dicyclohexyl disulfide.[6] Acetophenone is converted into di(α-phenylethyl) disulfide by ammonium polysulfide[7] and acetone into diisopropyl di-, tri-, and polysulfides by the action of hydrogen sulfide alone.[8] Thiols have also been postulated as intermediates in the Willgerodt reaction.[9]

Somewhat surprisingly, in the present investigation, the action of aqueous ammonium sulfide at 150° on both isobutyraldehyde and 2-ethylhexaldehyde produced considerable quantities (45 and 23%) of the respective thiols. Dialkyl di- and trisulfides accounted for the greater part of the remaining reaction products. That a reduction predominates, rather than the anticipated oxidation, can be assumed because of the relatively low ammonium polysulfide content of the reaction mixture as compared to the concentrations used in the Willgerodt reaction. Considerable variation in the ratio of thiol : disulfide : trisulfide isolated was frequently observed and may be caused by "minor" changes in the sulfide concentration and/or subtle differences in the work-up procedure, since all three products apparently can be in mutual equilibrium[9,10] in the presence of hydrogen sulfide and ammonia.

Experimental

Reaction of Isobutyraldehyde with Ammonium Sulfide.—A solution of 252 g. (7.9 moles) of hydrogen sulfide in 900 ml. (13.3 moles) of 28% aqueous ammonium hydroxide was charged, along with 144 g. (2 moles) of isobutyraldehyde, into a 3-l. stainless steel autoclave. The mixture was heated, with rocking, at 150° under autogenous pressure for 3.5 hr. and then cooled to 25°. Ether extraction of the reaction mixture followed by fractionation of the extracts yielded the following: (A) 80 g. (45%) of isobutyl mercaptan, b.p. 87°, $n^{30}\text{D}$ 1.4340; (B) 31 g. (18%) of diisobutyl disulfide, b.p. 60–75° (4.0 mm.), $n^{20}\text{D}$ 1.4882; (C) 9 g. (4%) of diisobutyl trisulfide, b.p. 86–92° (2.5 mm.), $n^{30}\text{D}$ 1.5215. The structure of A was confirmed by comparison of its physical properties to those of an authentic sample, b.p. 88°, $n^{30}\text{D}$ 1.4345, and the identity of the infrared spectra of the two.

From another experiment in which the mercaptan was not isolated there was obtained 65 g. (37%) of diisobutyl disulfide, b.p. 49–51° (0.45 mm.), $n^{30}\text{D}$ 1.4822, and 58 g. (27%) of diisobutyl trisulfide, b.p. 65–75° (0.3 mm.), $n^{30}\text{D}$ 1.5129–1.5219. Redistillation of the disulfide afforded pure material, of b.p. 55° (0.5 mm.), $n^{50}\text{D}$ 1.4822, which was found to be identical to an authentic sample, b.p. 43° (0.25 mm.), $n^{30}\text{D}$ 1.4819, prepared by the iodine oxidation of isobutyl mercaptan.

Anal. Calcd. for $C_8H_{12}S_2$: C, 53.91; H, 10.18; S, 35.91. Found: C, 53.91; H, 9.89; S, 35.80.

The structure of the trisulfide is based on its elemental analysis and infrared spectrum. A purified sample was obtained as a slightly yellow liquid, b.p. 70° (0.3 mm.), $n^{30}\text{D}$ 1.5219.

Anal. Calcd. for $C_8H_{16}S_3$: C, 45.70; H, 8.63; S, 45.67. Found: C, 46.00; H, 8.46; S, 45.42.

