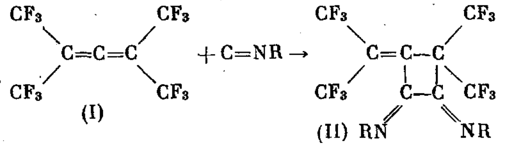
REACTION OF FLUORO-CONTAINING ALLENES WITH ISONITRILES

É. A. Avetisyan and N. P. Gambaryan

UDC 542.91:547.315'161:547.239.1

It is known that isonitriles react easily with such heterocumulenes as ketenimines [1, 2] and ketenes [3, 4], but information on the reaction of isonitriles with allenes was lacking up to now.

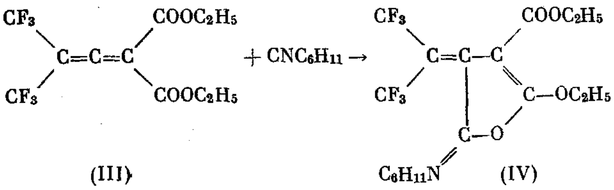
We found that the symmetrically polarized cumulene tetrakis(trifluoromethyl)allene (I), which is a very active electrophile, reacts even at 0° with isonitriles to form cycloadducts (II) with a 1 : 2 ratio of the reactants, and not 1 : 1 (in the case of ketenimines [1]) or 2 : 1 (in the case of ketene [4]).



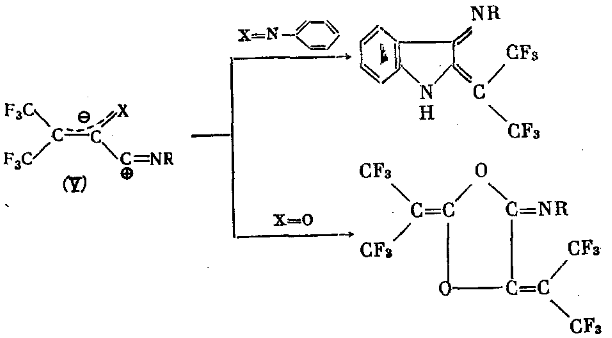
R=C(CH₃)₃ (a), C₆H₁₁ (b)

The formed compounds are obtained as brightly colored crystals that are easily hydrolyzed in the air.

The unsymmetrically polarized 1,1-dicarbethoxy-3,3-bis(trifluoromethyl)allene (III) also reacts with an isonitrile at 0°, but instead of the cyclobutanedione derivative it gives the 1,4-addition product of 1 mole of the isonitrile to the allene (IV) (the carbethoxyl group of the allene is involved).*



It is possible to assume that when isonitriles are reacted with either ketenimines or with a ketene the end product is formed via the intermediate bipolar ion (V), with subsequent cyclization to a ring (in the case of ketenimines) or the addition of a second molecule of the dipolarophile (in the case of ketenes).



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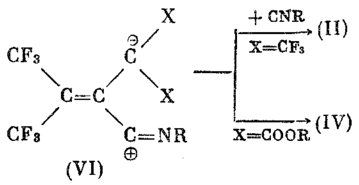
*A similar cyclization occurs when an N-alkyldicarbethoxyketenimine is reacted with an isonitrile [2].

Institute of Heteroorganic Compounds, Academy of Sciences of the USSR, Moscow. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 8, pp. 1904-1905, August, 1974. Original article submitted February 13, 1974.

When isonitriles are reacted with allenes the analogous bipolar ion (VI) is evidently stabilized either by the addition of a second molecule of the isonitrile* [formation of (II)], or by closure to a five-membered ring [formation of (IV)].



(VI)

As a result, fluoro-containing allenes† react with isonitriles under mild conditions, which represents a simple method for the synthesis of fluoro-containing derivatives of cyclobutanedione and dihydrofuran with an exocyclic double bond.

