FLUORO-CONTAINING ALLENES

COMMUNICATION 5*. REACTION OF TETRAKIS(TRIFLUOROMETHYL)ALLENE WITH UNSATURATED COMPOUNDS

N. S. Mirzabekyants, M. D. Bargamova,
Yu. A. Cheburkov, and I. L. Knunyants

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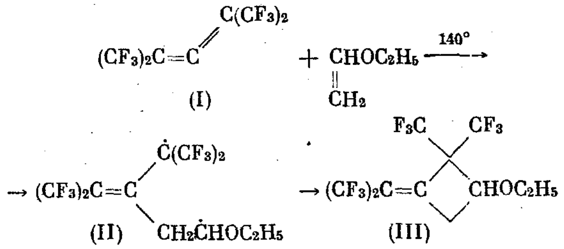
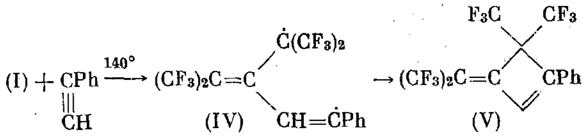
The reaction of allenes with unsaturated compounds has been studied inadequately [2] and usually leads to cyclic products as the result of cycloaddition reactions. Cyclobutane derivatives [3] are obtained with monoolefins, while dienes react to give, besides cyclobutanes, also six-membered adducts [4]. These cycloaddition reactions of the allenes are frequently ambiguous due to the ease of dimerization of the allenes and their tendency to isomerize to conjugated dienes. In this respect tetrakis(trifluoromethyl)allene (I) is a convenient study object, since it does not dimerize or isomerize [5].

In the present paper we studied the reaction of allene (I) with vinyl ethyl ether, phenylacetylene, isobutylene, furan, and butadiene. Allene (I) reacts with vinyl ethyl ether at 140°C on the type of [2+2]-cycloaddition reactions to give 2-ethoxy-3,3-bis(trifluoromethyl)-4-hexafluoroisopropylidenecyclobutane (III).



The structure of the obtained ethoxycyclobutane (III) is confirmed by the ^{1}H and ^{19}F NMR spectra. Its orientation corresponds to the polarity of the reactants. By analogy with the literature data, it may be assumed that this reaction proceeds as a two-step radical process [3], in which connection the stable allyl biradical (II) should be formed in the first step. The radical mechanism also finds confirmation in the relatively high initiation temperature (cf. with the other radical reactions of allene (I) [6, 7]).

It is probable that the reaction of allene (I) with phenylacetylene is realized in a similar manner via radical (IV); 2-phenyl-3,3-bis(trifluoromethyl)-4-hexafluoroisopropylidenecyclobutane (V) is obtained as a result.



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*See [1] for Communication 4.

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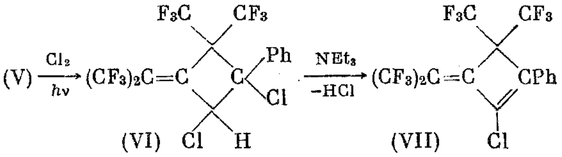
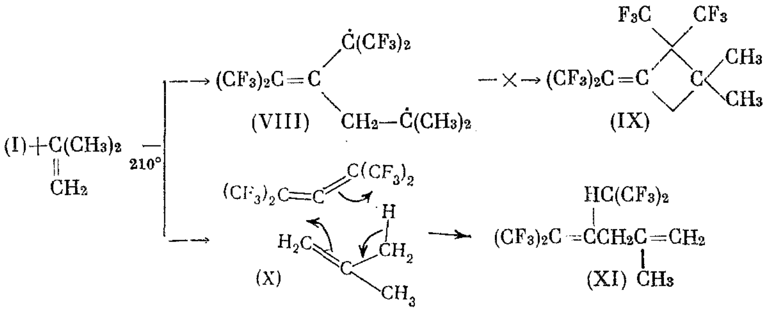
Phenylcyclobutane (V) is chlorinated smoothly in the presence of UV light to give a mixture of the diastereoisomers of 1,2-dichloro-2-phenyl-3,3-bis(trifluoromethyl)-4-hexafluoroisopropylidenecyclobutane (VI). The exocyclic double bond and the benzene ring are practically not involved here, and only one of the possibilities is realized, namely the chlorination of the double bond of the 4-membered ring. The treatment of dichlorocyclobutane (VI) with Et_3N leads to 1-chloro-2-phenyl-3,3-bis(trifluoromethyl)-4-hexafluoroisopropylidene-1-cyclobutene (VII).

