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SYNTHESIS OF ALLENES CONTAINING GEMINAL TRIFLUOROMETHYL GROUPS

I.L. KNUNYANTS, L.A. ROZOV, Yu.V. ZEIFMAN and Yu.A. CHEBURKOV

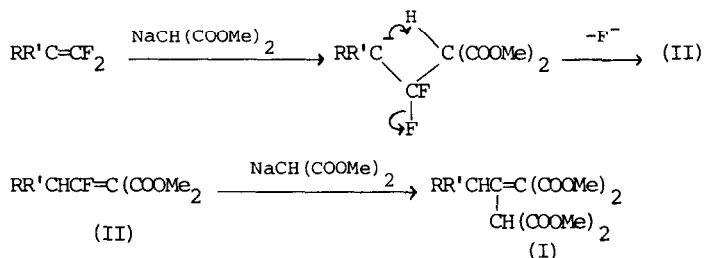
Institute of Organoelement Compounds, the U.S.S.R. Academy of Sciences,  
 Vavilova St., 28, Moscow 117312 (U.S.S.R.)

SUMMARY

Allenes  $(CF_3)_2C=C(COOMe)_2$  and  $(CF_3)_2C=C(COOEt)Ph$  were prepared by Cs-catalyzed condensation of octafluoroisobutene with dimethyl malonate and ethyl phenylacetate respectively. A stable salt  $[(CF_3)_2C:::CF:::C-(COOMe)_2]^-Cs^+$  is formed from  $(CF_3)_2C=C(COOMe)_2$  and CsF. Similar salts were prepared through the condensation of octafluoroisobutene with ethyl cyanoacetate and malononitrile. Allenes  $(CF_3)_2C=C=OMe_2$  and  $(CF_3)_2C=C=CHPh$  were synthesized by dehydrofluorination of olefines  $(CF_3)_2CHCF=CRR'$  under the action of octafluoroisobutene and CsF mixture; the latter allene has been isolated only as a cycloadduct with octafluoroisobutene.

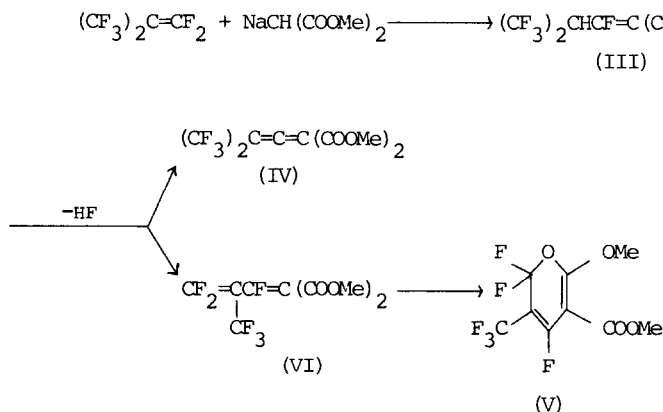
INTRODUCTION

We demonstrated previously [1,2] that a number of fluoroolefines reacted with dimethyl sodiomalonate to give polycarboxylic acid esters (I). Alkylidenemalonate (II) was evidently the intermediate reaction product, its fluorine atom being substituted by the malonate residue.

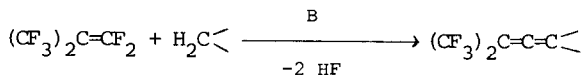


RR': F,F; F,Cl; F,CF<sub>3</sub>; COOMe, COOMe.

Quite another result was obtained in the similar reaction of dimethyl sodiomalonate with octafluoroisobutene (OFIB) [3]. In this case the intermediate alkylidenemalonate (III) undergoes dehydrofluorination. The resultant products were 1,1-bis(trifluoromethyl)-3,3-bis(carbomethoxy)-allene (IV) and 2,2,4-trifluoro-3-trifluoromethyl-5-carbomethoxy-6-methoxy-pyran (V); the latter was, evidently, formed through cyclization of the intermediate diene (VI).



The formation of allene (IV) in the reaction of OFIB with dimethyl sodiomalonate is of particular interest. The reaction is an example of the direct transformation of a fluoroolefin into an allene by replacement of two difluoromethylene fluorine atoms by a substituted methylene residue.



We know only one case of the use of such a reaction for an allene preparation: tetraphenylallene has been prepared from 1,1-diphenyl-2,2-dichloroethylene and diphenylmethane in the presence of sodium amide [4].

