BISTRIFLUOROMETHYLKETENE

COMMUNICATION 7. STRUCTURE OF THE DIMER

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One of the reactions which distinguishes bistrifluoromethylketene from its unfluorinated analogs is that of dimerization catalyzed by triethylamine. This is the standard method for the preparation of dimers from ketenes, and in this case it leads not to cyclic compounds (β-diketones [1] or β-lactones [2]), but to a linear dimer, which will be discussed in detail below.

We have prepared bistrifluoromethylketene previously [3, 4], but its chemical structure was unknown. In the present work we synthesized it by two additional methods. We repeated the reaction which we have described [3] between 3,3,3-trifluoro-2-(trifluoromethyl)propionyl chloride and triethylamine and found that when an equimolecular mixture of the reactants was left at room temperature the main product was bistrifluoromethylketene dimer, which was accompanied by the monomer and 3,3,3-trifluoro-2-(trifluoromethyl)propionyl fluoride, the mechanism of whose formation has been discussed previously:

$$(CF_3)_2CH-COCl + NR_3 \xrightarrow{-NR_3\cdot HCl} (CF_3)_2C=$$
$$=CO \text{ (monomer + dimer)} \quad + (CF_3)_2CHCOF.$$

It was found that the same dimer is readily obtained by the action of triethylamine or cesium fluoride on perfluoromethacryloyl fluoride (I)*

$$\text{(I)} \quad CF_2=C(CF_3)-COF \xrightarrow{NR_3 \text{ or } CsF} (CF_3)_2C=CO - \text{dimer.}$$

In the case of the reaction of the acid fluoride (I) with cesium fluoride the dimer was not isolated, and after the reaction the mixture was immediately treated with methanol. For the moment we will not discuss the structure of the main reaction product (the product of the methanolysis of the dimer), but we must mention that there is also formed the known methyl 3,3,3-trifluoro-2-(trifluoromethyl)propionate (II), which results from the alcoholysis of unchanged acid fluoride and subsequent hydrofluorination of the perfluoromethacrylic ester:

$$CF_2=C(CF_3)-COF + CH_3OH \rightarrow [CF_2=C(CF_3)-COOCH_3 + HF] \rightarrow$$
$$\rightarrow (CF_3)_2CHCOOCH_3 \text{ (II)}.$$

In the reaction mixture we also found methyl 3,3-difluoro-3-methoxy-2-(trifluoromethyl)propionate (III), formed by the addition of alcohol at the double bond [5]:

$$CF_2=C(CF_3)-COF + 2CH_3OH \rightarrow CH_3OCF_2-CH(CF_3)-COOCH_3 \text{ (III)}.$$

When the reaction mixture was poured into water, (III) was hydrolyzed into dimethyl (trifluoromethyl)malonate (IV):

$$CH_3OCF_2-CH(CF_3)-COOCH_3 \xrightarrow{H_2O} CF_3CH(COOCH_3)_2 \qquad \text{(IV)}.$$

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*In this work the known perfluoromethacryloyl fluoride [5] was synthesized in high yield by a new method: the thermal rearrangement of bistrifluoromethylketene over glass wool at 440°:

$$(CF_3)_2C=CO \xrightarrow{\text{rearrangement}} CF_2=C(CF_3)-COF.$$

We carried out this work in collaboration with L. Alekseeva.

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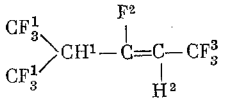
Bistrifluoromethylketene dimer is perfluoro(2,4,4-trimethylglutaconoyl) fluoride (V), which follows from its reactions and spectra (IR absorption maxima: double bond at 1690 and carbonyl groups at 1805 and 1835 cm^{-1}). We tried to establish the presence of a double bond by a chemical method, as well as by the IR spectrum, but, for example, we were unable to bring about the additon of chlorine to the dimer. The latter remained unchanged when irradiated in presence of chlorine in a sealed tube. The structure of the dimer was proved by its chemical transformations. Thus, under the action of water the acid fluoride (V) was converted into a mixture of cis- and trans-2H, 4H-heptafluoro-4-(trifluoromethyl)-2-pentenes (VI):

$$\text{(V)}\ FOC-C(CF_3)_2-CF=C(CF_3)-COF \xrightarrow{H_2O} [HOOC-C(CF_3)_2-CF=C(CF_3)-COOH] \xrightarrow{-2CO_2} (CF_3)_2CHCF=CHCF_3\ \text{(VI)}.$$

In the IR spectrum of the mixture of olefins the double bond absorption is at 1712 cm^{-1}, the shift toward shorter waves from the band in the spectrum of the acid fluoride (V) being due to the loss of the conjugation with the carbonyl group in the decarboxylation.