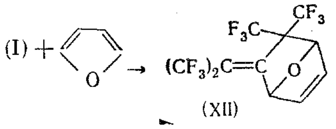


The reaction of allene (I) with isobutylene begins at 210° and leads to 5-trifluoromethyl-6,6,6-trifluoro-4-hexafluoroisopropyl-2-methyl-1,4-hexadiene (XI), which is evidently obtained as the result of the coordinated ene process [8, 9]. Cyclobutane derivative (IX) is not formed in this case, apparently due to the steric hindrance to the formation of biradical (VIII).

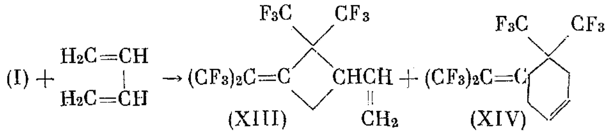


Allene (I) in the reactions with vinyl ethyl ether and phenylacetylene resembles not only the allenes, but also the fluoroolefins, which are good enophiles and react with unsaturated compounds (including dienes) to give cyclobutane derivatives [10, 11]. Allene (I) differs from the fluoroolefins in the fact that it enters into the diene synthesis with dienes like furan and butadiene. The Diels–Alder reaction of allenes with furan and its derivatives has received little study. Only a single example is known where cyanoallene is reacted with 2,5-dimethylfuran and 2-furaldehyde [12] (also see [13]).

Allene (I) reacts with furan even at 20° to give 3,3-bis(trifluoromethyl)-2-hexafluoroisopropylidene-7-oxabicyclo[2.2.1]-5-heptene (XII) in good yield. The IR spectrum of (XII) has a characteristic band in the 1580-cm^{-1} region, which corresponds to the absorption of the C=C bonds in bicyclic furan derivatives [14].



The reaction of allene (I) with butadiene proceeds under more drastic conditions (140-160°), in which connection allene (I) functions simultaneously as an enophile and as a dienophile to respectively give 2-vinyl-3,3-bis(trifluoromethyl)-4-hexafluoroisopropylidenecyclobutane (XIII) and 4,4-bis(trifluoromethyl)-5-hexafluoroisopropyldiene-1-cyclohexene (XIV). The yield of isomer (XIV) is increased slightly when



the temperature is raised to 200°. The fact that cyclobutane (XIII) is not isomerized by heat to adduct (XIV) serves as the most likely evidence that the [2 + 2]- and [4 + 2]-cycloaddition reactions proceed simultaneously.

Despite the fact that allene (I) resembles the unfluorinated allenes in cycloaddition reactions, still important differences exist. The ene reactions, which are widely depicted for its analog, tetramethylallene, are not inherent to allene (I). Another difference is the high electrophilicity of the cumulene system of bonds in allene (I), which exerts an effect on the choice of addenda for the cycloaddition reactions. For example, allene (I) could not be reacted with such electrophilic olefins as acrylonitrile and styrene, which reactions are known for tetramethylallene and other unfluorinated allenes [15-18].

EXPERIMENTAL METHODS

The PMR spectra (δ, ppm) were recorded on a Perkin-Elmer R-12 and R-20 spectrometer using TMS as the external standard. The ^{19}F NMR spectra (δ, ppm from CF_3COOH as the external standard) were taken on a Hitachi H-6013 spectrometer (56.46 MHz).

The fine structure of ethoxycyclobutane (III) was established by the NMR* method on an NR-2308 spectrophotometer, using the double and triple resonances based on ^{1}H and ^{19}F and the indors based on ^{1}H under the conditions of the noise suppression of ^{19}F.

