BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 39 2444—2449 (1966)

Heptafulvenes. V. Some Substitution Reactions of 2, 3-Dimethoxy-8, 8-dicyanoheptafulvenes

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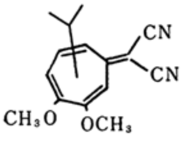
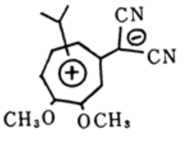
(Received February 19, 1966)

Methoxyl groups of alkyl-2, 3-dimethoxy-8, 8-dicyanoheptafulvenes were easily replaced by various kinds of nucleophilic reagents to give the corresponding substituted-8, 8-dicyanoheptafulvenes. There exists a difference in reactivity between the two methoxyl groups located at the 2 and 3 positions of 8, 8-dicyanoheptafulvenes. The isopropyl group at the 4 position of 2, 3-dimethoxy-8, 8-dicyanoheptafulvene hindered some substitution reactions of the methoxyl group at the 3 position.

The previous paper[1] reported the formation of 2, 3-dimethoxy-8, 8-dicyanoheptafulvene and its alkyl derivatives. Since isopropyl-2, 3-dimethoxy-8, 8-dicyanoheptafulvene (I) possesses the large dipole moment of 8.85 Debye units, there may be considered to be a large contribution of the ionic structure (II).[2a] The π-electron density at each atom in the heptafulvene derivative has also been calculated by Katagiri[2b] (Fig 1).



(I)



(II)

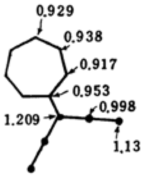
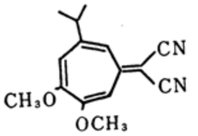


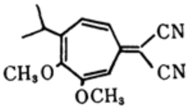
Fig. 1. π-Electron density at each atom in 8,8-divinyl heptafulvene (by Katagiri).

On the basis of these data, the methoxyl groups at the 2 and 3 positions of I may be expected to undergo various kinds of nucleophilic substitution reactions, and it is reasonable to expect that there is a difference between the reactivities of the methoxyl groups at the 2 and 3 positions and that the group at the 3 position might be more reactive if other factors are not considered.

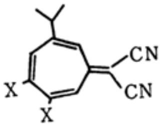
When 5-isopropyl-2, 3-dimethoxy-8, 8-dicyano-heptafulvene (III) is allowed to react with such amines as ammonia, methylamine and dimethylamine, the disubstituted products, V, VI and VII, respectively, are formed.



(III)



(IV)



(V) $X=NH_2$
(VI) $X=NHCH_3$
(VII) $X=N(CH_3)_2$

V reacts with acids or acid chlorides to give as products VIII, IX, X and XI, all of which have an imidazole nucleus. The possibility of these condensation products being 1, 3-diazaazulene derivatives (structure b) was eliminated by an examination of their infrared and ultraviolet absorption spectra. The infrared spectra of these compounds show conjugated nitriles at 2175 and 2195 cm^{-1}, and their ultraviolet spectra are completely different from that of 1, 3-diazaazulene.[3] III reacts with guanidine to give the corresponding condensation product. From its molecular formula and its spectral data, it was concluded

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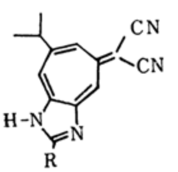
[1] Y. Kitahara, K. Doi and T. Kato, This Bulletin, **37**, 1747, 1750 (1964).

[2a] S. Katagiri, K. Doi, Y. Kitahara and H. Azumi, ibid., to be published. T. Nozoe and K. Takase, "Dai Yuki Kagaku" (Comprehensive Organic Chemistry), **13**, Asakura-shoten, Tokyo (1960), p. 531.

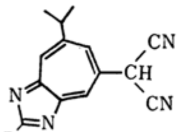
[2b] By private communication, Katagiri calculated the π-electron density at each atom of the hypothetical 8, 8-divinyl heptafulvene.

[3] I. Murata, This Bulletin, **33**, 56 (1960).

that the product has the heptafulvene structure (XIIa or XIIb).

