 1404, 1370, 1332, 1285, 1250, 1207, 1095, 1028, 850, 735, 700 (b)
IV	256(3.76)	2990, 2250(CN), 1732(CO), 1610, 1445, 1396, 1270, 1257, 1211, 1197, 1107, 1015, 1005, 747, 740, 702, 687 (a)
V	257.5 (3.49)(c)	2967, 1730(CO), 1443, 1440, 1365, 1305, 1265, 1230, 1170, 1112, 1095, 1030, 860, 744, 703 (b)
VI	225(4.01) 255(4.08) 384(4.36)	2205(CN), 1633*, 1585, 1520*, 1490*, 1406, 1269*, 885*, 830*, 763* (a)
VIII	254(3.96) 386(4,22)	2200(CN), 1693(CO), 1630*, 1530*, 1500*, 1483, 1420, 1412, 1390, 1255*, 1215, 1135, 1105, 1033, 830*, 820*, 780* (a)
X	246 355 (d)	1718(CO), 1685(CO), 1635*, 1545*, 1515*, 1430, 1369, 1260*, 1205, 1070, 1031, 877, 806*, 782*, 740, 704 (b) (d)

(a) KBr disk
(b) Liquid state
(c) Conrow's datum. See Ref. 12.
(d) X is comtaminated with V.

12) M. E. Vol'pin, I. S. Ahrem, D. N. Kursanov, *Isvest. Akad. Nauk U. S. S. R., Otdel Khim. Nauk*, **1957**, 1501; *Zhur. Obschchei Khim.*, **30**, 1187 (1960).

13) K. Conrow, *J. Am. Chem. Soc.*, **81**, 5461 (1959).

14) B. B. Corson and R. W. Stroughton, ibid., **50**, 2830 (1928).

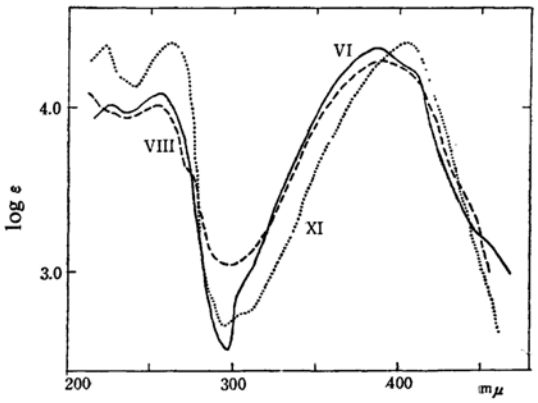
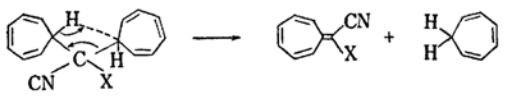


Fig. 1. Ultraviolet absorption spectra of VI (——), VIII (----) and XI (·····) in methanol.

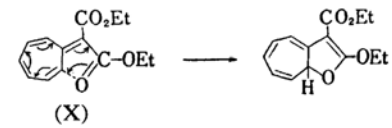
support that VI possesses the structure of 8, 8-dicyanoheptafulvene (heptafulvene-8, 8-dicarbonitrile). Heating of ditropylmalononitrile (II) at 140~150°C for 30 min. resulted in formation of VI and tropilidene in an almost quantitative yield. This reaction is considered to proceed through the intermediate depicted below (four-centered type reaction)[15].



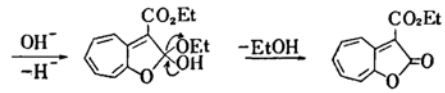
(II) X=CN (VI) X=CN
(IV) X=CO_2Et (VIII) X=CO_2Et