2-Ethoxy-3,3-bis(trifluoromethyl)-4-hexafluoroisopropylidenecyclobutane (III). A mixture of 7.42 g (0.025 mole) of allene (I), 3.8 g (0.05 mole) of vinyl ethyl ether, and a catalytic amount of hydroquinone was heated in a Carius tube for 6 h at 140°. After distillation of the mixture we obtained 6.17 g (67.5%) of (III) with bp 72° (24 mm), n_D^{20} 1.3465. Infrared spectrum: 1700 cm^{-1} (C=C), Mass spectrum: 384 (M), 369 (M − CH_3), 356 (M − C_2H_5), 336 (M − C_2H_5O − 3H), 163 [$(CF_3)_2CCH$]. Found: C 34.4; H 1.97; F 59.4%. $C_{11}H_8F_{12}O$. Calculated: C 34.4; H 2.10; F 59.4%. PMR spectrum: 1.02 t (CH_3); 3.33 center m [CH_2 (ethyl); CH_2 in ring]; 4.32 t (CH). ^{19}F NMR spectrum: −16.8 q. t (CF_3C=); −15.1 cm (CF_3C=); −11.5 m [$(CF_3)_2C$].

2-Phenyl-3,3-bis(trifluoromethyl)-4-hexafluoroisopropylidenecyclobutene (V). A mixture of 14.5 g (0.046 mole) of allene (I) and 4.74 g (0.046 mole) of phenylacetylene was heated in a Carius tube for 20 h at 140-170°. Fractional distillation gave 4.9 g of unreacted allene (I) and 9.7 g (77%) of (V) with bp 84-85° (4 mm), mp 20-22.5°, n_D^{20} 1.4701. Infrared spectrum (ν, cm^{-1}): 1450, 1495, 1570, 1592, 1660, 1682, (C=C). Ultraviolet spectrum: 302 nm, ε 408500. Found: C 43.2; H 1.47; F 54.9%. $C_{15}H_6F_{12}$. Calculated: C 43.0; H 1.43; F 54.3%. PMR spectrum: 7.0 q (ring CH); 7.3 center m (phenyl); $J_{H/F}$ = 3 Hz. ^{19}F NMR spectrum: −19 d. q (CF_3C=); −17.5 m (CF_3C)=); −12.5 q [$(CF_3)_2C$]; $J_{(CF_3)_2C/CF_3C=}$ = 10 $J_{CF_3C=/CF_3C=}$ = 6Hz.

1,2-Dichloro-2-phenyl-3,3-bis(trifluoromethyl)-4-hexafluoroisopropylidenecyclobutane (VI). A mixture of 4.9 g (0.012 mole) of 1-cyclobutene (V) and 0.84 g (0.012 mole) of chlorine in a Carius quartz tube was irradiated with UV light (PRK-2 lamp, 300 W) for 20 h. After distillation we obtained 4.1 g (71%) of (VI) as a mixture of two isomers (based on the GLC) with bp 72° (1 mm), n_D^{25} 1.4405. Infrared spectrum (ν, cm^{-1}): 1450, 1500, 1570, 1590, 1689 (C=C). Found: C 36.9; H 1.15; F 46.9; Cl 14.5%. $C_{15}H_6F_{12}Cl_2$. Calculated: C 37.1; H 1.23; F 47.1; Cl 14.6%. PMR spectrum: 5.8 br.s (CH); 7.4 center m (phenyl). ^{19}F NMR spectrum: −20.3 m (CF_3C=); −19.7 m (CF_3C=); −16.0 m[$(CF_3)_2C$].