From the mixture of cis and trans pentenes we were able to isolate the isomer present in the greater amount. This was probably the isomer in which the hydrogen and fluorine atoms at the double bond are in the trans position, which follows from the value of the spin-spin interaction constant (31.2 Hz) (cf. [6]). The PMR spectrum of the trans pentene (VI), determined at 40 MHz, is given below, and it contains multiplet signals from the two protons, one of which H(2) shows up as a doublet of quartets with a chemical shift of 5.53 p.p.m. and the other H(1) — in the form of 8 lines, which can be interpreted as two superimposed heptets with a chemical shift of 3.61 p.p.m. (Fig. 1).



The chemical shift of the H(2) atom is in accord with data in the literature [7]. As regards the H(1) atom, we compared its position on the δ scale with the chemical shifts of tertiary hydrogen atoms in a number of well known substances containing a 2,2,2-trifluoro-1-(trifluoromethyl)ethyl group, the structures of which are well established. The spectra were determined at room temperature in CCl_4 with hexamethyldisiloxane as internal reference substance. Chemical shifts are given relative to tetramethylsilane (Table 1).

It will be seen from Table 1 that the shift in the proton H(1) toward stronger fields is observed in those compounds which contain a larger number of fluorine atoms in the α-position relative to the proton under consideration and is greatly dependent on the structure of the rest of the molecule. It is interesting that in methyl 2H-pentafluoro-2-(trifluoromethyl)propyl ether (compound 2) the constants for spin-spin interaction with the atoms F(1) and F(2) are equal, which we have also observed previously for compounds of analogous structure [12]. Unlike the acid fluoride (V), 2H,4H-heptafluoro-4-(trifluoromethyl)-2-pentene readily combines with a chlorine molecule with formation of a mixture of diastereoisomers* of 2H,4H-3,4-dichloroheptafluoro-2-(trifluoromethyl)pentane (VII):

$$(CF_3)_2CH-CF=CH-CF_3 \xrightarrow[h\nu]{Cl_2} (CF_3)_2CH-C^{*}FCl-C^{*}HCl-CF_3\ \text{(VII)}.$$

Further confirmation of the structure of bistrifluoromethylketene dimer is provided by the reaction with methanol, in which we obtained dimethyl perfluoro(2,4,4-trimethylglutaconate) (VIII):

$$FOC-C(CF_3)_2-CF=C(CF_3)-COF \xrightarrow{CH_3OH} CH_3OOC-C(CF_3)_2-CF=C(CF_3)-COOCH_3\ \text{(VIII)}.$$

The IR spectrum of this compound contains an absorption band due to a double bond conjugated with a CO group and a doublet due to carbonyl groups. The presence of a conjugated $C=C-C=O$ grouping also follows from the UV spectrum, and the PMR spectrum contains two signals from methyl protons.

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*It forms two peaks on the chromatogram.

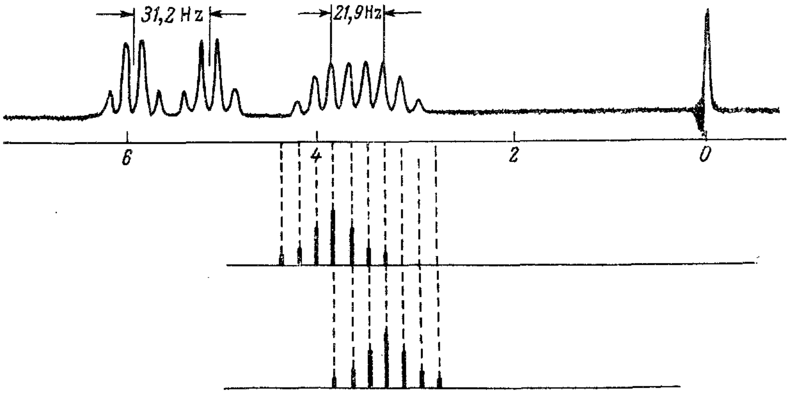


Fig. 1

For the purpose of assigning signals from these protons to the saturated or unsaturated end of the molecule we compared the NMR spectra of methyl esters of a number of saturated fluorinated acids with the spectrum of the perfluoromethacrylic ester (Table 2). The conditions under which these spectra were determined were the same as for the compounds containing the 2,2,2-trifluoro-1-(trifluoromethyl)ethyl group.

