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PREPARATION OF CHLOROFLUOROMETHYLENE OLEFINS VIA PHOSPHINE DECHLORINATION OF DICHLOROFLUOROMETHYLTRIS{DIMETHYLAMINO}PHOSPHONIUM CHLORIDE

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SUMMARY

The reaction of dichlorofluoromethyltris{dimethylamino}phosphonium chloride with tertiary phosphines provides a convenient preparation of the chlorofluoromethylenetris{dimethylamino}phosphonium ylide. This ylide provides reasonable yields of chlorofluoroolefins from aldehydes, activated ketones, non-activated ketones, and activated esters. The mechanism of phosphonium salt formation was shown to involve positive chlorine abstraction from $CFCl_3$ by $(Me_2N)_3P$ followed by recombination of the intermediate ion pair. Dechlorination of the resulting dichlorofluoromethyltris{dimethylamino}phosphonium chloride by triphenylphosphine gave an olefinating solution of reasonable stability. In contrast, the solution obtained by dechlorination of the phosphonium salt by tris{dimethylamino}-phosphine showed no stability.

INTRODUCTION

A variety of synthetic applications of the tertiary phosphine-polyhalomethane reaction have been successfully exploited in recent years [1-3]. One facet of this general reaction scheme, which has been of interest in our laboratories, has been the Wittig conversion of carbonyl-containing compounds to dihalomethylene olefins as illustrated in eq. 1.

$$2\ R_3P + CX_4 + >C{=}O \longrightarrow >C{=}CX_2 + R_3PO + R_3PX_2 \qquad \text{[eq. 1]}$$

Although much of the early work in this area employed carbon tetrachloride or carbon tetrabromide as a route to dichloro- or dibromomethylene olefins

[4-7], subsequent modifications have employed other reagents or catalysts. For example, trichlorobromomethane has been utilized in the preparation of dichloromethylene olefins [8-10], while dibromomethylene olefins are obtained in good yield from carbon tetrabromide by substitution of one equivalent of zinc dust for one equivalent of the tertiary phosphine [11-15].

The use of fluorohalomethanes in this type of approach has exhibited considerable promise in the preparation of fluoromethylene olefins [16-18], eq. 2.

$$2\ R_3P + CFXBr_2 + >C=O \xrightarrow{\Delta} >C=CFX + R_3PBr_2 + R_3PO \qquad \text{[eq. 2]}$$

R = Ph, Me_2N

X = F, Br

Although this route has served quite well for the preparation of difluoromethylene and bromofluoromethylene olefins, a notable lack of success has been achieved in the preparation of chlorofluoromethylene olefins [19]. The major difficulty has been the inability of the readily available methanes, $CFCl_3$ (I) and $CFHCl_2$ (II), to undergo a facile, clean reaction with triphenylphosphine (III). Under mild conditions, no reaction occurs, and under forcing conditions a complex mixture is obtained [19]. Alternatively, it was found that the synergistic effect of zinc dust and (III) on (I) in the presence of aldehydes and activated ketones did afford modest yields of chlorofluoromethylene olefins. However, this method suffers two disadvantages: (1) yields of olefins from aldehydes and activated ketones are, at best, modest, and (2), non-activated ketones show almost a total lack of reactivity.

Van Wazer et. al. [20] have reported that tris(dimethylamino)phosphine (IV) reacts with (I) to afford the expected dichlorofluoromethyltris(dimethylamino)phosphonium chloride (V) eq. 3.

$$\underset{\text{I}}{CFCl_3} + \underset{\text{IV}}{(Me_2N)_3P} \longrightarrow \underset{\text{V}}{[(Me_2N)_3\overset{\oplus}{P}CFCl_2]Cl^{\ominus}} \qquad \text{[eq. 3]}$$

We have found that dehalogenation of (V) with a second equivalent of a tertiary phosphine in the presence of the appropriate carbonyl component gives good to excellent yields of chlorofluoromethylene olefins from aldehydes, ketones (both activated and non-activated), and activated esters. The results of this generalized approach to the synthesis of chlorofluoromethylene olefins are summarized below.