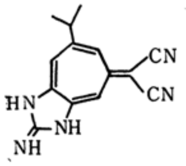


(a)

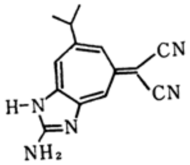


(b)

(VIII) $R=H$
(IX) $R=CH_3$
(X) $R=Ph$
(XI) $R=p\text{-}NO_2\cdot Ph$

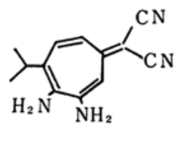


(XIIa)

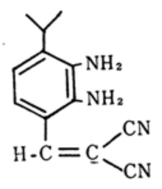


(XIIb)

4-Isopropyl-2, 3-dimethoxy-8, 8-dicyanoheptafulvene (IV) gave a yellow crystalline substance (XIII) and a white crystalline substance (XIV) in almost equal amounts upon reaction with liquid ammonia. The composition of both XIII and XIV satisfies $C_{13}H_{14}N_4$, but their ultraviolet absorption spectra are quite different. The spectrum of XIII is similar to that of 8, 8-dicyanoheptafulvene, but the spectrum of XIV, which shows no absorption in the longer wave region and which is similar to that of dicyanostyrene, suggests that XIV does not possess a heptafulvene structure. XIV seems to be a six-membered ring compound formed by rearrangement reaction* during the formation of XIII.

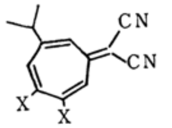


(XIII)

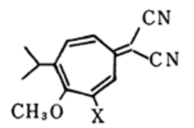


(XIV)

III readily undergoes substitution reactions with sodium ethoxide or sodium ethyl mercaptide, affording a disubstituted product, XV or XVI respectively. In the case of IV, however, the reaction with sodium ethyl mercaptide affords not a disubstituted product but monosubstituted product (XVII); this is due to the steric hindrance of the isopropyl group to the attack of the anionoid reagent.



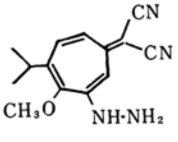
(XV) $X=OC_2H$
(XVI) $X=SC_2H_5$



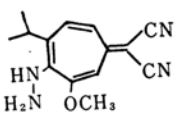
(XVII) $X=SC_2H_5$

IV reacts with hydrazine to afford a monohydrazino compound (XVIIIa or XVIIIb). The XVIIIa structure is more likely for the compound since the steric hindrance of the isopropyl group would be expected to prevent the 3-methoxyl group from substituting.

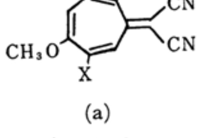
The reaction of III with sodium hydrogen sulfide gives a monosubstituted product whose composition corresponds to XIX. XIX is acidic, and the mercapto group is readily methylated by diazomethane to yield XX. By the reaction with ethylenediamine or with hydrazine, III does not afford a disubstituted product, but gives a monosubstituted product, XXI or XXII. For each of these monosubstituted products, there are two possible structures, a and b.



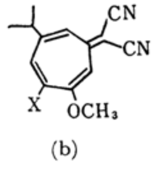
(XVIIIa)



(XVIIIb)



(a)



(b)

(XIX) $X=SH$
(XX) $X=SCH_3$
(XXI) $X=NH\cdot(CH_2)_2\cdot NH_2$
(XXII) $X=NH\cdot NH_2$

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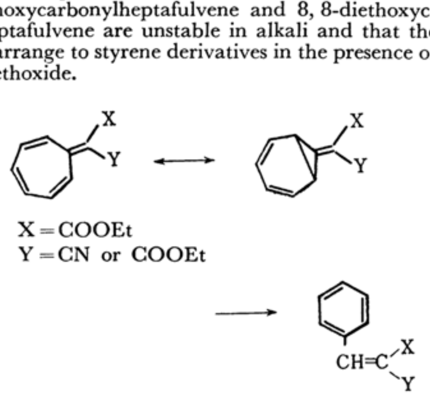
* However, the chemical proof of the structure of XIV will be the subject of further investigation. It is known that 8, 8-disubstituted heptafulvenes undergo a base-catalyzed rearrangement to styrene derivatives; for example, Kitahara and Doi[4] found that 8-cyano-8-ethoxycarbonylheptafulvene and 8, 8-diethoxycarbonylheptafulvene are unstable in alkali and that they easily rearrange to styrene derivatives in the presence of sodium methoxide.



$X=COOEt$
$Y=CN$ or $COOEt$

4) Heptafulvenes III, ibid., **37**, 1754 (1964).

It is not apparent that the methoxyl group at the 2 position of III is more reactive than that of the 3 position. Because III lacks the steric interference from an adjacent isopropyl group, unlike IV, the two possible structures, a and b, must be considered as equally likely. However, the ultraviolet and infrared absorption spectra support a.⁵⁾

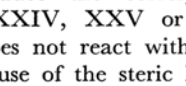
On the basis of these results, it may be concluded that there is a difference between the reactivities of the methoxyl groups at the 2 and 3 positions, and that the one at the 2 position undergoes nucleophilic substitution reactions more easily.