It will be seen from Table 2 that the signal from the methyl group of the unsaturated ester clearly lies in a stronger field, which is an argument in favor of an analogous assignment of the signals of the different methyl groups in the molecule of the diester (VIII). The resonance peak with $\delta = 3.96$ we attribute to an H(1) proton and that with $\delta = 3.83$ to an H(2) proton [$CH_3{}^1OOC-C(CF_3)_2-CF=C(CF_3)-COOCH_3{}^2$].

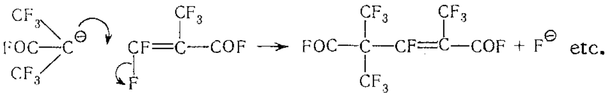
The mechanism of the formation of the linear dimer from bistrifluoromethylketene can be envisaged as follows. It is probable that dimerization is preceded by the isomerization of the ketene into the more stable perfluoromethacryloyl fluoride:

$$(CF_3)_2C=CO \rightarrow CF_2=C(CF_3)COF.$$

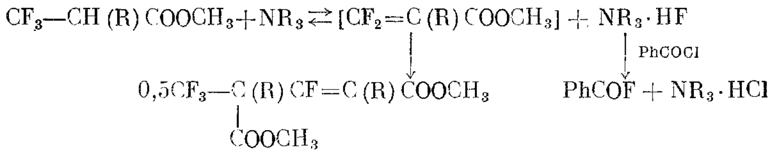
The active double bond of this compound is attacked by a fluoride ion, which may be provided by cesium fluoride or the product of the reaction of the unsaturated acid fluoride with triethylamine:

$$R_3N\ldots\rangle CF_2=C(CF_3)-COF \rightarrow F^{\ominus} + R_3\overset{\oplus}{N}-C_4F_5O$$
$$F^{\ominus}\ldots\rangle CF_2=C(CF_3)-COF \rightarrow (CF_3)_2\overset{\ominus}{C}-COF.$$

The anion of 3,3,3-trifluoro-2-(trifluoromethyl)propionyl fluoride formed at this stage again reacts with the unsaturated acid fluoride with replacement of the vinyl fluorine atom and formation of the dimer and a fluoride ion, which continues the reaction:



Thus, we are inclined to regard "bistrifluoromethylketene dimer" as being rather the dimer of perfluoromethacryloyl fluoride, and this unusual condensation is probably general for fluorine-containing acids with an active double bond. For example, in an attempt to prepare unsaturated esters from 3,3,3-trifluoro-2-(trifluoromethyl)propionic or (trifluoromethyl)malonic esters by the action of triethylamine in presence of benzoyl chloride* we isolated only the dimers of the expected unsaturated esters, one of which ($R=CF_3$) was found to be identical to the product obtained from the dimer (V) and methanol:



$$CF_3-CH(R)COOCH_3+NR_3 \rightleftarrows [CF_2=C(R)COOCH_3] + NR_3\cdot HF$$
$$\downarrow \qquad\qquad \downarrow{\scriptstyle PhCOCl}$$
$$0{,}5\,CF_3-\underset{\substack{|\\ COOCH_3}}{C}(R)CF=C(R)COOCH_3 \qquad PhCOF + NR_3\cdot HCl$$

$$R=CF_3\ (VIII)\ \text{and}\ COOCH_3\ (IX).$$

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*This method of dehydrofluorination was proposed by us recently for the synthesis of unsaturated compounds whose double bond is active toward nucleophilic reagents [14].

TABLE 1

No.	Compound	δ H (1)	JH (1) F (1)	JH (1) F (2)	δ CH_3	δ H (2)	JH (1) H (2)
1	$(CF_3{}^1)_2CH^1{-}CF^2{=}CH^2{-}CF_3{}^3$	3.61	7.1	21.9		5.53	
2	$(CF_3{}^1)_2CH^1{-}CF_2{}^2{-}OCH_3$	3.53	7.0	7.0	3.70		
3	$(CF_3{}^1)_2CH{-}COF^2$ [8]	4.15	7.3	2.0			
4	$(CH_3{}^1)_2CH^1{-}COOCH_3$	4.25	7.6		3.89		
5	$(CF^1{}_3)_2CH{-}CN$	4.45	6.6				
6	$(CF^1{}_3)_2CH{-}Br$ [9]	4.39	6.4				
7	$(CF_3{}^1)_2CH^1{-}CH^2O$ [10]	4.15	8.4			9.87	2.0
8	$(CF_3{}^1)_2CH^1CON(CH_3)_2$ [11]	4.60	7.1		3.0 and 3.17		

The spectral characteristics of tetramethyl perfluoro(1-butene-1,1,3,3-tetracarboxylate) (IX) are identical to those of dimethyl perfluoro(2,4,4-trimethylglutaconate).