1-Chloro-2-phenyl-3,3-bis(trifluoromethyl)-4-hexafluoroisopropylidene-1-cyclobutene (VII). To 4.2 g (0.0087 mole) of dichlorocyclobutane (VI) in 10 ml of abs. ether was added 0.88 g (0.0087 mole) of abs. Et_3N in drops. At the end of exothermic reaction the mixture was refluxed for 1.5 h, poured into water, washed in succession with dilute HCl solution, $NaHCO_3$ solution, and water, and dried over $MgSO_4$. After distillation we obtained 3 g (78%) of (VII) with bp 86-88° (4 mm), n_D^{25} 1.4749. Infrared spectrum: (ν, cm^{-1}): 1450, 1500, 1570, 1590, 1680 (C=C). Found: C 39.8; H 1.10; F 50.5; Cl 8.03%. $C_{15}H_5F_{12}Cl$. Calculated: C 40.0; H 1.12; F 50.1; Cl 7.94%. ^{19}F NMR spectrum: −25.0 q (CF_3C=); −17.1 m (CF_3C=); −14.0

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*The spectra were taken by P. O. Okulevich and A. I. Lutsenko.

q $[(CF_3)_2C]$; $J_{CF_3C=/CF_3C=} = 11$, $J_{CF_3C=/(CF_3)_2C}$ 12 Hz.

5-Trifluoromethyl-6,6,6-trifluoro-4-hexafluoroisopropyl-2-methyl-1,4-hexadiene (XI). A mixture of 5.6 g (0.0179 mole) of allene (I), 1.4 g (0.025 mole) of isobutylene, and a catalytic amount of hydroquinone was heated in a Carius tube for 50 h at 210°. After distillation we obtained 2.9 g [66.5%, when based on reacted allene (I)] of (XI) with bp 132-133° (741 mm), n_D^{20} 1.3358. Infrared spectrum (ν, cm^{-1}): 1640, 1650 (C=C). Mass spectrum: 368 (M), 353 $(M - CH_3)$, 333 $(M - CH_3 - HF)$, 299 $(M - CF_3)$. PMR spectrum: 1.5 s $(CH_3, 3)$; 3.08 s $(CH_2, 2)$; 4.38 h $[(CF_3)_2CH, 1]$; 4.42 s $(CH_2=, 1)$; 4.7 s $(CH_2=, 1)$; $J_{H-F} = 7.45$ Hz. ^{19}F NMR spectrum: -22.1 br. q $(CF_3C=)$; -16.9 q $(CF_3C=)$; -14.2 d.q $[(CF_3)_2CH]$; $J_{CF_3C} = /_{CF_3C=} = 10.8$; $J_{CF_3C=/(CF_3)_2C} = 2.51$ Hz.

3,3-Bis(trifluoromethyl)-2-hexafluoroisopropylidene-7-oxabicyclo[2.2.1]-5-heptene (XII). A mixture of 4.62 g (0.015 mole) of allene (I) and 1.4 g (0.02 mole) of furan was kept in a Carius tube at 20°. After distillation we obtained 4.6 g (82.3%) of (XII) with bp 70° (20 mm), n_D^{20} 1.3682. Infrared spectrum (ν, cm^{-1}): 1580; 1670 (C=C). Mass spectrum: 380 (M), 361 $(M - F)$, 332 $(M - F - CHO)$, 313 $(M - C_4H_3O)$, 293 $(M - C_4H_4O - F)$, 263 $(M - CHO - F - CF_3)$, 163 $[(CF_3)_2CCH]$. Found: C 34.5; H 0.84; F 60.3%. $C_{11}H_4F_{12}O$. Calculated: C 34.8; H 1.05; F 60.0%. PMR spectrum: 5.45 s; 5.78 s (CH in ring); 6.55 s (CH=). ^{19}F NMR spectrum: -20.5 br. g $(CF_3C=)$; -17.1 m $(CF_3C=)$; -15.3 m (CF_3); -13.7 m (CF_3).