The above conclusion is not in accord with the results calculated by Katagiri. This inconsistency is considered to arise from the interaction between the adjacent two methoxyl groups, and from complication factors, such as the π-p conjugation between the lone paired electrons of the oxygen atom of the methoxyl and the electrons in the ring, which cause discrepancies in the simple calculation.

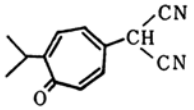
The hydrazino group of XVIII can be removed by treatment with cupric sulfate - acetic acid to give XXIII, which reacts readily with certain amines to produce the corresponding aminoheptafulvenes, XXIV, XXV or XXVI. However, XXIII does not react with dimethylamine, apparently because of the steric hindrance of the isopropyl group adjacent to the methoxyl group.

The methoxyl group of XXIII is readily hydrolyzed with alkali to yield the corresponding hydroxy compound, which is considered to have the XXVIIa structure rather than the tautomeric keto form, XXVIIb, on the basis of the following facts: (i) the ultraviolet absorption spectrum of the hydroxy compound is similar to that of heptafulvene, (ii) the infrared absorption spectrum of the compound indicates the presence of a conjugated nitrile, and (iii) the compound gives an acetate (XXVIII).

When treated with cupric sulfate - acetic or hydrochloric acid, XXIV affords 3-isopropyl-8, 8-dicyanoheptafulvene (XXIX) or 3-chloro-4-isopropyl-8, 8-dicyanoheptafulvene (XXX) respectively.



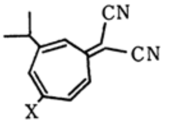
(XXIII) X=OCH_3 (XXVIIa) X=OH
(XXIV) X=$NH\cdot NH_2$ (XXVIII) X=OAc
(XXV) X=NH_2 (XXIX) X=H
(XXVI) X=$NHCH_3$ (XXX) X=Cl



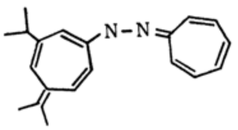
(XXVIIb)

XXII yields XXXI by the analogous dehydrazination reaction. The methoxyl group of XXXI is readily replaced by amino groups to produce the aminoheptafulvenes, XXXII, XXXIII or XXXIV. Because of the absence of the steric interference of the isopropyl group, XXXI gives XXXV by reaction with dimethylamine.

The dehydrazination of XXXII gives 2-isopropyl-8, 8-dicyanoheptafulvene XXXVI. XXXII readily condenses with tropone to yield the corresponding condensation products, XXXVII.



(XXXI) X=OCH_3 (XXXIV) X=$NHCH_3$
(XXXII) X=$NH\cdot NH_2$ (XXXV) X=$N(CH_3)_2$
(XXXIII) X=NH_2 (XXXVI) X=H



(XXXVII)

Experimental

The Reaction of 5-Isopropyl-2, 3-dimethoxy-8, 8-dicyanoheptafulvene (III) with Amines.—*Liquid Ammonia.*—A mixture of 1.5 g. of III and 30 ml. of liquid ammonia was allowed to stand at room temperature for 2 days. The evaporation of the resulting red solution left a yellow crystalline residue which was then dissolved in ethanol and chromatographed over alumina. The recrystallization of the eluted crystals from methanol gave orange needles of V, m. p. >260°C.

Found: C, 68.98; H, 5.92; N, 24.56. Calcd. for $C_{13}H_{14}N_4$: C, 69.00; H, 6.24; N, 24.76%.

UV λ_{max}^{MeOH} mμ (log ε): 245 (4.11), 335 (4.45), 405 (4.45).

Liquid Methylamine.—By a procedure similar to that described above, 500 mg. of III and 30 ml. of liquid methylamine afforded 430 mg. of orange scales (VI) after recrystallization from ethanol, m. p. 260—261°C (decomp.).

Found: C, 71.08; H, 6.54; N, 21.53. Calcd. for $C_{15}H_{18}N_4$: C, 70.83; H, 7.13; N, 22.03%.

UV λ_{max}^{MeOH} mμ (log ε): 258 (4.14), 330 (4.36), 425 (4.42).

Liquid Dimethylamine.—A mixture of 700 mg. of III and 50 ml. of liquid dimethylamine, after recrystallization from ethanol, yielded 500 mg. of VII as red prisms, m. p. 184—185°C.

Found: C, 72.14; H, 7.38; N, 19.44. Calcd. for $C_{17}H_{22}N_4$: C, 72.30; H, 7.85; N, 19.84%.