8-Cyano-8-ethoxycarbonylheptafulvene (VIII) as red crystals, m. p. 63.5°C was successfully synthesized in about a 40% yield by dehydrogenation of ethyl tropylcyanoacetate (III) with chloranil in boiling xylene. Pyrolysis of ethyl ditropylcyanoacetate (IV) gave also VIII in about a 25% yield. The reason why IV gave a poorer yield of VIII than in the case of pyrolysis of II can be attributed to the smaller electron-withdrawing power of ethoxycarbonyl than in the cyano group to split the bond between the tropyl group and the carbon atom to which it is attached. It was found that the reaction of III with *N*-bromosuccinimide under the condition described previously for I gave ethyl α-cyanocinnamate[16] (IX) rather than the expected VIII in a good yield. The absorption maxima of the infrared spectrum of VIII are given in the Table I. The shift of absorption bands of the carbonyl and cyano groups to a smaller wave number than those of III indicates the conjugation of these functional groups with the unsaturated system. On comparison of the infrared spectra of the two kinds of heptafulvenes, VI and VIII, it is learned that there are some absorption maxima characteristic to them. (indicated by an asterisk in the Table).

8, 8-Diethoxycarbonylheptafulvene (X) was obtained as a red oil by dehydrogenation of diethyl tropylmalonate (V) with chloranil. X was somewhat more labile than VI or VIII and tended to undergo polymerization on being left in the air. The structure of X is evident from the similarity of its ultraviolet spectrum with those of VI and VIII, and from the presence of absorption bands in its infrared spectrum characteristic to heptafulvenes (see Table 1). The absorption of carbonyl in X shifted to a small wave number from that of V. Bromination-dehydrobromination of diethyltropylmalonate (V) gave 3-ethoxycarbonyl-1-oxaazulan-2-one (XI)[17] whose formation may have passed through X as an intermediate, but this point requires further examination.



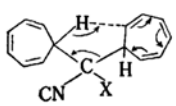
(X)



(XI)

In parallel with this work, Doi synthesized 3, 4-dihydroxy-8, 8-dicyanoheptafulvene by the reaction of 3-iodotropolone and malononitrile in the presence of sodium amide in liquid ammonia[18]. A few months later, Kitahara and Doi et al. successfully synthesized VI by condensation of tropone and malononitrile[19], and recently they obtained VI, VIII and X from tropylium ion and bromo compounds of malononitrile, ethyl cyanoacetate and diethyl malonate[20]. Their examination of the properties of heptafulvenes revealed some interesting facts as mentioned in Refs. 21 and 24.

15) A similar reaction mechanism involving an intermediate of a five membered ring can be possible. The examples of this type of reaction mechanism can be found in the explanation of the Cope Rearrangement. A. C. Cope, K. E. Hoyle and D. Heyl, *J. Am. Chem. Soc.*, 63, 1843 (1941); E. G. Foster, A. C. Cope and F. Daniels, ibid., 69, 1893 (1947).



16) J. T. Carrik, *J. Prakt. Chem.*, 45, 500 (1892).

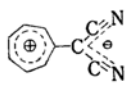
17) S. Seto, *Science Repts. Tohoku Univ., Ser. I*, 37, 367 (1954).

18) Paper presented at the Local Meeting of Tohoku District of the Chemical Society of Japan, Yamagata, June, 1959.

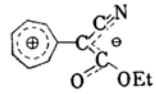
19) Paper presenteted at the General Meeting of Tohoku District of the Chemical Society of Japan, Akita, October, 1959.

20) Paper presented at the General Meeting of Hokkaido District of the Chemical Society of Japan, Sapporo, July, 1960.

8,8-Dicyanoheptafulvene (VI) is sparingly soluble in organic solvent and has a fairly high melting point, but 8-cyano-8-ethoxycarbonyl- (VIII) and 8,8-diethoxycarbonylheptafulvene (X) are more soluble than VI. VI and VIII do not form perchlorate, picrate, styphnate, or trinitrobenzene complex. VI and VIII are fairly stable to acids and do not change on being refluxed for 2 hr. with 6 N hydrochloric acid, while VI changes into a yellow solid on being heated with 75% sulfuric acid. On the other hand, VI and VIII are labile towards alkali[21]. Such behavior of 8,8-substituted heptafulvenes is different from that of heptafulvene (A)[10]. This is reminiscent of the fact that cyano and ethoxycarbonyl groups situated at 1- or 3-position of azulene are also difficult to hydrolyse with acids[22]. VI is stable to bromination and neither substitution nor addition reaction occurs on application of excess bromine in chloroform. These facts can be explained by the great contribution of the 6-π electron structures E and F due to electron-attracting groups at 8-position. In fact, as has been published[23], measurement of the dipole moment has shown that the value are 7.49 D (dioxane, 25°C) for VI and 4.40 D (benzene, 25°C) for VIII.