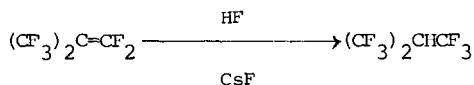
The study of OFIB condensation with dimethyl malonate under various conditions showed [3] that the best preparative method of allene (IV) formation is to carry out the process in the presence of  $\text{Et}_3\text{N} \cdot \text{BF}_3$  adduct. In this reaction the adduct acts both as a catalyst and a dehydrofluorinating agent (cf. ref. [5]). This reagent was also used to synthesize 1-

trifluoromethyl-1,3,3-tris(carbomethoxy) allene [2] as a result of dimethyl malonate condensation with methyl perfluoromethacrylate. However, attempts to extend this method for producing other allenes with geminal trifluoromethyl groups were unsuccessful. Thus, in the presence of  $\text{Et}_3\text{N}\cdot\text{BF}_3$  adduct OFIB does not react with ethyl phenylacetate, even under prolonged heating. Ethyl cyanoacetate reacts with OFIB and  $\text{Et}_3\text{N}\cdot\text{BF}_3$  under mild conditions, though the formation of a corresponding allene could not be detected in this case and only pyran was isolated.

In the present study we used cesium fluoride as a catalyst in the synthesis of allene by OFIB condensation with active methylene compounds. We also studied the synthesis of such allenes by dehydrofluorination of compounds  $(\text{CF}_3)_2\text{CHCF}=\text{CRR}'$  produced on the basis of OFIB reaction with  $\text{RR}'\text{CHMgX}$ -type Grignard reagents.

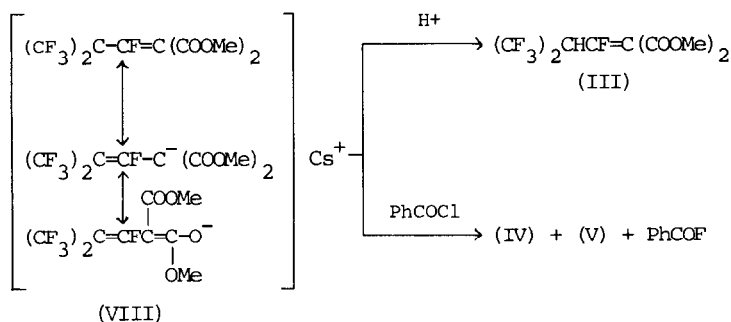
## RESULTS AND DISCUSSION

We have found that OFIB interaction with dimethyl malonate takes place in the presence of CsF catalytic quantities in monoglyme. Requirements for completion of the reaction are the OFIB excess and heating for 15 hours at 50 °C. The resultant products were allene (IV), pyran (V) and monohydroperfluoroisobutane. It is obvious that the reaction proceeds in the same manner as the OFIB interaction with dimethyl sodiomalonate, the function of the methylene component activator being performed by bases present in the reaction mixture - either by fluoride, or by the perfluoro-tert-butyl carbanion formed as a result of the reversible addition of  $\text{F}^-$  to OFIB [6]. The formation of  $(\text{CF}_3)_3\text{CH}$  shows that OFIB in this case behaves both as a substrate and as an HF acceptor. The latter evolves during the dehydrofluorination stages (cf. also ref. [7]).

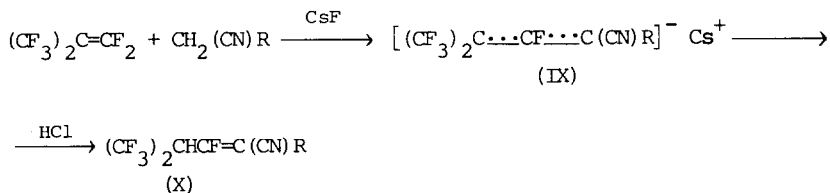


As should be expected, the OFIB reaction with ethyl phenylacetate, when catalysed by CsF, proceeds at an appreciable rate only under the more stringent conditions. Thus, heating of the reagents for 50 hours at 100 °C gives only 50% ethyl phenylacetate conversion, whereas in the presence





OFIB interaction with ethyl cyanoacetate and malononitrile in the presence of equimolar amounts of CsF leads to the same result. This reaction has yielded solutions of similar salts (IX), whose structure was confirmed by IR and  $^{19}\text{F}$  NMR spectra, as well as by transformation into unsaturated nitriles (X) caused by the action of anhydrous HCl.



