accommodate the strained B ring system. In the D ring C-13 lies 0.66 Å out of the plane of the other four atoms. The ethylene group in the side chain is found to be planar. Examination of the intramolecular distances leads to the conclusion that the packing of molecules in the crystal is determined by the bulk and shape of the molecules, and it is not influenced by specific interactions between molecules.

Registery No.—Photoisopyrocalciferyl *m*-bromobenzoate, 17448-36-1.

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Reactions of 1,2-Dichloroperfluorocycloalkenes and Perfluorocycloalkenes with Various Trivalent Phosphines

RICHARD F. STOCKEL, FREDERIC MEGSON, AND MICHAEL T. BEACHEM

American Cyanamid Company, Research and Development, Organic Chemicals Division,
Bound Brook, New Jersey 08805

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The reactions of trivalent phosphines with certain 1,2-dichloroperfluorocycloalkenes or perfluorocycloalkenes give the corresponding phosphobetaines in fair to excellent yields. Ample physical data are presented to substantiate the assigned structures. This includes ir, ^{19}F and ^{31}P nmr, and analytical data. Although the literature is voluminous with possible mechanistic paths of various nucleophiles with the above type olefins, there exists no proof of the suggested first intermediates involved. This paper describes the isolation and experimental results of the initial 1:1 adduct of triphenylphosphine and perfluorocyclobutene, as well as discussing a plausible mechanism for the formation of the phosphobetaine. The betaine 4,4,5,5-tetrafluoro-2-(triphenylphosphoranylidene)cyclobutane-1,3-dione undergoes several crystal structure changes and two melts before its final melting solid. This interesting and novel polymorphism is discussed.

When trialkyl phosphites and 1,2-dichlorohexafluorocyclopentene (DCHFC) are heated together, the corresponding tetraalkyl perfluoro-1-cycloalken-1,2-ylenediphosphonates are formed as the major products.[1] Owing to the extreme reactivity of trivalent phosphorus compounds towards electron-deficient olefins, we considered the possibility of preparing phosphobetaines by treating 1,2-dichloroperfluorocycloalkenes and perfluorocycloalkenes with trivalent phosphines. This was based on our previous work involving the reaction of certain tertiary amines with DCHFC, which gave nitrogen betaines under hydrolytic conditions,[2] and some unreported work involving the reaction of 1-chloro-2-methoxyhexafluorocyclopentene with triphenylphosphine. In the latter case the phosphobetaine was obtained in fair yields.

Our experimental approach was devised from a recent communication which illustrates the use of acetic acid and water for the preparation of the betaine 1-(3,3,4,4-tetrafluoro-2-hydroxy-5-oxo-1-cyclopenten-1-yl)pyridinium hydroxide, inner salt.[3] By adopting this procedure for our own work we were able to prepare various phosphobetaines in fair to excellent yields depending on the particular olefinic substrate.

Reactions Studied.—Although the reaction of several tertiary phosphines are included in this paper, only triphenylphosphine was extensively investigated with all of the halo olefins studied in this paper. These olefins include 1,2-dichlorooctafluorocyclohexene, 1,2-dichlorohexafluorocyclopentene, 1,2-dichlorotetrafluorocyclobutene, perfluorocyclohexene, perfluorocyclopentene, and perfluorocyclobutene. In the 1,2-dichloro series an interesting but not altogether unexpected trend was observed. The cyclobutene derivative was by far the most reactive, followed by the cyclopentene as depicted in Figure 1. The cyclohexene derivative does not give any phosphobetaine under these reaction conditions. Instead, only triphenylphosphine oxide and tars are found. Even under more strenuous conditions, using an auto-clave at temperatures above 125° under a slight nitrogen atmosphere, identical results were observed. In the perfluoro series a similar trend was observed, where perfluorocyclobutene and perfluorocyclopentene reacted readily, and perfluorocyclohexene remained unreacted. No effort was made to compare the reactivities of the 1,2-dichloro and perfluoro cyclic olefins.