Reaction of 2-Ethylhexaldehyde with Ammonium Sulfide.—In the manner described for the preceding reaction of isobutyraldehyde, 258 g. (2 moles) of 2-ethylhexaldehyde was treated with a solution of 248 g. (7.3 moles) of hydrogen sulfide in 900 ml. (13.3 moles) of 28% aqueous ammonium hydroxide. The reaction products were isolated similarly to give the following: (A) 67 g. (23%) of 2-ethylhexyl mercaptan, b.p. 78–82° (20 mm.) $n^{30}\text{D}$ 1.4512; (B) 161 g. (55%) of di(2-ethylhexyl) disulfide, b.p. 144–146° (1.5 mm.), $n^{30}\text{D}$ 1.4820; and (C) 48 g. of higher sulfides 15% calculated as di(2-ethylhexyl) trisulfide, b.p. 155–181° (1.5–3.0 mm.), $n^{30}\text{D}$ 1.5075. Redistillation of A afforded the mercaptan as a colorless liquid, b.p. 67° (10 mm.), $n^{30}\text{D}$ 1.4512 [reported,[3] b.p. 74–80 (19 mm.), $n^{25}\text{D}$ 1.4541].

Anal. Calcd. for $C_8H_{18}S$: C, 65.68; H, 12.40; S, 21.92. Found: C, 65.75; H, 12.31; S, 21.71.

The disulfide fraction B was redistilled to give a pure sample as a slightly yellow liquid, b.p. 168° (5 mm.), $n^{30}\text{D}$ 1.4833.

Anal. Calcd. for $C_{16}H_{34}S_2$: C, 66.13; H, 11.79; S, 22.07. Found: C, 66.01; H, 11.78; S, 22.35.

Fraction C could not be further purified by distillation. The material decomposed at 200° (2–3 mm.) into 2-ethylhexyl mercaptan and a nonvolatile residue.

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[7] E. Baumann and E. From, *Ber.*, **28**, 907 (1895).

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A Diene–Retrodiene–Diene Reaction. The Synthesis of 2,3,5,6-Tetrakis(trifluoromethyl)-7-oxabicyclo[2.2.1]-2,5-heptadiene

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In connection with studies on the activity of 3,4-dicyanofuran as a diene component and the retrogressive cleavage of its adducts,[1] we deemed it of interest to investigate the reaction between 3,4-dicyanofuran and hexafluoro-2-butyne as a dienophile to obtain 2,3-bis(trifluoromethyl)-5,6-dicyano-7-oxabicyclo[2.2.1]-2,5-heptadiene (I). Its retrodiene fission may occur with the predominant formation of either dicyanoacetylene or hexafluoro-2-butyne as products of the cleavage together with the corresponding furan derivatives.

The two components were unaffected by heating them together at 140° over a twenty-four-hour period in a sealed tube. A reaction occurred, however, on raising the temperature to 160° and yielded 2,3,5,6-tetracyano-7-oxabicyclo[2.2.1]-2,5-heptadiene (IV) and 2,3,5,6-tetrakis(trifluoromethyl)-7-oxabicyclo[2.2.1]-2,5-heptadiene (V) as the only products. They could be separated easily

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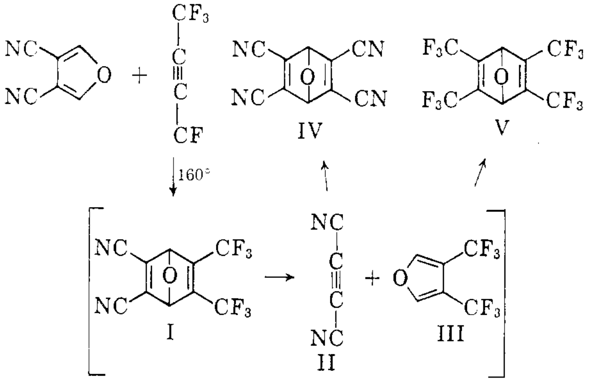
[1] C. D. Weis, *J. Org. Chem.*, **27**, 3520 (1962).

by sublimation because of the considerable volatility of the fluoro compound. The cyano compound was identified by comparison with a previously prepared sample.[1] The structure of the fluoro compound as a regular diene adduct was confirmed by analysis and supported by the n.m.r. spectrum.

