Journal of Fluorine Chemistry, 19 (1982) 601–615

REACTIVE ALKYNYL PERFLUOROALKANESULFONES

F. MASSA, M. HANACK* and L. R. SUBRAMANIAN

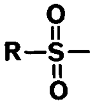
Institut für Organische Chemie der Universität Tübingen
Auf der Morgenstelle 18
D-7400 Tübingen (F.R.G.)

SUMMARY

The alkynylperfluoroalkanesulfones 5a-e have been prepared and their cycloaddition reactivity towards dienes and diazomethane has been studied. The faster reaction rate of 5b with cyclopentadiene than 5a and *vice versa* with tetracyclone (6) has been explained on steric and electronic affects. The alkynylperfluoroalkanesulfones are very reactive towards nucleophilic additions. Attempts to prepare the highly reactive bis-perfluoroalkanesulfonylacetylene (21) in the presence of cyclopentadiene led to the isolation of products 22, 23 and 24.

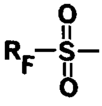
INTRODUCTION

Sulfone (1) is an important functional group in organic chemistry. It stabilizes an adjacent negative charge due to its electron-withdrawing power and functions as both an electrophile and as a nucleophile leaving group. These properties of the sulfonyl group have been exploited in organic synthesis [1-5].



$R-\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle O}{\|}}{S}}-$

1



$R_F-\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle O}{\|}}{S}}-$

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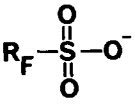


$R_F-\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle O}{\|}}{S}}-O^-$

3

$R_F = CF_3, C_4F_9$

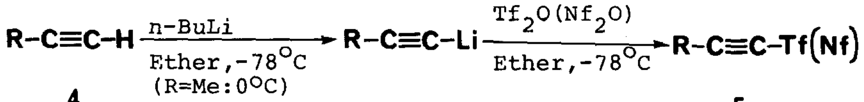
The electronegativity of the sulfonyl group can be increased by substitution of perfluoroalkane groups (2). The most common substituents used are the trifluoromethyl and the nonafluorobutyl groups. The early work carried out more than twenty years ago [6] established the trifluoromethanesulfonyl group (triflyl) as the strongest electron-withdrawing neutral group. This property of the triflyl group is not only due to its inductive effect, but also due to the distinct conjugation ability of the perfluoroalkanesulfone group. The better overlap of the 3d-orbitals of sulfur with the 2p-orbitals of oxygen is given as an explanation for the improved conjugation. The electron-withdrawing perfluoroalkyl group causes shrinking of the 3d-orbitals of the sulfur atom effecting a better overlap [7].

Our earlier work [8-13] and those of others [14-17] illustrate the versatile reactivity of perfluoroalkanesulfones. In testing the electron poor vinyl perfluoroalkane sulfones as dienophiles in the classical Diels-Alder reaction, it was demonstrated [11] that vinyl nonaflones react with dienes much faster than the conventional vinyl sulfones.

In our work on the preparative application of perfluoroalkanesulfonates [18,19] the more stronger electron-withdrawing ability of nonaflate anion (3, $R_F = C_4F_9$) *vs.* triflate anion have been studied. We report here the preparation and reactions of several alkinylperfluoroalkanesulfones, as well as the comparison of triflyl and nonaflyl groups with respect to the electron-withdrawing power and steric effects in Diels-Alder and other addition reactions.

RESULTS AND DISCUSSION

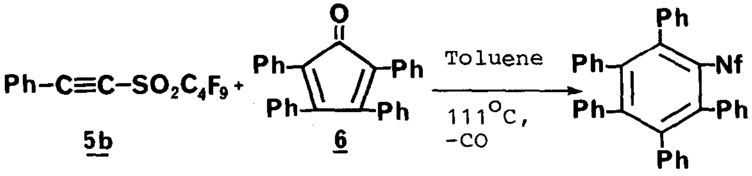
The triflones and nonaflones (5a-e) were prepared by the procedure reported for 5a [16]. The alkynes (4) were converted to their lithium salts by reaction with n-butyllithium at -78° C in ether and subsequently treated with trifluoromethanesulfonic acid anhydride (Tf_2O) [6,20] or nonafluorobutanesulfonic acid anhydride (Nf_2O) [21] to give the corresponding sulfones in moderate yields.



