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REACTION OF POLYFLUOROALKENES WITH DIPHENYLACETONITRILE CARBANION IN A TWO-PHASE SYSTEM

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SUMMARY

The carbanion of diphenylacetonitrile (DPA) generated in a catalytic two phase system reacts with polyfluoroalkenes to give addition-elimination products. Reaction of DPA with some polyfluorochloroalkanes was studied; elimination, addition-elimination and S_N2 reactions were observed.

INTRODUCTION

The addition of a variety of O,N and S nucleophiles (alcoholates, phenolates, thiolates etc.) to polyfluoroalkenes (PFA) giving rise to the formation of new carbon-heteroatom bonds was studied in detail [1]. In contrast to the above there are only few papers reporting addition of carbanions to PFA [2-8] although the fluoride ion catalysed oligomerisation of tetrafluoroethylene and hexafluoropropene obviously occurs *via* the nucleophilic addition of perfluoroalkylcarbanions to the parent olefins [9,10]. Examples of addition of carbanions to PFA include a reaction of chlorotrifluoroethylene with sodium dimethyl malonate [4] and organolithium and organomagnesium reagents [2,3,5-8]. There are also no reports on the application of the two-phase systems in reactions of organic anions with PFA, although those systems proved to be very efficient and convenient for a great variety of reactions of organic anions [11].

In a preliminary experiment benzyl alcohol was subjected to a reaction with chlorotrifluoroethylene 1a in the presence of concentrated aqueous sodium hydroxide and tetrabutyl ammonium hydrogen sulfate (TBAH) as a catalyst giving the expected addition product *viz* benzyl-2-chloro-1,1,2-trifluoroethylether 2a in a high yield. These conditions were also effective for the addition of n-butyl alcohol to 1a giving ether 2b. Ethers 2a and 2b were earlier obtained in the reaction of the corresponding alcohols with 1a in the presence of their alcoholates [12].

Another preliminary experiment has shown that the solid-liquid two-phase system involving anhydrous potassium carbonate as a base [13] is effective in the reaction of diethyl malonate with 1a; tetraethyl 2-(chlorofluoromethyl)-1-propene-1,1,3,3-tetracarboxylate 3 a product analogous to that obtained by Rozov [4]was formed in this reaction.

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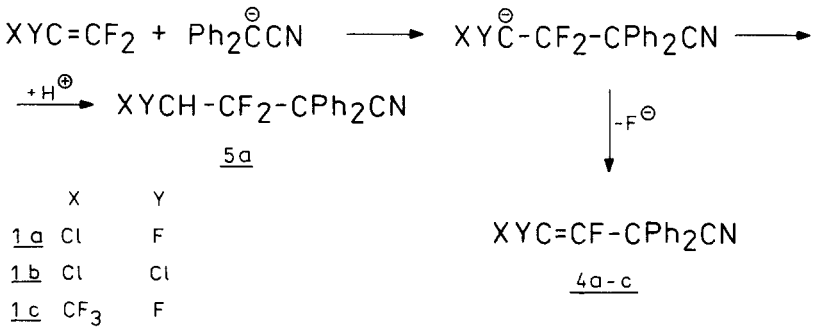
Derivatives of phenylacetonitrile which are easily deprotonated, giving highly nucleophilic carbanions [11,14] were chosen in our studies of the reactions of PFA with carbanions in the catalytic two-phase system.

RESULTS AND DISCUSSION

Reactions of phenylacetonitrile and 2-phenylbutyronitrile with chlorotrifluoroethylene 1a and hexafluoropropene 1c conducted in the presence of concentrated aqueous sodium hydroxide and TBAH in a variety of solvents (benzene, acetonitrile) failed. The alkenes were polymerized, whereas the nitriles were recovered almost quantitatively.

On the contrary, diphenylacetonitrile (DPA) reacted under these conditions with 1a-c in the expected way; the carbanion adds regiospecifically to form more stable fluorinated carbanions being subsequently stabilized by elimination of the fluoride ion to give products 4a-c. The overall stoichiometry corresponds to the vinylic substitution of the fluorine atoms. In the reaction of DPA with 1a stabilization of the intermediate carbanion occured also via protonation leading to the parallel formation of the addition product 5a.



The ratio of products 4a and 5a depends to some extent upon the conditions. The reaction carried out in acetonitrile or DMF in the presence of concentrated aqueous sodium hydroxide or potasium carbonate gave exclusively or mainly 5a. The same reaction in benzene resulted in the formation of 4a and 5a in the ratio of about 2.5.