RESULTS AND DISCUSSION

Previous work involving the preparation of difluoromethylene olefins in our laboratory has demonstrated the increased reactivity (nucleophilicity) of the tris(dimethylamino) ylide relative to the triphenyl ylide [18].

$$(Me_2N)_3\overset{\oplus}{P}\text{-}\overset{\ominus}{C}F_2 \;>>\; Ph_3\overset{\oplus}{P}\text{-}\overset{\ominus}{C}F_2$$

It was also qualitatively observed that (IV) was several orders of magnitude more reactive with CF_2Br_2 and $CFBr_3$ relative to (III) [21]. Therefore, it appeared that (IV) might succeed in reaction with (I), in contrast to our previous lack of success with (III) [19]. Indeed, the preparation of (V) has been reported in a previous totally unrelated study [20]. Thus, a reaction scheme similar to that outlined in equation 2 seemed possible for the 'insitu' generation of the chlorofluoromethylenetris(dimethylamino)phosphonium ylide (VI), eq. 4.

$$I + 2\ (IV) \longrightarrow \underset{VI}{[(Me_2N)_3\overset{\oplus}{P}\text{-}\overset{\ominus}{C}FCl]} + R_3PCl_2 \qquad \text{[eq. 4]}$$

However, several observations suggested this approach required some modification: (1) The ylide precursor, namely (V), forms very slowly. This slow rate of formation, coupled with the known reactivity of (IV) with numerous carbonyl compounds [22-25], indicated that polyhalogenated carbonyl-containing compounds would be totally consumed by (IV) before any significant amount of (VI) was formed; (2) the relative insolubility of (V) in ethereal solvents, such as Et_2O and THF, precluded their use for ylide reactions, although ethereal solvents served best for the preparation of (V). Consequently, a two step reaction sequence was indicated; initial preparation and isolation of (V) in ethereal solvents, followed by subsequent ylide generation in a polar aprotic solvent [26]. Benzonitrile was found to be a suitable solvent for this purpose. The overall reaction scheme is summarized in equation 5. Representative examples of

$$I + IV \xrightarrow[2)\ RT,\ overnight]{1)\ Et_2O,\ 0^\circ} V$$

$$V + R_3P + >C{=}O \xrightarrow[PhCN]{60^\circ} >C{=}CFCl + R_3PCl_2 + (Me_2N)_3PO \qquad \text{[eq. 5]}$$

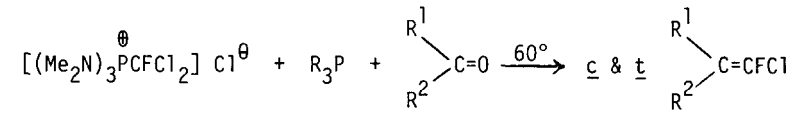
an aldehyde, activated ketone, non-activated ketone, and an activated ester were examined under these conditions and are summarized in Table I.

Several points of interest are worthy of note: (1) Reactions in THF lead to little, if any, of the expected chlorofluoromethylene olefins (Entries 1 and 2); (2) the use of benzonitrile in place of THF facilitates ylide formation (Entries 3 and 4); (3) the extent of successful olefination is dependent upon the nature of the tertiary phosphine employed as the dehalogenation reagent (Entries 5-8); (4) successful olefination of non-activated ketones can be attained by dechlorination of (V) with (IV) (Entry 7). In contrast, dechlorination of (V) with (III) affords only low yields of olefin (Entry 5); (5) successful olefination of an activated ester was achieved (Entries 6 and 8), the first successful olefination of an ester with a halomethylene ylide [27-29]. The vinyl ether product was extremely reactive and polymerized during all isolation attempts, therefore all structural assignments for this reactive compound are based on ^{19}F NMR evidence - which permits an unambiguous assignment [30,31]. Again, dechlorination with (IV) gives higher yields than when (III) is similarly employed (compare Entry 6 with 8). It is important to note that ester olefination occurs with no complications from side reactions of the ester with the generated dichlorophosphorane [32].