EXPERIMENTAL

The identification of all liquid compounds with known samples was conducted by gas-liquid chromatography. IR spectra were determined in the IR Spectroscopy Laboratory of the Institute of Heteroorganic Compounds with UR-10 and IKS-14 spectrophotometers. UV spectra were determined with an SFD-2 instrument in the Karpov Physicochemical Institute by Sh. Nadzhimutdinov. PMR spectra were recorded by I. P. Amiton with a TsLA-55-35 NMR spectrometer with hexamethyldisiloxane as an internal reference; chemical shifts are given on the δ scale relative to tetramethylsilane. Analyses were carried out in the Microanalytical Laboratory.

Perfluoromethacryloyl Fluoride (I). Bistrifluoromethylketene (147 g) contained in a glass trap was allowed to evaporate freely at room temperature into a glass tube filled with glass wool and heated to 440° over a length of 500 mm. A feeble stream of dry nitrogen was passed simultaneously through this tube. Beyond the heated zone the acid fluoride formed was condensed in a down-sloping condenser connected to the heated tube, and it flowed into a receiver; unchanged ketene was collected in a cooled trap. When the ketene had evaporated completely, the traps at the start and end of the apparatus were interchanged, and the condensate was again evaporated. In the trap at the end of the apparatus a gas condensed which came over below —10° and was not unchanged ketene; it was not investigated. By distillation of the liquid through a column we isolated 89.6 g (61%) of (I), b.p. 51.5°, identical to the preparation described previously [5]. IR spectrum (ν_{max}, cm^{-1}): 705, 980, 1040, 1060, 1167, 1270, 1385, 1700, and 1833 (only strong absorption).

Perfluoro(2,4,4-trimethylglutaconoyl) Fluoride (V) (Bistrifluoromethylketene Dimer). a) A mixture of 1.4 g of (I) and two drops of dry triethylamine was sealed in a glass tube at —78°, and the mixture was allowed to warm up to room temperature. When the weakly exothermic reaction stopped, the tube was heated to 100° for 1 h; it was then cooled and opened, and the contents were distilled. We obtained 1.1 g (79%) of a liquid of b.p. 110-117°, which froze to crystals when cooled and was identical to known dimer (V) [3, 4].

IR spectrum (ν_{max}, cm^{-1}): 740 m; 755 w; 770 w; 785 w; 825 m; 985 s; 1000 s; 1025 s; 1075 m; 1120 m; 1170-1300 v.s; 1345 v.s; 1390 v.s; 1500 w; 1540 w; 1690 s; 1805 v.s; 1835 (shldr). NaCl prism.

b) A mixture of 1 g of (I) and 0.3 g of cesium fluoride was left in a sealed tube at 20° for two days, and it was treated with methanol and then diluted with water. 1.1 g of an oil was obtained, and this was found to consist of 13% of methyl 3,3,3-trifluoro-2-(trifluoromethyl)propionate (II), 8% of methyl 3,3-difluoro-3-methoxy-2-(trifluoromethyl)propionate (III) [5], 6% of dimethyl (trifluoromethyl)malonate (IV) [14], and 73% of dimethyl perfluoro(2,4,4-trimethylglutaconate) (VIII), identical to the substance described below.