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5) Heptafulvenes VII, to be published.

UV $\lambda_{max}^{\mathrm{MeOH}}$ mμ (log ε): 285 (4.01), 340 (4.17), 455 (4.24).

The Reaction of 2, 3-Diamino-5-isopropyl-8, 8-dicyanoheptafulvene V with Acids or Acid Derivatives.—*With Formic Acid.*—A mixture of 5 ml. of 80% formic acid and 400 mg. of V was refluxed for 30 min. After the excess formic acid had been removed under reduced pressure, the resulting red crystalline material was recrystallized from methanol to yield 180 mg. of red scales (VIII), m. p. >280°C.

Found: C, 71.19; H, 4.74; N, 23.80. Calcd. for $C_{14}H_{12}N_4$: C, 71.16; H, 5.12; N, 23.72%.

UV $\lambda_{max}^{\mathrm{MeOH}}$ mμ (log ε): 245 (4.20), 290 (4.00), 410 (4.52).

With Acetic Anhydride.—A mixture of 300 mg. of V and 20 ml. of acetic anhydride was refluxed for one hr., after which the acetic anhydride was distilled off under reduced pressure. The addition of water to the residue precipitated red crystals (200 mg.) which, after filtration, were taken up in ethanol and passed through an alumina column. The recrystallization of the eluted material from ethanol gave red scales (IX), m. p. >300°C.

Found: C, 71.68; H, 5.11; N, 21.95. Calcd. for $C_{15}H_{14}N_4$: C, 71.97; H, 5.64; N, 22.39%.

UV $\lambda_{max}^{\mathrm{MeOH}}$ mμ (log ε): 250 (4.27), 295 (4.17), 415 (4.54).

With Benzoyl Chloride.—A solution of 400 mg. of V in 10 ml. of anhydrous pyridine was mixed with 1.5 mol. equivalents of benzoyl chloride and allowed to stand at room temperature overnight. After the pyridine had been distilled off, the residue was refluxed in 20 ml. of methanol for one hr. and then allowed to cool. The red crystalline deposit (300 mg.), after recrystallization from an ethyl acetate - methanol (1 : 1) mixture, afforded reddish violet scales (X), m. p. >300°C.

Found: C, 76.93; H, 4.71; N, 17.53. Calcd. for $C_{20}H_{16}N_4$: C, 76.90; H, 5.16; N, 17.94%.

UV $\lambda_{max}^{\mathrm{MeOH}}$ mμ (log ε): 240 (4.30), 265 (4.24), 330 (4.50), 410 (4.57).

With p-Nitrobenzoyl Chloride.—The reaction between V and *p*-nitrobenzoyl chloride was carried out in a manner similar to that described above. The crude crystals obtained from the reaction of 220 mg. of V and 200 mg. of *p*-nitrobenzoyl chloride in 10 ml. of pyridine were recrystallized from acetone to afford blackish-violet scales (XI), m. p.—300°C.

Found: C, 67.42; H, 4.21; N, 19.57. Calcd. for $C_{20}H_{15}N_5O_2$: C, 67.22; H, 4.23; N, 19.60%.

UV $\lambda_{max}^{\mathrm{MeOH}}$ mμ (log ε): 260 (4.31), 337 (4.57), 413 (4.62).

The Reaction of III with Guanidine.—III (500 mg.) was added to a solution of 200 mg. of guanidine hydrochloride in ethanolic sodium ethoxide (prepared from 50 mg. of sodium and 20 ml. of absolute ethanol), and the mixture was refluxed for 5 hr. The removal of the ethanol afforded a red oil which was then chromatographed over alumina. Ethyl acetate was used as the solvent; 100 mg. of the crystals were obtained from early fractions which, after recrystallization from ethyl acetate, afforded XV as orange plates, m. p. 143—144°C.

Found: C, 71.75; H, 6.86; N, 9.27. Calcd. for $C_{17}H_{20}N_2O_2$: C, 71.80; H, 7.09; N, 9.85%.

UV $\lambda_{max}^{\mathrm{MeOH}}$ mμ (log ε): 245 (4.29), 275 (4.16), 295 (4.17), 408 (4.45).

Then (1 : 1 ethyl acetate - methanol) crystals (210 mg.) were obtained; on recrystallization from ethanol, they gave XII as red needles, m. p. >290°C.

UV $\lambda_{max}^{\mathrm{MeOH}}$ mμ (log ε): 255 (4.13), 310 (4.23), 330 (4.28), 410 (4.54).