(E)



(F)

In order to examine the aromaticity and double bond character of heptafulvenes, Diels-Alder reaction and hydrogenation were carried out. 8,8-Diethoxycarbonylheptafulvene (X) tends to undergo polymerization, while 8,8-dicyanoheptafulvene (VI) does not form an adduct even on being refluxed with maleic anhydride in xylene. 8-Cyano-8-ethoxycarbonylheptafulvene (VIII) shows an intermediate reactivity and partially undergoes addition reaction with maleic anhydride to form the adduct (XII), which has an absorption at 247 mμ. VI resists catalytic hydrogenation over palladium carbon but easily absorbs three moles of hydrogen by the use of platinum oxide as catalyst and forms a pale yellow oil[24], which still retains the absorption at 239 mμ in its ultraviolet spectrum. On the other hand, X easily absorbs 4 mol. of hydrogen and forms an octahydro compound XIII, which was converted to cycloheptylmalonic acid[25] on hydrolysis.

These experimental results have shown that the stability of 8,8-disubstituted heptafulvenes depends on the nature of the substituent present and the high stability of the compound with a strongly negative group like the cyano group which agrees with the presumption.

Experimental[26,27]

The Condensation Reaction of Tropylium Bromide and Malononitrile.—To a solution of 2.41 g. (0.037 mol.) of malononitrile in 30 ml. of pyridine was gradually added 6 g. (0.035 mol.) of crude tropylium bromide[28] with stirring for 30 min. After stirring for 2 hr. at room temperature, the mixture was poured into 110 ml. of 6 N hydrochloric acid and extracted with benzene. The benzene extract was washed with water, diluted sodium hydrogen carbonate and water, dried over sodium sulfate and evaporated. The brown oily residue crystallized partly on standing. Addition of ethanol and cooling afforded 1.6 g. of crystals, m.p. 58~60°C, as first crop, 1.4 g. of crystals, m.p. 89~99°C, as second crop, and 2 g. of crystals, m.p. 38~48°C containing oil as third crop. Recrystallization of the first crop from benzene gave 1.24 g. (yield 22.7 %) of tropylmalononitrile (I) as colorless crystals, m.p. 61~62°C, which showed m.p. 62.8~63.5°C on recrystallization from benzene once more.

Found: C, 77.38; H, 5.26; N, 17.73. Calcd. for $C_{10}H_8N_2$: C, 76.90; H, 5.16; N, 17.94%.

The solution of the third crop in petroleum ether-benzene (1 : 2) was chromatographed through a column containing 40 g. of alumina. An elution with the same solvent gave 0.64 g. of crystals, m. p. 94~105°C. This substance and the second crop were combined and recrystallized from ethanol to give ditropylmalononitrile (II) as colorless prisms, m. p. 107~108°C.

Found: C, 82.78; H, 5.57; N, 11.15. Calcd. for $C_{17}H_{14}N_2$: C, 82.90; H, 5.73; N, 11.37%.

The Condensation Reaction of Tropylium Bromide and Tropylmalononitrile (I).—To a solution of 0.31 g. (2 mmol.) of I in 6.3 ml. of pyridine 0.35 g. (2 mmol.) of crude tropyl bromide was added and the solution resulted was heated on a water bath for 1.5 hr. After addition of 21.7 ml. of 6 N hydrochloric acid under ice-cooling, the mixture was extracted with benzene. The benzene extract was washed with diluted sodium hydrogen carbonate and water, dried over sodium sulfate and distilled to give 0.39 g. (yield 80%) of crystals, m.p. 102~104°C. Recrystallization from ethanol gave colorless crystals, m.p. 104~105.5°C, which showed no depression on admixture with II.