IR spectrum of (II) (ν_{max}, cm^{-1}): 730 s; 785 m; 864 m; 922 w; 1020 s; 1110 v.s; 1126 v.s; 1170 s; 1250 v.s; 1315 v.s; 1370 v.s; 1450 m; 1773 v.s (CO). NaCl prism.

c) A round-bottomed flask at —78° was charged with 16.8 g of 3,3,3-trifluoro-2-(trifluoromethyl)-propionyl chloride, and an equimolecular amount of dry triethylamine was added cautiously. The mixture

TABLE 2

Compound	Ref. to prepn.	δ OCH_3	δ CCH_3
$C_3F_7COOCH_3$		4.01	
$(CF_3)_3C-COOCH_3$	[11]	3.99	
$(CF_3)_2CH-COOCH_3$		3.90	
$(CF_3)_2C(CH_3)-COOCH_3$*		3.85	1.69
$CF_3COCOOCH_3$	[13]	3.83	
$CF_2=C(CF_3)-COOCH_3$	[5]	3.68	

*This ester was synthesized by Yu. E. Aronov from the corresponding acid fluoride (see Experimental).

was allowed to warm up to room temperature gradually (in the course of 3 h) with the flask connected to a cooled (—78°) trap. The apparatus was then connected to a water pump, and all the liquid in the flask (11 g) was distilled in a boiling water bath into the trap. Distillation of the condensate through a column gave 2.3 g (18%) of bistrifluoromethylketene, b.p. 5-10°, 1.3 g (9%) of 3,3,3-trifluoro-2-(trifluoromethyl)-propionyl fluoride, b.p. 30-33°, 1.4 g (15%) of a mixture of cis- and trans-2H,4H-heptafluoro-4-(trifluoromethyl)-2-pentenes [see experiment with (VI)], b.p. 71-80°, and 4.0 g (32%) of bistrifluoromethylketene dimer, b.p. 105-110°.

Chlorination of Bistrifluoromethylketene Dimer. An equimolecular mixture of the dimer (1 g) and chlorine was irradiated in a sealed quartz tube for 5 h with a PRK-2 lamp at a distance of 10 cm. At the end of the irradiation the tube was cooled to —78°, opened, and heated to 50° to remove chloride. The residue was identified as unchanged dimer.

trans-2H,4H-Heptafluoro-4-(trifluoromethyl)-2-pentene (VI). With cooling a sufficient amount of bis-2-methoxyethyl ether was added gradually to a mixture of 0.95 g of (V) and 1 ml of water in a round-bottomed flask with a reflux condenser to make the mixture homogeneous. At the end of the exothermic reaction the mixture was heated at 70° for 15 min (until no more CO_2 came off — identified by gas-liquid chromatography) and diluted with water; the precipitated oil (0.8 g) was separated and washed with water, and it was distilled from its mixture with an equal volume of concentrated H_2SO_4. We obtained 0.42 g (62%) of the olefin (VI), b.p. 71-79°, which was shown chromatographically to a mixture of the cis and trans isomers in about 1 : 5 proportions. The trans isomer was isolated by means of preparative chromatography,* and it had b.p. 68.5° (752 mm) (micro method); n_D^{20} 1.285. Found %: C 27.3; H 0.79; F 72.0. $C_6H_2F_{10}$. Calculated %: C 27.3; H 0.76; F 72.0.

IR spectrum of the mixture of isomers (ν_{max}, cm^{-1}): 695 w; 720 s; 735 m; 748 w; 769 w; 794 m; 820 w; 850 w; 890 s; 920 s; 978 s; 1000 s; 1100 s; 1140-1340 v.s; 1395 m; 1685 (shldr); 1705 (shldr); 1712 s; 1757 (shldr); 2985; 3088; 3140.

PMR spectrum: $(CF_3^1)_2CH^1-CF^2=CH^2-CF_3^3$ δH(1) 3.61; δH(2) 5.53; JH(1)F(1) 7.12 Hz; JH(1)F(2) 21.9Hz; JH(2)F(2) 31.2Hz; JH(2)F(3) 7.2Hz.

(±)-2H,4H-3,4-Dichloroheptafluoro-2-(trifluoromethyl)pentane (VII). A mixture of 8.1 g of (VI) and 3.02 g of chlorine was irradiated in a sealed glass tube with UV (PRK-2 lamp) for 6 h. The tube was cooled to —78°, opened, and warmed to room temperature; hydrogen chloride was liberated. In the distillation of the liquid obtained (8.7 g) through a column we isolated 6.5 g (63%) of a fraction of b.p. 114-118° and n_D^{20} 1.3356, which was found to be a mixture of two diastereoisomers of the chlorinated product, which were not completely separated on the chromatogram. Found %: C 21.0; H 0.62; F 56.7. $C_6H_2F_{10}Cl_2$. Calculated %: C 21.5; H 0.60; F 56.7. The IR spectrum of the sample contained no absorption in the region 1450-2200 cm^{-1} at a layer thickness of 60 μ.