In the reaction of DPA with dichlorodifluoroethylene 1b the situation was complicated by the fact that the available alkene was a mixture of three isomers: 1,1-dichloro-2,2-difluoroethylene and cis and trans 1,2-dichloro--1,2-difluoroethylenes in a 1:1:1 ratio (integrated ^{19}F NMR estimate; chemical shifts are 88.6; 112.7; and 105.2 ppm, respectively [15]). The reaction resulted in the formation of a single substitution product. Its ^{19}F NMR spectrum showed a signal due to a non-coupled fluorine atom. The yield of the product calculated on the original alkenes mixture never exceeds 30% suggesting that only one of the isomeric alkenes entered the reaction. Analysis of the ^{19}F NMR spectra of the mixture of dichlorodifluoroethylenes

before and after the reaction showed that the alkene ratio has changed from the initial value of 1:1:1 to 0.1:1:1. These data indicated unambigously that the reaction occured only with 1,1-dichoro-2,2-difluoroethylene 1b and so the product is 2,2-diphenyl-3-fluoro-4,4-dichlorobutene nitrile 4b. Variations of solvents and the reaction temperature had no influence on this result.

The above results proved the general rule which says that the isomers of PFA containing terminal difluoromethylene moiety are the most reactive towards nucleophiles. This regioselectivity is favoured also due to the formation of reasonably stabilized carbanion $CF_2R\text{-}\bar{C}Cl_2$.

The reaction of DPA with perfluoropropene proceeded regio- and stereospecifically as an addition-elimination reaction to give trans-1,1--diphenyl-2,3,4,4,4-pentafluoropentene nitrile 4c.

We have also studied reactions of DPA with such chlorofluoroalkanes which in basic conditions can eliminate hydrogen chloride to form PFA. Here the reaction can follow two pathways: direct S_N2 type nucleophilic substitution or initial elimination followed by addition to PFA generated in situ.

The reaction of 2,3-dichloro-1,1,1-trifluoropropene 6 with DPA in the catalytic two-phase system resulted in the formation of compound 8 as the main product. The reaction apparently occurs via initial elimination of hydrogen chloride to form alkene 7 [16] which adds the DPA carbanion giving (ii). The latter is stabilized via elimination of the fluoride ion to give a product of allylic substitution 8. In acetonitrile the DPA carbanion reacts also directly with 6 to give 9. The S_N2 pathway is supported by the fact that the reaction of DPA with alkene 7 gave no traces of 9. At higher temperature and in the presence of an excess of DPA the reaction gave product 10, which is obviously formed as a result of subsequent addition of the DPA carbanion to 8 followed by elimination of the fluoride ion and hydrogen cyanide.

Dependence of the product distribution on the reaction conditions is shown in Table 1.

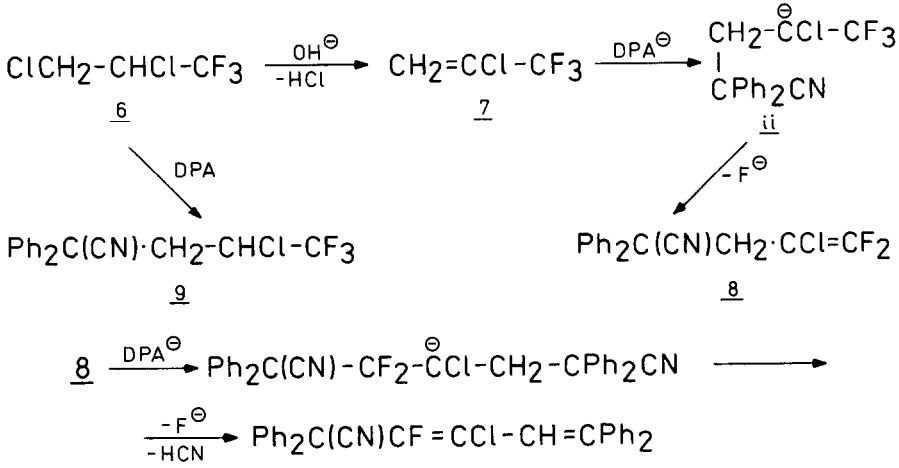


TABLE 1
Reaction of DPA with compounds 6 and 7 in benzene

6 : DPA [a]	Temperature (°C)	Time (h)	Total yield [b] (%)	Product composition % [c]		
				8	9	10
2 : 3	30	1	85	91	5	4
2 : 3 [d]	36	1.5	87	68	2	30
1 : 1	0 - 5	2	29	99	-	traces
1 : 1 [e]	0 [f]	0.25 [g]	81	66	30	4
	30	2				
2 : 3	25 [f]	0.25 [g]	95	50	4	46
	80	0.25				
1 : 2	24	2	96	83	8	9
7 [h] : DPA						
1 : 3	23	0.5	20	traces	-	99
1.4 : 1	23	0.5	25	73	-	27
1 : 2	25	0.5	20	46	-	54