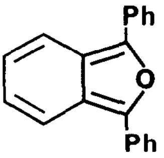
4 5

Sulfone	R	Sulfonyl rest	Yield(%)
5a	Ph	Tf	47 (see exptl.)
5b	Ph	Nf	28
5c	n-Pr	Nf	8
5d	n-Pr	Tf	7
5e	Me	Tf	14

The sulfone (5a) is a white crystalline solid melting at 31° C. The other sulfones (5b-e) are pale yellow liquids and are identified by their spectral data (exptl.). All alkynyl perfluoroalkane sulfones (5a-e) are thermally labile, but can be stored at 0° C for several months without decomposition. The nonaflone (5b) reacts with tetraphenylcyclopentadienone (tetracyclone) (6) as well as 1,3-diphenylisobenzofuran (8) to give the adducts 7 (-CO) and 9. They are characterized spectroscopically [8]. The n-propyl derivative (5c) yielded only the 1,3-diphenylisobenzofuran adduct (9, R = C_3H_7). With tetracyclone in p-cymene as solvent 5c gave the partially hydrogenated product (10). The hydrogenation of 6 took place most probably via a radical mechanism, while the hydrogen atom of p-cymene can be easily abstracted at higher temperatures. No reaction took place between p-cymene and tetracyclone in the absence of 5c.



5b 6 7



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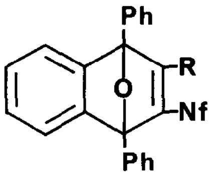
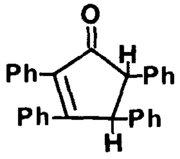


9 , R = Ph,C_3H_7



10

Ph-C≡C-X

11 , X = COCl,CN,CHO,COOMe,$SiMe_3$

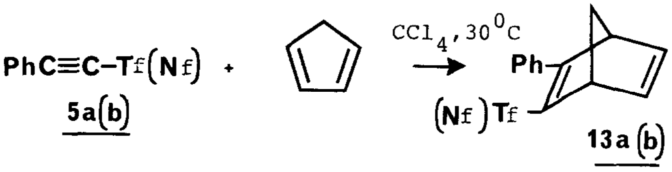
$PhCH{=}CHSO_2C_4F_9$

12

The kinetic studies of the Diels-Alder reaction of differently substituted phenylalkynes (11) give the highest reaction rate for 5a. 5a was found to be even more reactive than acetylenedicarboxylic ester as well as trans-(β-nonafluorobutanesulfonyl) styrene (12) [11]. Comparison of kinetic studies of 5a and 5b with tetracyclone (6) showed [8] that the triflone 5a reacts 2.4 times faster than the nonaflone 5b, which is opposite to the behaviour of triflates and nonaflates as leaving groups in solvolysis reactions [19].

The low reactivity of nonaflone 5b with the bulky diene component, tetracyclone, could be due to steric hindrance caused by both the reactants. To determine the extent of electronic influence of triflone and nonaflone on the dienophile activity of alkynes, cyclopentadiene was used as the diene, where steric effect play only a minor role.

5a and 5b were found to react with cyclopentadiene in CCl_4 at 30° C to give the adduct 13. The rate of the reaction was measured by IR spectroscopy by monitoring the decrease in the intensity of C≡C-streching band. The data given below show that 5b reacts faster than 5a with cyclopentadiene by a factor of only 1.3. This denotes that the substitution of the triflyl by the nonaflyl group does not bring practically any increase in the dienophilic character of alkynyl sulfones.