The similarity of olefin stereochemistry obtained from reaction of (V) and (III) with benzaldehyde and trifluoroacetophenone (Entries 3 and 4) as compared to other methods [31,33,34] suggests that an ylide is indeed the reactive intermediate in these reactions (cf. Mechanism section for additional evidence). It is of interest to note that (VI) gives identical stereochemical results to the triphenyl ylide [31,33] in these olefination reactions (Entries 3 and 4). The observed stereochemistry with acetophenone is that expected from our previous observations with aldehydes and activated ketones [31,33]. Ando [34] has also observed nonstereoselective olefinations with this type of ylide. The stereoselective olefination observed with the activated ester is surprising, and additional work is required before any detailed explanation can be offered for this unusual stereochemical behavior.

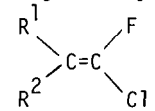
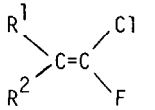
Table 1

Preparation of Chlorofluoromethylene Olefins: Carbonyl, Solvent, and Phosphine Survey



R	R^1	R^2	Solvent	Reaction[a] Duration(Hr)	Olefin[b] Yield(%)	cis:trans[c]
Ph	CF_3	Ph	THF	2	0	-------
Ph	CH_3	Ph	THF	10	3	53:47
Ph	CF_3	Ph	PhCN	1.5	83	42:58
Ph[d]	H	Ph	PhCN	3	60	56:44
Ph	CH_3	Ph	PhCN	11	3	50:50
Ph	CF_3	OC_3H_7-i	PhCN	144	40	10[e]
Me_2N	CH_3	Ph	PhCN	3	56	52:48
Me_2N[f]	CF_3	OC_3H_7-i	PhCN	2	67	10[e]

[a]Time when maximum olefin yield was initially realized. [b]Glpc yield based on starting carbonyl compound.

[c] cis:  ; trans: 

[d]Reaction at 100°C. [e]Determined by ^{19}F NMR, α,α,α-trifluorotoluene as internal standard. [f]Reaction at room temperature.

Since both the nature of the reactive intermediate and the observed stereochemistry parallel the detailed work of Krutzsch [31] and Ando [34], obvious extentions of this procedure can be predicted from these earlier reports. However, the main advantages of this procedure over these previous reports are: (1) availability of the common halomethane [35] and phosphine [36] precursors; (2) simplicity of the reaction; (3) extention to non-activated ketones and activated esters.

MECHANISM

Although a complete mechanistic study has not been conducted, several mechanistic experiments illustrate some aspects of this reaction sequence.

I. Formation of Dichlorofluoromethyltris{dimethylamino}phosphonium Chloride (V)

When the preparation of (V) was carried out in triglyme/ethanol, ^{19}F NMR analysis of the reaction mixture showed (II) (>99%) as the only fluorine-containing product; 93% of hexamethylphosphoramide was also observed by ^{1}H NMR (eq. 6).

$$I + IV + EtOH \xrightarrow[0°C]{TG} \underset{>99\%}{II} + \underset{93\%}{(Me_2N)_3PO} \qquad \text{[eq. 6]}$$

When the reaction of (I) and (IV) was carried out in the presence of TME, no 1-chloro-1-fluorotetramethylcyclopropane was detected. However, 97% of (V) was observed. The above evidence suggests that (V) is formed via abstraction of positive chlorine from (I), followed by a rapid recombination of the ion pair as outlined in equation 7. The reduced methane, (II), is formed by capture of the intermediate $CFCl_2^{\ominus}$ ion by ethanol [38]. An independent control experiment has demonstrated that (V) is not hydrolyzed by ethanol [41]. Therefore, (II) is formed via capture of a reaction intermediate and not by hydrolysis of (V). Similar stability of other tris{dimethylamino}phosphonium salts to hydrolysis has been previously observed in our laboratory [21].

$$I + IV \longrightarrow [(Me_2N)_3\overset{\oplus}{P}Cl]CFCl_2^{\ominus} \xrightarrow{\text{cyclization}} V$$
$$\downarrow EtOH \qquad \not\downarrow EtOH$$
$$II + (Me_2N)_3PO \qquad II \qquad \text{[eq. 7]}$$