[a] molar ratio, [b] yields are related to 6, [c] based on integrated ^{19}F NMR spectra, [d] 50% aqueous sodium hydroxide was added dropwise into a mixture of reagents, [e] CH_3CN was used as a solvent, [f] temperature at which 6 was added, [g] time of addition, [h] compound 7 was obtained by dehydrochlorination of 6 in an alkaline medium.

The reaction of DPA with 2,3-dichloro-1,1,1,4,4,4-hexafluorobutane 11 gave products 14 and 17. The first step of the reaction is the elimination of hydrogen chloride from 11 yielding alkene 12 and subsequently alkyne 13. The addition of DPA to alkyne 13 resulted in the formation of alkene 14, whereas the reaction with alkene 12 was more complicated. The addition - allylic elimination leads apparently to alkene 15 which eliminates another molecule of hydrogen chloride to form 16. Subsequent addition of DPA anion to 16 gives 2,3-disubstituted tetrafluorobutadiene 17.

TABLE 2

M.p. , B.p. and elemental analyses of compounds 4a-c, 5a, 8-10, 14, 17

Compound		M.p.	B.p.	Analyses (%)									
R = Ph_2CCN		(°C)	(°C/mmHg)	Calculated					Found				
nr	formula			C	H	N	F	Cl	C	H	N	F	Cl
4a	CFCl=CFR		123-5/0.2	66.3	3.5	4.8	13.1	12.3	66.4	3.5	4.6	13.3	12.3
4b	CCl_2=CFR	71-2		62.8	3.3	4.6	6.2	23.2	62.8	3.1	4.6	6.3	23.2
4c	CF_3-CF=CFR		134-6/3	63.2	3.1	4.3	29.4	-	63.1	3.0	4.4	29.3	-
5a	CHFCl-CF_2R	94		62.0	3.6	4.5	18.4	11.5	62.0	3.5	4.5	18.3	11.3
8	CF_2=$CClCH_2$R	62-3		67.2	4.0	4.6	12.5	11.7	67.4	3.9	4.9	12.7	11.7
9	CF_3-CHCl-CH_2R [a]		117-20/0.2	63.1	4.1	4.4	17.6	11.0	63.8	3.8	4.2	16.5	11.4
10	RCF=CCl-CH=CPh_2 [a]		140-5/0.2 decomposition	80.1	4.7	3.1	4.2	7.9	80.5	5.0	2.9	4.3	7.8
14	CF_3CH=CRCF_3	79-80		60.9	3.1	3.9	32.1	-	60.7	3.1	3.7	32.0	-
17	CF_2=CR-CR=CF_2	246		75.6	4.0	5.5	14.9	-	75.4	3.8	5.4	15.0	-

[a] compounds 9 and 10 were contaminated with trace amounts of DPA and of compound 8

TABLE 3

^{1}H and ^{19}F NMR spectra of compounds 4a-c, 5a, 8-10, 14, and 17 (in CCl_4)