EXPERIMENTAL METHOD

The IR spectra were taken on a UR-20 instrument; the ^{1}H NMR spectra were taken on a Perkin –Elmer R-12 instrument (60 MHz, internal standard = HMDS); the ^{19}F NMR spectra were taken on a Hitachi instrument (56.46 MHz, and the chemical shifts are given in parts per million relative to CF_3COOH as the external standard).

Reaction of Tetrakis(trifluoromethyl)allene (I) with Isonitriles. a) To a solution of 3.6 g of allene (I) in 10 ml of absolute ether at 0° was added in drops a solution of 1.4 g of tert-butyl isonitrile in 15 ml of absolute ether. The temperature was brought up to ~20°. Successive freezing from ether and alcohol gave 3.3 g (66%) of bright red crystals of (II) with mp 39-40°. Found: C 42.79; H 3.73; F 48.11%; mol. wt. 486 (mass spectrometry). $C_{17}H_{18}F_{12}N_2$. Calculated: C 42.68; H 3.76; F 47.7%. Infrared spectrum (ν, cm^{-1}): 1640, 1660, 1720, 1740 (sh) (C=C, C=N). ^{19}F NMR spectrum (in CCl_4): –17.4 m [$(CF_3)C=$], –18.3 q [$(CF_3)_2Cl$]; –20.1 q [$(CF_3)C=$].

b) Similar to the preceding experiment, from 3.1 g of allene (I) and 2.2 g of cyclohexyl isonitrile at 0° was obtained 3.8 g (72%) of bright orange crystals of (IIb) with mp 68-71°. Found: H 4.06; F 43.48; N 5.31%; mol. wt. 530 (mass spectrometry). $C_{21}H_{23}F_{12}N_2$. Calculated: H 4.15; F 43.19; N 5.28%. Infrared spectrum (ν, cm^{-1}): 1630, 1660, 1720 (C=C, C=N). ^{19}F NMR spectrum (in CCl_4): –13.1 m, –16.9 m, –20.1 m.

Reaction of 1,1-Dicarbethoxy-3,3-bis(trifluoromethyl)allene (III) with Cyclohexyl Isonitrile. To 2.0 g of allene (III) in 15 ml of absolute ether at 0° was added in drops a solution of 0.7 g of cyclohexyl isonitrile in 5 ml of absolute ether. The temperature was brought up to ~20°. The ether was vacuum-distilled. We obtained 1.54 g (56%) of (IV) with mp 83-84° (from alcohol). Found: C 49.96; H 5.09; F 26.48%. $C_{18}H_{21}F_6NO_4$. Calculated: C 50.34; H 5.12; F 26.57%. Infrared spectrum (ν, cm^{-1}): 1570, 1625, 1715 (C=C, C=N, COOR). ^{19}F NMR spectrum (in C_6H_6): –20.5 q, –22.0 q (CF_3), J_{FF} = 8.4 Hz. ^{1}H NMR spectrum (δ, ppm, CCl_4): 1.35 t and 1.50 t (CH_3); 4.23 q and 4.65 q (OCH_2); 1.2-2 m [$(CH_2)_5$]; 4-4.9 m (CH).

CONCLUSIONS

Fluoro-containing allenes react easily with isonitriles. Tetrakis(trifluoromethyl)allene gives the addition product of two molecules of the isonitrile to one double bond of the allene, while unsymmetrical 1,1-dicarbethoxy-3,3-bis(trifluoromethyl)allene gives the 1,4-cycloaddition product of one molecule of the isonitrile with involvement of the carbethoxyl group of the allene.

LITERATURE CITED

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*The addition of two molecules of the isonitrile to the multiple bond was observed in the reactions with carbonyl compounds [5] and with dicyanobis(trifluoromethyl)ethylene [6].

†In contrast to the fluorinated allenes, chloromethylallene $CH_2=C=CH-CH_2Cl$ does not react with cyclohexyl isonitrile even after a month at ~20°.

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