(41% yield) of product, b.p. 68.5–70.5°. The infrared spectrum and analysis corresponded to 1,3,3,4,4,4-hexafluoro-2-butanone hydrate.

Anal. Calcd. for $C_4H_4F_6O_2$: C, 24.25; H, 2.03; mol. wt., 198.07. Found: C, 24.58; H, 2.22; mol. wt., 189 (freezing point depression of benzene).

Stability of ethyl N-methyl-N-n-perfluoropropylcarbamate toward hydrolysis to fluoride ion. As a basis for comparison, the alizarin-zirconium test for fluoride ion was found to be sensitive to 0.05 mg. of fluoride ion in 1 ml. of water. A 10-mg. sample of ethyl *N*-*n*-perfluoropropylcarbamate shaken with 1 ml. of water for 1 min. gave a strong positive test for fluoride ion. A 40-mg. sample of ethyl *N*-methyl-*N*-*n*-perfluoropropylcarbamate shaken with 1 ml. of water for 30 min. gave no test for fluoride ion and only a very faintly positive test after an additional 30 min. of heating at 100°. The extent of alpha fluorine hydrolysis was estimated to be less than 1%.

CLEVELAND 6, OHIO

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF FLORIDA]

Fluoroolefins. IX. The Reaction of Chlorotrifluoroethylene with Olefins[1]

PAUL TARRANT, ROBERT W. JOHNSON, JR., AND WALLACE S. BREY, JR.

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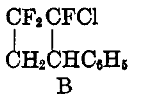
Chlorotrifluoroethylene has been found to react with a variety of olefins to give cyclobutane derivatives. With terminal olefins, addition occurs to give the —CH_2CF_2— structure and a mixture of *cis-trans* isomers is obtained where this type of isomerism is possible. Infrared and nuclear resonance spectra were used to establish the structures of the products. The effects of substituents in the cyclobutane ring on the chemical shift differences between nonequivalent fluorines attached to the ring are found to be approximately additive.

The formation of a variety of cyclobutane derivatives by the reaction of tetrafluoroethylene and unsaturated compounds was reported by Coffman *et al.*[2] in 1949. It is somewhat surprising that the readily available chlorotrifluoroethylene has not been widely employed in cycloalkylation reactions to give a series of similar cyclobutyl derivatives. The dimerization of chlorotrifluoroethylene and similar compounds to substituted cyclobutanes was reported some years ago by Henne and Ruh.[3] Barney and Cairns[4] established the structure of the reaction product of acrylonitrile and chlorotrifluoroethylene as A, while Roberts[5] found that the product from styrene and the fluoroolefin had structure B. Since the completion of our work, Park *et al.*[6] have established that perhaloethylenes react with vinylsilanes; chlorotrifluoroethylene gave compounds such as C while iodotrifluoroethylene gave products represented by D.

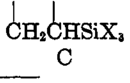
$\begin{array}{l} CF_2CFCl \\ |\quad\ | \\ CH_2CHCN \end{array}$

