

dihydro-2-pyridone and glutarimide. Purification of 6-methyl-4,5-dihydro-2-pyridone was accomplished by preparative vpc ($1/4$ in. \times 12 ft Al, 5% Versamide on Chromosorb G, DMCS treated, acid washed, 175°, 120 cc/mm He, retention time 11.2 min): mp 113–115°; nmr (CDCl_3) δ 1.81 (s, 3, $\text{CH}_3\text{C}=\text{C}$), 2.34 (m, 4, $-\text{CH}_2-$), 4.78 (m, 1, $-\text{CH}=\text{C}-$), 8.5 (broad singlet, 1, NH); ir (KBr) 3150 (NH), 1670 (amide CO), 1239, 1179, 918, 813, 762, 663 cm^{-1} .

Anal. Calcd for $\text{C}_8\text{H}_9\text{ON}$: C, 64.84; H, 8.16; N, 12.60. Found: C, 64.80; H, 8.46; N, 12.80.

Fraction 2, bp 130–160° at 2 mm, was recrystallized from isopropyl alcohol-*n*-hexane: mp 143–145°; nmr (CDCl_3) δ 1.40 (d, 3, CH_3CH), 2.67 (s, 4, CH_2CO), 3.98 (q, 1, CHCH_3), 7.76 (broad singlet, 1, NH); ir (KBr) 3200 (NH), 1725 ($\text{C}=\text{O}$), 1670 cm^{-1} (amide $\text{C}=\text{O}$).

Anal. Calcd for $\text{C}_8\text{H}_9\text{O}_2\text{N}$: C, 56.68; H, 7.14; N, 11.02. Found: C, 56.79; H, 6.97; N, 10.79.

This compound was identified as 6-methyl-5-oxo-2-piperidone.

Oxidation of 3-Carboxy-2-piperidone.—Peracetic acid (32 g, 25%, 0.1 mol), 3-carboxy-2-piperidone (8.55 g, 0.05 mol), and manganic acetylacetonate (50 mg) were allowed to react in the usual manner. Evaporation under vacuum afforded VI as a white solid (6.4 g, 69% yield) which, after two recrystallizations from ethanol, had mp 74–76°; ir (KBr) 3100 (hydrogen bonded NH), 1745 (ester $\text{C}=\text{O}$), 1708 (sh), 1690 cm^{-1} (imide $\text{C}=\text{O}$); nmr (CDCl_3) δ 1.29 (t, 3, CH_3CH_2-), 2.24 (m, 2, $-\text{CH}_2-\text{CH}-$), 2.66 (m, 2, CH_2CO), 3.6 (t, 1, $-\text{CHCH}_2$), 4.27 (q, 2, CH_2CH_3).

Anal. Calcd for $\text{C}_8\text{H}_{11}\text{O}_4\text{N}$: C, 51.88; H, 5.99; N, 7.56. Found: C, 51.60; H, 5.81; N, 7.32.

Oxidation of 2-Pyrrolidone.—Peracetic acid (64 g, 25%, 0.2 mol) treatment of 2-pyrrolidone (8.5 g, 0.1 mol) and manganic acetylacetonate (50 mg) in ethyl acetate (50 ml) was carried out in the usual manner. Filtration and evaporation provided succinimide (5.7 g, 63.7% yield) as a white crystalline material whose melting point (124°, ethanol recrystallization) and infrared spectrum were identical with those of an authentic sample.

Oxidation of N-Methyl-2-pyrrolidone.—Peracetic acid (64 g, 25%, 0.2 mol), N-methyl-2-pyrrolidone (9.9 g, 0.1 mol), and manganic acetylacetonate (50 mg) in ethyl acetate (50 ml) were

allowed to react in the usual manner. Work-up afforded N-methylsuccinimide (6.25 g, 55.3% yield), mp 64°. The structure was verified by infrared comparison with an authentic sample.

