The Stereochemistry of Addition of Methanol to Hexafluoro-2-butyne and Trifluoromethylacetylene

E. K. Raunio*[1] and T. G. Frey

Department of Chemistry, University of Idaho, Moscow, Idaho 83843

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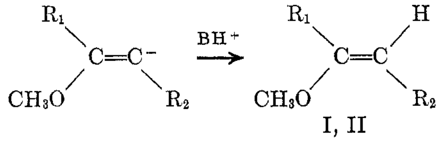
The stereochemistry of the products from the methoxide ion and the triethylamine-catalyzed addition of methanol to hexafluoro-2-butyne and to trifluoromethylacetylene have been determined. In all cases the addition is predominantly trans and is consistent with previously proposed mechanisms for nucleophilic additions to activated triple bonds. A small amount of *trans*-1,1,1,2,4,4,4-heptafluoro-2-butene was formed in the triethylamine-catalyzed addition to hexafluoro-2-butyne and a small amount of the geminal addition product of methanol to trifluoromethylacetylene was formed in the methoxide-catalyzed addition.

That the stereochemistry of nucleophilic additions to activated triple bonds is related to the nature of the activating groups is illustrated by the fact that the tertiary amine catalyzed addition of methanol to ethyl propiolate is 68% cis addition, whereas the similar addition of methanol to dimethyl acetylenedicarboxylate is 90% trans addition.[2] Although the stereochemistry of nucleophilic additions to various activated triple bonds has been reported,[3-14] little attention has been directed to the stereochemical course of additions to trifluoromethyl activated triple bonds.[15-21] The stereochemistry of these additions is of particular interest since in contrast to carbonyl, carboxylate, and cyanide activated triple bonds, the activation here should be largely inductive in nature. The sodium alkoxide catalyzed addition of alcohols to trifluoromethylacetylene and to hexafluoro-2-butyne has been studied,[15,16] but there are no reports on the stereochemistry of the products.

We have found that the sodium methoxide catalyzed addition of methanol to trifluoromethylacetylene ($R_1 = H; R_2 = -CF_3$) and both the sodium methoxide and the triethylamine catalyzed additions of methanol to hexafluoro-2-butyne ($R_1 = R_2 = -CF_3$) are predominantly trans additions (>97%) yielding I and II, respectively. Triethylamine failed to catalyze the addition of methanol to trifluoromethylacetylene, even at elevated temperature, and no detectable addition to either hexafluoro-2-butyne or trifluoromethylacetylene took place in the absence of catalyst. The cis isomer (III) was not isomerized under the reaction conditions, indicating that the trans isomer obtained in the reaction is the kinetic product.

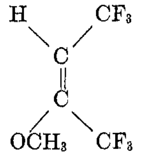
$$CH_3OH + B \longrightarrow CH_3O^- + BH^+$$

$$CH_3O^- + R_1C{\equiv}CR_2 \longrightarrow$$



I, II

$I, R_1 = H; R_2 = CF_3$
$II, R_1 = CF_3; R_2 = CF_3$

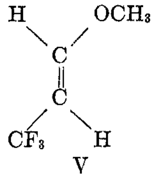


III

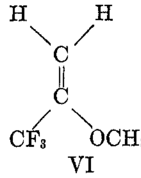
The stereochemistry of the reaction can be accounted for by assuming that it goes in accord with the mechanism proposed by Truce[4] and Miller[5] to account for the invariably trans addition which is observed in nucleophilic additions of thiols to acetylenes. Truce proposed that the approach of the negatively charged anion to the triple bond pushes an electron pair to the opposite side of the reaction intermediate where it is protonated (presumably by either protonated base molecules or by molecules of the addend), accounting for the observed trans addition.

The reaction products were analyzed by gas-liquid chromatography. In addition to the trans isomer, small amounts of the cis isomer III and of the HF addition product IV were isolated from the triethylamine-catalyzed addition of methanol to hexafluoro-2-butyne. Cullen and Dawson[18] also obtained IV from the reaction of hexafluoro-2-butyne, trimethylamine, and water in 27% yield. These authors proposed the reactions shown in Scheme I as one possible mechanism. Only the cis and trans isomers, II and III, were formed when sodium methoxide rather than triethylamine was the catalyst.