Picrate: m. p. 262—263°C (decomp.) Found: C, 49.95; H, 3.47; N, 23.02. Calcd. for $C_{14}H_{13}N_5\cdot C_6H_3N_3O_7$: C, 50.00; H, 3.35; N, 23.32%.

The Reaction of III with Sodium Ethyl Mercaptide.—A mixture of 250 mg. of III and 20 ml. of ethyl mercaptan containing 50 mg. of sodium was refluxed for 8 hr., and then most of the mercaptan was distilled off. The residue was diluted with 50 ml. of water, and extracted with ethyl acetate. The ethyl acetate extract was washed with water, dried over magnesium sulfate, and evaporated to yield 150 mg. of red crystals which, after recrystallization from ethanol, gave red scales of XVI, m. p. 106—107°C.

Found: C, 64.17; H, 6.34; N, 8.50. Calcd. for $C_{17}H_{20}N_2S_2$: C, 64.54; H, 6.37; N, 8.86%.

UV $\lambda_{max}^{\mathrm{MeOH}}$ mμ (log ε): 295 (sh.), 345 (4.27), 438 (4.45).

The Reaction of III and Sodium Hydrogen Sulfide.—A sodium ethoxide solution (prepared from 5 ml. of absolute ethanol and 70 mg. of sodium) was saturated with hydrogen sulfide, and then 200 mg. of III was added. After the mixture had been heated for several minutes, the ethanol was removed and the residue was diluted with dilute sulfuric acid to afford 200 mg. of yellow crystals (XIX), m. p. 219—220°C (decomp.). When XIX was heated in ethanol, it changed into an insoluble blackish-red material which could not be purified.

A suspension of 200 mg. of the crude XIX in ethanol was treated with an excess of diazomethane. After the solvent had been removed, the residue was dissolved in benzene and passed through an alumina column. The evaporation of the solvent afforded red needles (XX), m. p. 174—175°C.

Found: C, 66.13; H, 6.14; N, 9.97. Calcd. for $C_{15}H_{16}N_2OS$: C, 66.16; H, 5.92; N, 10.29%.

UV $\lambda_{max}^{\mathrm{MeOH}}$ mμ (log ε): 260 (4.15), 330 (4.04), 415 (4.47).

The Reaction of III with Ethylenediamine.—To a solution of 50 ml. of absolute ethanol containing 90 mg. of sodium, 260 mg. of ethylenediamine hydrochloride and 510 mg. of III were added, the mixture was then refluxed for one hr. The removal of the ethanol afforded a red oil which, after being chromatographed over alumina using ethanol, yielded 300 mg. of crystals. Recrystallization from ethanol gave orange plates (XXI), m. p. 248—250°C (decomp.).

Found: C, 67.77; H, 6.77; N, 19.37. Calcd. for $C_{16}H_{20}N_4O$: C, 67.58; H, 7.09; N, 19.71%.

UV $\lambda_{max}^{\mathrm{MeOH}}$ mμ (log ε): 250 (4.17), 350 (4.55), 410 (4.37).

The Reaction of III with Hydrazine.—A large excess of 80% hydrazine was added to a suspension of 400 mg. of III in 40 ml. of ethanol at 50°C. The mixture was heated for 5 min., and then diluted with 200 ml. of water to give 260 mg. of crystals. Recrystallization from an ethanol - ethyl acetate mixture afforded orange scales (XXII), m. p. 204—205°C (decomp.).

Found: C, 65.72; H, 5.93; N, 21.84. Calcd. for $C_{14}H_{16}N_4O$: C, 65.60; H, 6.29; N, 21.86%.

UV $\lambda_{max}^{\mathrm{MeOH}}$ mμ (log μ): 240 (4.24), 325 (4.33), 405 (4.44).

The Reaction of 4-Isopropyl-2, 3-dimethoxy- 8, 8-dicyanoheptafulvene (IV) with Liquid Ammonia.—A mixture of 450 mg. of IV and 40 ml. of liquid ammonia was allowed to stand overnight at room temperature, and then the ammonia was distilled off. The residue was treated with methanol. The methanol-insoluble yellow crystalline material (150 mg.) was dissolved in ethanol and chromatographed over alumina to afford yellow crystals (XIII), m. p. >260°C.

Found: C, 68.93; H, 6.23; N, 24.95. Calcd. for $C_{13}H_{14}N_4$: C, 69.00; H, 6.24; N, 24.76%.

UV $\lambda_{max}^{\mathrm{MeOH}}$ mμ (log ε): 225 (4.25), 245 (4.01), 330 (4.38), 410 (4.47).

From the methanol-soluble part, 150 mg. of white needles (XIV), m. p. >270°C, were obtained.