II. Formation of Chlorofluoromethylenetris{dimethylamino}phosphorane (VI)

In order to demonstrate that (VI) was indeed formed in this reaction, the reaction of (V) with (III) was conducted in benzonitrile/ethanol. ^{19}F NMR analysis after 6 hours at 45°C indicated that the major product was chlorofluoromethyltris{dimethylamino}phosphonium chloride (VII), eq. 8, resulting from protonation of (VI).

$$III + V \xrightarrow[45°]{PhCN} [VI] + Ph_3PCl_2 \xrightarrow{EtOH} [(Me_2N)_3\overset{\oplus}{P}CFHCl]Cl^{\ominus} + EtCl + Ph_3PO \quad \text{[eq. 8]}$$

VII, 92%

III. Reactivity and Stability of (VI)

When (III) was employed as the dechlorination agent of (V) in the presence of acetophenone (Entry 5, Table 1), only traces of olefin were observed after 11 hours. In contrast, the use of (IV) (Entry 7) gave a reasonable yield of olefin in only 3 hours. In order to establish that (VI) was indeed formed in the first reaction above, and to gain some insight into the reactivity and stability of the different intermediates, the following experiments were carried out:

(a) Dehalogenation of Dichlorofluoromethyltris{dimethylamino}phosphonium Chloride (V) with Triphenylphosphine (III) in the Presence of Acetophenone, Followed by Addition of Trifluoroacetophenone, eq. 9

$$III + V + PhC(O)CH_3 \xrightarrow[60°C,\ 24\ hrs.]{PhCN} [\text{Reaction Soln.}] + Ph(CH_3)C{=}CFCl \ (c/t,\ 6\%)$$

$$[\text{Reaction Soln.}] \xrightarrow[2\ hrs.,\ 60°C]{PhC(O)CF_3} Ph(CF_3)C{=}CFCl \quad (c/t,\ 50\%) \qquad \text{[eq. 9]}$$

Although only 6% of cis- and trans-1-chloro-1-fluoro-2-phenylpropene was formed from acetophenone after 24 hours, immediate reaction occurred upon addition of the more reactive trifluoroacetophenone [43]. These results suggest that this dehalogenation step is reversible, eq. 10, similar to the equilibrium observed with (III) or (IV) and CF_2Br_2 [44]. The lack of

$$III + V \rightleftharpoons VI + Ph_3PCl_2 \qquad \text{[eq. 10]}$$

reaction with acetophenone under these conditions suggests that recapture

of chlorine from the dichlorotriphenylphosphorane by (VI) is faster than its reaction with acetophenone. When the more electrophilic ketone, trifluoroacetophenone, is added, Wittig olefination successfully competes with recapture of halogen by the ylide. Since successful olefination of trifluoroacetophenone still occurs after a 24 hour reaction at 60°C, it is obvious that the reaction mixture retains olefinating ability for an extended period. Indeed, we have followed the olefinating ability of a benzonitrile solution of (III) and (V) [prepared at room temperature] by reacting aliquots with benzaldehyde at 70°C/2 hrs. Although the yield of chlorofluorostyrenes decreases with time, the original solution retains olefinating ability for >500 hours [45].

In contrast to the stability of the olefinating solution prepared from (III) and (V), when (IV) and (V) are reacted at 60°C in benzonitrile for 1.5 hours, followed by the addition of acetophenone, no 1-chloro-1-fluoro-2-phenylpropenes were observed, indicating that this solution has limited, if any, stability [46]. We suggest that this behavior is a reflection of the ease of loss of positive chlorine from $(Me_2N)_3PCl_2$ relative to Ph_3PCl_2. Therefore, the reaction of (IV) and (V) does not result in an equilibrium situation, and no pathway is available to prevent ylide decomposition. Thus, in the absence of a trapping agent such as a carbonyl compound, only ylide decomposition is observed. Similar lack of stability of the difluoromethylene ylide has been observed in the absence of a pathway to stabilize the ylide by halogen capture from a dihalophosphorane [44]. These observations suggest that the ease of recapture of halogen from a dihalophosphorane is dependent upon both the nature of the halogen and the substituents attached to phosphorus. However, since no related work of this nature is available in the literature, additional work is required to delineate all the features of this recapture mechanism.