The formation of IV and V as the only products is explained by a Diels-Alder addition of hexafluoro-2-butyne to 3,4-dicyanofuran to yield I. This, however, has only a transient existence and decomposes under the conditions of its formation to yield dicyanoacetylene (II) and 3,4-bis(trifluoromethyl)furan (III) by a retrodiene reaction. These two fragments recombine in a consecutive diene reaction with the starting materials and give finally IV and V.



I could not be detected among the reaction products. The reaction is accompanied by a considerable formation of carbonaceous material as is often observed during the more complex reactions of dicyanoacetylene at elevated temperature.

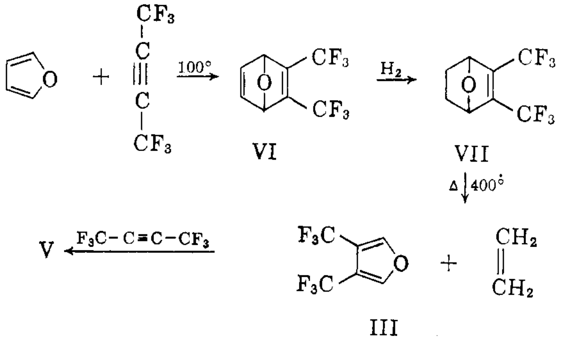
Although I is so unstable that it is already cleaved under the conditions of its formation, it seemed surprising that dicyanoacetylene and methyl acetylenedicarboxylate formed stable compounds with 3,4-dicyanofuran.[1]

V is a white crystalline compound which has some volatility at room temperature. It did not add triphenylphosphine as has been reported for IV.[1] No retrodiene fission could be noticed on heating it to 300° in a sealed tube.

V could be conveniently prepared in larger quantities by the reaction sequence outlined below.

Hexafluoro-2-butyne was added to furan in tetrahydrofuran as solvent at 100° and gave 2,3-bis(trifluoromethyl)-7-oxabicyclo[2.2.1]-2,5-heptadiene (VI) in 72% yield. The subsequent hydrogenation of the unsubstituted double bond was carried out with platinum catalyst in methanol. 2,3-bis(Trifluoromethyl)-7-oxabicyclo[2.2.1]-2-hexene (VII) was isolated in 70% yield.

Its thermal cleavage was achieved at 400° with the almost quantitative formation of 3,4-bis(trifluoromethyl)furan and ethylene. After heating a mixture of III and hexafluoro-2-butyne to 160° in a sealed tube, V was isolated in 86% yield. The reaction product proved to be identical to the previously isolated one by comparison of their infrared and n.m.r. spectra.



Experimental

2,3,5,6-Tetracyano-7-oxabicyclo[2.2.1]-2,5-heptadiene (IV) and 2,3,5,6-Tetrakis(trifluoromethyl)-7-oxabicyclo[2.2.1]-2,5-heptadiene (V).—A mixture of 2,4-dicyanofuran (0.5 g., 0.042 mole) and hexafluoro-2-butyne (1.5 g., 0.088 mole) was heated in a sealed tube for a period of 24 hr. The excess of hexafluoro-2-butyne was evaporated and the residue (0.98 g.) subjected to sublimation at a bath temperature of 50–60° at 760 mm.; 0.23 g. (30%) of V was collected in the form of long white needles, m.p. 57°.

Anal. Calcd. for $C_{10}H_2OF_{12}$: C, 32.80; H, 0.55; F, 62.27. Found: C, 32.75; H, 0.85; F, 62.47. Mol. wt. 366 (mass spectrometer).

The infrared spectrum showed a band for C=C at 5.95 μ (7-cm. gas cell, 3-mm. pressure). The n.m.r. spectrum exhibited only one type of hydrogen.