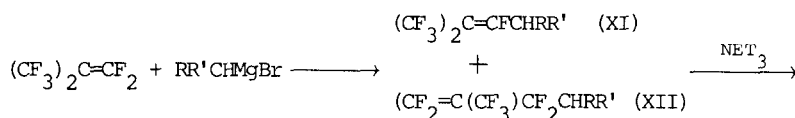
R: COOEt (a), CN (b).

It should be pointed out that the fore-mentioned ability to form stable adducts with CsF observed for certain fluorine-containing allenes is a general property of highly electrophilic unsaturated fluorine compounds. Indeed,  $\text{COF}_2$  [8],  $(\text{CF}_3)_2\text{C}=\text{O}$  [9],  $\text{CF}_3\text{N}=\text{CF}_2$  [10],  $\text{CF}_3\text{NOO}$  [11] and  $(\text{CF}_3)_2\text{C}=\text{C}=\text{NSO}_2\text{Ph}$  [7] are known to give stable adducts with CsF. Recently tetrakis-(trifluoromethyl)allene and bis(trifluoromethyl)ketene were also shown to give stable adducts with CsF [12].

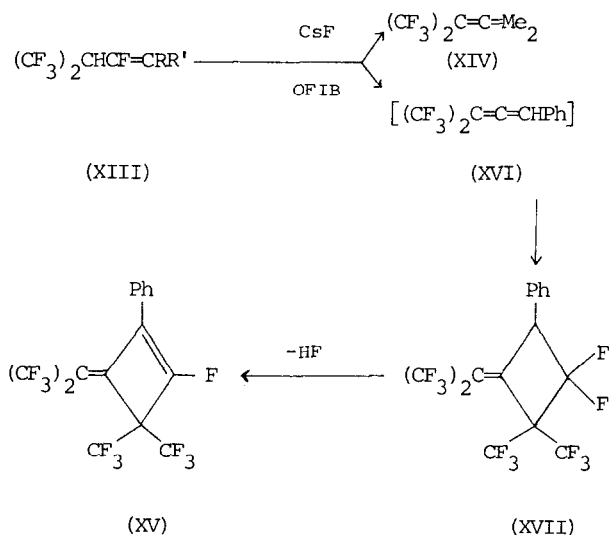
Attempts to prepare corresponding allenes by thermal decomposition of adducts (IX) or by treating them with benzoyl chloride proved unsuccessful. In all cases only intensive tar formation was observed. Reaction between OFIB and ethyl cyanoacetate in the presence of catalytic amounts of CsF did not give 1,1-bis(trifluoromethyl)-3-cyano-3-carbethoxyallene either. In this case only intermediate unsaturated nitrile (Xa) was identified in the reaction mixture. The reasons for the unsuccessful synthesis of allenes with the CN group are not completely clear; it may be due to their high reactivity (cf. ref. [13]).

Another method of synthesizing allenes with geminal trifluoromethyl groups is based on the OFIB reaction with Grignard reagents. We demonstrated earlier [14] that this reaction gives a mixture of vinyl (XI) and allyl (XII) substitution products. Under the action of bases these products both isomerize into olefines (XIII) with the  $(CF_3)_2CH$  group. Such a sequence of transformations allows one to obtain the initial compounds for the synthesis of allenes which cannot be prepared by OFIB condensation with poor CH-acids. For instance, diphenylmethane does not react with OFIB in the presence of CsF, even at 150 °C.

Thus, the reaction of olefines (XIIIa) with OFIB and CsF results in dehydrofluorination producing 1,1-bis(trifluoromethyl)-3,3-dimethylallene (XIV) with a 67% yield. The reaction of olefine (XIIIb) with OFIB and CsF is more complicated. It yields a mixture of products, from which fluorine-containing cyclobutene (XV) was isolated; it could result from cycloaddition of OFIB to the corresponding allene (XVI) and subsequent cycloadduct (XVII) dehydrofluorination.



RR': Me, Me(a); H, Ph(b)



Products of type (XVII) were not observed in other similar reactions studied in the present work. However, this kind of OFIB cycloaddition to bis(trifluoromethyl)ketenimines is known to take place under conditions of nucleophilic catalysis [15].