A



$\begin{array}{l} CF_2CFCl \\ |\quad\ | \\ CH_2CHC_6H_5 \end{array}$

B



$\begin{array}{l} CF_2CFCl \\ |\quad\ | \\ CH_2CHSiX_3 \end{array}$

C

$CF_2{=}CHCH_2CHISiX_3$

D

The purpose of the present research was to determine the extent of the reaction of chlorotrifluoroethylene with olefins and to determine the structures of the reaction products. Chlorotrifluoroethylene reacted with a wide variety of olefins and good conversions to cyclobutyl derivatives were obtained in several reactions as indicated in Table I. Reactive olefins such as styrene and acrylonitrile gave conversions of 65% while the lowest conversions (7–8%) were obtained with allyl chloride. Tetrafluoroethylene is somewhat more reactive than chlorotrifluoroethylene as the conversion was smaller with the latter and higher reaction temperatures are necessary. The order of reactivity of styrene with various fluoroolefins is as follows, based on conversions: $CF_2{=}CFCl > CF_2{=}CFCN > CF_2{=}CFBr > CF_2{=}CFI \gg CF_2{=}CFCF_3 = CF_2{=}CFH$. No appreciable amounts of cyclobutane derivatives were obtained with the latter olefins. These results are related to the ease with which the individual fluoroolefins form cyclic dimers. For instance, chlorotrifluoroethylene readily gives the cyclic dimer[3] at 200° and even lower while a temperature of 350° is required for the cyclic dimerization of perfluoropropylene in comparable conversion.[7] Perfluoroacrylanitrile gave a 30% conversion to dimer[8] and 100% yield at 230°. It is difficult to explain these results on the basis of electrical or steric factors singly. The differences between the size and electrical effects of the nitrile and trifluoromethyl groups seem too small to account for the rather large

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[1] Paper VIII, *J. Org. Chem.*, **25**, 2254 (1960).

[2] D. D. Coffman, P. L. Barrick, R. D. Cramer, and M. S. Raasch, *J. Am. Chem. Soc.*, **71**, 490 (1949).

[3] A. L. Henne and R. P. Ruh, *J. Am. Chem. Soc.*, **69**, 279 (1947).

[4] A. L. Barney and T. L. Cairns, *J. Am. Chem. Soc.*, **72**, 3193 (1950).

[5] E. F. Silversmith, Y. Kitahara, M. C. Caserio, and J. D. Roberts, *J. Am. Chem. Soc.*, **80**, 5840 (1958).

[6] J. D. Park, J. D. Graves, and J. R Lacher, *J. Org. Chem.*, **25**, 1628 (1960).

[7] M. Hauptschein, A. H. Feinberg, and M. Braid, *J. Am. Chem. Soc.*, **80**, 842 (1958).

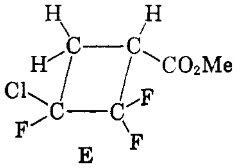
[8] J. D. La Zerte, D. A. Rausch, R. J. Kashar, J. D. Park, W. H. Pearlson, and J. R. Lacher, *J. Am. Chem. Soc.*, **78**, 5639 (1956).

differences in reactivity. That steric factors are not involved is indicated by the behavior of trifluoro- and iodotrifluoroethylene, for the former does not react with styrene while the latter gives a 33% conversion to cyclobutane even at 125°.

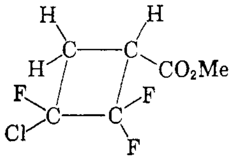
The reaction products were identified as cyclobutane derivatives from evidence in the infrared and NMR spectra. The characteristic band near 11 μ was present in the infrared spectrum of each product. The NMR spectrum in each case indicated the presence of two nonequivalent fluorine atoms attached to the same carbon atom, along with a third fluorine attached to the neighboring carbon atom. Such a configuration is consistent with the presence of a four-membered ring. In other work in these laboratories, to be described in detail in another publication, olefins were added to butadienes to form molecules containing six-membered rings having CF_2 groups. It has been found that, in such rings, inversion is sufficiently rapid to remove the nonequivalence of two fluorines attached to the same carbon atom.

The typical fluorine NMR spectrum obtained for the product of a reaction contained ten peaks. An example is shown in Figure 1. There were two groups of four peaks, each of these groups constituting a nonequivalence quartet. The particular peaks to be assigned as members of a group could readily be identified by the intensity ratios between the outer and inner members of the quartet, which increase toward unity as the chemical shift between the two atoms represented by the nonequivalence quartet increases. In addition, both peaks in either half of a nonequivalence quartet show precisely the same fine structure. As discussed below, each quartet arises from the CF_2 group of one of the pair of isomers, chromatographically inseparable, which were present in the products. Each of the remaining two of the ten peaks in the spectrum corresponds to the third fluorine atom in one of the isomers. The nonequivalence quartets were analyzed for chemical shifts by the usual procedure.[9]

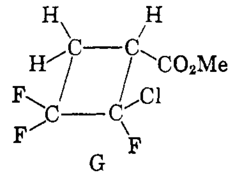
In every case except that of the reaction of isobutylene there were formed two isomers, and these were formed in nearly equal amounts. In general four products are possible in the reaction of two unsymmetrically substituted olefins, as indicated for methyl acrylate and chlorotrifluoroethylene.