Found: C, 68.43; H, 6.01; N, 24.42. Calcd. for $C_{13}H_{14}N_4$: C, 69.00; H, 6.24; N, 24.76%.

UV $\lambda_{max}^{\mathrm{MeOH}}$ mμ (log ε): 225 (4.26), 300 (4.36).

The Reaction of IV with sodium Ethyl Mercaptide.—To 30 ml. of ethyl mercaptan containing 80 mg. of sodium, 500 mg. of IV were added, and then the mixture was refluxed for 8 hr. After the ethyl mercaptan had been removed, the residue was treated with water and extracted with ethyl acetate. The ethyl acetate extract was washed with dilute sulfuric acid and then with water. Drying over magnesium sulfate and the removal of the solvent afforded 500 mg. of a red oil, which was then taken up in benzene and chromatographed on alumina. Red plates (XVII), m. p. 131—132°C, were obtained after recrystallization from ethanol.

Found: C, 66.82; H, 6.06; N, 9.63. Calcd. for $C_{16}H_{18}N_2OS$: C, 67.11; H, 6.34; N, 9.78%.

UV $\lambda_{max}^{\mathrm{MeOH}}$ mμ (log ε): 225 (3.87), 335 (4.26), 442 (4.42).

The Reaction of IV with Hydrazine.—By the procedure described for the formation of XXII from III, 200 mg. of red needles (XVIII), m. p. 208—209°C, were obtained from 300 mg. of IV.

Found: C, 65.98; H, 6.06; N, 21.99. Calcd. for $C_{14}H_{16}N_4O$: C, 65.60; H, 6.29; N, 21.86%.

UV $\lambda_{max}^{\mathrm{MeOH}}$ mμ (log μ): 243 (4.09), 315 (4.24), 405 (4.42).

The Dehydrazination of 2-Hydrazino-5-isopropyl-3-methoxy-8, 8-dicyanoheptafulvene (XXII).—Into a boiling suspension of 200 mg. of XXII in a mixed solvent of 5 ml. of acetic acid and 5 ml. of water, 10 ml. of a 10% aqueous cupric sulfate solution was stirred, drop by drop. The boiling was continued for 20 min., after which time gas evolution ceased. The reaction mixture was allowed to come to room temperature, and then diluted with water and extracted with ethyl acetate. The ethyl acetate extract was washed with a dilute aqueous sodium hydroxide solution and then with water, dried over magnesium sulfate, and evaporated. The brown crystalline residue was dissolved in ethyl acetate and passed through an alumina column. The crystals (100 mg.) so obtained were recrystallized from ethanol to give orange needles (XXXI), m. p. 175.5—177.5°C.

Found: C, 74.09; H, 5.85; N, 12.51. Calcd. for $C_{14}H_{14}N_2O$: C, 74.31; H, 6.24; N, 12.38%.

UV $\lambda_{max}^{\mathrm{MeOH}}$ mμ (log ε): 238 (4.29), 280 (3.85), 418 (4.48).

The Dehydrazination of XVIII.—The procedure was the same as that described for the dehydrazination of XXII. Red prisms (XXIII), m. p. 141—142°C, after recrystallization from ethanol, were obtained from XVIII.

Fonnd: C, 74.36; H, 6.12; N, 12.54. Calcd. for $C_{14}H_{14}N_2O$: C, 74.31; H, 6.24; N, 12.38%.

UV $\lambda_{max}^{\mathrm{MeOH}}$ mμ (log ε): 238 (4.03), 250 (4.04), 428 (4.50).

Depending on the experimental conditions, orange needles, m. p. 255°C (decomp.), could be obtained in addition to XXIII.

Found: C, 64.36; H, 5.74; N, 18.63. Calcd. for $C_{16}H_{18}N_4O_2$: C, 64.41; H, 6.08; N, 18.78%.

UV $\lambda_{max}^{\mathrm{MeOH}}$ mμ (log ε): 240 (4.09), 307 (4.29), 410 (4.58).

IR: 3250 (NH), 1660, 1626, 1285 cm^{-1}.

From the results of microanalysis and a study of its infrared spectrum, the above compound was deduced to be 2-acetylhydrazino-4-isopropyl-3-methoxy-8, 8-dicyanoheptafulvene.

The Reaction of XXIII with Hydrazine.—To a solution of 100 mg. of XXIII in 2 ml. of ethanol there was added 27 mg. of a 80% hydrazine hydrate aqueous solution. The concentration of this solution afforded 50 mg. of red crystals which were recrystallized from ethanol to give red prisms (XXIV), m. p. 187—188°C (decomp.).