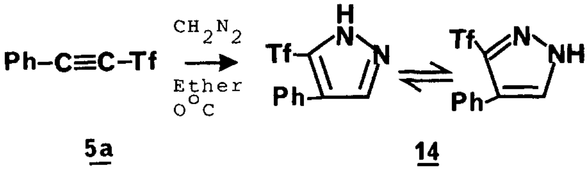
5a(b)

13a(b)

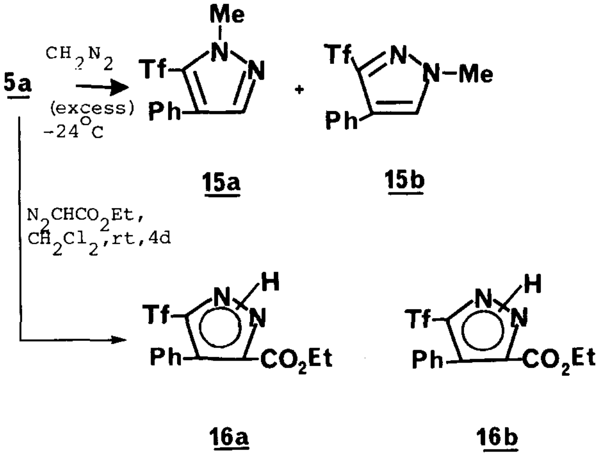
Dienophile	k_2 ($l.mol^{-1}$ sec^{-1})	Yield
5a	2.7×10^{-3}	40
5b	3.5×10^{-3}	44

The 1,3-dipolar addition reaction of diazomethane and ethyldiazoacetate with 5a and 5b was also studied. The cycloaddition reaction of diazoalkanes with alkynes is a synthetic route to pyrazoles [22]. The reaction takes place faster when the alkyne component carry electron-withdrawing substituents which also increase the regioselectivity of the addition reaction [23,24].

Diazomethane reacts with 5a already at 0° C regiospecifically yielding the pyrazole (14). An excess of diazomethane causes N-methylation of pyrazole (14) and the two isomers 15a and 15b are formed in a ratio of 1:1.



5a **14**

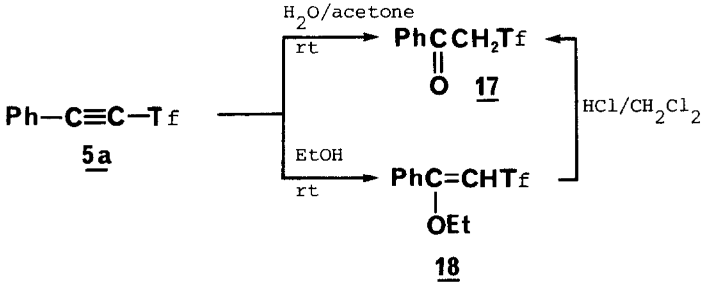


15a **15b**

16a **16b**

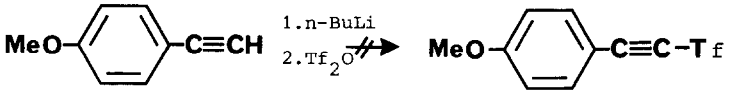
The addition of ethyldiazoacetate to 5a takes place slowly yielding a mixture of 16a and 16b in a ratio of 5:2 as determined by ^{1}H-NMR spectroscopy. The regioselectivity found in the addition of ethyldiazoacetate to 5a is unexpectedly small. In fact the slower reaction rate should have increased the regioselectivity.

Nucleophiles like thiophenol add to the triple bond in 5a in the presence of catalytic amount of sodium phenolate [16]. We have investigated the reactivity of 5a with weak nucleophiles like ethanol and water without the addition of a catalyst. Stirring a homogeneous mixture of 5a with water in acetone for 3 days gave the β-ketotriflone (17). Similarly a solution of 5a in absolute ethanol forms the enol ether (18) within a day. The enol ether 18 could be hydrolyzed to the β-ketosulfone (17) with HCl.



The addition of water to alkynes normally require mercuric salts as catalyst [19]. The surprisingly easy addition of water to 5a without a catalyst at room temperature is due to the strong electron-withdrawing effect of the triflyl group. The more nucleophilic ethanol reacts with 5a even faster.

Attempts to prepare p-methoxyphenyl (triflyl)acetylene (19) in an analogous manner failed, yielding only polymerized products. Similarly it was not possible to convert ethoxyacetylene to the corresponding perfluoroalkanesulfone (20). 19 and 20 could also not be captured *in situ* in the presence of cyclopentadiene.