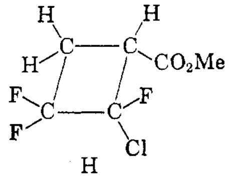
E



F



G

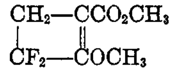


H

Several considerations lead to the conclusion that the product mixtures consist of pairs of *cis-trans* isomers corresponding to forms G and H above. Firstly, the addition products of methyl acrylate and of acrylonitrile lost hydrogen chloride readily when treated with base, while those from isobutylene and from methacrylonitrile, which in forms G and H do not have a hydrogen on a carbon adjacent to that bearing the chloride, did not dehydrochlorinate. Thus a CH_2—CF_2 linkage, rather than a CH_2—CFCl linkage, is present.

Secondly, if one of the forms E or F and one of the forms G or H constituted the mixture of isomers, the isobutylene addition product would also be expected to show the presence of more than one isomer. This was the only product obtained, however, in which but a single isomer was present.

Thirdly, the product of dehydrochlorination of VIII (Table I) by treatment with KOH in methanol can, on the basis of composition and NMR spectrum, have only the following structure:



$$\begin{array}{l}CH_2\text{—}CCO_2CH_3\\ |\qquad\ \ \|\\ CF_2\text{—}COCH_3\end{array}$$

In addition to the two methyl groups, there are present two hydrogens, neither of which is attached to doubly-bonded carbon. Furthermore, the presence of a plane of symmetry in the molecule is indicated by the fact that the two fluorines are equivalent in the NMR spectrum. Thus, if dehydrochlorination has occurred between adjacent carbon atoms, the structure of VIII is determined.

Fourthly, the NMR chemical shifts of the fluorine atoms in the compounds given in Table II can be interpreted consistently and satisfactorily only in terms of the existence of the CH_2—CF_2 linkage, as demonstrated in detail in the following paragraphs.

In a pair of *cis-trans* isomers, the nonequivalence of the fluorines in the CF_2 group arises in part from the dissymmetry of substitution in the parent trifluoro olefin and also in part from the dissymmetry of the olefin to which the trifluoro olefin adds. The present data afford a test of the question whether these two effects are substantially independent of one another and therefore can be treated as additive. It is concluded that they are indeed additive to the extent that it is possible to use the chemical shifts to establish the direction of addition of the olefin to the trifluoroolefin.

To test the hypothesis of additivity, we first assume that it applies and discuss the manner in which individual group contributions to fluorine nonequivalence may be extracted from the spectral data. As the nonequivalences of the coupled fluorines in the CF_2 groups of two members of a pair of

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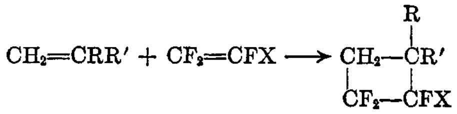
[9] J. A. Pople, W. G. Schneider, and H. J. Bernstein, *High-resolution Nuclear Magnetic Resonance*, McGraw-Hill, 1959, p. 122.

TABLE I

PROPERTIES OF SOME FLUORINE-CONTAINING CYCLOBUTANE DERIVATIVES



$$CH_2{=}CRR' + CF_2{=}CFX \longrightarrow \begin{array}{c} \quad\quad R \\ \quad\quad | \\ CH_2{-}CR' \\ |\quad\quad | \\ CF_2{-}CFX \end{array}$$