It should be pointed out that some reactions are known which lead to allenes with geminal trifluoromethyl groups. Such allenes were obtained, for instance, from bis(trifluoromethyl)ketene and triethyl phosphite [16] or [17], and also by the ketene reaction with ethoxyacetylene [18] or dimethylketene [19] through decomposition of corresponding cycloadducts. The allenes were prepared also by fluorination of 1,1,1-trifluoro-2-trifluoromethyl-3-butyn-2-ol with sulfur tetrafluoride [20] or by dehydrofluorination of the products of perfluoro-2-iodopropane addition to vinylidene fluoride [21]. 1,1-Bis(trifluoromethyl)-3,3-dichloroallene obtained from OFIB and chloroform was isolated as a cycloadduct with furan [22]. The suggested methods therefore substantially expand the scope of the available methods for the synthesis of allenes.

#### EXPERIMENTAL

$^1\text{H}$  NMR spectra were recorded on a Perkin-Elmer R-12 spectrometer at 60 MHz; chemical shifts are given in  $\delta$ -values from  $(\text{CH}_3)_4\text{Si}$  (external standard).  $^{19}\text{F}$  NMR spectra were recorded on a Hitachi H-6013 instrument at 56.46 MHz; chemical shifts are given in ppm from  $\text{CF}_3\text{COOH}$  (external standard). IR spectra were recorded on an UR-10 spectrometer.

#### 1,1-Bis(trifluoromethyl)-3,3-bis(carbomethoxy)allene (IV)

A mixture consisting of freshly calcined CsF (1.0 g), dimethyl malonate (9.0 g) and OFIB (72.0 g) was heated at  $50^\circ\text{C}$  in dry monoglyme (60 ml) in a sealed glass tube for 15 h. The unreacted OFIB,  $(\text{CF}_3)_3\text{CH}$  and the solvent were distilled off in vacuo; distillation of the residue gave 8.9 g (43%) of allene (IV), b.p.  $41 - 43^\circ\text{C}/3 \text{ mmHg}$  (cited in ref. [3]:  $42 - 44^\circ\text{C}/3 \text{ mmHg}$  and 2.0 g (10%) of pyran (V), b.p.  $60 - 63^\circ\text{C}/0.05 \text{ mmHg}$  (cited in ref. [3]:  $61 - 62^\circ\text{C}/0.05 \text{ mmHg}$ ).

Reaction of allene (IV) with CsF

A mixture consisting of allene (IV) (1.1 g), CsF (0.57 g) and dry monoglyme (10 ml) was stirred at  $\sim 20^{\circ}\text{C}$  until completely homogenized. A salt solution (VIII) was obtained which had adsorption bands at 1605, 1630 (C=C) and 1705 (C=O)  $\text{cm}^{-1}$ .

$^{19}\text{F}$  NMR spectrum: a multiplet  $\text{CF}_3$ , CF at -21.3 (4F) and a multiplet  $\text{CF}_3$  at -18.2 (3 F).

Reactions of OFIB with active methylene compounds in the presence of equimolar amounts of CsF(a) With dimethyl malonate

OFIB (35.0 g) was introduced into a suspension of CsF (5.75 g) in dry monoglyme (80 ml) with vigorous stirring. In 20 minutes a solution of dimethyl malonate (5.0 g) in dry monoglyme (20 ml) was added dropwise at  $\sim 0^{\circ}\text{C}$ ; the reaction mixture was stirred at this temperature for 2 h and then kept at  $\sim 20^{\circ}\text{C}$  until the OFIB content stopped diminishing ( $\sim 36$  h). Volatile products and about 30 ml of the solvent were distilled off in vacuo. These residue was a salt solution (VIII) (NMR and IR spectra see above).

(b) With ethyl cyanoacetate

In a manner similar to that described above, reaction of CsF (6.75 g), OFIB (45.0 g) and ethyl cyanoacetate (5.0 g) in dry monoglyme (100 ml) yielded a salt solution (IXa).

$^{19}\text{F}$  NMR spectrum: a multiplet  $\text{CF}_3$  at -23.8 (3 F), a multiplet  $\text{CF}_3$  at -21.3 (3 F) and a multiplet CF at -5.8 (1 F). IR spectrum: 1600 and 1630 (C=C), 2190 (CN)  $\text{cm}^{-1}$ .

(c) With malononitrile

In a similar manner, reaction of CsF (6.9 g), OFIB (40.0 g) and malononitrile (3.0 g) in dry monoglyme (100 ml) yielded a salt solution (IXb).

$^{19}\text{F}$  NMR spectrum: a multiplet  $\text{CF}_3$  at -25.0 (6 F) and a multiplet CF at +2.6 (1 F). IR spectrum: 1605 (C=C), 2180 and 2200 (CN)  $\text{cm}^{-1}$ .