A plausible explanation for this observed deviation can be rationalized from Table I.[4] This shows a noticeable reduction of the double-bond strain in cyclohexene. By applying this reasoning to the perhalo olefins it becomes apparent why the six-membered cyclic compounds are less reactive than the corresponding four-, five-, and seven-membered compounds. Although this

TABLE I

Ring size	Excess strain of cyclo olefin, kcal/mol
C_3	54.3
C_4	
C_5	5.9
C_6	0
C_7	5.2

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[1] A. W. Frank, *J. Org. Chem.*, **30**, 3663 (1965).

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[3] S. E. Ellzey, Jr., and W. A. Gueee, *J. Org. Chem.*, **31**, 1300 (1966).

[4] N. S. Zefirov and V. I. Sokolov, *Russ. Chem. Rev.*, **36** (2), 90 (1967).

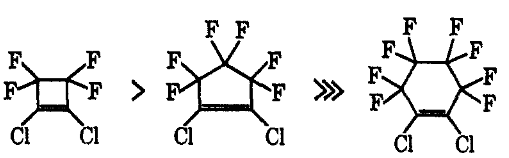


Figure 1.

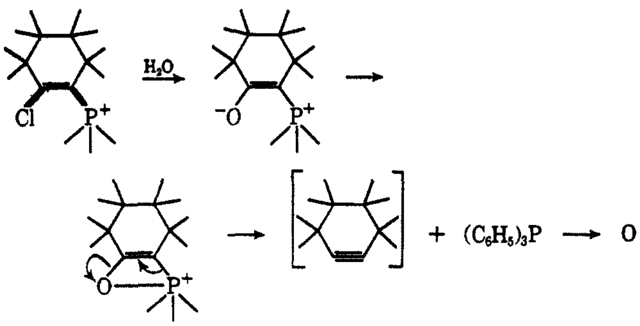


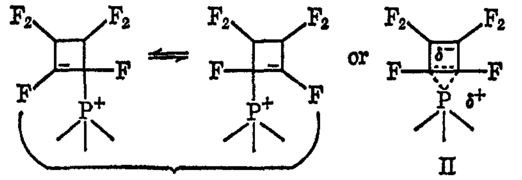
Figure 2.

order is in contrast to the scheme of *I* strain,[5] a number of cyclic systems have been studied which show this trend.[6,7]

An alternate possibility which cannot be ruled out because of the observed facts involves the intervention of a intramolecular Wittig reaction.[8] In this case the six-membered ring, more so than the other homologs, is ideally set up sterically and electronically for this possibility. This would lead to an extremely reactive cyclohexyne intermediate as illustrated in Figure 2, which would result in a variety of products. Thus far trapping experiments have failed to reveal the presence of this species.

During the course of this study we were able to isolate under anhydrous conditions a 1:1 adduct of perfluorocyclobutene and triphenylphosphine. Recent investigators have been trying to prove that that carbanions are the first formed intermediates in the reactions of nucleophiles with perhalo olefins. In certain cases it appears that the stability of the postulated initial intermediate carbanion influences the reaction path,[9] while in other examples this apparently is not so important as other factors.[10] However, the formation of a carbanion as the first step has been a hypothesis up to the present time, and no experimental proof existed.

The 1:1 adduct which we have succeeded in isolating can perhaps be best explained by an equilibrating 1,3-dipolar species I, although a nonclassical structure II cannot be excluded. We feel that this lends credibility to the carbanion mechanism. In a sense this is a carbanion stabilized electrostatically by a positive P atom.



I II

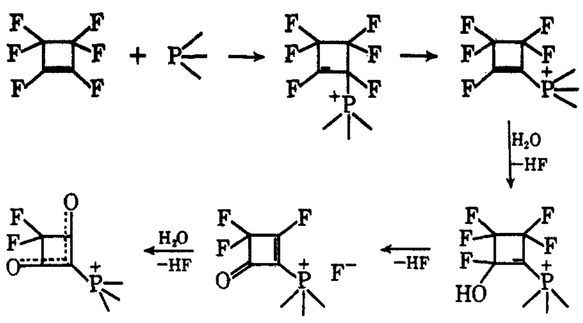


Figure 3.