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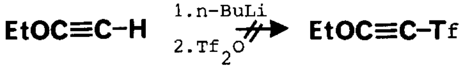


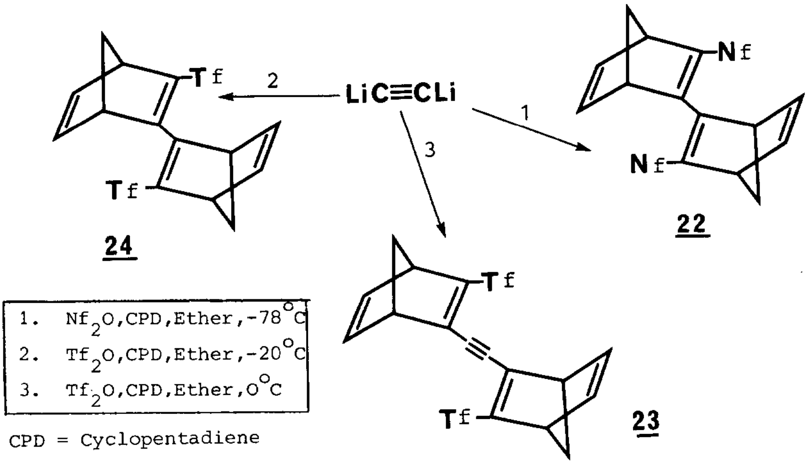
$$EtOC{\equiv}C\text{-}H \;\not\xrightarrow[2.\,Tf_2O]{1.\,n\text{-}BuLi}\; EtOC{\equiv}C\text{-}Tf$$

20

Bis-(perfluoroalkanesulfonyl)acetylene (21) is unknown. 21 should be an even more electron poor acetylene than 5a-e and therefore more reactive towards electron rich dienes. However our efforts to prepare 21 by reacting dilithium acetylide or the corresponding di-Grignard compound with Tf_2O or Nf_2O failed to yield any products. An attempt to capture the disulfone 21 *in situ* with cyclopentadiene lead mostly to polymeric materials beside the Diels-Alder adducts (22, 23, 24). They are not formed via the expected bis-(perfluoroalkanesulfonyl)acetylene (21). 22 and 24 are the cycloaddition products of the diynes 25

$R_FSO_2C{\equiv}CSO_2R_F$

21



1. Nf_2O,CPD,Ether,-78°C
2. Tf_2O,CPD,Ether,-20°C
3. Tf_2O,CPD,Ether,0°C

CPD = Cyclopentadiene

and 26 to two moles of cyclopentadiene. The adduct 23 is formed by the reaction of triyne 27 to two moles of cyclopentadiene.

$TfC\equiv C-C\equiv C-Tf$ **25**

$NfC\equiv C-C\equiv C-Nf$ **26**

$TfC\equiv C-C\equiv C-C\equiv C-Tf$ **27**

$$\underset{\mathbf{28}}{PhC\equiv CLi} \xrightarrow[\text{Ether, }-78^{\circ}]{C_4F_9SO_2F} \underset{\mathbf{5b}}{PhC\equiv CNf} + \underset{\mathbf{29}}{PhC\equiv C-C\equiv C-Ph}$$

$$\mathbf{5b} + \mathbf{28} \not\rightarrow \mathbf{29}$$

The diynes 25 and 26 and triyne 27 are probably formed by an oxidative coupling of dilithiumacetylide with the perfluoroalkanesulfonic acid anhydrides (Nf_2O,Tf_2O). The alternative reaction path of coupling of the alkynyl nonaflone intermediates to give the diynes and triynes was ruled out based on the following experiment. Reaction of phenylethynyllithium (28) with $C_4F_9SO_2F$ gives diphenylbutadiyne (29) as the major product. However 29 does not form when phenylethynyllithium was allowed to react with 5b. These results support that products 25 - 27 are formed by an oxidative coupling mechanism.

Further reactions of these new class of compounds are in progress.

EXPERIMENTAL

General method of preparation of alkynyl perfluoroalkanesulfones

Trifluoromethanesulfonicacid anhydride /nonafluorobutanesulfonicacid anhydride (50 mmol) in dry ether (100 ml) was added dropwise with stirring to lithium alkynides (50 mmol) prepared from the corresponding alkynes and n-butyllithium (50 mmol) in dry ether (100 mmol) at -70° C. Only in the case of 5b, the lithium alkynide was added to nonafluorobutanesulfonicacid anhydride. The reaction mixture was allowed to come to room temperature slowly. It was then washed with aq. $NaHCO_3$, aq. HCl and brine and dried over anhydrous $MgSO_4$. The solvent was removed under reduced pressure and the residue was purified by Kugelrohr distillation twice.