No.	R	R′	X	% Conversion	B.P.	Mm.	Temp.	n_D^t	d_4^t	C Calcd.	C Found	H Calcd.	H Found
I	H	C_6H_5	Cl	67.0	109–110[a]	20	21	1.4829	1.3071	54.44	54.63	3.64	3.91
II	H	C_6H_5	Br	43.0	65	0.5	21	1.5026	1.5313	45.31	45.38	3.04	3.41
III	H	C_6H_5	I	33.3	82–83	0.5	21	1.5408	1.7346	38.48	39.34	2.58	2.68
IV	H	C_6H_5	CN	56.6	75	3.0	22	1.4743	1.2340	62.56	62.58	3.82	4.05
V	H	CH_3	Cl	35.4	99–100	760	21	1.3702	1.2582	37.87	37.44	3.81	3.85
VI	CH_3	CH_3	Cl	20.2	114–115	760	25	1.3827	1.2140	41.75	41.57	4.68	4.84
VII	H	CH_2Cl	Cl	7.8	141–144	760	21	1.4130	1.4275	31.11	31.79	2.61	2.91
VIII	H	CO_2CH_3	Cl	47.4	82	42	19	1.3980	1.3947	35.57	36.14	2.98	3.26
IX	H	CN	Cl	65.0	82[b]	40	20	1.4012	1.4332	35.42	35.77	1.78	1.90
X	CH_3	CN	Cl	30.6	80	34	20	1.4013	1.3513	39.26	39.54	2.75	2.94

[a] Previous literature values.[5] [b] Previous literature values.[4]

TABLE II

FLUORINE CHEMICAL SHIFTS OF CYCLOBUTANE DERIVATIVES

(Values are in parts per million from external reference ethyl trifluoroacetate)

				CF_2						CF[a]		
								Nonequivalence contribution[b]				
No.	R	R′	X	Isomer 1		Isomer 2		[Position 2]	[Position 3]	1′ Isomer	2′ Isomer	Difference
I	H	C_6H_5	Cl	21.15	41.31	30.55[c]		10.1	10.1	58.69	30.55[c]	28.14
II	H	C_6H_5	Br	14.29	41.33	24.91	29.01	15.57	11.47	57.18	27.62	29.56
IV	H	C_6H_5	CN	16.88	42.46	26.74	30.89	14.88	10.73	104.70	78.90	25.80
V	H	CH_3	Cl	22.20	40.14	27.75	31.17	10.68	7.26	59.43	34.73	24.70
VI	CH_3	CH_3	Cl	24.13	32.40	—	—	8.27	—	49.71	—	—
VIII	H	CO_2CH_3	Cl	20.58	37.61	27.43	30.76	10.18	6.85	53.01	34.06	18.95
IX	H	CN	Cl	19.93	39.29	26.10	31.28	12.27	7.09	47.80	35.35	12.45
X	CH_3	CN	Cl	20.32	31.58	23.26	31.61	9.81	1.46	49.18	40.65	8.53

[a] The CF chemical shift labeled "Isomer 1′" does not necessarily correspond to the CF_2 shift labeled "Isomer 1." [b] Refer to text for explanation. [c] In compound I, two of the resonance patterns fall nearly at the same place in the spectrum, and the exact position of each is slightly obscured.

isomers are the sum and difference of the contributions of the CFX group and the CRR′ group (Table I), it follows that one of the contributions is numerically equal to the average of the two nonequivalences in the isomer pair and the other contribution is equal to the difference between this average and the nonequivalence found in either isomer of the pair. For example, in compound II (Table II), the nonequivalences are (41.33 − 14.29) or 27.04 parts per million for one isomer and (29.01 − 24.91) or 4.10 p.p.m. for the other isomer. The average of these two values is 15.57 and the difference between the average and either value is 11.47 p.p.m. Corresponding results for each compound are listed in columns 9 and 10 of Table II.