Structure assignment of the adduct is based on analytical results and ir and nmr spectroscopic data. The ^1H spectrum [$(CH_3)_4Si$ as the internal standard] shows only aromatic absorption. The ^{31}P spectrum [$(CH_3CH_2)_3PO_4$ as the internal standard] shows a broad peak at −5.6 ppm, which is in the correct region for a tetravalent positively charged phosphorus atom.[11] In fact this value is very close to that found for the phosphobetaine product of this adduct. The ^{19}F nmr spectrum (CCl_3F as the internal standard) shows two clusters of peaks at ϕ 86.1 and 124.2. Using allyl trifluoroacetate as an internal standard the H:F(86.1):F(124.2) ratio is 15:4:2. These multiplets give symmetrical spin-coupling patterns, but the coupling constants could not be measured because of their complexity.

Further probes in the area of ^{19}F nmr studies are currently in progress. These include low-temperature examination and a study involving computer analysis. We hope to report shortly on these findings as soon as meaningful information is ascertained.

Supplementary proof is derived from the analysis of $C_{22}H_{15}F_6P$ (*Anal.* Calcd: C, 62.26, H, 3.53; P, 7.31. Found: C, 62.75; H, 3.55; P, 7.50.) and the ir spectrum. The latter gives strong bands[12] at 7.0, 13.22, and 14.54 μ due to P-phenyl, and strong bands at 8 μ due to the CF_2 absorption. There was no absorption centered around 1665 cm^{-1} due to the O=C=C=C=O functional group.[13] Final support is the ease in which the 1:1 adduct readily reacts with water to give the phosphobetaine II.

Analogously, tributylphosphine and butylidiphenylphosphine give the corresponding betaines with DCHFC in comparable yields as indicated in Table II p. 4396.

Reaction Mechanism.—The 1:1 adduct supports an addition–elimination path similar to that of other nucleophiles studied using this substrate. However, in this instance the addition product happens to be isolable as has been found with some alicyclic perhalo olefins. Even when excess phosphine is present the major product is still the phosphobetaine. This is in sharp contrast to other nucleophiles studied on these halo olefin substrates. With perfluorocycloalkenes, the products are 1,2 disubstituted.[14,15] The same types

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TABLE II

PHYSICAL DATA ON PHOSPHOBETAINES

Compound	Yield, %	Mp, °C	Ir,[a] μ	Nmr[b]		Anal., % C	H	P
A, 4,4-Difluoro-2-(triphenylphosphoranylidene)-cyclobutane-1,3-dione	42[c]	228–229	5.68	^{31}P −4.1 ppm	Calcd	69.47	3.94	8.15
	60[d]		6.03	^{19}F ϕ +118.4	Found	69.29	4.10	8.18
$C_{22}H_{15}F_2O_2P$			6.16					
B, 4,4,5,5-Tetrafluoro-2-(triphenylphosphoranylidene)cyclopentane-1,3-dione	81[e]	173–174	5.85	^{31}P −10.2 ppm	Calcd	64.18	3.48	7.20
	75[f]		5.98	^{19}F ϕ +128.3	Found	64.1	3.46	7.18
$C_{23}H_{15}F_4O_2P$			6.10					
C, 4,4,5,5-Tetrafluoro-2-(butyldiphenylphosphoranylidene)cyclopentane-1,3-dione	72[g]	148–149	5.82	^{31}P −12.8 ppm	Calcd	61.46	4.63	7.56
			5.95	^{19}F ϕ +128.5	Found	61.46	4.68	7.61
$C_{21}H_{19}F_4O_2P$			6.08					
D, 4,4,5,5-Tetrafluoro-2-(tributylphosphoranylidene)cyclopentane-1,3-dione	60[h]	68–69	5.75	^{31}P −21.7 ppm	Calcd	55.13	7.28	8.38
			5.85	^{19}F ϕ +128.4	Found	54.90	7.31	8.37
$C_{17}H_{27}F_4O_2P$			6.08					