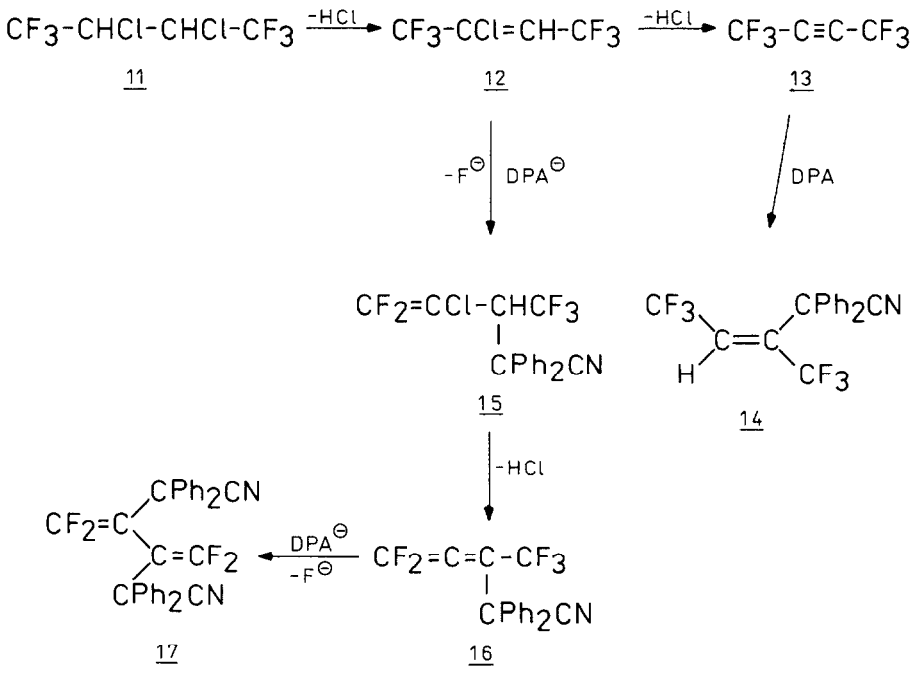
Compound R=Ph_2CCN	Chemical shifts δ(ppm) [a]	Chemical shifts ϕ(ppm) [b]	coupling constant J(Hz)
$CFCl{=}\overset{\alpha}{C}F\overset{\beta}{}R$ 4a	Ph 7.50 (bs)	F_α and F_β 110 (d) and 138 (d)	$^{3}J(FF) = 142.0$
$CCl_2{=}CFR$ 4b	Ph 7.35 (s)	F 90.8 (s)	
$CF_3\overset{\alpha}{C}F{=}\overset{\beta}{C}FR$ 4c	Ph 7.30 (bs)	CF_3 67.0 (dd) F_α 158.8 (ds) F_β 134.6 (dq)	$^{3}J(C\underline{F}_3F) = 10.0$ $^{3}J(F_\alpha F_\beta) = 139.0$ $^{4}J(C\underline{F}_3F) = 22.0$
$CHFCl\text{-}\overset{\alpha}{C}F_2R$ 5a	Ph 7.40 (s) H 5.66-6.33 (m)	F_α 148.5 (ddd) CF_2 107.0, 113.0 (AB pattern)	$^{2}J(FH) = 46.3$ $^{2}J(C\underline{F}_2) = 263.3$ $^{3}J(C\underline{F}_2H) = 13.3, 2.2$ $^{3}J(F_\alpha C\underline{F}_2) = 13.4, 16.4$

CF_2=CCl-CH_2R 8	Ph 7.50 (bs) CH_2 3.36 (dd)	CF_2	85.5 90.3 (AB pattern)	$^2J(CF_2)$ = 34.4 $^4J(HF)$ = 1.7
CF_3-CHCl-CH_2R 9	Ph 7.20-7.70 (m) H 3.95-4.95 (m) H 2.98-3.18 (m)	CF_3	75.1 (d)	$^3J(H_\alpha H_\beta)$ = 7.0 $^3J(CF_3H_\alpha)$ = 7.4
Ph_2C=CH-CCl=CFR 10	Ph 7.0 -8.0 (m) H 3.63 (d)	CF	94.7 (d)	$^4J(HF)$ = 2
CF_3-CH=CR-CF_3 14	Ph 7.35 (bs) CH 6.70 (q)	F_α F_β	56.4 (dm) 60.8 (bs)	$^3J(F_\alpha H)$ = 9.5 $^5J(F_\alpha F_\beta)$ = 2
CF_2=CR-CR=CF_2 [c] 17	Ph 6.80-7.40 (m)	F_α and F_β	68.2 and 69.2 (m)	$^2J(FF)$ = 12.0

s - singlet, bs - broad singlet, d - doublet, t - triplet, q - quartet, m - multiplet

[a] relative to internal TMS, [b] relative to internal CCl_3F (positive upfield), [c] in $(CD_3)_2CO$

It was shown in a separate experiment, that the reaction of DPA with hexafluorobutyne 13 gave no compound 17, and so the reaction pathway may be as follows:



Structures of all new compounds were established on the basis of elemental analysis (Table 2) and ^{1}H, ^{19}F NMR, IR, and MS spectral data.

^{1}H and ^{19}F NMR spectra of all compounds are fully consistent with the structure (Table 3).

Signals of geminal fluorine in the terminal CF_2 groups followed the typical AB pattern. Structures of compounds 4a and 4c were confirmed by coupling constant values typical for trans fluorine atoms and for fluorine cis to the CF_3 groups. In the ^{19}F NMR spectrum of 14 a long-range coupling between the CF_3 groups was observed; the coupling constant ($^{5}J(FF)$ = ca 2 Hz) confirms the trans structure of this compound.