CONCLUSION

The dechlorination of dichlorofluoromethyltris{dimethylamino}phosphonium chloride by tertiary phosphines provides a facile route to the corresponding chlorofluoromethylene ylide. This ylide successfully olefinates aldehydes, activated ketones, non-activated ketones, and activated esters. A stable ylide solution is obtained from the reaction of the phosphonium salt and triphenylphosphine.

EXPERIMENTAL

Solvents and Reagents:

All reactions proved to be extremely moisture sensitive, requiring scrupulously dried reagents. THF (MCB) and triglyme (Ansul) were predried by stirring over sodium followed by distillation from a sodium benzophenone ketyl. Benzonitrile (MCB) was washed with aqueous sodium carbonate, water, and dried overnight over calcium chloride prior to vacuum distillation from P_2O_5. Both solvents were stored over 4 Å (Linde) molecular sieves in dark septum-capped bottles under a dry nitrogen atmosphere. Triphenylphosphine (Cincinnati-Milacron) was heated at 50°C/0.1 mm overnight then stored in a desiccator under nitrogen over P_2O_5. Tris{dimethylamino}phosphine was prepared by the Organic Synthesis procedure [37]. Trichlorofluoromethane [35] was utilized as received.

Generally, all solid dried reagents were handled in a glove bag under a dry nitrogen atmosphere, and transferred to reaction flasks via Fieser side-arm addition tubes [47]. Carbonyl compounds were purified by standard literature procedures [48]. Isopropyltrifluoroacetate was prepared by modification of the produce of Miller and Woolf [49], and was dried prior to use by distillation from P_2O_5.

Analytical Instrumentation and Reaction Apparatus

Details of the analytical instrumentation employed in this work and the typical reaction apparatus have been described in detail [19]. Glpc analyses of reaction solutions from attempted acetophenone olefinations were conveniently analyzed on a 10 ft x 1/4 in. O.D. stainless steel column packed with 25% FFAP on 80-100 mesh Chromosorb P (Column C).

Preparation of Dichlorofluoromethyltris{dimethylamino}phosphonium Chloride (V)

(IV) (44.3 g, 0.27 mole) in 75 ml dry ether was added dropwise over a two hour period to a stirred, 0°C solution of (I) (49.9 g, 0.36 mole) in 350 ml dry ether. Subsequent stirring for two hours at 0°C was followed by overnight stirring at room temperature under a nitrogen atmosphere. Filtration of the hygroscopic tan precipitate in a fritted Schlenk funnel [47] under nitrogen, followed by additional ether washes and drying with a stream

of dry nitrogen, afforded 75.5 g (0.25 mole, 93%) of (V). The melting point of (V) was characterized by softening at 151°C and decomposition at 218°C. Anal: Calculated for $C_7H_{18}N_3PCl_3F$: C, 27.97; H, 6.04; N, 13.98. Found: C, 27.89; H, 5.92; N, 13.88%. ^1H NMR ($CDCl_3$, internal TMS): δ = 3.09, d(CH_3); $J(^1H-^{31}P)$ = 10 Hz; ^{19}F NMR ($CDCl_3$, internal $CFCl_3$): Ø* = 58.3 ppm, d($PCFCl_2$); $J(^{19}F-^{31}P)$ = 82.5 Hz; ^{31}P NMR ($CDCl_3$, external H_3PO_4): δ = -43.5 ppm, d($PCFCl_2$); $J(^{31}P-^{19}F)$ = 84.2 Hz. Reported: ^{31}P NMR (EtOH, external H_3PO_4): δ = -44 ppm [20].

General Olefination Procedure

Solvents were first added via predried syringe, followed by the addition of (V) and (III). The carbonyl component was then added via syringe, followed by heating to the reaction temperature. When (IV) was used as the dechlorination agent, (V) and the carbonyl component were first added and dissolved in the reaction solvent followed by either slow syringe addition (~ 1 minute) or dropwise addition (30-60 minutes in the case of isopropyltrifluoroacetate) of (IV) at room temperature, followed by heating to reaction temperature.