Oxidation of N-Ethylacetamide.—A solution of N-ethylacetamide (8.7 g, 0.1 mol) and manganic acetylacetonate (50 mg) in ethyl acetate (50 ml) was treated with peracetic acid (64 g, 25%, 0.2 mol) in the usual manner. Filtration and evaporation provided an oil which, upon distillation, yielded a small amount of acetamide and diacetamide: 5.9 g (58.4%); bp 80–90° at 1.4 mm; mp 75.5–77°; nmr (CDCl_3) δ 2.32 (s, 6, CH_3C), 9.73 (s, 1, NH). Spectral (ir, nmr) comparisons with an authentic sample verified the structure as that of diacetamide. A mixture melting point was undepressed.

Oxidation of N-Formylpiperidine.—N-Formylpiperidine (11.3 g, 0.1 mol) and manganous chloride (5×10^{-3} mol) in ethyl acetate (50 ml) were treated with peracetic acid (120, 25%, 0.4 mol) in the usual manner. Fractional distillation gave a mixture of starting material and N-formyl-2-piperidone (bp 80–82° at 3 mm). Preparative-scale vpc (6 ft \times $1/4$ in. Al, 20% Tergitol N-P44 on Chromosorb W, 170°) provided pure N-formyl-2-piperidone: nmr (CDCl_3) δ 1.87 (m, 4, CH_2), 2.56 (m, 2, $\text{CH}_2\text{C}=\text{O}$), 3.60 (m, 2, $-\text{CH}_2\text{N}$), 10.43 (s, 1, CHO); ir (neat) 1720 (CHO), 1690 cm^{-1} ($-\text{NHCO}-$).

Anal. Calcd for $\text{C}_8\text{H}_9\text{O}_2\text{N}$: C, 56.68; H, 7.14. Found: C, 56.28; H, 7.28.

Registry No.—1-[H]-7-Oxo-4,5-dihydroazepine, 2228-76-4; adipamic acid ethyl ester, 1190-69-8; 3,4-dihydro-2-pyridone, 24058-44-4; 6-methyl-6-hydroperoxy-2-piperidone, 24058-46-6; 6-methyl-5,6-dihydro-2-piperidone, 24058-47-7; 6-methyl-4,5-dihydro-2-pyridone, 24058-29-5; 6-methyl-5-oxo-2-piperidone, 24058-30-8; N-formyl-2-piperidone, 24058-32-0; Mn(acac)₂, 14024-58-9; Mn(acac)₃, 14284-89-0; IV, 24058-45-5; VI, 24058-31-9.

(17) A. Labruto, *Gazz. Chim. Ital.*, **63**, 266 (1933).

(18) I. M. Heilbron, *ibid.*, **63**, 845 (1933).

Fluoro Olefins. III. The Synthesis of β -Substituted 1-Chloroperfluoro Olefins¹

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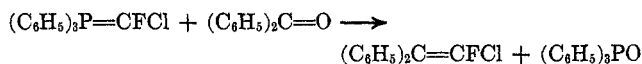
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The reaction of polyfluorinated ketones with chlorofluoromethylenetriphenylphosphorane, $(\text{C}_6\text{H}_5)_3\text{P}=\text{CFCl}$, generated *in situ* from sodium dichlorofluoroacetate and triphenylphosphine, provides a general, one-step route to β -substituted 1-chloroperfluoro olefins. The β substituent can either be an aryl or alkyl group. The reaction of this ylide with several typical aldehydes and ketones was also briefly studied. The proposed mechanism for the formation of the chlorofluoromethylene ylide involves the decomposition of an intermediate phosphobetaine salt. An alternate route to the chlorofluoromethylene ylide, *via* reaction of dichlorofluoromethane with potassium *t*-butoxide and triphenylphosphine, is also presented.

Earlier reported preparations of 1-chlorofluoro olefins generally required several steps, involving Grignard reagents and zinc dehalogenations.^{3–7} Reaction of the chlorofluoromethylene ylide with a carbonyl moiety offers a simple, one-step route to these olefins. Particularly, reaction with polyfluorinated ketones offers a facile synthesis of β -substituted 1-chloroperfluoro olefins.