21) Y. Kitahara et al. reported that VI and VIII rearranged to the corresponding styrene derivatives on treating with dilute alkali.

22) Unpublished work by T. Asano and M. Tada in this Laboratory.

23) M. Yamakawa, H. Watanabe, T. Mukai, T. Nozoe and M. Kubo, *J. Am. Chem. Soc.*, **82**, 5665 (1960).

24) Y. Kitahara et al. found that VI absorbed 4 mol. of hydrogen to give an octahydro compound which on hydrolysis gave cycloheptylmalonic acid.

25) I. Vogel, *J. Chem. Soc.*, **1928**, 2025.

26) All melting points and boiling points were uocorrected.

27) The microanalyses were performed by Mr. S. Azumi and Miss A. Iwanaga to whom the authors expressed their gratitude.

28) Tropylium bromide was synthesized from tropilidene by the method of Doering and Knox. *J. Am. Chem. Soc.*, **79**, 352 (1957).

The Condensation Reaction of Tropylium Bromide and Ethyl Cyanoacetate.—To a solution of 16.4 g. (0.145 mol.) of ethyl cyanoacetate in 150 ml. of pyridine, 20.4 g. (0.12 mol.) of crude tropyllium bromide was gradually added with stirring under ice-cooling. The reaction mixture was allowed to stand overnight at room temperature to which 260 ml. of concentrated hydrochloric acid was added dropwise under ice-cooling. The acidic solution was extracted with ether and the ether extract was filtered off, washed with diluted sodium hydrogen carbonate and water, and dried over sodium sulfate. Evaporation of ether gave 22.30 g. of a brown oil which crystallized partially on standing. Filtration afforded 6.3 g. of crystals, m.p. 115~117°C, which were recrystallized from ethanol to give 5.3 g. (yield 15%) of ethyl ditropylcyanoacetate (IV) as colorless prisms, m.p. 124~125°C.

Found: C, 78.12; H, 6.35; N, 4.84. Calcd. for $C_{19}H_{19}O_2N$, C, 77.79; H, 6.53; N, 4.77%.

Distillation of the filtrate in reduced pressure gave 10.97 g. (yield 45.0%) of ethyl tropylcyanoacetate (III) as orange viscous oil, b.p. 130~135°C /4 mmHg. After one more distillation, the oil of b.p. 125~130°C/2 mmHg was submitted for microanalysis and spectrum determination.

Found: C, 70.22; H, 6.45; N, 7.06. Calcd. for $C_{12}H_{13}O_2N$. C, 70.91; H, 6.45; N, 6.89%.

The Condensation Reaction of Tropylium Bromide and Ethyl Tropylcyanoacetate (III).—A solution of 0.43 g. (2.5 mmol.) of crude tropyl bromide and 0.5 g. (2.5 mmol.) of III in 10 ml. of pyridine was warmed at 40~50°C in a water bath for 30 min. Under ice-cooling, the reaction mixture was neutralized by adding 36 ml. of 6 N hydrochloric acid and extracted with benzene. The benzene extract was washed with water, dried over sodium sulfate and evaporated. Recrystallization of residual crystals from ethanol gave 0.57 g. (yield 78%) of colorless crystals, m. p. 122~123°C, which were proved to be identical with IV by mixed melting point determination.

Bromination and Dehydrobromination of Tropylmalononitrile (I).—A solution of 0.32 g. (2 mmol.) of bromine in 0.3 ml. of chloroform was added dropwise to a solution of 0.31 g. (2 mmol.) of I in 3 ml. of chloroform at room temperature. During stirring for 40 min., the color of bromine disappeared and evaporating chloroform in reduced pressure at room temperature gave a pale orange oil. Heating the oil in a boiling water bath for 10 min., it changed to orange red crystals with the evolution of hydrogen bromide gas. Addition of ethanol and filtration affored 150 mg. (yield 50%) of reddish crystals, m.p. 180~185°C, which on recrystallization from ethanol gave 8, 8-dicyanoheptafulvene (VI) as red needles, m.p. 198~199°C.

