

5. P. W. Albro, C. E. Parker, G. D. Marburu, O. Hermander, and F. T. Corbin, *Appl. Spectrosc.*, **4**, 556 (1984).
6. J. Gut, M. Prystas, and M. Jonas, *Coll. Czech. Chem. Commun.*, **26**, 986 (1961).
7. D. Libermann and R. Jacquier, *Bull. Soc. Chim. France*, No. 2, 383 (1961).

# FEATURES OF THE (2 + 3)-CYCLOADDITION OF TRIFLUOROACETONITRILE OXIDE

T. D. Truskanova, N. V. Vasil'ev, A. F. Gontar',  
A. F. Kolomiets, and G. A. Sokol'skii

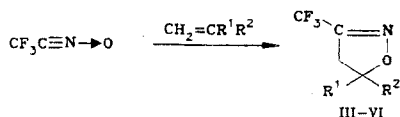
UDC 547.464.5'422'239.04:543.87

The (2 + 3)-cycloaddition of trifluoroacetonitrile oxide is a function of the donor and steric properties of dipolarophiles and usually proceeds regiospecifically. A significant temperature effect was found for the cycloaddition of trifluoroacetonitrile oxide to dipolarophiles with low donor capacity.

Trifluoroacetonitrile oxide [1] has high reactivity toward donor alkenes and extremely low activity in reactions with acceptor dipolarophiles. In the present communication, results are given for a more detailed study of the reactions of oxide I with donor dipolarophiles, cyclic alkenes, and dipolarophiles with low donor capacity.

The cycloaddition of oxide I to unconjugated monosubstituted alkenes is a function of the donor properties of these substrates. The yields of the cycloadducts, which are greatest using ethyl vinyl ether, decrease with decreasing donor properties in the cases of vinyl acetate and allyl bromide.

These reactions are regiospecific. The orientation of the substituents occurs only at C(5) of the ring formed as indicated by NMR spectral analysis. Complete regiospecificity is also found for reaction with other mono- and disubstituted alkenes.



III R<sup>1</sup>=OC<sub>2</sub>H<sub>5</sub>, R<sup>2</sup>=H (65%); IV R<sup>1</sup>=OAc, R<sup>2</sup>=H; V R<sup>1</sup>=CH<sub>2</sub>Br, R<sup>2</sup>=H; VI R<sup>1</sup>=CH<sub>3</sub>, R<sup>2</sup>=CH<sub>3</sub>

The presence of two geminal methyl groups in isobutylene produces steric hindrance in the transition state and the yield of oxazoline VI is low.\*

The reactivity of oxide I relative to cyclohexene and cyclopentene increases significantly with the calculated ring strain (2.61 and 6.93 kcal/mole, respectively [3]).

The reaction of oxide I with cyclopentadiene as a representative of conjugated cyclic alkenes proceeds rather readily but the reaction is nonregioselective. <sup>19</sup>F NMR spectroscopy indicated the formation of a 2:3 mixture of cycloadducts. However, the isomers could not be assigned using <sup>1</sup>H NMR spectroscopy.

Other conjugated alkenes such as styrene and ethyl acrylate as well as N-methylbenzalimine react smoothly with oxide I. Styrene, which is a good donor, proved the most active and phenyloxazoline X is formed in this case in 80% yield. N-Methylbenzalimine, which is a

\*An opposite effect is found in the analogous reactions of nonfluorinated nitrile oxides. Isobutylene is a more active dipolarophile than, for example, allyl bromide [2].

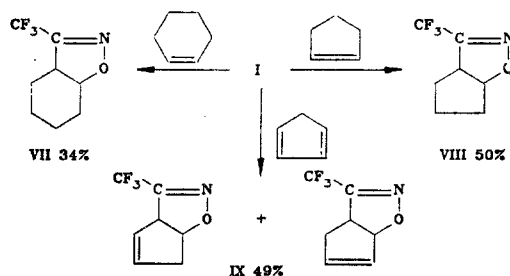
TABLE 1.  $^{19}\text{F}$  and  $^1\text{H}$  NMR Spectra of IV-X and XII

Compound	Chemical shifts, ppm (coupling constant, Hz)
IV	-11.5 (3F, s, $\text{CF}_3$ ); 3.2 (2H, m, 4- $\text{CH}_2$ ); 6.7 (H, d.d, 5-CH); ( $J_{45}=3.0$ ; $J_{46}=5.5$ ); 2.0 (3H, s, $\text{CH}_3$ )
V	-11.4 (3F, s, $\text{CF}_3$ ); 3.1 (2H, m, 4- $\text{CH}_2$ ); 5.1 (H, m, 5-CH); 3.5 (2H, d, $\text{CH}_2\text{Br}$ ) ( $J_{\text{CHCH}_2\text{Br}}=5.0$ )
VI	-9.5 (3F, s, $\text{CF}_3$ ); 3.2 (2H, m, 4- $\text{CH}_2$ ); 1.7 (6H, m, $\text{CH}_3$ )
VII	-12.3 (3F, s, $\text{CF}_3$ ); 3.1 (1H, m, 4-CH); 1.7 (8H, m, $\text{CH}_2$ ); 5.1 (1H, m, 5-CH)
VIII	-13.0 (3F, s, $\text{CF}_3$ ); 3.0 (1H, m, 4-CH); 1.6 (6H, m, $\text{CH}_2$ ); 4.9 (1H, m, 5-CH)
IX	-12.9 (3F, s, $\text{CF}_3$ ); 3.8 (1H, m, 4-CH); 5.5...6.0 (2H, m, $\text{HC}=\text{CH}$ ); 2.5 (2H, m, $\text{CH}_2$ ); 5.6 (1H, m, 5-CH)
X	-11.5 (3F, s, $\text{CF}_3$ ); 2.9 (2H, m, 4- $\text{CH}_2$ ); 5.4 (1H, m, 5-CH); 7.1 (5H, m, Ph)
XII	-11.9 (3F, s, $\text{CF}_3$ ); 2.6 (3H, s, $\text{CH}_3$ ); 6.1 (1H, s, 5-CH); 7.4 (5H, m, Ph)