2-Vinyl-3,3-bis(trifluoromethyl)-4-hexafluoroisopropylidenecyclobutane (XIII) and 4,4-bis(trifluoromethyl)-5-hexafluoroisopropylidene-1-cyclohexene (XIV). A mixture of 21 g (0.067 mole) of allene (I), 8.8 g (0.162 mole) of butadiene, and a catalytic amount of hydroquinone was heated in a Carius tube for 30 h at 140-150°. After fractional distillation we obtained: 1) 7 g (31.8%) of (XIII) with bp 154-157° (757 mm), n_D^{20} 1.3540. Infrared spectrum: (ν, cm^{-1}): 1650, 1700 (C=C). Mass spectrum: 366 (M), 347 $(M - F)$, 327 $(M - HF - F)$, 297 $(M - CF_3)$, 271 $(M - CF_3 - HF)$, 283 $(M - CF_3 - CH_2)$, 263 $(M - CF_3 - CH_2 - HF)$, 227 $(M - 2CF_3 - H)$. Found: C 36.4; H 1.63; F 62.2%. $C_{11}H_6F_{12}$. Calculated:C 36.1; H 1.64; F 62.3%. PMR spectrum: 2.6 m $(CH, CH_2$ in ring); 4.4 m $(CH_2=)$; 5.6 m (CH=). ^{19}F NMR spectrum: -9.7 m of 9 lines $[(CF_3)_2C]$; -11.4 h $[(CF_3)_2C]$; -15.1 m $(CF_3C=)$; -17.2 q. t $(CF_3C=)$; $J_{H/F} = 2.4$ $J_{H/F} = 14$, $J_{CF_3C=/CF_3C=} = 7.5$; $J_{(CF_3)_2C/(CF_3)_2C} = 7.5$ Hz. 2) 1.7 g (7.8%) of (XIV) with bp 178-179° (757 mm), n_D^{20} 1.3668. Infrared spectrum: 1610 cm^{-1} (C = C). Mass spectrum: 366 (M), 347 $(M - F)$, 327 $(M - HF - F)$, 297 $(M - CF_3)$, 277 $(M - CF_3 - HF)$, 227 $(M - 2CF_3 - H)$. Found: C 36.2; H 1.67; F 62.3%. $C_{11}H_6F_{12}$. Calculated: C 36.1; H 1.64; F 62.3%. PMR spectrum: 2.64 br. s (CH_2); 3.09 br. s (CH_2); 5.91 m (CH=). ^{19}F NMR spectrum: -15 q $[(CF_3)_2C]$; -18 m $(CF_3C=)$; -20.7 q $(CF_3C=)$; $J_{CF_3C=/CF_3C=} = 11.3$; $J_{(CF_3)_2C/CF_3C=} = 16.9$ Hz.

CONCLUSIONS

1. Tetrakis(trifluoromethyl)allene enters into the cycloaddition reaction with vinyl ethyl ether and phenylacetylene to respectively give 2-ethoxy-3,3-bis(trifluoromethyl)-4-hexafluoroisopropylidenecyclobutane and 2-phenyl-3,3-bis(trifluoromethyl)-4-hexafluoroisopropylidenecyclobutene.

2. The above-mentioned allene reacts with isobutylene to give the alkylation product, and specifically 5-trifluoromethyl-6,6,6-trifluoro-4-hexafluoroisopropyl-2-methyl-1,4-hexadiene.

3. Tetrakis(trifluoromethyl)allene enters into the diene synthesis with furan and butadiene to respectively give 3,3-bis(trifluoromethyl)-2-hexafluoroisopropylidene-7-oxabicyclo[2.2.1]-5-heptene and 4,4-bis(trifluoromethyl)-5-hexafluoroisopropylidene-1-cyclohexene.

LITERATURE CITED

1. L. A. Rozov, Yu. E. Zeifman, Yu. A. Cheburkov, and I. L. Knunyants, Izv. Akad. Nauk SSSR, Ser. Khim., 1975, 188.
2. D. R. Taylor, Chem. Rev., 67, 317 (1967).
3. D. R. Taylor, M. R. Warburton, and D. B. Wright, J. Chem. Soc. Perkin Trans. 1, 11, 1365, (1972).
4. W. J. Feast, W. K. R. Musgrave, and R. G. Weston, J. Chem. Soc., C 1971, 937.
5. Yu. E. Aronov, Yu. A. Cheburkov, and I. L. Knunyants, Izv. Akad. Nauk SSSR, Ser. Khim., 1967, 1758.