At present, two reports other than our own¹⁰ have appeared in the literature which describe the chlorofluoromethylene ylide route to 1-chlorofluoro olefins. Speziale and Ratts⁸ prepared 1,1-diphenyl-2-fluoroethylene *via* the following sequence.⁹ The chloro-



fluoromethylene ylide was generated from dichlorofluoromethane, potassium *t*-butoxide, and triphenyl-

(1) (a) Presented in part: Abstracts, 154th National Meeting of the American Chemical Society, Chicago, Ill., Sept 1967, p 2k. (b) Taken in part from the Doctoral Dissertation of H. C. Krutzsch, The University of Iowa, Aug 1968. (c) Preliminary report: *Tetrahedron Lett.*, 71 (1968). (d) Part II: *J. Org. Chem.*, **33**, 1854 (1968).

(2) National Institutes of Health Predoctoral Fellow, 1965–1968.

(3) S. G. Cohen, H. T. Wolosinski, and P. J. Scheuer, *J. Amer. Chem. Soc.*, **72**, 3952 (1950).

(4) P. Tarrant and D. A. Walker, *ibid.*, **76**, 1624 (1954).

(5) S. Dixon, *J. Org. Chem.*, **21**, 400 (1956).

(6) E. D. Bergmann, *et al.*, *J. Amer. Chem. Soc.*, **79**, 4174 (1957).

(7) T. Ando, *et al.*, *Bull. Chem. Soc. Jap.*, **40**, 1275 (1967).

(8) A. J. Speziale and K. W. Ratts, *J. Amer. Chem. Soc.*, **84**, 854 (1962).

(9) We have been unable to substantiate this earlier report. In our experiments, benzophenone did not react with the fluorochloro ylide. Professor Ando¹⁰ has also informed us that his group was also unsuccessful in duplicating this report.

(10) Professor T. Ando, private communication. We are indebted to Professor Ando for communicating some of his unpublished data to us.

TABLE I
 PHYSICAL PROPERTIES OF β -SUBSTITUTED 1-CHLOROPERFLUORO OLEFINS

AR(R)	R _f	Isomer ^a	Bp, °C (mm)	n _D ²⁰	ν_{C-Cl} , μ	Cyclohexane, λ_{max} , m μ (ϵ)	Ethanol, λ_{max} , m μ (ϵ)
C ₆ H ₅	CF ₃	A	75 (40)	1.4558	5.97	221 (5,730)	221 (5,380)
		B	77 (40)	1.4636	6.01	227 (8,350)	227 (7,790)
C ₆ H ₅	C ₂ F ₅	A	75 (30)	1.4334	6.02	222 (5,350)	222 (4,750)
		B	77 (30)	1.4401	6.04	223 (7,460)	223 (6,500)
C ₆ H ₅	<i>n</i> -C ₃ F ₇	A	83 (25)	1.4181	6.01	222 (4,800)	222 (4,730)
		B	85 (25)	1.4243	6.05	223 (7,300)	223 (6,400)
<i>p</i> -ClC ₆ H ₄	CF ₃	A	94 (20)	1.4788	5.98	226 (10,300)	225 (9,150)
		B	97 (20)	1.4874	6.02	231 (11,600)	231 (10,900)
<i>p</i> -CH ₃ OC ₆ H ₄	CF ₃	A	104 (15)	1.4736	5.98	246 (5,400)	246 (5,160)
		B	107 (15)	1.4846	6.02	252 (7,360)	251 (6,420)
<i>p</i> -FC ₆ H ₄	CF ₃	A	84 (40)	1.4435	5.97	222 (5,130)	223 (4,690)
		B	86 (40)	1.4508	6.02	228 (7,370)	228 (6,980)
<i>p</i> -CH ₃ C ₆ H ₄	CF ₃	A	90 (25)	1.4606	5.98	228 (6,050)	230 (5,340)
		B	93 (25)	1.4697	6.02	233 (8,940)	231 (8,550)
C ₆ H ₅	CF ₂ Cl ^b	A	78 (15)	1.4895	5.98	223 (5,940)	223 (5,460)
		B	78 (15)	1.4941	6.03	227 (7,580)	227 (7,280)
C ₆ H ₁₁	CF ₃	A	76 (35)	1.4181	6.00		
		B	76 (35)	1.4204	6.01		
<i>n</i> -C ₄ H ₉	CF ₂ ^b	A	114 (739)	1.3753	5.94		
		B	114 (739)	1.3775	5.95		
C ₆ H ₅ CH ₂	CF ₃	A + B ^c	81 (20)	1.4647	5.95		
		(50/50)					