5a: yield 47%, white crystalline solid, m.p. 31° C. The spectral data are in accordance with the literature values [16].
5b: yield 28%, pale yellow oil, b.p. 80° C/2.7 Pa. - IR(Film): 2200 ($C\equiv C$), 1608, 1500 (Phenyl), 1395 (S=O), 1250 - 1180 (CF), 1150 (S=O) cm^{-1}. - ^{1}H-NMR (CCl_4): δ = 7.15 - 7.85 (Phenyl) ppm. Analysis: Found C, 38.12; H, 1.35%. $C_{12}H_5O_2F_9S$ requires C, 37.5; H, 1.3%.
5c: yield 8%, pale yellow liquid, b.p. 90° C/4 Pa. The product contaminated with acidic impurities was purified by shaking with dry $NaHCO_3$ in petrol ether (30-50° C). - IR(Film): 2200 ($C\equiv C$), 1394 (S=O), 1250-1180 (C-F), 1150 (S=O) cm^{-1}. - ^{1}H-NMR (CCl_4): δ = 1.05 (t,3H); 1.68 (m,2H); 2.55 (t,2H) ppm. - Analysis: Found C, 30.21; H, 1.94. $C_9H_7O_2F_9S$ requires C, 30.86; H, 2.0%.
5d: yield 7%, pale yellow liquid, b.p. 110° C/6.7 Pa. The product contaminated with acidic impurities was purified by shaking with dry $NaHCO_3$ in petrol ether (30-50° C). IR(Film): 2218 ($C\equiv C$), 1382 (S=O), 1218 (C-F), 1133 (S=O) cm^{-1}. - ^{1}H-NMR (CCl_4): δ = 1.10 (t,3H); 1.78 (m,2H); 2.57 (t,2H). - Analysis: Found C, 35.51; H, 3.49. $C_6H_7O_2F_3S$ requires C, 36.0; 3.52.
5e: yield 35%, colorless liquid, b.p. 50° C/133 Pa. IR(Film): 2205, 2075 ($C\equiv C$), 1380 (S=O), 1212 (C-F), 1130 (S=O) cm^{-1}. - ^{1}H-NMR (CCl_4): δ = 2.28 (s) ppm. - Analysis: Found C, 27.53; H, 1.72. $C_4H_3O_2F_3S$ requires C, 27.91; H, 1.76.

Addition of Phenyl (triflyl) acetylene (5a) and Phenyl (nonaflyl) acetylene (5b) to cyclopentadiene.

(i) Kinetic studies: A 0.04 molar solution of 5a and 5b in abs. CCl_4 was thermostatically controlled at 30° C. Equimolar amount of cyclopentadiene was added to the solution separately. The zero time was taken to be that time at which constant internal temperature was reached. Aliquots were removed every half hour and the IR absorption in the region 2000 - 2500 was measured. The concentration of reactants remaining and products formed were calculated by comparing the absorptions around 2200 cm^{-1} with spectra of known concentration for the pure compounds. The constant k_2 was graphically determined.

(ii) Product studies

3-Triflyl-2-phenylbicyclo[2.2.1]hepta-2,5-diene (13a):

The samples from kinetic measurement were mixed together and the solvent evaporated to give a colorless oil. A white crystalline solid is precipitated on titruation with petrol ether (30-50° C). Yield 40%, m.p. 75-76° C. IR(KBr): 1592, 1483 (phenyl), 1570, 1550 (C=C), 1350 (S=O), 1195 (C-F), 1120 (S=O) cm^{-1}. - ^{1}H-NMR (CCl_4): δ = 2.05 - 2.60 (m, 2H, $-CH_2-$); 3.86 - 4.25 (m,2H, methine protons); 7.0 (m, 2H, olefinic protons); 7.37 (s,5H, phenyl) ppm - MS: m/e = 300 (M^+, 39%), 231 ($M-CF_3$, 8%), 167 ($M-SO_2CF_3$, 97%), 66 (C_5H_6, 100%). - Analysis: Found C, 56.14; H, 3.65 $C_{14}H_{11}O_2F_3S$ requires C, 56.0; H,3.67.