Found: C, 78.09; H, 4.20; N, 17.77. Calcd. for $C_{10}H_6N_2$: C, 77.90; H, 3.92; N, 18.17%.

Dehydrogenation of Tropylmalononitrile (I) with *N*-Bromosuccinimide.—Five hundred milligrams (3.2 m mol.) of I and 550 mg. (3.0 m mol.) of *N*-bromosuccinimide were added to a solution of 11 ml. of *tert*-butanol, 2 ml. of pyridine and 1 ml. of water and the mixture was allowed to stand at room temperature for 90 hr. During this period, reddish needles separated. The filtration gave 250 mg. of red needles, m.p. 194~199°C. After adding 60 ml. of water, the filtrate was extracted with ether. The ether extract was washed with water, dried over magnesium sulfate and evaporated to 160 mg. red needles, m. p. 195~198°C and the filtrate was dissolved in benzene and chromatographed using 3 g. of alumina. After evaporation, the first elutes with benzene gave 65 mg. of colorless needles, m. p. 81~82°C, (VII) which showed no depression on admixture with benzalmalononitrile, m. p. 83°C[14]. The second elutes with benzene gave 60 mg. of red needles, m. p. 194~198°C. Three hundred and fifty milligrams (yield 70%) of total red needles were combined and recrystallized from ethanol to give red needles, m. p. 198~199°C, which is identical with VI.

Dehydrogenation of Tropylmalononitrile (I) with Chloranil.—Three hundred milligrams (1.9 mmol.) of I and 510 mg. (2.1 mmol.) of chloranil were added to 5 ml. of xylene and the mixture was refluxed for 2 hr. The dark brown precipitate separated on cooling was filtered and dissolved in benzene. The benzene solution was washed with 1 N sodium hydroxide solution and water and dried over sodium sulfate. Epaporation of benzene gave 60 mg. of orange red crystals, m. p. 179~188°C. Recrystallization from ethanol gave 50 mg. (yield 17%) of red needles, m. p. 189~199°C, which showed no depression on admixture with the authentic sample VI.

Thermal Decomposition of Ditropylmalononitrile (II).—One gram (6.4 mmol.) of II was placed in the sublimation apparatus with a cold-finger condenser and heated at 140~150°C in an oil bath for 30 min. Sublimation in 2 mmHg at the same temperature gave 540 mg. (yield 86%) of red needles, m.p. 188~193°C. Recrystallization from ethanol afforded red crystals, m.p. 199~200°C, which showed to be identical with VI on admixture with the authentic sample. During thermal decomposition and sublimation, about 200 mg. of a yellowish oil was caught in a trap cooled with dry ice-acetone. One hundred and twenty five milligrams of this oil and 147 mg. (1.5 mmol.) of maleic anhydride were added to 1.5 ml. of xylene and the mixture was refluxed for 4.5 hr. An addition of 5 ml. of petroleum ether to the solution gave 110 mg. (yield 41%) of pale yellow crystals, m. p. 98~99°C, on cooling. Recrystallization from carbon tetrachloride afforded crystals, m. p. 99~100°C, which showed no depression on admixture with adduct, m. p. 99~100°C. of tropilidene and maleic anhydride[29].

Dehydrogenation of Ethyl Tropylcyanoacetate (III) with Chloranil.—To 100 ml. of xylene, 19.6 g. (0.08 mol.) of chloranil and 10 g. (0.051 mol.) of III were added and the mixture was refluxed for 1.5 hr., while a lot of dark brown crystals separated. The crystals (A) obtained by filtration were digested several times with methanol (B) and then benzene (C). Thus 7.1 g. of chloranil was recovered as an insoluble part. The residue obtained from ethanol washings (B) by evaporation was digested with benzene (D) to give 2.1 g. of dihydrochloranil. The washings C and D were

29) K. Alder and G. Jacobs, *Ber.*, **86**, 1528 (1953).

combined and chromatographed through a column containing 60 g. of alumina. Elution of a dark red band with benzene and evaporation of benzene gave 2.84 g. of dark red oil (E) which crystalized partially. The xylene filtrate from A was evaporated in reduced pressure and the residue obtained was washed with methanol (F) to give 2.1 g. of chloranil. Methanol washings were evaporated and the residue was dissolved in benzene and chromatographed using 60 g. of alumina. Evaporation of red benzene eluates affored 1.66 g. of red crystals (G), m.p. 46~54°C. Four and a half grams (yield 45%) of the combined red crystals, E and G were dissolved in benzene and chromatographed again using alumina to give 8-cyano, 8-ethoxycarbonylheptafulvene (VIII) as red crystals, m. p. 61~63°C. Recrystallization from petroleum ether gave red prisms, m. p. 63.5°C.

