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CONVERSION OF A CUMULENE SYSTEM TO A DIENE SYSTEM IN THE REACTIONS

OF TETRAKIS (TRIFLUOROMETHYL) ALLENE AND N-PHENYL-BIS (TRIFLUOROMETHYL) KETENIMINE

WITH NUCLEOPHILES

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Tetrakis(trifluoromethyl)allene (I) reacts with nucleophilic reagents to give products of addition or cycloaddition at one of the cumulene C=C bonds. The nucleophilic reagent attacks the central carbon atom [1]. A fluoride anion is lost from the CF₃ group and the 1,2-diene bond system is converted to a 1,3-diene system upon the reactions of (I) with the anions of metal carbonyls [2]. The products of the ionic hydrogenation of one of the C=C bonds were obtained in the reaction of allene (I) with tertiary amines such as triethylamine [3] and 1,3-dimethylbenzimidazoline [4].

Bis(dialkylamino)methanes, similarly to their cyclic analog 1,3-dimethylbenzimidazoline, would be expected to serve as a hydride ion source or give products of insertion at the CH_2 -N bond due to its facile electrophilic cleavage in the methylenediamine system upon reaction with (I) [5]. However, we have found that allene (I) and bis(dialkylamino)methanes react under mild conditions to give amino derivatives of 1,3-dienes (II). The primary products of these transformations are probably bipolar ions (III) ((IIIa) and (IIIb) were detected by ¹⁹F NMR spectroscopy as two signals of equal intensity at -25 and -24 ppm), which very rapidly lose fluoromethylamine (detected by ¹⁹F NMR spectroscopy) to form dienes (II)

 $(CF_3)_2C = C = C(CF_3)_2 + R_2NCHNR_2 \rightarrow \begin{bmatrix} CF_3 \\ \odot & | \\ (CF_3)_2C = C - CF_3 \\ (I) & | \\ R' \end{bmatrix} \xrightarrow{[]{}} (CF_3)_2C = C - C = CF_2 + FCHNR_2 \\ \downarrow \\ R_2NCHNR_2 \\ \vdots \\ R' \\ (III) \end{bmatrix} \xrightarrow{[]{}} (II)$

R' = H, $R_2N = Me_2N$ (a), Et_2N (b); R' = Ph, $R_2N = O(CH_2CH_2)_2N$ (c).

The conversion of the allene system to a 1,3-diene system was also found in the reaction of allene (I) with triethyl phosphite. In this case, the primary adducts apparently rearrange to a phosphorane which gives diene (IV) by the elimination of ethyl fluoride.

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$$(I) + (EtO)_{3}P \rightarrow \begin{bmatrix} CF_{3} & CF_{3} \\ (CF_{3})_{2}C = C - C \\ (EtO)_{3}P \oplus \\ (EtO)_{3}P \oplus \\ CF_{3} \end{bmatrix} \xrightarrow{I} (CF_{3})_{2}C = C - C = CF_{2} \\ (EtO)_{3}P \oplus \\ CF_{3} \end{bmatrix} \xrightarrow{I} (CF_{3})_{2}C = C - C = CF_{2} \\ (EtO)_{2}P = O \\ (IV)$$

In attempts to extend these reactions for other cumulene systems, we found that N-phenylbis(trifluoromethyl)ketenimine (V),* dimerizes by the action of Et_3N or $P(OEt)_3$ [6] and reacts with bis(dialkylamino)methanes to give products of addition at the C=N bond, namely, aminals (VI). On the other hand, bis(trifluoromethyl)ketene forms amides as a result of the addition of diaminomethane at a C=C bond [8] and isomerizes by the action of the action of perfluoromethacrylic acid [9].

Aminals (VI) are stable at 0-5°C but only briefly at 20°C. Upon the action of nucleophiles, aminals (VI) lose fluoromethylamine to form an intermediate amidine, which reacts with dimethylamine to give the product of the replacement of one fluorine atom by a difluoromethylene group, namely, enamine (VII) and with ethanol by the replacement of two fluorine atoms to give acetals (VIII).



Thus, the transformation of the cumulene system to the 1,3-diene system by the action of nucleophiles is rather general in nature.

EXPERIMENTAL

The NMR spectra were taken on a Perkin-Elmer R-32 spectrometer. The ¹⁹F NMR spectra were taken at 84.6 MHz relative to CF_3CO_2H as the external standard. The ¹H NMR spectra were taken at 90 MHz relative to TMS as the external standard (δ , ppm). The IR spectra were taken on a UR-20 spectrometer. The mass spectra were taken on a Varian MAT CH-6 mass spectrometer at 70 eV ionizing voltage.