3-Nonaflyl-2-phenylbicyclo[2.2.1]hepta-2,5-diene (13b):

Removal of solvent from the combined samples from kinetic experiment gave an oil, which was purified by chromatography over silica gel. yield, 44%. - IR(Film): 1610, 1495 (phenyl), 1585, 1568 (C=C), 1370 (S=O), 1225 (C-F), 1142 (S=O) cm^{-1}. - ^{1}H-NMR (CCl_4): δ = 2.07, 2.56 (m, 2H, $-CH_2-$); 3.87 - 4.25 (m, 2H, methine protons); 7.0 (m,2H, olefinic protons); 7.40 (s, 5H, phenyl) ppm. - MS: m/e = 450 (M^+, 30%), 431 (M-F,2%), 384 ($M-C_5H_6$,1%), 231 ($M-C_4F_9$,8%), 167 ($M-C_4F_9SO_2$, 100%), 66 (C_5H_6, 64%). - Analysis: Found C, 45.96; H, 2.46. $C_{17}H_{11}O_2F_9S$ requires C, 45.34, H, 2.46.

Addition of diazomethane to phenyl(triflyl)acetylene (5a)
3-Triflyl-4-phenylpyrazol (14):

To 5a (234 mg, 1 mmol) in dry ether (20 ml) was added dropwise an equimolar amount of an ethereal solution of diazomethane at 0° C. The yellow color of diazomethane was decolorized immediately. After removal of solvent and crystallization from CCl_4 one obtains a white powder. Yield 128 mg (43%), m.p. 102-104° C. - IR(KBr): 1605 - 1408 (phenyl and pyrazolring - several bands), 1371 (S=O), 1202 (C-F), 1103 (S=O) cm^{-1}. - ^1H-NMR ($CDCl_3$): δ = 7.57 (m, 5H, phenyl); 8.03 (s,1H, = CH in pyrazol ring); 11.47 (s,1H,NH) ppm. - MS: m/e = 276 (M^+, 57%), 207 ($M-CF_3$, 100%). - Analysis: Found C, 42.93; H, 2.48, N, 9.75. $C_{10}H_7N_2O_2F_3S$ requires C, 43.48; H, 2.55, N, 10.14.

3-Triflyl-2-methyl-4-phenylpyrazol (15a) and 3-Triflyl-1-methyl-4-phenylpyrazol (15b):

5a (263 mg, 1.12 mmol) in dry ether (20 ml) was treated with a threefold excess of ethereal diazomethane within 15 min at -24° C. The cooling was removed after 30 min and left aside for 2 h. Removal of solvent and crystallization from CCl_4 gave white crystals. Yield 105 mg (32%), m.p. 116 - 117° C. - IR (KBr): 1540 - 1435 (phenyl and pyrazol ring, several bands) 1385 (S=O), 1220 (C-F), 1118 (S=O) cm^{-1}. - ^1H-NMR ($CDCl_3$). δ = 4.01 (s,3H,-CH_3); 4.07 (s,3H, -CH_3); 7.3 - 7.9 (m, 11H, =CH-, phenyl and pyrazol ring); 8.14 (s,1H, =CH-, pyrazol ring) ppm. MS: m/e = 290 (M^+, 100%), 220 ($M-CF_3-H$,80%). - Analysis: Found C, 45.25; H, 3.09; N, 9.58. $C_{11}H_9N_2O_2F_3S$ requires C; 45.52; H, 3.13; N, 9.65.

Addition of ethyldiazoacetate to phenyl(triflyl)acetylene (5a)

Ethyl 5-triflyl-4-phenylpyrazol-3-carboxylate (16a) and ethyl-4-triflyl-5-phenylpyrazol-3-carboxylate (16b).