Found: C, 72.06; H, 5.50; N, 6.78. Calcd. for $C_{12}H_{11}O_2N$: C, 71.62; H, 5.51; N, 6.9%.

Thermal Decomposition of Ethyl Ditropylcyanoacetate (IV).—One gram (3.4 mmol.) of IV in a small Claisen flask was heated at 170~195°C in an oil bath and distilled in 2 mmHg at the same temperature to give a red viscous oil. Addition of a little amount of ethanol afforded yellow crystals, m.p. 118~120°C, which proved to be starting IV, by mixed m.p. determination. The red filtrate, after evaporating ethanol, was dissolved in benzene and chromatographed using alumina. An elution of a red absorption band with benzene and evaporation of benzene gave 150 mg. (yield 22%) of a red oil which crystallized on standing and showed m.p. 55~60°C. Repeated recrystallization from petroleum ether gave red prisms, m.p. 63°C, which showed no depression on admixture with VIII.

The Reaction of Ethyl Tropylcyanoacetate (III) and *N*-Bromosuccinimide. — Four hundred milligrams (2 mmol.) of III and 420 mg. (2.4 mmol.) of *N*-bromosuccinimide were dissolved in a mixture of 10 ml. of *tert*-butanol, 2 ml. of pyridine and 1 ml. of water. The reaction mixture was allowed to stand at room temperature for about 1 week, then poured to 30 ml. of water and extracted with ether. The ether extracts were washed with diluted hydrochloric acid and water, dried over magnesium sulfate and evaporated to 340 mg. of brown oil. On adding a small amount of ethanol. it crystallized to give 300 mg. of crystals, m.p. 45~47°C. Recrystallization from petroleum ether afforded colorless plates (IX), m. p. 49~50°C, which showed no depression on admixture with authentic ethyl α-cyanocinnamate, m. p. 50°C[16].

Dehydrogenation of Diethyl Tropylmalonate (V) with Chloranil.—To boiling xylene were added 7.5 g. (0.03 mol.) of V and 8.8 g. (0.036 mol.) of chloranil and the reaction mixture was refluxed for 1.5 hr. After cooling, dark red crystals separated, and this was filtered to give 2.8 g. of dihydrochloranil as crystals, m.p. 228°C. Distillation of xylene from the filtrate under reduced pressure afforded precipitates from which 2.0 g. of chloranil, m.p. 285°C, were obtained by washing with methanol (A). The washings A were evaporated and the residue was dissolved in benzene and chromatographed through a column containing 50 g. of alumina. An elution of a red band with benzene and evaporation of solvent gave 4.1 g. of red oil (B). It seemed to contain a little amount of starting material, because of the presence of infrared absorption at 705 and 740 cm^{-1} due to tropilidene nucleus. The distillation of the oil (B) in reduced pressure gave the following fractions. 1) 0.32 g. of oil, b.p. 122~130°C/3 mmHg. 2) 1.00 g. of red oil, b.p. 130~140°C/3 mmHg. 3) 0.63 g. of red oil, b.p. 140~150°C/3 mmHg and a considerable amount of residue.

Found: C, 67.77; H, 6.54 (for fr. 3); C, 67.42; H, 6.91 (for fr. 2). Calcd. for $C_{14}H_{16}O_4$: C, 67.73; H, 6.50%.

Fraction 2 (0.68 g.) was allowed to stand at room temperature for about 2 weeks, thereby red gelatinous material was obtained. On being dissolved in hot ethanol and cooled, it gave 0.35 g. of pale yellow amorphous product which softens at about 120°C. This is sparingly soluble in ether and ethanol, but soluble in acetone, benzene and ethyl acetate. It has a weak absorption maximum at 255 mμ.