Preparation of Chlorofluoromethylene Olefins

All reactions were carried out with an excess of (V) and tertiary phosphine relative to the carbonyl component. Olefin yields are based on the carbonyl component. Product chlorofluoromethylene olefins were unambiguously identified by comparison of their spectroscopic properties relative to authentic samples [19,31].

(1) Carbonyl Survey

(a) Use of Triphenylphosphine (III)

The following procedure is representative. Reaction of trifluoroacetophenone (1.73 g, 9.9 mmoles) with (V) (4.04 g, 13.5 mmoles) and (III) (3.89 g, 14.8 mmoles) in 60 ml THF for 2 hours at 60°C showed 0% (via glpc analysis on Column A) of the expected chlorofluoromethylene olefins, and 99% unreacted ketone.

(b) Use of Tris{dimethylamino}phosphine (IV)

Acetophenone (1.05 g, 8.7 mmoles) and (V) (3.29 g, 11.0 mmoles) were dissolved in 20 ml benzonitrile. Subsequent syringe addition of (IV) (1.89 g, 11.6 mmoles) was followed by heating at 55°C for 3 hours. Glpc analysis (Column C) showed 56% (4.9 mmoles) of cis- and trans-1-chloro-1-fluoro-2-phenylpropene in an isomer ratio of 52:48.

Mechanistic Experiments:

(a) Protonation of Chlorofluoromethylenetris{dimethylamino}phosphorane (VI)

A homogeneous solution of (V) (2.03 g, 6.8 mmoles) and absolute ethanol (0.56 g, 12.3 mmoles) was prepared in benzonitrile and stirred at 45°C for 1 hour. Subsequent addition of (III) (1.78 g, 6.8 mmoles) was followed by heating at 45°C for 6.5 hours. ^{19}F NMR analysis of the reaction mixture showed 8% (0.6 mmoles) of (V) and 92% (6.2 mmoles) of (VII) [50].

(b) Capture of $CFCl_2^{\ominus}$

To the standard apparatus was added 15 ml of triglyme, (I) (1.2 cc, 17.8 mmoles) and absolute ethanol (0.92 g, 20.0 mmoles). Then, (IV)(1.56 g, 9.6 mmoles) in 10 ml triglyme was added dropwise to this solution at 0°C over a 40 minute period, resulting in the formation of a slightly yellow, homogeneous solution. After stirring for 4 hours at 0°C, ^{19}F NMR analysis of the reaction solution indicated the formation of 9.6 mmoles (99%) (II) [Ø* = 80.2 ppm, d, $J(^1H-^{19}F)$ = 52 Hz]. ^1H NMR analysis indicated the formation of 8.9 mmoles (93%) of $(Me_2N)_3PO$ [δ = 2.57, d; $J(^1H-^{31}P)$ = 9.0 Hz]. Enhancement of the $(Me_2N)_3PO$ peak was also observed by the addition of authentic $(Me_2N)_3PO$.

(c) Reaction of Trichlorofluoromethane (I) and Tris{dimethylamino}phosphine (IV) in the Presence of TME

To the standard apparatus was added 15 ml of triglyme, (I) (1.1 cc, 16.5 mmoles), 1.49 g (17.8 mmoles) of tetramethylethylene (TME), and benzene (glpc internal standard). To this solution, (IV) (1.62 g, 9.9 mmoles) in 10 ml triglyme was added dropwise over a 40 minute period, keeping the reaction solution at 0°C. Precipitation occurred within one hour. After stirring for an additional 6 hours at 0°C, glpc analysis showed that 33% (I) remained. No 1-chloro-1-fluorotetramethylcyclopropane was detected, and 91% TME was observed by glpc. Filtration of the reaction mixture via a fritted Schlenk funnel gave 97% isolated (V) - identified via ^{19}F NMR.