The difference in chemical shifts between the CFX fluorine (*i.e.*, at position 2) in each of the two isomers in a pair (column 13, Table II) is solely the result of the difference between the groups designated R and R′, which might be located either at the position adjacent to the CFX or across the ring from it. In order to assign this nonequivalence contribution[10] and those in columns 9 and 10 of Table II, the magnitudes may be compared within the groups of figures themselves and also with data reported by Phillips[11] for tetrafluorocyclobutanes. For all adducts except those containing a CN group, the difference in chemical shifts for the CFX fluorines is 19 to 30 p.p.m. This is of the order of magnitude found by Phillips for the nonequivalence of fluorines in position 2 of unsymmetrically substituted tetrafluorocyclobutanes (23.5 p.p.m. for H/phenyl nonequivalence contribution and 19.37 for H/methyl) and is much larger than he found for

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[10] Because efforts at separation of the two isomers by vapor phase chromatography, as well as by other methods, failed, a CF resonance can not be unequivocally associated with a particular CF_2 resonance pattern on the basis of data in this paper. This question will be considered further in a subsequent paper dealing with NMR spin-spin coupling constants of these and other cyclic fluorine compounds.

[11] W. D. Phillips, *J. Chem. Phys.*, 25, 949 (1956).

TABLE III

CONDITIONS FOR THE CYCLOALKYLATION REACTIONS

Reagents					Time,	Product	
Fluoroolefin	Moles	Olefin	Moles	Temperature	Hr.	Formula	Wt., g.
$CF_2{=}CFCl$	0.43	Styrene	0.48	100	22	I	63.5
$CF_2{=}CFBr$	0.50	Styrene	0.50	125	16	II	57
$CF_2{=}CFI$	0.97	Styrene	0.19	125[a]	16	III	10
$CF_2{=}CFCN$	0.079	Styrene	0.19	100[a]	14	IV	9.5
$CF_2{=}CFCF_3$	0.10	Styrene	0.16	125[a]	16		0
$CF_2{=}CFCl$	0.47	Propylene	0.43	275	18	V	48
$CF_2{=}CFCl$	0.26	Isobutylene	0.31	310	3	VI	9
$CF_2{=}CFCl$	0.34	Allyl chloride	0.33	240[b]	2	VII	5
$CF_2{=}CFCl$	0.52	Methyl acrylate	0.52	140	18	VIII	48
$CF_2{=}CFCl$	0.47	Acrylonitrile	0.47	155	8	IX	52
$CF_2{=}CFCl$	0.52	Methacrylonitrile	0.50	140–150	16	X	28

[a] Sealed glass tube. [b] Considerable charring took place and HCl evolved.

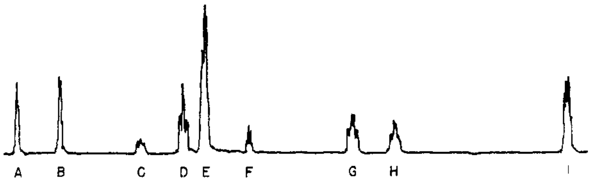

Fig. 1. Fluorine NMR spectrum of Compound II. Field increases from left to right. Peaks A, B, G, and H constitute one nonequivalence quartet. Peaks C, D, F, and part of E constitute a second nonequivalence quartet. The remaining portions of peak E and peak I each correspond to a single fluorine atom in the CFBr group of one of the isomers.

the fluorines in position 3 (10.03 and 6.60 p.p.m., respectively, for the same cases). Thus in the present compounds, the CFX must be adjacent to the unsymmetrically substituted carbon.

The nonequivalence contributions to the CF_2 shifts must now be assigned. This has been done in Table II. The entry labeled "Position 2" in column 9 is the value we attribute to the effect of substituent X as compared to fluorine, and it is seen that the values assigned for this effect when X = Cl vary between extremes of 8.27 and 12.27, but are between 9.8 and 10.7 for four of the six compounds. Turning to the cross-ring, or "Position 3" contribution as assigned, we note that the H/phenyl pair gives values of 10.1 in I, 11.47 in II, and 10.73 in IV, compared to Phillips' value of 10.03. The same effect for H/methyl is 7.26 compared to 6.60.

In compounds IX and X, which contain CN groups, the qualitative agreement with Phillips' data is less satisfactory, although the general pattern is similar and the results confirm the structural assignments. Thus in IX the effect of the H/cyano pair on the adjacent fluorines is 12.45 compared to 9.47 for the tetrafluorocyclobutane case; the same effect for methyl/cyano is 8.53 compared to 6.17.