Found: C, 67.46; H, 6.24. Calcd. for $C_{14}H_{16}O_4$: C, 67.73; H, 6.50%. mol. wt.: 1000 (by Rast method using camphor).

Bromination and Dehydrobromination of Diethyl Tropylmalonate (V).—To a solution of 0.96 g. (4 mmol.) of V in 5 ml. of chloroform was added a solution of 0.64 g. of bromine (4 mmol.) in 2 ml. of chloroform. After stirring for 30 min., the solvent was evaporated from the mixture to give 1.5 g. of a pale yellow oil. Heating the oil in a boiling water bath for 60 min. resulted in evolution of hydrogen bromide gas to give 1.1 g. of a brownish oil. It was dissolved in benzene and the benzene layer was washed with diluted sodium hydrogen carbonate and water, dried over sodium sulfate and chromatographed through a column containing 20 g. of alumina. The evaporation of benzene elutes gave 350 mg. of red oil which has an ultraviolet absorption maxima at 274 and 355 mμ. An elution with ethyl acetate afforded 300 mg. of brown oil which crystallized. Recrystallization from ethanol gave 50 mg. of yellow crystals (XI), m.p. 130°C, which proved to be identical with 3-ethoxycarbonyl 1-oxaazulan-2-one, m.p. 130°C, by mixed melting point determination[17].

Behavior of 8,8-Disubstituted Heptafulvene, VI and VIII against Acid and Alkali. — a) 6 N Hydrochloric acid and ethanol: 60 mg. of VI was dissolved in a mixture of 3 ml. of concentrated hydrochloric acid and 3 ml. of ethanol and the solution was refluxed for 2 hr. On cooling, red needles were crystallized and 40 mg. of starting material, m.p. 198°C, was collected by filtration.

One hundred miligrams of VIII was treated in the same way as above and the reaction mixture was poured into 50 ml. of water and extracted with benzene. The benzene extracts were washed with water, dried over sodium sulfate and evaporated to 85 mg. of red oil which crystallized and showed m.p. 59~61°C. Recrystallization from petroleum ether gave red prisms, m.p. 62~63°C, which was proved to be identical with starting VIII.

b) 75% sulfuric acid: 100 mg. of VI was added to 2.5 ml. of 75% sulfuric acid and the mixture was heated in a boilding water bath. After 6 hr.,

all crystals were dissolved and no carbon dioxide evolved. Dilution with 5 ml. of water and addition of sodium hydrogen carbonate to pH 2.5 separated an yellow amorphous material which is sparingly soluble in water or ether, but soluble in sodium hydrogen carbonate.

c) 2 N potassium hydroxide and ethanol solution: 50 mg. of VI was dissolved in 1 ml. of 6 N potassium hydroxide and 2 ml. of ethanol and the resulted mixture was refluxed for 1 hr. 20 mg. of solid resinous material separated. Extraction of the filtrate with benzene gave no starting VI.

Bromination of 8, 8-Dicyanoheptafulvene (VI).—To a solution of 80 mg. (0.55 mmol.) of VI in 3 ml. of chloroform was added a solution of 160 mg. of bromine (1 mmol.) in 0.6 ml. of chloroform and the reaction mixture was stirred at room temperature for 4 hr. Bromine still remained. Evaporation of chloroform at room temperature gave 70 mg. of red needles, m.p. 192~194°C, which were recrystallized from ethanol to give a starting material (VI) as crystals, m.p. 199~200°C.

Reaction of 8-Cyano, 8-Ethoxycarbonylheptafulvene (VIII) and Maleic Anhydride.—A solution of 300 mg. (1.5 mmol.) of VIII and 176 mg. (1.8 mmol.) of maleic anhydride in 6 ml. of xylene was refluxed for 34 hr. After xylene was distilled under reduced pressure and a small amount of methanol was added, a red viscous oil crystallized. Sixty milligrams (yield 13.4%) of light yellow crystals, m. p. 170~174°C, were obtained by filtration and recrystallized from methanol to give an adduct (XII) as crystals, m.p. 177°C.