The *trans*-1-methoxy-3,3,3-trifluoropropene (the result of cis addition) (V) and the *gem*-trifluoromethyl-



V



VI

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SCHEME I

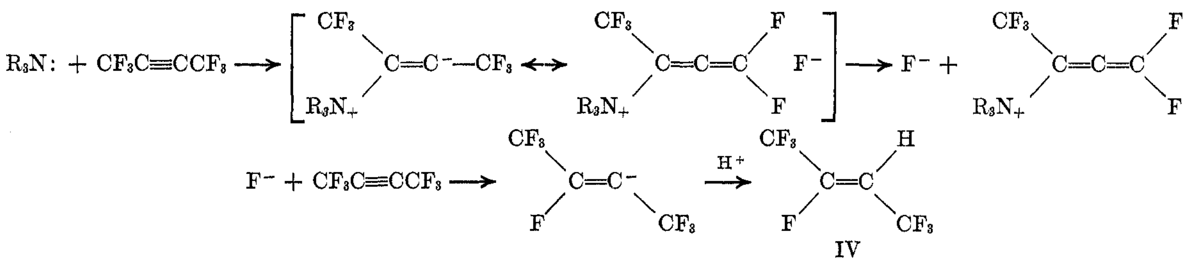
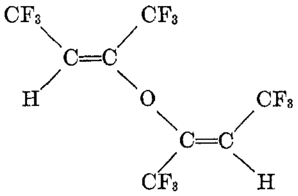

IV

TABLE I

NMR DATA FOR COMPOUNDS I, II, III, V, AND VI

	H¹ nmr			F¹⁹ nmr		
Compd	Group	Shift, δ	*J*, Hz	Group	Shift, ppm	*J*, Hz
I	CH_3O	3.70 (s)		${}^{CF_3}{>}C{=}$	+58.0 (d)	8.2
	${}^{CF_3}_{H}{>}C{=}$	4.58 (m), a quartet of doublets	8.2 7			
	$={C}<^{OCH_3}_{H}$	6.21 (d)	7			
II	CH_3O	3.90 (s)		${}^{CF_3}_{H}{>}C{=}$	+57.8 (d)	8
	$={C}<_{H}$	5.66 (q)	8	$={C}<^{OCH_3}_{CF_3}$	+71.0 (s)	
III	CH_3O	3.66 (s)		${}^{CH_3}_{H}{>}C{=}$	+54.5 (m), a quartet of doublets	11 8
	$={C}<^{H}$	5.04 (q)	8	$={C}<^{CF_3}_{OCH_3}$	+68.9 (q)	11
V	CH_3O	3.56 (s)		${}^{CF_3}{>}C{=}$	+60.4 (m), a doublet of doublets	6.3 2.0
	${}^{CF_3}_{H}{>}C{=}$	4.88 (m), a quartet of doublets	6.3 13			
	$={C}<^{H}_{OCH_3}$	6.03 (m), a quartet of doublets	2 13			
VI	CH_3O	3.58 (s)		${}^{CF_3}{>}C{=}$	+73.5 (d)	1.8
	$={C}<^{H}$	4.28 (m), a quartet of doublets	1.8 3.5			
	$={C}<^{H}$	4.72 (d)	3.5			

methoxyethene (VI) were formed in small amounts (1.8 and 1.5%, respectively) in the sodium methoxide catalyzed addition to trifluoromethylacetylene. Assignments of stereochemistry and of structure are based primarily on nmr spectroscopy. The stereochemical assignments are based on ones made by Cullen and Dawson[18] for the analogous compound VII. The nmr data are summarized in Table I.


VII

Experimental Section

All reactions were carried out by use of a vacuum line. The hexafluoro-2-butyne was obtained from Peninsular ChemResearch, Inc., Gainesville, Fla.

The proton nmr spectra were determined on a Varian HA-100 spectrometer, using tetramethylsilane as an internal standard. The fluorine nmr spectra were determined on a Varian HA-100-MHz spectrometer, using $CFCl_3$ as an internal standard. All positive values given for F^{19} nmr are upfield from $CFCl_3$. A Beckman IR5A was used to obtain infrared spectra. All infrared bands are given in reciprocal centimeters (cm^{-1}). Gas chromatographic analysis was carried out using a Varian-Aerograph Model 90-P equipped with a 12-ft copper column (0.25 in.) packed with 10% QF-1 on 60–70 Chromosorb W. Mass spectra were obtained from a RMU-6E Hitachi mass spectrometer.

Hexafluoro-2-butyne, Methanol, and Triethylamine.—Hexafluoro-2-butyne (1.62 g, 10 mmol) and 10 mmol (0.32 g) of absolute methanol were condensed into a 500-ml reaction vessel and allowed to come to room temperature. After 2 days, infrared showed no reaction had occurred. Triethylamine (0.101 g, 1 mmol) was then condensed into the vessel. After 24 hr, a strong absorption at 1695 cm^{-1} was found. A crude separation was accomplished by passing the volatile components through a −78° (acetone–Dry Ice) slush bath and a −196° (liquid nitrogen) bath. No unreacted butyne was found in either trap. Three components were isolated by gas chromatography of the material which condensed in the −78° trap.