The addition product of propylene and 1,1-dichloro-2,2-difluoroethylene showed the characteristic cyclobutane infrared band at 11.02 mμ and the NMR spectrum of a four-membered ring. The chemical shifts for the CF_2 group, at 18.74 and 26.13 p.p.m., represent a nonequivalence of 7.39, which is very close to the H/methyl effect of 7.26 in V, and is comparable with the Phillips value of 6.60 for the cross-ring effect. Thus this adduct, too, has a CH_2—CF_2 linkage.

EXPERIMENTAL[12]

General procedure. In general all cycloalkylation reactions were carried out in either a .3 l. stainless steel reaction vessel fitted with a valve, pressure gauge, and blow-out assembly or in a 120 ml., sealed, thick-walled Pyrex glass tube. The polymerization inhibitor was in all cases *p-t*-butylcatechol. If the reactants were gases at room temperature, they were condensed either in a thick-walled glass tube and weighed or were condensed in a cold trap cooled to Dry Ice temperature, weighed, and poured into the autoclave which was cooled to Dry Ice temperature. The autoclave was then sealed, fitted with a high pressure valve, rocked, and heated at the desired temperature. After the heating process, the reaction vessel was cooled and opened, and any unchanged material was collected in a cold trap cooled to Dry Ice temperature. The remaining liquid material was subjected to fractional distillation. The reaction conditions are shown in Table III.

A gas chromatographic column, 20 ft. in length and of $^1/_4$-in. aluminum tubing packed with 0.6 g. of dinonyl phthalate per 1.0 g. of Chromosorb, 35–80 mesh, was used to determine the number of components in the fractionated samples except for the high boiling styrene derivatives. Helium was used as the carrier gas.

No separation of geometrical isomers occurred with this column and the sample submitted for NMR analysis showed a single peak on the vapor chromatogram.

2,2-Dichloro-1,1-difluoro-3-methylcyclobutane (XI). The autoclave was charged with 21 g. (0.50 mole) of propene, 70 g. (0.53 mole) of 1,1-dichloro-2,2-difluoroethylene, and 2 g. of inhibitor. The autoclave was then sealed and heated while rocking for sixteen hours at 225°. The resulting liquid was treated with 63.5 g. (1 g.-atom) of zinc dust in 200 ml of dioxane in order to remove 1,1,2,2-tetrachlorotetrafluorocyclobutane from the reaction mixture. This material and the desired product have similar boiling points. The mixture was then filtered to remove the solid material, the remaining liquid washed several times with water to remove the dioxane and dried over calcium chloride. Fractional distillation gave 14.5 g. (17% conversion) of material, b.p. 131°, n_D^{21} 1.4170, d_4^{21} 1.3175.

Anal. Calcd. for $C_5H_6F_2Cl_2$: MR_D, 33.30; %C, 34.31; %H, 3.46. Found: MR_D, 33.41; %C, 34.53; %H, 3.68.

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(12) Analyses by Galbraith Laboratories, Knoxville, Tenn., and Weiler and Strauss, Oxford, England.

The reaction of VIII *with methanolic potassium hydroxide.* To a 250 ml., three necked flask fitted with a reflux condenser, a stirrer, and a dropping funnel was added 30 g. (0.148 mole) of VIII. Potassium hydroxide (17 g., 0.30 mole) dissolved in 100 ml. of methyl alcohol was added dropwise while the reaction flask was maintained at 30–40°. After addition was complete, the reaction mixture was poured into 500 ml. of cold water. The organic layer was separated, washed with water, dried over calcium chloride, and distilled to give 8 g. (30.2% conversion) of material, b.p. 181°, n_D^{19} 1.4290, d_4^{19} 1.2654.

Anal. Calcd. for $C_7H_8F_2O_3$: MR_D, 35.63; %C, 47.19; %H, 4.53; %F, 21.33. Found: MR_D, 36.44; %C, 47.18; %H, 4.68; %F, 21.12.