^a A = $\text{AR(R)}_{\text{R}_f} > \text{C}=\text{C} < \begin{matrix} \text{Cl} \\ \text{F} \end{matrix}$, B = $\text{AR(R)}_{\text{R}_f} > \text{C}=\text{C} < \begin{matrix} \text{F} \\ \text{Cl} \end{matrix}$. Registry numbers in descending order are 19302-03-5, 19302-02-4, 24165-18-2, 24165-19-3, 24165-20-6, 24165-21-7, 19302-07-9, 19302-06-8, 19302-11-5, 19302-10-4, 19302-05-7, 19302-04-6, 19302-09-1, 19302-08-0, 24165-29-5, 24164-51-0, 24164-52-1, 24299-52-9, 24164-53-2, 24164-54-3, 16205-21-3 (A), 16205-22-4 (B). ^b Isomers were not separable by distillation. ^c Isomers were inseparable by distillation or preparative glpc.

 TABLE II
 β -SUBSTITUTED 1-CHLOROPERFLUORO OLEFINS

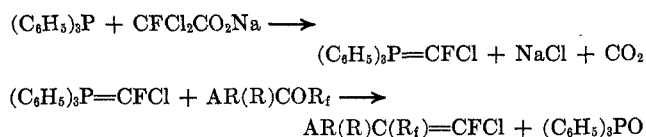
AR(R)	R _f	Yield, % ^a	A/B ratio ^b	C, %		H, %		Cl, %		F, %	
				Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found
C ₆ H ₅	CF ₃	56	53/47	48.10	47.99	2.23	2.21	16.04	15.81	33.85	33.90
C ₆ H ₅	C ₂ F ₅	42	59/41	43.70	43.98	1.82	1.63	12.94	13.02	41.50	41.66
C ₆ H ₅	<i>n</i> -C ₃ F ₇	41	60/40	40.65	40.39	1.54	1.39	10.93	11.06	46.80	48.74
<i>p</i> -ClC ₆ H ₄	CF ₃	53	55/45	41.75	42.06	1.55	1.59	27.40	27.60	29.40	30.22
<i>p</i> -CH ₃ OC ₆ H ₄	CF ₃	67	52/48	47.25	47.54	2.75	3.01	13.93	13.69	29.85	30.09
<i>p</i> -FC ₆ H ₄	CF ₃	27	55/45	44.50	44.77	1.65	1.61	14.65	15.42	39.20	39.63
<i>p</i> -CH ₃ C ₆ H ₄	CF ₃	48	53/47	50.30	50.18	2.94	2.91	14.90	15.40	31.85	32.67
C ₆ H ₅ CH ₂	CF ₃	37	50/50	50.43	50.58	2.94	2.86	14.90	15.42	31.85	32.15
C ₆ H ₁₁	CF ₃	70	42/58	47.00	47.25	4.78	4.88	15.40	15.30	32.90	33.09
<i>n</i> -C ₄ H ₉	CF ₂	34	48/52	41.20	41.33	4.41	4.54	17.36	17.23	37.15	37.10
C ₆ H ₅	CF ₂ Cl	29 ^c	52/48	44.80	44.50	2.07	2.22				

^a Glpc yield was based on starting ketone. ^b This was the *cis/trans* ratio afforded from the olefination reaction. A and B are the same as in Table I. ^c This olefin was prepared from the chlorofluoromethylenetriphenylphosphorane ylide generated from potassium *t*-butoxide, dichlorofluoromethane, and triphenylphosphine.

phosphine. Ando and coworkers¹¹ have prepared this ylide by the reaction of methyl dichlorofluoroacetate with triphenylphosphine and sodium methoxide in petroleum ether.

Results and Discussion

Chlorofluoromethylenetriphenylphosphorane, generated from sodium dichlorofluoroacetate and triphenylphosphine, reacted with polyfluorinated ketones to afford the corresponding *cis-trans* β -substituted 1-



(11) H. Yamanaka, T. Ando, and W. Funaka, *Bull. Chem. Soc. Jap.*, **41**, 757 (1968).

chloroperfluoro olefins in yields of 34–70%. The polyfluorinated ketones were prepared by reaction of the appropriate Grignard reagent with a polyfluorinated acid.¹² Reaction of the chlorofluoromethylene ylide with several typical nonfluorinated aldehydes and ketones afforded the corresponding chlorofluoro olefins in yields of 9 to 49%.