The triflone 5a (477 mg, 2.04 mmol) dissolved in CH_2Cl_2 (5 ml) was allowed to react with a dichloromethane (5 ml) solution of ethyldiazoacetate [26] (233 mg, 2.04 mmol) at room temperature for 30 min. The reaction was monitored by TLC ($CHCl_3$). The solvent was removed after 4 days and the residue was crystallized from CCl_4 to give white crystalline needles. Yield 510 mg (72%), m.p. 147 - 165° C. - IR(KBr): 3260 (NH), 1740, 1722 (C=O), 1560 - 1448 (phenyl and pyrazol ring), 1378

(S=O), 1205 (C-F), 1120 (S=O) cm^{-1}. - ^1H-NMR ($CDCl_3$): δ = 1.1 (t, 3H, CH_3 of 16a, J = 7 Hz); 1.41 (t,3H, CH_3 of 16b, J = 7 Hz); 4.22 (q, 2H, $-CH_2-$ of 16a, J = 7 Hz); 4.35 (q, 2H, $-CH_2$ of 16b, J = 7 Hz); 7.14 (s, 5H, phenyl of 16a); 7.56 (s, 5H, phenyl of 16b) ppm. Integration: 5a:5b = 5:2. - MS: m/e = 348 (M^+, 100%), 333 ($M-CH_3$, 4%), 320 ($M-N_2$, 9%), 303 ($M-C_2H_5O$, 21%) 279 ($M-CF_3$, 22%). - Analysis: Found C, 44.88; H, 3.23; N, 7.96. $C_{13}H_{11}N_2O_4F_3S$ requires C, 44.83; H, 3.18; N, 8.04.

Addition of water to phenyl(triflyl)acetylene (5a)
Benzoyl(triflyl)methane (17):

5a (470 mg, 2 mmol) was stirred with water (1.7 ml, 94 mmol) in acetone (4 ml) for 3 days at room temperature. The solvent and water was removed under reduced pressure and the residue was crystallized from petrol ether (30 - 50° C) and dichloromethane mixture to give colorless crystals. Yield 240 mg (47%), m.p. 35-36° C. - IR(Film): 1686 (C=O), 1595, 1578 (phenyl), 1375 (S=O), 1214 (C-F), 1122 (S=O) cm^{-1}. - ^1H-NMR ($CDCl_3$): δ = 4.90 (s,2H); 7.45 - 8.11 (m, 5H) ppm. - MS: m/e = 252 (M^+, 48%), 183 ($M-CF_3$, 28%), 119 ($M-SO_2CF_3$, 13%), 105 ($M-CH_2SO_2CF_3$, 100%). - Analysis: Found C, 43.21; H, 2.84. $C_9H_7O_3F_3S$ requires C, 42.86; H, 2.8.

Addition of ethanol to phenyl(triflyl)acetylene (5a)
2-Triflyl-1-ethoxy -1-phenylethene (18:

5a (65 mg, 0.28 mmol) and abs. ethanol (5 ml) was stirred at room temperature for one day. After removal of ethanol, the residue was crystallized from ethanol-water to give colorless needles. Yield 42 mg (53%), m.p. 97 - 97.5° C. - IR(KBr): 1583 (C=C), 1505 (phenyl), 1378 (S=O), 1212 (C-F), 1123 (S=O), 1027 (C-O) cm^{-1}. - ^1H-NMR (CCl_4): δ = 1.47 (t,3H, J = 7 Hz); 4.09 (q, 2H, J = 7 Hz); 5.46 (s, 1H); 7.43 (s, 5H). - MS: m/e = 280 (M^+, 9%), 211 ($M-CF_3$, 68%), 147 ($M-SO_2CF_3$, 48%) . - Analysis: Found C, 46.87; H, 3.90, $C_{11}H_{11}O_3F_3S$ requires C, 47.14, H, 3.96.