(d) Stability of Triphenylphosphine (III)/Dichlorofluoromethyltris{dimethylamino}phosphonium Chloride (V) at 60°C

Addition of (I) (7.27 g, 27.7 mmoles), (V) (2.64 g, 8.8 mmoles) and acetophenone (1.03 g, 8.6 mmoles) to benzonitrile was followed by heating for 24 hours at 60°C. Glpc analysis on Column C showed only 6% (mesitylene

as internal standard) cis- and trans-1-chloro-1-fluoro-2-phenylpropene. Addition of trifluoroacetophenone (1.57 g, 9.0 mmoles) was followed by an additional 2 hour heating at 60°C. Glpc analysis (Column A) showed 50% (4.4 mmoles) cis- and trans-1-chloro-2-phenylperfluoropropene. All product propenes were identified by comparison of their glpc retention times with authentic samples.

(e) Stability of Tris{dimethylamino}phosphine (IV)/Dichlorofluoromethyltris{dimethylamino}phosphonium Chloride (V) at 60°C

The addition of (V) (3.58 g, 11.9 mmoles) to benzonitrile in a standard apparatus was followed by syringe addition of (IV) (2.04 g, 12.5 mmoles). An immediate exothermic reaction occurred and the reaction mixture turned from light yellow to dark brown. After heating at 60°C for 1.5 hours, acetophenone (1.11 g, 9.2 mmoles) was added. Glpc analysis (Column C) after an additional 1.5 hours at 60°C, showed none of the cis- or trans-1-chloro-1-fluoro-2-phenylpropene and 80% (7.4 mmoles) remaining acetophenone.

ACKNOWLEDGEMENT

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32 D. J. Burton and W. M. Koppes, J. Org. Chem., 40 (1975) 3026.

33 D. J. Burton and H. C. Krutzsch, Tetrahedron Lett., (1968) 71.

34 H. Yamanaka, T. Ando, and W. Funasaka, Bull. Chem. Soc. Japan, 41 (1968) 756.

35 $CFCl_3$ (Freon® 11) is available from E. I. duPont de Nemours.

36 (III) and (IV) are available from several chemical supply houses. (IV) can also be prepared via the Organic Synthesis procedure [37].

37 Organic Synthesis, Volume 46, John Wiley & Sons Inc., New York, N. Y., 1966, p. 47.

38 This mechanistic sequence is similar to that first suggested by Miller [39] and later verified by Downie [40].

39 B. Miller, Topics In Phosphorus Chemistry, Vol. 2, Interscience, New York, N. Y., 1965.

40 I. Downie, J. Lee, and M. Matough, Chem. Comm., (1968) 1350.

41 Similar hydrolytic stability was observed with the analogous trichloromethyltris(dimethylamino)phosphonium chloride by Ried and Appel [42].

42 W. Ried and H. Appel, Liebigs Ann., 679 (1964) 51.

43 A number of reports have indicated the enhanced reactivity of trifluoroacetophenone in ylide reactions relative to acetophenone [16,31,34].

44 D. G. Naae, H. S. Kesling, and D. J. Burton, Tetrahedron Lett., (1975) 3789.

45 This work represents the first report of a stable Wittig olefination system for a chlorofluorophosphonium ylide [compare stability of [31] and [34]].

46 Acetophenone reacts readily 'insitu' with (IV) and (V) under these conditions to give the chlorofluoroolefins. Trifluoroacetophenone is not used here, since if an equilibrium solution is obtained, the trifluoroacetophenone would react rapidly with (IV).

47 D. Shriver, Manipulation of Air-Sensitive Compounds, McGraw Hill, New York, N. Y., 1969.

48 D. D. Perrin, W. L. F. Armarego, and D. R. Perrin, Purification of Laboratory Chemicals, Pergamon Press, Oxford, 1st Ed., 1966.

49 C. Miller and C. Woolf, Chem. Abstr., 52 (1958) 13779 d, e, f.

50 (VII) was characterized by the following spectral data: ^1H NMR ($CDCl_3$, internal TMS) δ = 2.99 d (CH_3); J(^1H-^{31}P) = 10.1 Hz; δ = 7.88 dd (CHFCl) J(^1H-^{19}F) = 45 Hz, J(^1H-^{31}P) = 11.5 Hz; ^{19}F NMR ($CDCl_3$, internal $CFCl_3$) $\emptyset^*$ = 153.6 ppm, dd (CHFCl); J(^{19}F-^{31}P) = 78 Hz.