The first peak was identified as *trans*-1,1,1,2,4,4,4-heptafluoro-2-butene (IV): ir (vapor) 1722 (C=C), 1404 (CF), 1309 (CF) 1272 (CF), 1220 (CF), 1192 (CF), 862 ($C{=}C<^{H}$), 735 (CF); mass spectrum (70 eV) *m/e* (relative intensity) 182 (11), 163 (34), 113 (100), 69 (25). This agreed closely with the data obtained by Cullen and Dawson.[18] The second peak was identified as *trans*-1,1,1,4,4,4-hexafluoro-2-methoxy-2-butene (II): ir (vapor) 2940 (CH), 1695 (C=C), 1469 (CH_3), 1399 (CH_3), 1300 (CF), 1272 (CF), 1212 (CF), 1170 (CF), 1100 (CO), 866 ($C{=}C<^{H}$);

mass spectrum (70 eV) m/e (relative intensity) 194 (48), 175 (20), 110 (19), 91 (100), 69 (33). *Anal.* Calcd for $C_5H_4F_6O$: C, 30.94; H, 2.08. Found: C, 30.62; H, 2.07. The third peak was identified as *cis*-1,1,1,4,4,4-hexafluoro-2-methoxy-2-butene (III): ir (vapor) 1680 (C═C), 1466 (CH_3), 1400 (CH_3), 1320 (CF), 1269 (CF), 1181 (CF), 1125 (CO), 914 ($\mathrm{C{=}C{<}^{H}}$); mass spectrum (70 eV) m/e (rel intensity) 194 (48), 175 (14), 110 (19), 91 (100), 69 (36).

Hexafluoro-2-butyne, Methanol, and Sodium Methoxide.—Hexafluoro-2-butyne (1.30 g, 8 mmol) and 8 mmol (0.256 g) of absolute methanol were condensed into a 500-ml reaction vessel containing *ca.* 0.8 mmol (42.9 mg) of sodium methoxide and the resulting solution was allowed to stand (room temperature) for 10 hr. The infrared showed a strong absorption at 1695 cm^{-1} and showed that no butyne was present. The procedure described above was used to isolate the components from the reaction mixture. Two major peaks accounting for 98.6% of the material present were collected by glc and identified as *trans*-1,1,1,4,4,4-hexafluoro-2-methoxy-2-butene (II), 97.8%, and *cis*-1,1,1,4,4,4-hexafluoro-2-methoxy-2-butene (III), 2.2%. No peak corresponding to *trans*-1,1,1,2,4,4,4-heptafluoro-2-butene (IV) appeared.

Attempted Isomerization of *cis*-1,1,1,4,4,4,Hexafluoro-2-methoxy-2-butene (III) with Triethylamine.—*cis*-1,1,1,4,4,4-Hexafluoro-2-methoxy-2-butene (0.0305 g, 0.157 mmol) was sealed in an nmr tube with 0.015 mmol (0.0015 g) of triethylamine and 0.75 mmol of tetramethylsilane. The nmr taken immediately after the sample tube had reached room temperature and the nmr taken after 3 days at room temperature were identical with the spectrum of the *cis*-vinyl ether (III). Then 0.015 mmol (4.8×10^{-4} g) of absolute methanol was condensed into the nmr tube containing the cis compound and the triethylamine. After 3 days, the nmr spectrum showed only the cis compound III present.

Trifluoromethylacetylene, Methanol, and Triethylamine.—Trifluoromethylacetylene (0.376 g, 4 mmol) and 4 mmol (0.128 g) of absolute methanol were condensed into a 500-ml reaction vessel and allowed to come to room temperature. After 20 hr, infrared analysis showed no reaction. Triethylamine (0.04 g, 0.4 mmol) was then condensed into the reaction vessel. After 7 hr, no reaction could be detected, so another 0.4 mmol (0.04 g) of triethylamine was added. After 39 hr, the reaction mixture had turned brown, but no carbon–carbon double bond could be found in the ir. Unreacted $CF_3C{\equiv}CH$ (0.229 g, 2.44 mmol) was recovered from the reaction.