IR spectra of the compounds obtained showed weak absorptions of the CN groups (2240-22-30 cm^{-1}), and strong bands of the C=C double bond (1600-1750 cm^{-1}) and the aromatic ring (1600-1450 cm^{-1}).

In the MS spectra of compounds 2 and 4 molecular ions were observed and the fragmentation patterns confirmed the suggested structures.

EXPERIMENTAL

Boiling and melting points are uncorrected. NMR spectra were recorded with a JEOL JNM-4H-100 spectrometer; chemical shifts are in ppm from internal CCl_3F for ^{19}F spectra (positive upfield) and from internal TMS for ^1H spectra (positive downfield). Mass spectra were obtained with an Analytical GCMS System LKB-2091 and IR spectra were recorded on a Beckman Acculab (film for liquids, and nujol suspension for solids were used).

Benzyl 2-chloro-1,1,2-trifluoroethyl ether 2a

Trifluorochloroethylene was introduced from a gas burette to a vigorously stirred mixture of benzyl alcohol (2.5 g, 23 mmoles), benzene (10 ml), 50% aqueous sodium hydroxide (6 ml) and TBAH (0.08 g) at a rate allowing temperature to be kept below 35° (an exothermic reaction). When the required amount of the olefin was introduced the reaction was continued at 20° for an additional half an hour, then the mixture was diluted with water and the organic layer extracted three times with benzene. The product was isolated and purrified by vacuum distillation. The yield was 4 g (81%). B.p. 62-64°/0.4 mmHg (ref.[12] 93°/13 mmHg) ^1H and ^{19}F NMR (in CCl_4) : $\delta(CH_2)$ = 1.36 ppm (m), $\delta(CH_2)$ = 4.36 ppm (m), $\delta(CHF)$ = 5.90 ppm (dt), δ(Ph) = 7.28 ppm (bs), $\Phi_2(CF_2)$ = 86.7, 87.3 ppm (AB pattern), $\Phi(CHF)$ = 152.4 ppm (dt), $^2J(HF)$ = 47.8 Hz, $^3J(FF)$ = 4.4 Hz, $^3J(HF)$ = 4.1 Hz, IR(film): ν(C-O-C) = 1100 cm^{-1}

n-Butyl-2-chloro-1,1,2-trifluoroethyl ether 2b

The reaction of trifluorochloroethylene with n-butanol carried out according to the above procedure gave compound 2b in an 80% yield B.p.= 125° (ref.[12]124.5°). ^1H and ^{19}F NMR (in CCl_4) : $\delta(CH_3)$ = 0.83 ppm (t), $\delta(CH_2)$ = 1.32 ppm (m), 1.48 ppm (qn), 3.78 ppm (t), $\delta(CHF)$ = 5.91 ppm (dt), $\Phi_2(CF_2)$ = 88.0 ppm, 88.6 ppm (AB pattern), $\Phi(CHF)$ = 154.2 ppm (dt), $^2J(HF)$ = 48.0 Hz, $^2J(FF)$ = 143.0 Hz, $^3J(FH)$ = 4.2 Hz, $^3J(HH)$ = 7.5 Hz, 6.3 Hz, IR(film) : ν(C-O-C) = 1090 cm^{-1}

Tetraethyl-2-(chlorofluoromethyl)-1-propene-1,1,3,3-tetracarboxylate 3

Trifluorochloroethylene 1a (15 mmoles) was slowly introduced from a gas burette, keeping the reaction temperature at about 35°, to a vigorously stirred mixture of diethylmalonate (4 g, 25 mmoles), DMF (5 ml), anhydrous potassium carbonate (4.6 g, 33 mmoles), and TBAH (0.09 g). After addition of the alkene was completed the reaction mixture was stirred at room temperature for half an hour then diluted with water and the organic product was extracted three times with ether. The product was isolated and purified by vacuum distillation. B.p. = 168-70°/0.4 mmHg. The yield was 7.4 g (75%). Calculated for $C_{16}H_{22}O_8FCl$: C, 48.4; H, 5.6; F, 4.8;

Cl, 8.9%. Found: C, 48.4; H, 5.7; F, 4.9; Cl, 9.0%. ^{1}H and ^{19}F NMR (in CCl_4) : $\delta(CH_3)$ = 1.36 ppm (m), $\delta(CH_2)$ = 4.30 ppm (m), $\delta(CH)$ = 4.75 ppm (s), $\delta(CHF)$ = 7.29 ppm (d), $\Phi(CHF)$ = 136.6 ppm (d), $^{2}J(HF)$ = 50 Hz. IR (film) : $\nu(C=O)$ = 1750 cm^{-1}, $\nu(C=C)$ = 1650 cm^{-1}, $\nu(C-H)$ = 2985 cm^{-1}.