On a small-scale basis these reactions were carried out by simply heating a triglyme solution of the carbonyl compound, triphenylphosphine, and sodium dichlorofluoroacetate at 80 to 90° for a period of several hours. For preparative-scale reactions, a solution of sodium dichlorofluoroacetate in triglyme was added dropwise to a mixture of triphenylphosphine and carbonyl compound in triglyme at 80–90°. This procedure prevented a rapid uncontrollable evolution of carbon dioxide. The results of these reactions, in-

(12) K. T. Dishart and R. Levine, *J. Amer. Chem. Soc.*, **78**, 2268 (1956).

TABLE III
 MISCELLANEOUS β -CHLOROFLUORO OLEFINS

Chlorofluoro olefin	Yield, % ^a	Bp, °C (mm) ^b	A/B ratio ^c	C, %		H, %		Cl, %		F, %	
				Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found
C ₆ H ₅ CH=CFCl ^d	49	63 (16)	56/44	61.30	61.19	3.83	4.10	22.70	22.40	12.15	12.29
n-C ₄ H ₉ CH=CFCl ^e	25	108 (738)	61/39	52.75	52.83	7.33	7.36	26.00	25.74	13.92	14.21
CH ₂ (CH ₂) ₃ C=CFCl ^f	9	59 (75)		53.50	53.43	5.95	6.08	26.40	26.11	14.11	14.42
CH ₂ (CH ₂) ₃ C=CFCl	23 ^g										
(C ₆ H ₅) ₂ C=CFCl	0										

^a Glpc yield was based on starting ketone. ^b Boiling point of *cis-trans* mixture obtained from ylide reaction. ^c This was the *cis/trans* ratio of product afforded from the olefination reaction; A = $\text{AR(R)}>\text{C}=\text{C}<\begin{smallmatrix} \text{Cl} \\ \text{F} \end{smallmatrix}$, B = $\text{AR(R)}>\text{C}=\text{C}<\begin{smallmatrix} \text{F} \\ \text{Cl} \end{smallmatrix}$. ^d n^{20}_{D} 1.5410 (*cis-trans* mixture), $\nu_{\text{C-Cl}}$, 5.98 μ (*cis-trans* mixture). Registry numbers are 16205-22-4 (A), 16629-98-4 (B). ^e n^{20}_{D} 1.4090 (*cis-trans* mixture), $\nu_{\text{C-Cl}}$, 5.93 (*cis-trans* mixture). Registry numbers are 24164-59-8 (A), 24164-60-1 (B). ^f n^{20}_{D} 1.4456, $\nu_{\text{C-Cl}}$, 5.87 μ . Registry number is 24164-76-9. ^g Tributylphosphine was used in place of triphenylphosphine.

cluding some of the physical properties of these olefins are summarized on Tables I-III.

Concentration studies demonstrated that for best results a mole ratio of 1.5:1.5:1.0 of triphenylphosphine, sodium dichlorofluoroacetate, and carbonyl compound, respectively, should be used. The *cis-trans* olefin was isolated by flash distillation of the reaction mixture into a Dry Ice cooled receiver. Careful distillation on a spinning-band column and/or preparative glpc yielded pure *cis* and *trans* olefin. *cis-trans* isomer assignments for the olefins were based on $J_{\text{F,CF}}$, or $J_{\text{H,F}}$.