Reactions of salts (VIII), (IXa) and (IXb)

(a) With HCl

A salt solution (VIII), prepared from CsF (5.75 g), OFIB (35.0 g) and dimethyl malonate (5.0 g) in dry monoglyme (100 ml), was evaporated in vacuo till dry. Dry  $\text{CH}_2\text{Cl}_2$  (100 ml) was added to the solid residue, and dry HCl was passed with stirring for one hour into the resultant suspension. The precipitate was filtered off and distillation of the residue yielded 7.1 g (60%) of dimethyl 1,3,3,3-tetrafluoro-2-trifluoromethylpropylidene-malonate (III), b.p. 79 - 80 °C/11 mmHg (cited in ref. [23]: 77 °C/11 mmHg).

In a manner similar to that described above, reaction of salt (IXa) gave 61% of ethyl 1,3,3,3-tetrafluoro-2-trifluoromethylpropylidene-cyanoacetate (Xa), b.p. 52 - 53 °C/3 mmHg,  $n_D^{20}=1.3880$ . Analysis: C, 36.8; H, 2.04; F, 45.4; N, 4.97%.  $\text{C}_9\text{H}_6\text{F}_7\text{O}_2\text{N}$  requires C, 36.9; H, 2.05; F, 45.4; N, 4.78%.

$^1\text{H}$  NMR spectrum: 1.2 (triplet  $\text{CH}_3$ ); 4.2 (quartet  $\text{CH}_2$ ); 5.9 (doublet of heptets CH);  $J(\text{CH}_3-\text{CH}_2)=7.7$  Hz;  $J(\text{CH}-\text{CF})=29.2$  Hz.  $^{19}\text{F}$  NMR spectrum: a triplet  $(\text{CF}_3)_2\text{CH}$  at -14.6 and a multiplet CF at -5.4;  $J(\text{CF}_3-\text{CH})=J(\text{CF}_3-\text{CF})=8.0$  Hz. IR spectrum: 1660 (C=C), 1740 (C=O), 2230 (CN)  $\text{cm}^{-1}$ .

A similar reaction of salt (IXb) yielded 71% of 1,3,3,3-tetrafluoro-2-trifluoromethylpropylidene-malononitrile (Xb), b.p. 141 - 142 °C (cited in ref. [24]: 138 - 140 °C).

(b) With PhCOCl

Salt solution (VIII) was treated with an equimolar amount of freshly distilled benzoyl chloride. The reaction mixture was stirred for 3 h at  $\sim 20$  °C, the solvent was distilled off in vacuo, and the residue distillation yielded a fraction with b.p. 40 - 120 °C/3 mmHg, comprised of, according to GLC data, 30% PhCOF, 40% allene (IV), 10% ester (III), 5% PhCOCl and 5% pyran (V).

1,1-Bis(trifluoromethyl)-3-phenyl-3-carbethoxyallene (VII)

OFIB (90.0 g) was introduced into a suspension of CsF (19.0 g) in dry monoglyme (75 ml) with vigorous stirring. After 20 minutes ethyl phenylacetate (20.6 g) was added dropwise, stirring was continued for another

2 h, and then the reaction mixture was allowed to stand for 12 h. Volatile products and the solvent were distilled off in vacuo, a mixture of dry ether (30 ml) and dry chloroform (30 ml) was added, and the precipitate was filtered off. Distillation of the residue gave 26.7 g (63%) of allene (VII), b.p. 77 - 78 °C/3 mmHg,  $n_D^{20}$  = 1.4620. Analysis: C, 51.1; H, 3.10; F, 35.5%.

$C_{14}H_{10}F_6O_2$  requires C, 51.8; H, 3.09; F, 35.2%.

$^1H$  NMR spectrum: 0.5 (triplet  $CH_3$ ); 3.5 (quartet  $CH_2$ ); 6.7 (multiplet Ph);  $J(CH_3-CH_2)$  = 6.7 Hz.  $^{19}F$  NMR spectrum: a singlet  $CF_3$  at -17.5. IR spectrum: 1740 (C=O), 1970 (C=C)  $cm^{-1}$ .