NMR spectra. Spectra were obtained for solutions of 1:1 volume ratio in carbon tetrachloride, using a Varian high-resolution spectrometer operating at a frequency of 56.4 megacycles. The reference was ethyl trifluoroacetate in the external part of a precision coaxial tube. Sidebands were applied by an audio oscillator continuously monitored by a Hewlett-Packard frequency counter, and the results were averaged for several sweeps through the spectrum of each sample. A shift of resonance up-field is reported as a positive chemical shift. The maximum uncertainty of the chemical shifts is estimated to be 0.03 p.p.m.

Acknowledgment. We wish to acknowledge the financial support of this research by the Office of the Quartermaster General under Contract DA-19-129-QM-500, Dr. J. C. Montermoso as project officer. We wish to thank Dr. L. D. La Zerte of the Minnesota Mining & Manufacturing Co. for furnishing the sample of perfluoroacrylonitrile used in the experiments.

GAINESVILLE, FLA.

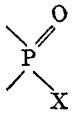
[CONTRIBUTION FROM THE RESEARCH LABORATORIES, ARMOUR INDUSTRIAL CHEMICAL COMPANY, McCOOK, ILL.]

A New Phosphorylation Reaction of Olefins.
I. Scope of the Reaction

ERIC JUNGERMANN,[1] J. J. McBRIDE, JR., R. CLUTTER, AND AGO MAIS

Received July 7, 1961

A new general method for forming a phosphorus-carbon bond at an olefinic linkage is described. It is based on the reaction of an olefin with phosphorus trichloride in the presence of aluminum chloride. The resultant products are saturated phosphorus-containing acids or acid chlorides of the type



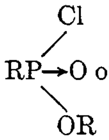
$\overset{O}{\underset{X}{P}}$

, where X = OH or Cl. Esters can be prepared by reaction of the chlorides with alkoxides.

Among the olefins investigated are: 2,4,4-trimethyl-2-pentene; propylene trimer, tetramer, and pentamer, methyl oleate, tricosene-11, 2-pentene, 2-methyl-2-butene, 4-methyl-2-pentene, and cyclohexene. The effect of reaction conditions on the products formed is discussed in some detail. This reaction offers a new, versatile procedure for synthesizing organic phosphorus compounds from olefins.

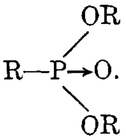
As part of a program of finding new derivatives of fatty acids, it was decided to investigate the possibility of adding a phosphorus containing moiety to the double bond of oleic acid. Several techniques had been reported previously: Sasin *et al.*[2] and Stiles *et al.*[3] had reported the preparation of dialkyl alkyl phosphonates by the free radical addition of dialkyl phosphites to olefins, including methyl oleate, using a peroxide catalyst. The direct addition of yellow phosphorus in the presence of oxygen has also been the subject of numerous discussions in the literature.[4,5] The free radical catalyzed addition of phosphorus trichloride to *alpha*-olefins had been reported by Kharasch,[6] but yields were low, and the scope of the reaction was limited. No work has been reported in the literature on the formation of carbon-phosphorus bonds by the addition of phosphorus trichloride to olefins under ionic conditions.

About ten years ago Clay[7] and Kinnear and Perren[8] reported that alkyl halides react with phosphorus trichloride in the presence of aluminum chloride to form a complex $[RPCl_3]^+[AlCl_4]^-$. Controlled hydrolysis of the complex yields the alkylphosphonyl chloride. Hoffmann[9] extended the reaction and by a simple batch process obtained the corresponding alkyl alkylphosphonochloridates,



$R\overset{Cl}{\underset{OR}{P}}\rightarrow O$

or the dialkyl alkylphosphonates



$R—\overset{OR}{\underset{OR}{P}}\rightarrow O$.

The reaction is formally related to the conventional Friedel-Craft condensation for the preparation of aromatic phosphorus halides. $ArH+PCl_3 \xrightarrow{AlCl_3}$

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