TABLE 2. Indices of Compounds Synthesized

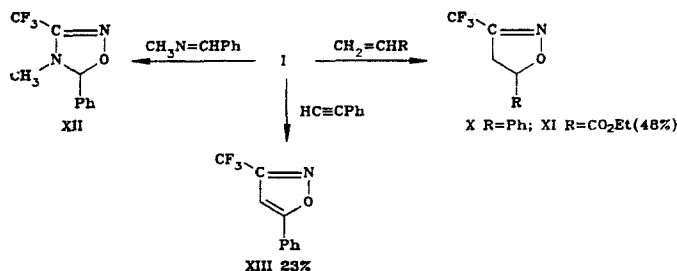
Compound	Chemical formula	mp, °C (P, hPa)	$n_D^{20}$	IR spectrum, $\text{cm}^{-1}$	Yield, % (20°C)
IV	$\text{C}_6\text{H}_6\text{F}_3\text{NO}_3$	62...63 (0,7)	1,3890	1620 (C=N); 1770 (C=O)	24
V	$\text{C}_5\text{H}_5\text{BrF}_3\text{NO}$	55...56 (0,7)	1,4222	1625 (C=N)	21
VI	$\text{C}_6\text{H}_8\text{F}_3\text{NO}$	62...67 (17)	1,3951	1650 (C=N)	16
VII	$\text{C}_8\text{H}_{10}\text{F}_3\text{NO}$	72...81 (20)	1,4080	1620 (C=N)	34
VIII	$\text{C}_7\text{H}_8\text{F}_3\text{NO}$	62 (12)	1,4010	1620 (C=N)	50
IX	$\text{C}_7\text{H}_6\text{F}_3\text{NO}$	60 (12)	1,4170	1600 (C=N); 1720 (C=C)	49
X	$\text{C}_{10}\text{H}_8\text{F}_3\text{NO}$	90 (0,7)	1,4721	1610...1640 (C=N), (Ph)	80
XII	$\text{C}_{10}\text{H}_9\text{F}_3\text{N}_2\text{O}$	107 (3)	1,4790	1620 (C=N); 1680...1710 (Ph)	41

better donor and one of the most active dipolarophiles, reacts with oxide I somewhat less well, apparently due to steric hindrance. Ethyl acrylate, which has less donor capacity, reacts with a satisfactory yield.



The reaction of oxide I with dipolarophiles with acceptor properties such as maleic anhydride, esters of maleic and fumaric acids, and polyfluoroalkenes does not occur even in the case of a large excess of these reagents and extended reaction time.

Among acetylenic compounds, only phenylacetylene was found to undergo cycloaddition to oxide I. Oxazole XIII is formed in this case



We should note that the rate of (2 + 3)-cycloaddition of oxide I at  $-20^{\circ}\text{C}$  is significantly reduced, especially for dipolarophiles with weak donor properties.

The present results and literature data [1, 4] are in accord with the predominant participation of the lowest unoccupied molecular orbital of oxide I and highest occupied molecular orbital of the dipolarophile in formation of the transition states in these reactions.

#### EXPERIMENTAL

The IR spectra were taken on KBr plates on a Perkin-Elmer R-225 spectrometer. The  $^{19}\text{F}$  and  $^1\text{H}$  NMR spectra were taken for chloroform solutions on a Hitachi R-20 spectrometer at 56.46 MHz for the  $^{19}\text{F}$  NMR spectra and 60 MHz for the  $^1\text{H}$  NMR spectra and are given in Table 1. The chemical shifts are given for the  $^1\text{H}$  nuclei relative to tetramethylsilane as an internal standard and for the  $^{19}\text{F}$  NMR spectra relative to trifluoroacetic acid as an external standard. The physicochemical indices and IR spectra data for the compounds synthesized are given in Table 2. Products III, XI, and XIII were described by Gambaryan et al. [1]. The elemental analysis data of all these compounds for C, H, N, and F corresponded to the calculated values.

General Method for the Preparation of Cycloadducts. A solution of 0.223 mole of the corresponding dipolarophile in 100 ml ether was added with stirring to a solution of 0.203 mole trifluoroacetonitrile oxide in 100 ml dry ether and then a solution of 0.203 mole triethylamine in 100 ml dry ether was added. The reaction mixture was stirred for 10 h and filtered. The filtrate was fractionated in vacuum.

At  $-20^{\circ}\text{C}$ , the yields of III, IV, XI and XII were 48, 11, 10 and 8%, respectively.

#### LITERATURE CITED

1. N. D. Del'tsova, É. S. Ananyan, and N. P. Gambaryan, *Izv. Akad. Nauk SSSR, Ser. Khim.*, No. 2, 362 (1971).
2. V. Grundman and P. Grünager, *The Nitrile Oxides*, Springer Verlag, Berlin (1971).
3. N. L. Allinger and J. T. Sprague, *J. Am. Chem. Soc.*, **94**, 5734 (1972).
4. K. Tanaka, H. Masuda, and K. Mitsuhashi, *Bull. Chem. Soc. Jpn.*, **57**, 2184 (1984).