Found: C, 63.67; H, 4.08; N, 4.62. Calcd. for $C_{16}H_{13}O_5N$: C, 64.21; H, 4.38; N, 4.68%. λ_{max}^{MeOH} 297 mμ (log ε 4.23).

Evaporation of methanol from the filtrate gave 250 mg. of a red oil which was dissolved in benzene and chromatographed through column containing 6 g. of alumina. An elution with benzene afforded 100 mg. (yield 33%) of VIII as red crystals, m.p. 50~55°C.

Reaction of 8, 8-Dicyanoheptafulvene (VI) and Maleic Anhydride.—Two hundred and fifty milligrams (1.7 mmol.) of VI and 190 mg. (1.9 mmol.) of maleic anhydride was added to 6 ml. of xylene and the resulted mixture was refluxed for 13 hr. On cooling, red needles crystallized. Evaporation of xylene and addition of ethanol to residue gave 200 mg. of starting VI as red needles, m. p. 195°C.

Catalytic Reduction of 8, 8-Dicyanoheptafulvene (VI).—a) One hundred milligrams (0.65 mmol.) of VI was dissolved in 40 ml. of ethanol and hydrogenated in the presence of 30 mg. of Pd-carbon (5%) at ordinary temperature and pressure. Only 20 ml. (0.9 mmol.) of hydrogen was absorbed for 6 hr. Treated in the usual way, 90 mg. of red needles, m.p. 184~188°C were obtained which was identical with VI.

b) With Pt-oxide. A solution of 120 mg. (0.82 mmol.) of VI in 55 ml. of ethanol was hydrogenated in the presence of 15 mg. of Pt-oxide at ordinary temperature and pressure. After 42 ml. (2.3 mmol.) of hydrogen had been absorbed, the color of the solution changed and at 57 ml. (3.1 mmol.) of hydrogen the velocity became slow and at 61 ml. (3.3 mmol.) hydrogenation was stopped. Catalysts were filtered and the filtrate was evaporated to give 120 mg. of yellow oil which showed infrared absorption at 3345, 3445 cm^{-1} due to NH_2 group. It was dissolved in benzene and passed through a column containing 9 g. of alumina. Evaporation of the benzene eluate gave 30 mg. of a colorless oil which has no infrared absorption maximum due to NH_2 or NH group, but showed an absorption maximum at 239 mμ in methanol. Evaporation of the ether eluates gave 45 mg. of a brown oil which has infrared absorption at 3345 and 3445 cm^{-1}.

Catalytic Reduction of 8, 8-Diethoxycarbonylheptafulvene (X).—A solution of 500 mg. (2 mmol.) of X in 40 ml. of ethanol was hydrogenated in the presence of 10 mg. of Pt-oxide as catalyst at ordinary temperature and pressure. After 107 ml. (4.9 mmol.) of hydrogen had been absorbed, the red color of the solution disappeared and the absorption of hydrogen almost ceased at 175 ml. (7.8 mmol.). The filtrate obtained by removal of the catalyst was evaporated to 400 mg. of an yellow oil (XIII). It has no absorption maximum in the ultraviolet spectrum.

Two hundred and fifty milligrams of XIII was added to a mixture of 2.5 ml. of 6 N potassium hydroxide and 2.5 ml. of ethanol and the solution was refluxed for 2 hr. After evaporating ethanol and diluting with water, the reaction mixture was acidified with diluted hydrochloric acid and extracted with ether. The ether extracts were washed with water, dried over sodium sulfate and evaporated to 200 mg. of colorless crystals, m. p. 145~149°C (decomp.). Repeated recrystallization from a mixture of carbon tetrachloride and acetone gave colorless crystals, m. p. 160~161°C (decomp.).

Found: 60.49; H, 7.72. Calcd. for $C_{10}H_{16}O_4$: C, 59.98; H, 8.05%.

Reported melting point for cycloheptylmalonic acid is 164.5°C[25].

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