<u>Reaction of Tetrakis(trifluoromethyl)allene (I) with Bis(dialkylamino)methanes.</u> a) A sample of 1 g bis(dimethylamino)methane was added with stirring and cooling to 1.8 g (I). After homogenization, the ¹⁹F NMR spectrum showed two signals of equal intensity at -25.2 and -24.8 ppm, which completely disappeared after about 0.5 h and the ¹⁹F NMR spectrum corresponded to (IIa). Distillation of the mixture gave 1.8 g (87%) 2,4-bis(trifluoromethyl)-3-dimethylaminopentafluoro-1,3-pentadiene, bp 71-73°C (4 mm). Found: C 32.2; H 1.9; F 61.0%. Calculated for C₉H₆F₁₁N: C 32.0; H 1.8; F 62.0%. IR spectrum (ν , cm⁻¹): 1650, 1670 (C=C). PMR spectrum: 2.9 s (CH₃). ¹⁹F NMR spectrum: -23.3 m (CF₃, 3F), -21.4 m (CF₂, 2F), -19.1 m (CF₃, 3F).

b) Under analogous conditions, 2 g allene (I) and 1 g bis(dimethylamino)methane gave 1.8 g (77%) diene (IIb), bp 68-71°C (2 mm). Found: C 36.1; H 2.8; F 57.2%. Calculated for $C_{11}H_{10}F_{11}N$: C 36.1; H 2.7; F 57.3%. Mass spectrum, m/z: 365 M⁺. PMR spectrum: 1.3 t (CH₃), 3.4 q (CH₂), J_{H-H} = 7.3 Hz. ¹⁹F NMR spectrum: -23.2 m (CF₃, 3F), -20.9 m and -14.4 m (CF₂, 2F), -18.5 m (CF₃, 3F(, -17.1 m (CF₃, 3F).

^{*}Bis(trifluoromethyl)ketenimines react with nucleophiles to give the products of addition or cycloaddition [6] and only react with metal carbonyl anions similarly to allene (I) to give azabutadiene derivatives [7].

c) A sample of 1.3 g dimorpholinophenylmethane in 2 ml abs. ether was added to 1.5 g allene (I). After 20 h, ether was distilled off in vacuum to give 1 g (55%) 2,4-bis(tri-fluoromethyl)-3-morpholinopentafluoro-1,3-pentadiene (IIc), mp 77-78°C (from petroleum ether). Found: C 34.8; H 2.0; F 55.0%. Calculated for $C_{11}H_8F_{11}NO$: C 34.8; H 2.1; F 55.1%. Mass spectrum, m/z: 379 M⁺. IR spectrum: 1635, 1670 (C=C). PMR spectrum (in acetone): 3.15 m (CH₂), 3.5 m (CH₂). ¹⁹F NMR spectrum (in acetone): -23.4 d. m (CF₃, 3F), -18.7 m (CF₃, 3F), -17.3 m (CF₃, 3F), -18.7 m and -11.5 m (CF₂, 2F).

Reaction of Allene (I) with Triethyl Phosphite. A sample of 1 g (P(OEr)₃ was added with ice cooling to 2 g allene (I) in an argon atmosphere. The mixture formed two layers and was periodically removed from the ice and vigorously shaken. After about 15 min, the mixture became homogeneous. The red-orange solution obtained colorless upon standing for 15 h at $\sim 20^{\circ}$ C. Distillation gave 2.6 g (94%) 2,4-bis(trifluoromethyl)-1,3-pentafluoropentadien-3-yl-0,0-diethylphosphonate (IV), bp 77-78°C (4 mm). Found: C 30.7; H 2.6; F 47.4%. Calculated for C₁₁H₁₀F₁₁PO₃: C 30.6; H 2.3; F 48.5%. Mass spectrum, m/z: 430 M⁺. IR spectrum: 1640, 1740 cm⁻¹ (C=C). PMR spectrum: 1.2 t (CH₃), 4.0 d. q (CH₂), J_{H-H} = 7.3, J_{H-P} = 10 Hz. ¹⁹F NMR spectrum: -19.1 m (CF₃, 6F), -18.2 m (CF₃, CF₂, 5F).

Bis(trifluoromethyl)ketene animals (VI). a) A solution of 1.5 g ketenimine (V) in 1 ml abs. ether was added dropwise with cooling to a solution of 0.6 g bis(dimethylamino)methane in 2 ml abs. ether and the mixture was left with cooling for ~ 20 h. Distillation of the ether gave 1.8 g N,N-dimethyl-N'-phenyl-N'-dimethylaminomethylaminal (VIa), mp 95-97°C (from pentane). Found: C 50.8; H 5.2; F 32.2%. Calculated for $C_{15}H_{19}F_6N_3$: C 50.7; H 5.3; F 32.1%. IR spectrum: 1580, 1590 (C=C). PMR spectrum (in CCl₄): 2.25 s (2CH₃), 2.35 s (CH₃), 2.4 s (CH₃), 2.9 s (CH₂), 6.9-7.3 m (C₆H₅). ¹⁹F NMR spectrum (in CCl₄): -23.4 q (CF₃), -24.4 q (CF₃), JF-F = 7.5 Hz.

b) Under analogous conditions, 2.3 g ketenimine (V) and 1.44 g bis(diethylamino)methane in 5 ml abs. ether gave 3.4 g N,N-diethyl-N'-phenyl-N'-diethylaminomethylaminal (VIb) as an oil. ¹⁹F NMR spectrum (in ether): -22.4 q (CF₃), -24.6 q (CF₃), $J_{F-F} = 7.4$ Hz.