2,2-Diphenyl-3,4-difluoro-4-chlorobutenenitrile 4a (nc) and 2,2-diphenyl-3,3,4-trifluoro-4-chlorobutanenitrile 5a (nc)

Diphenylacetonitrile (3.8 g, 20 mmoles), benzene (10 ml), 50% aqueous sodium hydroxide (6 ml), and TBAH (0.07 g) were vigorously stirred and an equimolar amount of olefin 1a was gradually introduced from a gas burette. The reaction was carried out at 45-48° (a moderate exothermic effect). After addition of 1a, the reaction mixture was stirred at room temperature for one hour, then diluted with water. The organic layer was separated and the aqueous layer was extracted with benzene. The extracts were combined and after removal of the solvent the residue was distilled to give 5 g of a viscous liquid. B.p. 121-6°/0.2 mmHg. The product was isolated by column chromatography on silica gel using benzene as eluent to give 4a (B.p. = 123.5°/0.2 mmHg), and 5c (M.p. = 94° from hexane). Yields were 3.2 g (55%) and 4 g (22%), respectively.

2,2-Diphenyl-3-fluoro-4,4-dichlorobutenenitrile 4b (nc)

A mixture of isomeric dichlorodifluoroethenes (9 g) in benzene (5 ml) was added dropwise at room temperature to a stirred of diphenylacetonitrile (3.8 g, 20 mmoles), 50% aqueous sodium hydroxide (7 ml), benzene (10 ml) and TBAH (0.07 g). The reaction was carried out for one hour, then the reaction mixture was diluted with water and the product was extracted with benzene. The extract was initially purified by filtering trough a layer of silica gel. After evaporation of the solvent the residue was treated with n-hexane and the unreacted DPA was filtered off. Evaporation of the hexane solution gave product 4b. M.p. = 72° (from methanol). Yield was 4.6 g (75%).

2,2-Diphenyl-3,4,5,5,5-pentafluoropentenenitrile 4c (nc)

Reaction of DPA with hexafluoropropene was carried out as with CF_2CFCl (1a) at 10-15° for one hour.
A 77% yield of compound 4c was obtained. B.p. = 134°/3 mmHg

2,2-Diphenyl-4-chloro-5,5-difluoropentenenitrile 8 (nc)

1,2-Dichloro-3,3,3-trifluoropropane (6) (1.7 g, 10 mmoles) dissolved in benzene (5 ml) was added dropwise to a stirred mixture of DPA (2.9 g, 15 mmoles), benzene (10 ml), 50% aqueous sodium hydroxide (3 ml),

and TBAH (0.05 g). The temperature was kept at 30°. The reaction mixture was then stirred at room temperature for an additional hour, then diluted with water and extracted with benzene. The extract was initially purified by passing through a layer of silica gel. After evaporation of the solvent the residue was treated with CCl_4 (10 ml) and unreacted DPA was filtered off. The product was purified by column chromatography on silica gel using benzene as eluent to give 2.3 g (77% yield) of 8. M.p. 62-3°.

2,2-Diphenyl-3-(trifluoromethyl)-5,5,5-trifluoropentenenitrile 14 (nc) and 1,4,4-tetrafluoro-2,3-di-(cyanodiphenylmethyl)-butadiene 17 (nc)

1,1,1,4,4,4-Hexafluoro-2,3-dichlorobutane (2.4 g, 10 mmoles)(11) disolved in benzene was added dropwise to a stirred mixture of DPA (2.3 g, 15 mmoles), benzene (5 ml), 50% aqueous sodium hydroxide (3 ml), and TBAH (0.05 g). The temperature was kept at 35° (exothermic effect occured). The reaction was carried out for an additional hour and worked up as above. After evaporation of the solvent the residue was treated with methanol. A white precipitate of 17 deposited. Yield 0.9 g (18%). M.p. = 246°. The analytical sample was obtained by recrystallisation from dioxane. The methanolic solution was evaporated and the residue chromatographed on silica gel, using benzene as eluent. A 50% yield (1.8 g) of compound 14 was obtained. M.p. 79-80°.

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