To determine the effect solvent had on reaction yields and *cis/trans* ratios, a variety of dipolar aprotic solvents was studied, using trifluoroacetophenone as a model ketone. The results are summarized in Table IV. As the results of this table illustrate, the *cis/trans*

 TABLE IV
 EFFECT OF SOLVENTS ON THE REACTION OF TRIFLUOROACETOPHENONE WITH TRIPHENYLPHOSPHINE AND SODIUM DICHLOROFLUOROACETATE AT 90°

Solvent	Time, min ^a	Yield, %		
		Carbon dioxide	Olefin ^b	A/B ratio ^c
Dimethylformamide	21	100	20	55/45
N-Methyl-2-pyrrolidone	23	77	20	54/46
Monoglyme	281	88	27	54/46
Diglyme	135	88	54	55/45
Triglyme	90	86	56	53/47
Dimethyl sulfoxide ^d				

^a Time required for the maximum amount of carbon dioxide to be evolved. ^b Glpc yield based on starting ketone. ^c This was the *cis/trans* ratio of product afforded from the olefination reaction; A = $\text{C}_6\text{H}_5>\text{C}=\text{C}<\begin{smallmatrix} \text{Cl} \\ \text{F} \end{smallmatrix}$, B = $\text{C}_6\text{H}_5>\text{C}=\text{C}<\begin{smallmatrix} \text{F} \\ \text{Cl} \end{smallmatrix}$. ^d Rapid evolution of dimethyl sulfide precluded any further measurements.

isomer ratios are not affected by a change in solvent.¹³ When dimethyl sulfoxide was used as the solvent for the reaction, a competing side reaction took place, which produced dimethyl sulfide [isolated as its mercuric chloride adduct, 2(CH₃)₂S-3HgCl₂¹⁴]. Heating a solu-

tion of sodium dichlorofluoroacetate in dimethyl sulfoxide also caused evolution of dimethyl sulfide.

Several workers have claimed that addition of lithium ion or iodide ion to a Wittig reaction mixture has a noticeable effect on the *cis/trans* ratio of the product.¹⁵⁻¹⁷ However, others have disputed this claim.^{18,19} In this work the product *cis/trans* ratio was not significantly affected when the reaction with trifluoroacetophenone was carried out in the presence of lithium ion (as CFCl₂CO₂Li) or in the presence of iodide ion (as NaI); the isomer ratio in the presence of lithium ion was 51/49, and in the presence of iodide ion was 54/46.

However, an increase in the size of the perfluoroalkyl group did affect the *cis/trans* isomer ratio. When trifluoroacetophenone was allowed to react with the chlorofluoromethylene ylide, 53% of the product was the isomer bearing the phenyl and chlorine groups *cis*, and with pentafluoropropiophenone the percentage of the corresponding isomer increased to 59%. The substitution of an aliphatic group for an aromatic group also had an effect on the *cis/trans* isomer ratio, but in the opposite direction. When a cyclohexyl group was substituted for a phenyl group, the percentage of the corresponding isomer decreased to 42%. A butyl or a benzyl group had less effect in this respect. *para* substituents on the aromatic ring had little effect on the product *cis/trans* isomer ratio. When an aldehyde was allowed to react with the chlorofluoromethylene ylide, the less sterically favored isomer was formed in greater amounts. For example, 56% of the chlorofluoro olefin from the reaction of benzaldehyde with the chlorofluoromethylene ylide was the olefin bearing the phenyl and chlorine groups *cis*. With valeraldehyde, the percentage of the corresponding isomer was 61%. This anomaly is rationalized by assuming hydrogen bonding between the aldehydic proton and the ylide fluorine in the betaine-forming step, thus producing more of the betaine that yields the less sterically favored *cis* isomer upon decomposition into chlorofluoro olefin and triphenylphosphine oxide. Ando and coworkers have also carried out the reaction of benzaldehyde with the chlorofluoromethylene ylide. Their

(15) L. D. Bergelson and M. M. Shemyakin, *Tetrahedron*, **19**, 149 (1963).

(16) L. D. Bergelson, *et al.*, *Tetrahedron Lett.*, 2669 (1964).

(17) M. Schlosser, G. Mueller, and K. F. Cristmann, *Angew. Chem. Int. Ed. Engl.*, **5**, 667 (1964).

(18) G. Drefahl, D. Lorenz, and G. Schmitt, *J. Prakt. Chem.*, **23**, 143 (1964).

(19) H. O. House, V. K. Jones, and G. A. Frank, *J. Org. Chem.*, **29**, 3327 (1964).

(13) Although we have found no solvent effects in the reaction of the fluorochloro ylide generated *via* sodium dichlorofluoroacetate, Ando and coworkers¹⁰ have found that, when the ylide is generated from methyl dichlorofluoroacetate, the *cis/trans* product ratios do vary with the polarity of the solvent.