Found: C, 68.92; H, 5.81; N, 25.13. Calcd. for $C_{13}H_{14}N_4$: C, 69.00; H, 6.24; N, 24.76%.

UV $\lambda_{max}^{\mathrm{MeOH}}$ mμ (log ε): 250 (4.12), 330 (3.89), 465 (4.56).

The Reaction of XXIII with Ammonia.—A mixture of 50 mg. of XXIII and 10 ml. of methanolic ammonia was allowed to stand overnight at room temperature; then the solvent was removed. The resulting crystalline material was recrystallized from ethanol to give orange prisms (XXV), m. p. 234—235°C (decomp.).

Found: C, 73.90; H, 5.67; N, 20.27. Calcd. for $C_{13}H_{13}N_3$: C, 73.90; H, 6.20; N, 19.89%.

UV $\lambda_{max}^{\mathrm{MeOH}}$ mμ (log ε): 250 (4.17), 308 (3.88), 465 (4.59).

The Reaction of XXIII with Methylamine.—To a solution of 50 mg. of XXIII in 4 ml. of ethanol, 1 ml. of a 40% aqueous methylamine solution was added; the mixture was then refluxed for 5 min. On cooling to room temperature, 50 mg. of orange needles (XXVI), m. p. 256—257°C (decomp.), were obtained.

Found: C, 75.05; H, 6.26; N, 18.64. Calcd. for $C_{14}H_{15}N_3$: C, 74.64; H, 6.71; N, 18.65%.

UV $\lambda_{max}^{\mathrm{MeOH}}$ mμ (log ε): 220 (4.31), 255 (4.10), 325 (3.85), 465 (4.57).

The Reaction of XXIII with Dimethylamine.—To a solution of 50 mg. of XXIII in 6 ml. of ethanol, 1 ml. of a 33% aqueous dimethylamine solution was added. The concentration of this mixture afforded 20 mg. of orange needles, m. p. 255—256°C (decomp.), which were identified as XXVI by microanalysis and by a study of their infrared spectrum. XXVI seems to be formed by the reaction of XXIII with the methylamine contained in the dimethylamine.

3-Hydroxy-4-isopropyl-8, 8-dicyanoheptafulvene (XXVII).—A mixture of 200 mg. of XXIII, 20 ml. of water, and 2 N sodium hydroxide was heated. The acidification of the resulting red solution with sulfuric acid precipitated crystals which were recrystallized from benzene-methanol to afford orange prisms (XXVII), m. p. 226—227°C (decomp.).

Found: C, 73.36; H, 5.23; N, 13.40. Calcd. for $C_{13}H_{12}N_2O$: C, 73.56; H, 5.70; N, 13.20%.

UV $\lambda_{max}^{\mathrm{MeOH}}$ mμ (log ε): 243 (4.19), 295 (3.64), 440 (4.60).

The Acetylation of XXVII.—After a mixture of 150 mg. of XXVII and 2 ml. of acetic anhydride has been refluxed for 1 hr., the solvent was distilled off. The recrystallization of the residue from methanol afforded 80 mg. of orange scales (XXVIII) m. p. 137—138°C.

Found: C, 71.07; H, 5.24; N, 11.28. Calcd. for $C_{15}H_{14}N_2O_2$: C, 70.85; H, 5.55; N, 11.02%.

UV $\lambda_{max}^{\mathrm{MeOH}}$ mμ (log ε): 235 (4.10), 257 (4.11), 397 (4.43).

3-Chloro-4-isopropyl-8, 8-dicyanoheptafulvene (XXX).—Into a boiling solution of 2 g. of cupric sulfate in 4 ml. of water, a solution of 100 mg. of XXIV in 6 ml. of concentrated hydrochloric acid was stirred, drop by drop. The heating was continued until the evolution of nitrogen gas ceased. After it had then been allowed to cool to room temperature, the mixture was diluted with water and extracted with ethyl acetate. The extract was washed with water and dried over magnesium sulfate, and the solvent was distilled off. The red, oily residue, after being chromatographed over alumina using a mixed solvent of benzene and ethyl acetate (5 : 1), afforded 20 mg. of orange needles (XXX), m. p. 143—144°C.

Found: C, 68.08; H, 4.59; N, 12.20. Calcd. for $C_{13}H_{12}N_2Cl$: C, 67.69; H, 4.81; N, 12.15%.

UV $\lambda_{max}^{\mathrm{MeOH}}$ mμ (log ε): 240 (4.07), 257 (4.09), 397 (4.40).