### 2-Methyl-3,5,5,5-tetrafluoro-4-trifluoromethylpentene-2 (XIIIa)

To 23.6 g of a mixture consisting of 1,1,1,3-tetrafluoro-2-trifluoromethyl-4-methylpentene-2 (XIa) (70%) and 1,1,3,3-tetrafluoro-2-trifluoromethyl-4-methylpentene-1 (XIIa) (30%) (prepared as described in ref. [14]) triethylamine (10.7 g) was added and the mixture refluxed for 25 h and poured into water; the lower oil layer was taken into ether, washed with 5% HCl and dried with  $CaCl_2$ . After the removal of the ether the residue was distilled over an equal volume of concentrated  $H_2SO_4$  in vacuo (3 mmHg) into a trap (-78 °C). Redistillation gave 14.7 g of a fraction with b.p. 92 - 97 °C, comprised of according to GLC data, 90% olefine (XIIIa) and 10% allene (XIV).

For (XIIIa):  $^1H$  NMR spectrum: 1.4 (singlet  $CH_3$ ); 1.3 (doublet  $CH_3$ ); 3.9 (doublet of heptets CH);  $J(CH_3-CF)$  = 8.0;  $J(CH-CF_3)$  = 8.0;  $J(CH-CF)$  = 26.6 Hz.  $^{19}F$  NMR spectrum: a triplet  $CF_3$  at -11.5; a multiplet CF at + 48.0;  $J(CF_3-CH) = J(CF_3-CF) = 8.0$  Hz. IR spectrum: 1720 (C=C)  $cm^{-1}$ .

### 1,1-Bis(trifluoromethyl)-3,3-dimethylallene (XIV)

OFIB (9.0 g) was introduced into a suspension of CsF (3.4 g) in dry diglyme (25 ml) with vigorous stirring, and in 20 minutes a diglyme solution (10 ml) of pentene (XIIIa) (5.0 g) contained an admixture of 10% allene (XIV) was added dropwise. The stirring was continued at  $\sim 20$  °C for 3 h and volatile products were removed into a trap (-78 °C) in vacuo (3 mmHg). The contents of the trap were washed with warm HCl and with water, then

dried with  $\text{CaCl}_2$  and distilled to give 3.1 g (67%) of pure allene (XIV), b.p.  $85 - 87^\circ\text{C}$  (cited in ref. [19]:  $45 - 50^\circ\text{C}/195\text{ mmHg}$ ).

$^1\text{H}$  NMR spectrum: 1.5 (singlet  $\text{CH}_3$ )  $^{19}\text{F}$  NMR spectrum: a singlet  $\text{CF}_3$  at  $-15.0$ . IR spectrum:  $2000\text{ (C=C=C)}\text{ cm}^{-1}$ .

1-Phenyl-2-fluoro-3,3-bis(trifluoromethyl)-4-hexafluoroisopropylidenecyclobutene (XV)

OFIB (20.0 g) was introduced into a suspension of CsF (4.0 g) in dry monoglyme (50 ml) with vigorous stirring. On completion of the exothermal reaction the mixture was cooled to  $0^\circ\text{C}$  and a solution of 1-phenyl-2,4,4,4-tetrafluoro-3-trifluoromethylbutene-1 (XIIIb) (7.1 g) (prepared as described in ref. [14]) in dry monoglyme (10 ml) was added to it dropwise. In 24 h the volatile products and solvent were distilled off in vacuo. The residue distillation yielded 6.4 g of a fraction with b.p.  $70 - 75^\circ\text{C}/3\text{ mmHg}$ , containing 80% of cyclobutene (XV). By preparative GLC (chromatograph Carlo Erba, column QF-1, carrier gas He,  $130^\circ\text{C}$ ) pure cyclobutene (XV) was isolated, b.p.  $61 - 62^\circ\text{C}/3\text{ mmHg}$ ,  $n_D^{20} = 1.4085$ . Analysis: C, 41.7; H, 1.00; F, 57.3%.  $\text{C}_{15}\text{H}_5\text{F}_{13}$  requires: C, 41.6; H, 1.16; F, 57.3%.

$^1\text{H}$  NMR spectrum: 7.1 (singlet Ph).  $^{19}\text{F}$  NMR spectrum: a quartet  $\text{CF}_3$  at  $-20.6$ ; a multiplet  $\text{CF}_3$  at  $-15.8$ ; a doublet of quartets  $\text{CF}_3$  at  $-10.5$ ; a heptet  $\text{CF}$  at  $+12.4$ ;  $J(\text{CF}_3-\text{CF}_3) = J[(\text{CF}_3)-(\text{CF}_3)_2] = 10.0$ ;  $J[(\text{CF}_3)_2\text{C}-\text{CF}] = 4.0\text{ Hz}$ . IR spectrum:  $1610, 1660\text{ cm}^{-1}$ .

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