Dimethyl Perfluoro(2,4,4-trimethylglutaconate) (VIII). A mixture of 10.2 g of bistrifluoromethylketene dimer and 30 ml of absolute methanol was boiled in a flask with a reflux condenser for 2 h and then diluted with water. The precipitated oil was separated, dried with P_2O_5, and distilled. We obtained 7.5 g (69%) of the dimethyl ester (VIII), b.p. 71-75° (11 mm) and 175-178° (760 mm).

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*The work was carried out by R. V. Golovnya and A. V. Sklyarov with a Virus Gasofract 3000PR chromatograph.

A chromatographically pure sample had b.p. 75° (11 mm) and n_D^{20} 1.3570. Found %: C 31.4; H 1.68; F 49.4. $C_{10}H_6F_{10}O_4$. Calculated %: C 31.6; H 1.58; F 50.0.

IR spectrum (ν_{max}, cm^{-1}): 590 m; 630 w; 650-675 m (doublet), 710 w; 727 m; 745 s; 760 m; 930-945 w (doublet), 990 s; 1040 s; 1080 s; 1150-1340 v.s; 1440 s; 1675 s (C=C), 1760-1775 s (doublet CO). UV spectrum: in alcohol log ε_{max} 2.994 at 226 mμ; in hexane log ε_{max} 2.725 at 228 mμ. PMR spectrum: δCH_3 3.83 and 3.96 p.p.m. with ratio of intensities of 1:1.

17 g of benzoyl chloride was added dropwise in the course of 1 h to an equimolecular mixture of methyl 3,3,3-trifluoro-2-(trifluoromethyl)propionate (21.6 g) and triethylamine in a round-bottomed three-necked flask fitted with stirrer, dropping funnel, and reflux condenser. The mixture was heated in a water bath at 100° for 2 h and then diluted with 50 ml of water. The oil was separated and washed with hydrochloric acid, and the residue was refluxed with ethanol for 3 h. The solution was diluted with water, and the oil was separated, dried with magnesium sulfate, and distilled. We obtained 10.8 g (55%) of the dimethyl ester (VIII), b.p. 72-78° (9 mm), identical with the sample described above and 11.8 g of ethyl benzoate, b.p. 89-90° (9 mm).

Tetramethyl Perfluoro(1-butene-1,1,3,3-tetracarboxylate) (IX). In an analogous way, 10.4 g of benzoyl chloride was added to a mixture (equimolecular) of 19.7 g of methyl (trifluoromethyl)-malonate and 7.5 g of triethylamine, and the resulting mixture was heated at 60° for 3 h. It was treated with water and washed with hydrochloric acid; the oil was taken up in ether and dried with magnesium sulfate. Ether was driven off, and the residue was vacuum-distilled. We obtained 9 g (98%) of benzoyl fluoride, b.p. 27-45° (9 mm), identical to a known sample, and 6.2 g (47%) of the tetramethyl ester (IX), b.p. 152° (0.2 mm) and n_D^{20} 1.4291. Found %: C 40.0; H 3.32; F 22.1. $C_{12}H_{12}F_4O_8$. Calculated %: C 40.0; H 3.33; F 21.1.

IR spectrum (ν_{max}, cm^{-1}): 1030 m; 1055 s; 1083 s; 1170 s; 1210-1320 v.s; 1443 s; 1460 (shldr); 1475 (shldr); 1673 m (C=C), 1745-1775 v.s (CO). NaCl prism. PMR spectrum: δCH_3 3.76 and 3.97 p.p.m.

Methyl 3,3,3-Trifluoro-2-methyl-2-(trifluoromethyl)propionate. This was prepared in the usual way from 3,3,3-trifluoro-2-methyl-2-(trifluoromethyl)propionyl fluoride [15] and methanol in 64% yield; b.p. 98.5-99° (745 mm). Found %: C 32.3; H 2.31; F 50.2. $C_6H_6F_6O_2$. Calculated %: C 32.1; H 2.68; F 50.9.

IR spectrum (ν_{max}, cm^{-1}): 740 s; 765 m; 795 s; 885 s; 980 s; 1075-1325 v.s; 1400 m; 1450 s; 1600 w; 1760 v.s; 2100 v.w.

CONCLUSIONS

1. Unlike other known ketenes, bistrifluoromethylketene forms a linear dimer under the action of triethylamine.

2. A new reaction was discovered: the linear dimerization of functional derivatives of perfluoromethacrylic and (difluoromethylene)malonic acids.

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