The residue was sublimed at 1-mm. pressure and 3,4-dicyanofuran (0.11 g.) was collected at a bath temperature of 70–150°. IV (0.16 g., 35% yield), m.p. 325°, was obtained at 220–230° and identified by comparison of the infrared spectrum with the spectrum of an authentic sample.

2,3-Bis(trifluoromethyl)-7-oxabicyclo[2.2.1]-2,5-heptadiene (VI).—Hexafluoro-2-butyne (16 g., 0.1 mole) was condensed at −60° into a heavy wall tube and tetrahydrofuran (50 ml.) and furan (7 g., 0.1 mole) were added. The mixture was heated in the sealed tube on a steam bath for 6 hr. Three separate runs prepared under identical conditions were combined, the solvent distilled through a column, and the main fraction collected at 100–126°/760 mm. Redistillation gave VI as a colorless liquid (51.3 g., 72%), $n^{26}D$ 1.3584.

Anal. Calcd. for $C_8H_4F_6O$: C, 41.75; H, 1.75; F, 57.81. Found: C, 41.45; H, 1.32; F, 58.13.

A 0.375-g. sample was hydrogenated in methanol (11 ml.) in the presence of a platinum catalyst and consumed 41.1 ml. (calcd. 40.7 ml.) of hydrogen. A band for the absorption of the trifluoromethyl substituted double bond was found at 5.89 μ.

2,3-Bis(trifluoromethyl)-7-oxabicyclo[2.2.1]-2-heptene (VII).—VI (102 g., 0.443 mole) was dissolved in tetrahydrofuran (210 ml.)and hydrogenated in the presence of a platinum catalyst in a Parr apparatus. The hydrogen uptake ceased sharply after the consumption of one equivalent of hydrogen. The tetrahydrofuran was distilled from the filtered solution through a column until the temperature in the still head reached 100°. Then the main fraction (63.7 g.) was collected at 100–129°. The tetrahydrofuran fraction was added to water (1000 ml.) and the oil (7.4 g.) which separated was dried over sodium sulfate and combined with the main fraction. A total yield of 71.1 g.

(70%) of VII was obtained. Redistillation at 125–128° yielded a colorless liquid, $n^{26}\text{D}$ 1.3612.

Anal. Calcd. for $C_8H_6OF_6$: C, 41.38; H, 2.59; F, 49.10. Found: C, 41.62; H, 2.40; F, 49.42.

The infrared spectrum showed a band for the double bond at 5.89 μ.

3,4-Bis(trifluoromethyl)furan (III).—VII (32 g., 0.138 mole) was passed dropwise in a slow current of nitrogen through a glass tube (450 mm. × 19 mm.) heated to 400°. The product was collected in a Dry Ice trap (22.1 g., 96.5%). Distillation at 88–89°/760 mm. gave a colorless liquid, $n^{25}\text{D}$ 1.3302.

Anal. Calcd. for $C_6H_2F_6O$: C, 35.51; H, 0.99; F, 55.86. Found: C, 35.23; H, 1.38; F, 55.60. The infrared spectrum showed the peak of the furan aromaticity at 6.32.

2,3,5,6-Tetrakis(trifluoromethyl)-7-oxabicyclo[2.2.1]-2,5-heptadiene (V).—III (4 g., 0.0196 mole) and hexafluoro-2-butyne (3.5 g., 0.0216 mole) were heated together in a sealed tube at 140° for 24 hr. Evaporation of the excess hexafluorobutyne left V (6.18 g., 86%) as a white crystalline solid. It was purified by sublimation at 40–50° (bath temperature) and obtained as long white needles. The identity with the previously obtained material was confirmed by their superimposable infrared spectrum and by the n.m.r. spectrum.