Trifluoromethylacetylene, Methanol, and Sodium Methoxide.—Trifluoromethylacetylene (0.780 g, 8.3 mmol) and 8 mmol (0.256 g) of absolute methanol were condensed into a 1-l. reaction vessel with 1.6 mmol (0.0534 g) of sodium methoxide and allowed to come to room temperature. After 3 hr, an absorbance at 1690 cm^{-1} was observed in the ir. After 45 hr of reaction, the mixture was separated *via* slush baths. The material from a −98° trap [CH_3OH, N_2(liquid)] was separated *via* glc. Separation was carried out at room temperature. The material isolated from the liquid N_2 trap was unreacted $CF_3C{\equiv}CH$ (44.5%). Three major peaks were collected by glc of the contents of the −98° trap. The first peak collected was identified as *gem*-trifluoromethylmethoxyethene (VI): ir (vapor) 2941 (CH_3), 1667 ($\mathrm{C{=}C{<}^{H}_{H}}$), 1399 ($\mathrm{C{=}C{<}^{H}_{H}}$), 1370 ($CH_3$), 1277 (CO), 1205 (CF), 1177 (CF), 1156 (CF), 843 ($\mathrm{C{=}C{<}^{H}_{H}}$); mass spectrum (70 eV) m/e (rel intensity) 126 (100), 107 (8.5), 95 (20), 91 (17), 76 (14), 69 (35), 57 (33), 43 (31), 42 (32). The second peak corresponded to *trans*-1-methoxy-3,3,3-trifluoropropene (V): ir (vapor) 2933 (CH_3), 1672 ($\mathrm{{}_{H}{>}C{=}C{<}^{H}}$), 1454 ($CH_3$), 1351 ($\mathrm{{}_{H}{>}C{=}C{<}^{H}}$), 1242 (CF), 1178 (CF), 1123 (CF), 953 ($\mathrm{{}_{H}{>}C{=}C{<}^{H}}$); mass spectrum (70 eV) m/e (rel intensity) 126 (100), 111 (6), 107 (19), 95 (42), 91 (33), 77 (34), 76 (18), 69 (38), 57 (18), 37.5 (0.5), 31 (92). The third peak corresponded to *cis*-1-methoxy-3,3,3-trifluoropropene (I): ir (vapor) 2933 (CH_3), 1692 ($\mathrm{{}^{H}{>}C{=}C{<}^{H}}$), 1464 ($CH_3$), 1280 (CF), 1203 (CF), 1148 (CF), 718 ($\mathrm{{}_{H}{>}C{=}C{<}_{H}}$); mass spectrum (70 eV) m/e (rel intensity) 126 (100), 111 (9), 107 (39), 95 (44), 91 (54), 77 (47), 76 (26), 69 (51), 59 (25), 51 (15), 37.5 (0.5), 31 (57). *Anal.* Calcd for $C_4H_5F_3O$: C, 38.11; H, 4.00. Found: C, 38.38; H, 4.40.

Registry No.—I, 26885-67-6; II, 400-21-5; III, 26885-69-8; IV, 17157-69-6; V, 26885-71-2; VI, 26885-72-3; methanol, 67-56-1; hexafluoro-2-butyne, 692-50-2; trifluoromethylacetylene, 661-54-1.

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The Synthesis of Fluorine-Containing Heterocyclic Nitramines[1]

John A. Young,* Josef J. Schmidt-Collerus, and John A. Krimmel[2]

Denver Research Institute, University of Denver, Denver, Colorado 80210

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Trifluoroacetaldehyde reacted readily with ammonia to give 2,4,6-tris(trifluoromethyl)hexahydro-*s*-triazine (**1d**), which on nitrosation gave the 1,3,5-trinitroso derivative **1e**. 2,4,6-Trimethyl-1,3,5-trinitrosohexahydro-*s*-triazine (**1f**) could not be converted to the trinitro compound; the fluorine-containing trinitroso compound underwent this conversion successfully, although a displacement rather than an oxidation reaction was indicated. 2,2-Diaminohexafluoropropane condensed with formaldehyde and methylenedinitramine to give a mixture of 2,2-bis(trifluoromethyl)-5-nitrohexahydro-*s*-triazine (**2b**) and 2,2-bis(trifluoromethyl)-5,7-dinitro-1,3,5,7-tetraazacyclooctane (**3c**). Several *N*-nitroso and *N*-nitro derivatives of these two ring systems were prepared.

Saturated cyclic polyamines with rings composed of alternating carbon and nitrogen atoms, as in Chart I, tend to be unstable. Solutions of formaldehyde and ammonia contain hexahydro-*s*-triazine (**1a**), but it cannot be isolated from solution and probably is in equilibrium with open-chain forms and with ammonia and formaldehyde.[3,4] Reported derivatives of **1a** always have been stabilized by structural features such as the condensed tricyclic system in hexamethylenetetramine, the electronegative groups in RDX (1,3,5-trinitrohexahydro-*s*-triazine (**1b**), or the C-substituted alkyl groups in 2,4,6-trimethylhexahydro-*s*-triazine (**1c**); the cyclic

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[2] Research and Development Department, Whittaker Chemical Corp., San Diego, Calif.

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