Reaction of dilithium acetylide with trifluoromethanesulfonic acid anhydride and nonafluorobutanesulfonicacid anhydride

(i) Adduct of two moles of cyclopentadiene with bis-(triflyl)-butadiyne (25)

Acetylene was passed through a solution of n-butyllithium 62.5 ml of 1.6 M in hexane100 mmol) in dry ether (150 ml) at 0°C. Cyclopentadiene (9 ml) was then added followed by trifluoromethanesulfonicacid anhydride (28.0 g, 100 mmol) in ether (50 ml) in about 4 h. The reaction mixture was allowed to come to room temperature. It was worked up by washing with aq. $NaHCO_3$ and brine and dried over $MgSO_4$. Removal of solvent left a black viscous mass, which was extracted with petrol ether ($30-50^{\circ}$ C) (2 x 100 ml). The residue obtained by removing the petrol ether was chromatographed over silica gel with benzene as eluent. The benzene fraction was concentrated and treated with a small amount of petrol ether ($30-50^{\circ}$ C) and left overnight at 0°C to crystallize. Yield 434 mg (4%), yellow crystals, m.p. $77-78^{\circ}$ C. - IR(KBr): 1598 (C=C), 1365 (S=O), 1207 (C-F), 1127 (S=O) cm^{-1}. - ^{1}H-NMR ($CDCl_3$): δ = 2.51 (m, 4H, $-CH_2-$); 3.72 (m, 2H, methine protons); 4.13 (m, 2H, methine protons); 7.11 (m, 4H, olefinic protons) ppm. - MS: m/e = 446 (M^+, 6%), 312 ($M-CF_3SO_2H$, 30%), 178 ($M-2\ CF_3SO_2H$, 100%). Analysis: Found C, 43.15; H, 2.72. $C_{16}H_{12}O_4F_6S_2$ requires C, 43.05; H, 2.71.

(ii) Adduct of two moles of cyclopentadiene to bis(nonaflyl)-butadiyne (26):

The reaction was carried out as described above, however at -70° C. Yield 740 mg (4%), m.p. $76-77^{\circ}$ C. - IR(KBr): 1569, 1525 (C=O), 1369 (S=O), 1220 (C-F), 1142 (S=O) cm^{-1}. - ^{1}H-NMR ($CDCl_3$): δ = 2.24 (m, 2H, $-CH_2-$); 2.7 (m, 2H, $-CH_2$); 3.73 (m, 2H, methine protons); 4.1 (m, 2H, methine protons); 6.77 - 7.23 (m, 4H, olefinic protons). - MS: m/e = 746 (M^+ 1%), 462 ($M-C_4F_9SO_2H$, 25%), 178 ($M-2\ C_4F_9SO_2H$, 100%). - Analysis: Found C, 35.46; H, 1.61. $C_{22}H_{12}O_4F_{18}S_2$ requires C, 35.4; H, 1.62.

(iii) Adduct of two moles of cyclopentadiene to bis(triflyl)-hexatriyne (27):

To trifluoromethanesulfonicacid anhydride (28.0 g, 100 mmol) and cyclopentadiene (9 ml) in ether (150 ml) cooled to -20° C was added an ethereal suspension of dilithiumacetylide (from 62.5 ml of n-butyllithium and acetylene) dropwise within an hour. The reaction mixture was allowed to come to room temperature and washed with aq. $NaHCO_3$ and brine. After drying over $MgSO_4$ and removal of solvent, the black viscous product obtained was extracted with petrol ether (30-50° C) (2 x 100 ml). The residue after removal of the solvent was chromatographed over silica gel with chloroform as eluant. The chloroform was then removed and a small amount of petrol ether (30-50° C) was added to the residue and left in the frig for 5 weeks. The solid obtained was filtered and washed with a small amount of cold petrol ether. Yield 105 mg (1.3%), yellow crystals, m.p. 119 - 120° C. - IR(KBr): 2218 (C≡C), 1611 (C=C), 1375 (S=O), 1215 (C-F), 1143 (S=O) cm^{-1}. - ^1H-NMR ($CDCl_3$): δ = 2.43 (m, 4H, $-CH_2-$); 4.09 (m, 4H, methine protons); 7.02 (m, 4H, olefinic protons) ppm. - MS: m/e = 470 (M^+, 70%), 336 ($M-CF_3SO_2H$, 39%), 202 ($M-2\ CF_3SO_2H$, 100%). Analysis: Found C, 45.40; H, 2.59. $C_{18}H_{12}O_4F_6S_2$ requires C, 45.96; h, 2.57.

ACKNOWLEDGEMENT

We thank the Deutsche Forschungsgemeinschaft for financial support.

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