[a] Mineral oil mulls on a Perkin-Elmer Model 317 spectrophotometer. [b] Varian HR-60 compounds were measured as 10% solutions, F in $CFCl_3$, and P in $(Et)_3PO_4$ as internal standards. [c] Reactants: triphenylphosphine and 1,2-dichlorotetrafluorocyclobutene. [d] Reactants: triphenylphosphine and perfluorocyclobutene. [e] Reactants: triphenylphosphine and 1,2-dichlorohexafluorocyclopentene. [f] Reactants: triphenylphosphine and perfluorocyclopentene. [g] Reactants: butyldiphenylphosphine and 1,2-dichlorohexafluorocyclopentene. [h] Reactants: tributylphosphine and 1,2-dichlorohexafluorocyclopentene.

of disubstituted products are observed with 1,2-dichlorofluorocycloalkenes when the nucleophiles are phosphorus, sulfur, and arsenic,[16] but otherwise these latter types of olefins give 1,3,3-trisubstituted derivatives.[17,18] The reason for this difference with phosphines is probably due to electronic and steric factors. Once the initial addition–elimination is complete C-2 becomes susceptible to attack by water because of the positive phosphorus atom. Furthermore this course of events are probably the only possibility that could occur because additional attack by phosphine would be inhibited at C-1 or C-2 due to steric hindrance. Finally water reacts a second time at C-4 to give the final stable phosphobetaine. See Figure 3.

Recent studies indicate that once the initial carbanion is formed elimination can occur at two different sites.[19,20] The mode of elimination depends on the effect which the α substituents have on the stability of the carbanion.[9,21] In our studies, the elimination of the halogen vicinal to the phosphorus atom appears to be the predominant leaving group. This is actually what one would predict.

Physical Data.—Nuclear magnetic resonance confirms the assigned structures of the betaines prepared. The ^{31}P signal in all cases is of the right field strength expected from a tetravalent phosphorous atom.[11] Furthermore the ^{19}F nmr complements the proposed structure by indicating the equivalency of the fluorine atoms due to the molecules symmetry.

The ir spectra are also diagnostic because of the characteristic $O=C=C=C=O$ system.[13] In each case three bands are evident as shown in Table II. Actually, four bands should be present due to the two $C=O$ and two $C=C$ bands; however, one of these centered around 8 μ is not observed owing to C—F absorption. Other bands observed were due to P-phenyl, 7.0, 13.22, and 14.54 μ;[12] however, in the case of the tributyl derivative the band at 6.82 μ is blocked out by the mineral oil.

The microanalyses for C, H, and P were all satisfactory.

The ability of a compound to exist in at least two distinctly different crystalline phases is actually a common occurrence in organic chemistry. However, unlike most polymorphic compounds, crystals of B in Table I show two phases stable below the melting point, and two quite different phases are obtained on cooling the melt. Table III lists transition temperatures for the polymorphs of B. Further microscopic investigation is in progress with similar type compounds.

TABLE III

Polymorphic form	Transition temp, °C
$1 \rightarrow 2$	164–168
2	178–179, melts
$3 \rightarrow 4$	124.0–124.5
4	181–182, melts

Experimental Section

General Procedure for the Preparation of Betaines.—Equivalent amounts of phosphine and halo olefin (usually 0.1 mol were used) were added to 100 ml of glacial acetic acid and 10 ml of water. (Similar results are obtained with commercial DMF). The solution was refluxed from 8–15 hr. After the reflux 300 ml of water was added, which caused precipitation. The precipitate was then recrystallized from methanol–water.

The Preparation of the 1:1 Adduct of Perfluorocyclobutene and Triphenylphosphine.—Into a three-necked flask equipped with a Dry Ice–acetone condenser was added 20 g (excess) of perfluorobutene. Then with stirring 26 g (0.1 mol) of triphenylphosphine dissolved in 150 ml of ethyl ether which was added to the flask. A white precipitate immediately was formed. This was filtered off and washed with more ethyl ether. Approximately 42 g of the adduct was isolated.

Registry No.—I, 17447-55-1; Table II—A, 17447-51-7; B, 17447-52-8; C, 17447-53-9; D, 17447-54-0.

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