3,4,5-Tricyanopyrazole

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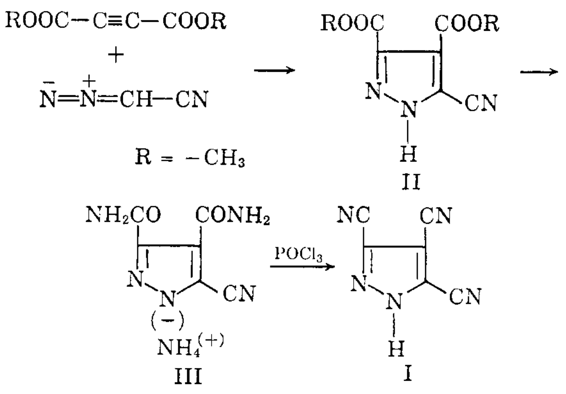
It is reported that the multiple dehydration of tri- or tetracarbamoylamides bearing the functional groups on adjacent carbon atoms proceeds well only under selected conditions[1] and is often thwarted entirely.[2]

We have encountered a similar situation in the heterocyclic series while attempting to prepare 3,4,5-tricyanopyrazole (I) by dehydration of 3,4,5-tricarbamoylpyrazole[3] with phosphorus oxychloride. Only a mixture of partially dehydrated compounds was obtained, the separation of which proved to be rather cumbersome.

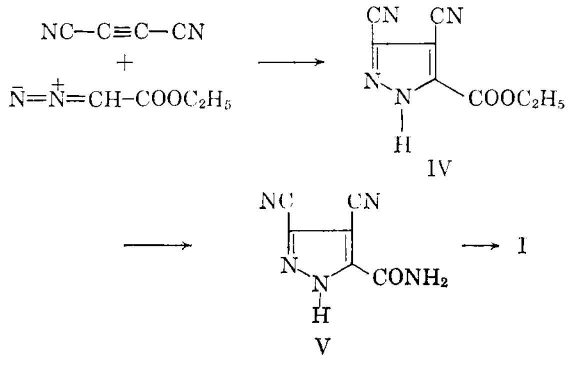
Therefore, the preparation of I was attempted by way of a Büchner pyrazole synthesis that is illustrated below. By choosing a combination of suitable starting materials—*e.g.* compounds bearing nitrile groups—the multidehydration of amide groups was circumvented.

Whereas dicyanoacetylene and diazoacetonitrile gave only a tarry product in ether solution, dimethyl acetylenedicarboxylate and a freshly prepared ethereal solution of diazoacetonitrile gave dimethyl 5-cyanopyrazole-3,4-dicarboxylate (II).

Ammonolysis of the cyanopyrazole ester (II) in aqueous ammonia at room temperature furnished a monocarbamoyl derivative which reacted further at room temperature over a period of four to five days to yield the ammonium salt of 3,4-dicarbamoyl-5-cyanopyrazole (III). The reaction could be conveniently accelerated by carrying it out in a sealed tube at elevated temperature. The neighboring cyano group causes the N-bonded hydrogen to exhibit acidic properties sufficient to form a stable ammonium salt. Subsequent dehydration in refluxing phosphorus oxychloride occurred smoothly with the formation of 3,4,5-tricyanopyrazole (I).



An alternative route is based on the treatment of dicyanoacetylene with ethyl diazoacetate which yielded ethyl 3,4-dicyanopyrazole-5-carboxylate (IV) together with an oily by-product. The ammonolysis of IV occurred smoothly at room temperature yielding 3,4-dicyano-5-carbamoylpyrazole (V). In this case no ammonium salt of V was formed. It was subsequently dehydrated with phosphorus oxychloride to I, which was found to be identical with a previously prepared sample.



I is a colorless crystalline compound which dissolves slightly in water to give a strongly acid solution. Salts are easily formed by neutralization of the aqueous solution and I is recovered upon acidification with mineral acids. With diazomethane, N-methyl-3,4,5-tricyanopyrazole (VI) is obtained. The silver salt of I was found to be light stable upon exposure to daylight over a period of several months; it is similar in this respect to the silver salt of cyanoform.

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