3-Isopropyl-8, 8-dicyanoheptafulvene (XXIV).—Into a boiling solution of 5 g. of cupric sulfate in 10 ml. of water and 5 ml. of acetic acid, 180 mg. of XXIV were stirred and then the mixture was heated for 10 min. After being allowed to cool to room temperature, the reaction mixture was extracted with ethyl acetate. The extract was washed with dilute sodium hydroxide and then with water, and dried. The removal of the solvent afforded orange crystals which, after being chromatographed over alumina using a benzene-ethyl acetate (10 : 1) mixture, gave 50 mg. of crystals. Recrystallization from ethanol-cyclohexane gave red needles (XXIX), m. p. 120—121°C.

Found: C, 79.49; H, 5.83; N, 14.33. Calcd. for $C_{13}H_{12}N_2$: C, 79.56; H, 6.16; N, 14.28%.

UV $\lambda_{max}^{\mathrm{MeOH}}$ mμ (log ε): 232 (4.06), 255 (4.10), 397 (4.42).

3-Hydrazino-5-isopropyl-8, 8-dicyanoheptafulvene (XXXII).—By the procedure described for the formation of XXIV from XXIII, 200 mg. (after recrystallization from ethanol) of red prisms (XXXII), m. p. 218—219°C (decomp.), were obtained from 300 mg. of XXXI.

Found: C, 69.12; H, 5.73; N, 24.65. Calcd. for $C_{13}H_{14}N_4$: C, 69.00; H, 6.24; N, 24.76%.

UV $\lambda_{max}^{\mathrm{MeOH}}$ mμ (log ε): 244 (4.20), 330 (3.93), 465 (4.50).

The Condensation Reaction of XXXII with Tropone.—To a solution of 50 mg. of XXXII in 10 ml. of methanol, 4 drops of tropone were added; this mixture was then refluxed for 1.5 hr. After the methanol had been removed, 30 mg. of crystals were obtained. Recrystallization from ethanol gave reddish-violet scales (XXXVII), m. p. 227°C (decomp.).

Found: C, 76.38; H, 5.74; N, 17.47. Calcd. for $C_{20}H_{18}N_4$: C, 76.40; H, 5.77; N, 17.82%.

UV $\lambda_{max}^{\mathrm{MeOH}}$ mμ (log μ): 515 (4.64).

The Reaction of XXXI with Ammonia.—According to the procedure described for the formation of XXV from XXIII, 100 mg. of red prisms (XXXIII), m. p. 260—261°C (decomp.), were obtained from 150 mg. of XXXI.

Found: C, 73.80; H, 5.85; N, 19.91. Calcd. for $C_{13}H_{13}N_3$: C, 73.90; H, 6.20; N, 19.89%.

UV $\lambda_{max}^{\mathrm{MeOH}}$ mμ (log. ε): 242 (4.19), 315 (3.81), 455 (4.48).

The Reaction of XXXI with Methylamine.—When treated by the procedure used for the conversion of XXIII into XXVI, 100 mg. of XXXI afforded 90 mg. of orange needles (XXXIV), m. p. 247—248°C (decomp.).

Found: C, 74.96; H, 6.29; N, 19.27. Calcd. for $C_{14}H_{13}N_3$: C, 75.31; H, 5.87; N, 18.82%.

UV $\lambda_{max}^{\mathrm{MeOH}}$ mμ (log ε): 245 (4.32), 300 (sh.) 320 (3.93), 355 (3.93), 463 (4.53).

The Reaction of XXXI with Dimethylamine.—To a solution of 100 mg. of XXXI in 2 ml. of ethanol, 3 ml. of 33% aqueous dimethylamine was added, then the mixture was refluxed for 1 hr. The concentration of the reaction mixture afforded 40 mg. of red prisms (XXXV) after recrystallization from ethanol.

Found: C, 75.48; H, 6.72; N, 18.00. Calcd. for $C_{15}H_{17}N_3$: C, 75.28; H, 7.16; N, 17.56%.

UV $\lambda_{max}^{\mathrm{MeOH}}$ mμ (log μ): 250 (4.19), 333 (3.90), 465 (4.53).

2-Isopropyl-8, 8-dicyanoheptafulvene (XXXVI).—The procedure was the same as that described for the dehydrazination of XXIV. From 100 mg. of XXXII, 40 mg. of red needles (XXXVI), m. p. 111°C, were obtained.

The authors gratefully acknowledge the award of Maintenance Grants from Sankyo Co. Thanks are also due to Miss Yoko Endo and Miss Yukiko Endo for their elemental analyses.