6. M. D. Bargamova, N. S. Mirzabekyants, E. I. Mysov, Yu. A. Cheburkov, and I. L. Knunyants, Izv. Akad. Nauk SSSR, Ser. Khim., 1974, 830.
7. N. S. Mirzabekyants, M. D. Bargamova, Yu. A. Cheburkov, and I. L. Knunyants, Izv. Akad. Nauk SSSR, Ser. Khim., 1974, 2545.
8. T. L. Gilchrichst and R. C. Storr, Organic Reactions and Orbital Symmetry, Cambridge (1972).
9. H. A. Chia, B. E. Kirk, and D.R. Taylor, J. Chem. Soc. Perkin Trans. 1, 1974, 1209.
10. J. Roberts and K. M. Shartz, in monograph "Organic Reactions" [Russian translation], Vol. 12, "Mir" (1965), p. 7.
11. P. D. Bartlett, Science, 159, 833 (1968).
12. P. Kurtz, H. Gold, and H. Disselnkoter, Ann. Chem., 624, 1 (1959).
13. B. L. Dyatkin, N. I. Delyagina, E. I. Mysov, and I. L. Knunyants, Tetrahedron, 30, 4031 (1974).
14. A. R. Katritskii, Physical Methods in the Chemistry of Heterocyclic Compounds [in Russian], "Nauka" (1966), p. 430.
15. J. C. Martin, P. L. Carter, and J. L. Chitwood, J. Org. Chem., 36, 2225 (1971).
16. H. N. Cripps, J. K. Williams, and W.H. Sharkey, J. Am. Chem. Soc., 81, 2723 (1959).
17. D. R. Taylor and D. B. Wright, J. Chem. Soc., C 1971, 391.
18. J. E. Baldwin and U. V. Roy, Chem. Commun., 1969, 1225.

SYNTHESIS AND PROPERTIES OF PYRIMIDINYLALKYLSULFONAMIDES.

COMMUNICATION 1. INTERACTION OF CERTAIN ω-HALOALKYLURACILS WITH p-TOLUENESULFAMIDE

Yu. S. Shvetsov, A. N. Shirshov,
and V. S. Reznik

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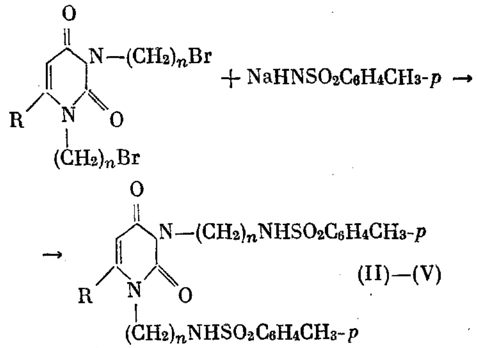
To study N-alkyl derivatives of uracil containing the sulfonamide grouping in the alkyl chain we investigated the interaction of certain N-(ω-bromoalkyl)uracils with p-toluenesulfamide (I). The corresponding 1,3-bis[ω-(p-toluenesulfonamido)alkyl]uracils (II)-(V) in yields of 45-80% are formed upon reaction of 1,3-bis(ω-bromoalkyl)uracils with the Na salt of (I).



(II)—(V)

R = H; $n = 4$ (II); R = CH_3, $n = 4$ (III); R=H, $n = 3$ (IV); R = CH_3, $n = 3$ (V)

Compounds (II)-(V) are stiff oils or crystalline materials having limited solubility in $CHCl_3$ and being insoluble in water. IR Spectra of (II)-(V) have intense bands in the region of stretching vibrations of the C=O group (1627-1665 and 1682-1710 cm^{-1}). Stretching vibration

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A. E. Arbuzov Institute of Organic and Physical Chemistry, Kazan Branch of the Academy of Sciences of the USSR. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 5, pp. 1103-1106, May, 1976. Original article submitted May 19, 1975.