(14) W. F. Farragher, J. C. Merrel, and S. Conroy, *J. Amer. Chem. Soc.*, **51**, 2774 (1929).

TABLE V
COMPARISON OF DECARBOXYLATION^a AND BASE PLUS HALOFORM^b METHODS OF YLIDE GENERATION

Starting ketone	Decarboxy ^c yield, %	Base ^c yield, %	Decarboxy ^d A/B ratio	Base ^d A/B ratio
Benzaldehyde	49	39	56/44	56/44
Trifluoroacetophenone	56	31	53/47	52/48
Cyclopentanone	9	27		
Cyclopentanone ^e	23	0		
Benzophenone	0	0		

^a Decarboxylation method: $(C_6H_5)_3P + CFCl_2CO_2Na \longrightarrow (C_6H_5)_3P=CFCl + CO_2 + NaCl$. ^b Base + haloform method: $(C_6H_5)_3P + CHFCl_2 + t-BuOK \longrightarrow (C_6H_5)_3P=CFCl + t-BuOH + KCl$. ^c Glpc yield based on starting ketone. ^d This was the *cis/trans* ratio of product afforded from the olefination reaction, $A = \begin{matrix} C_6H_5 \\ >C=C < \\ CF_3(H) \end{matrix} \begin{matrix} Cl \\ \\ F \end{matrix}$, $B = \begin{matrix} C_6H_5 \\ >C=C < \\ CF_3(H) \end{matrix} \begin{matrix} F \\ \\ Cl \end{matrix}$. ^e Tri-*n*-octylphosphine substituted for triphenylphosphine.

results indicated that 56% of the chlorofluoro olefin from the reaction was the isomer bearing the phenyl and chlorine groups *trans*, just the opposite of our results. We are unable at present to account for this disparity between our results and theirs.

The reaction of dichlorofluoromethane with potassium *t*-butoxide and triphenylphosphine as an alternate route to the chlorofluoromethylene ylide was also investigated. Briefly, the procedure used was to add dichlorofluoromethane to a slurry of potassium *t*-butoxide and triphenylphosphine in heptane at 0°. Then the desired carbonyl compound was added. The ratio of reactants was formally the same as that used in the decarboxylation method of ylide generation previously described. The resulting mixture was stirred for several hours at room temperature, then subjected to product separation. Product yields and isomer ratios were determined by glpc analysis. The results obtained from this method of ylide generation are compared with the decarboxylation method of ylide generation in Table V. The results in this table illustrate that reaction temperature and changes in solvent have no influence on the *cis/trans* ratio of product. These data also demonstrate that the decarboxylation method used in conjunction with aldehydes and reactive (polyfluorinated) ketones generally enables somewhat higher yields of olefins. With unreactive ketones, such as cyclopentanone, the reactivity and stability of the intermediate ylide become more important. At the higher reaction temperature of the decarboxylation method of ylide generation, most of the ylide decomposes before reaction with the unreactive carbonyl species. At the lower temperature of the haloform and base method of ylide generation, however, the ylide is more stable, and hence reaction even with an unreactive carbonyl compound gives a higher yield of olefin. Although the ylide (from sodium dichlorofluoroacetate) decomposes at the higher temperature, rapid cooling and addition of a reactive carbonyl component showed that a reasonable amount of ylide still remained, since a 36% yield of product was obtained when trifluoroacetophenone was added to the reaction mixture of triphenylphosphine and sodium dichlorofluoroacetate in triglyme after carbon dioxide evolution had ceased. When tri-*n*-butylphosphine was substituted for triphenylphosphine, a more reactive chlorofluoromethylene ylide was formed. For example, a 25% yield of chlorofluoro olefin was obtained with cyclopentanone when tri-*n*-butylphosphine was substituted for triphenylphosphine in the decarboxylation method of ylide generation. However, this alkyl ylide is much less stable. When cyclopentanone was added to the