<u>N,N-Dimethyl-N'-phenylamidine of α -trifluoromethyl- β -dimethylamino- β -fluoroacrylic acid (VII). Excess Me₂NH was bubbled into a solution of 17 g aminal (VIa) in 10 ml abs. ether with stirring. After 48 h at 20°C, the precipitate was filtered off. The filtrate gave 1.3 g (90%) amidine (VIIa), mp 37-40°C (from pentane, sublimation). Found: C 55.4; H 5.5; F 24.8; N 13.8%. Calculated for C₁₄H₁₇F₄N₃: C 55.4; H 5.6; F 25.1; N 13.9%. Mass spectrum, m/z: 303 M⁺. IR spectrum (ν , cm⁻¹): 1580, 1590 (C=C), 1570 (C=N). PMR spectrum (in CCl₄): 2.55 s (CH₃), 3.2 s (CH₃), 6.7=7.4 m (C₆H₅). ¹⁹F NMR spectrum (in CCl₄): -1.1 q. m (CF), -24.4 d (CF₃), J_{F-F} = 15.1 Hz.</u>

<u> α -Trifluoromethyl- β , β -diethoxyacrylic Acid Amidines (VIII).</u> a) A sample of 3 ml abs. ethanol was added to 2.2 g aminal (VIa). After about 20 h at \sim 20°C, the volatile products were distilled off in vacuum and the hydrofluoride residue was dissolved in water. An aqueous solution of NaHCO₃ was added to pH 7.5-8 and the mixture was extracted with ether. The extract was dried over MgSO₄. Distillation of the ether gave 0.9 g (44%) N,N-dimethyl-N'-phenylamidine (VIIIa), bp 110-114°C (4·10⁻³ mm). Found: 58.2; H 6.5; F 16.5; N 8.6%. Calculated for C₁₆H₂₁F₃N₂O₃: C 59.2; H 6.4; F 17.3; N 8.5%. Mass spectrum, m/z: 330 M⁺. IR spectrum: 1595, 1610 (C=C), 1670 (C=N). PMR spectrum (in CCl₄): 12.2 t (CH₃), 1.45 t (CH₃), 3.2 s (Me₂N), 3.92 q (CH₂O), 4.24 q (CH₂O), 6.8-7.6 m (C₆H₅), J_{H-H} = 7.4 Hz. ¹⁹F NMR spectrum (in CCl₄): -22.2 s (CF₃).

b) Under analogous conditions, 3.4 g aminal (VIb) and 3 ml abs. ethanol gave 1 g N,N-diethyl-N'-phenylamidine (VIIIb), bp 105-108°C (0.15 mm). Found: C 59.6; H 6.6; F 16.7; N 7.7%. Calculated for $C_{19}H_{25}F_{3}N_{2}O_{2}$: C 60.3; H 7.0; F 15.9; N 7.8%. IR spectrum: 1590 (C=C), 1660 (C=N). ¹⁹F NMR spectrum: -22.2 s (CF₃).

CONCLUSION

1. Tetrakis(trifluoromethy1)allene reacts with bis(dialkylamino)methanes and triethyl phosphite to form substituted 1,3-dienes.

2. N-Phenylbis(trifluoromethyl)ketenimine reacts with bis(dialkylamino)methanes to give products of addition at the C=N bond, namely amidines which are converted by the action of nucleophiles to azabutadiene derivatives.

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VIBRATIONAL SPECTRA AND STRUCTURE OF SYMMETRICAL GLYOXIMES

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In the present work, we studied the structure of disubstituted symmetrical glyoximes with the general formula

where R = H, CH_3 , CI, CN, NH_2 , and Ph by IR and Raman spectroscopy. The structures of only a few glyoximes have been established by x-ray diffraction structural analysis, namely for unsubstituted glyoxime (I), dimethyl- (II), difuryl- (III), methyl(carbamoylaziridino)- (IV) and methyl(dimethylamino)glyoximes (V). Glyoximes (I)-(IV) have trans-anti configuration, while (V) has trans-amphi configuration [1-5].

Symmetrically disubstituted glyoximes may exist in six configurations:



X-ray diffraction structural data [1, 2] indicate that (I) and (II) in the crystalline state have trans-anti configuration, their molecules are centrosymmetric and the glyoxime fragments are planar.

The alternation prohibition should hold for the vibrational spectra of these molecules, i.e., the vibrational bands permitted in the IR spectra should be prohibited in the Raman spectra and vice versa.

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