reaction mixture of tri-*n*-butylphosphine and sodium dichlorofluoroacetate in triglyme (85°) after all carbon dioxide evolution, no chlorofluoroolefin was obtained. Similarly, no chlorofluoro olefin was obtained when cyclopentanone was added to the reaction mixture of dichlorofluoromethane, potassium *t*-butoxide, and tri-*n*-butylphosphine in heptane (0°). Benzophenone failed to react under either method of chlorofluoromethylene ylide generation.⁹ By increasing the ratio of chlorofluoromethylene ylide precursor (triphenylphosphine, potassium *t*-butoxide, and dichlorofluoromethane) to carbonyl compound from 1.5 to 3 to 1 in the haloform plus base method of ylide generation, the yield of chlorofluoro olefin from trifluoroacetophenone increased from 31 to 55%. Thus, the utility of the cheaper haloform method can be increased by employing a large excess of the fluorochloromethylene ylide.

The identification of the chlorofluoro olefins was based primarily on elemental analysis and infrared, ultraviolet, and proton and fluorine nmr spectroscopy. The infrared spectra of the chlorofluoro olefins always exhibited a strong $>C=CFCl$ absorption between 5.97 and 6.05 μ . The position at which the $>C=CFCl$ absorption occurred in any pair of *cis-trans* isomers differed by 0.05 μ or less.

The ultraviolet spectra of the β -aryl substituted 1-chloroperfluoro olefins exhibited a decrease in extinction coefficient between cyclohexane and ethanol. The $\pi \rightarrow \pi^*$ primary absorption band in the *para*-substituted 2-phenyl-1-chloroperfluoro olefins showed an increasing wavelength value in the following order: $p-CH_3-O > p-CH_3 > p-H > p-F$. In the homologous 2-phenyl-1-chloroperfluoropropene, butene, and pentene series, the value of the absorption maxima and extinction coefficient decreased with increasing perfluoroalkyl group size in the order $CF_3 > C_2F_5 > n-C_3F_7$. Apparently, the larger the perfluoroalkyl group, the more the phenyl ring was twisted out of conjugation with the double bond, lowering both the wavelength and the extinction coefficient.

In any given pair of *cis-trans* isomers, both the absorption maxima and the extinction coefficient were larger in the isomer bearing the aryl and chlorine groups in a *trans* configuration than in the isomer bearing the aryl and chlorine groups *cis*. This effect could be rationalized in terms of steric crowding between the aromatic ring and the chlorine atom. When the phenyl and chlorine groups occupied *cis* positions, the phenyl ring was twisted out of conjugation to a greater extent with the double bond than when the phenyl and chlorine groups occupied *trans* positions.

The fluorine nmr data were also consistent for the assigned structures of the β -substituted 1-chloroperfluoro olefins, and were used to assign the configurations of the *cis* and *trans* isomers on the basis of the F,CF_3 or F,CF_2X coupling constants across the double bond (see Table VI). The *trans* F,CF_3 or F,CF_2X ($X =$

TABLE VI
FLUORINE NMR^a SPECTRAL DATA OF β -SUBSTITUTED
1-CHLOROPERFLUORO OLEFINS
 $AR(R)C(CF_2X)=CFCl$

AR(R)	X	Iso- mer ^b	$J_{1,2}$	ϕ_1	ϕ_2
C ₆ H ₅	F	A	24	64.1	59.0
		B	13	61.7	59.0
<i>p</i> -ClC ₆ H ₄	F	A	24	62.8	59.0
		B	13	60.5	59.2
<i>p</i> -CH ₃ OC ₆ H ₄	F	A ⁴	24	64.2	59.4
		B	13	62.4	59.3
<i>p</i> -FC ₆ H ₄ ^c	F	A	24	63.2	59.1
		B	13	61.5	59.3
<i>p</i> -CH ₃ C ₆ H ₄	F	A	24	64.3	59.4
		B	13	62.2	59.2
C ₆ H ₁₁	F	A	26	64.6	57.3
		B	12	64.5	59.7
<i>n</i> -C ₄ H ₉	F	A	21	65.8	61.1
		B	12	68.0	60.2
C ₆ H ₅	Cl	A	31	63.3	46.1
		B	12	63.4	46.2
C ₆ H ₅	CF ₃	A	27	60.9	108.8
		B	7	52.8	109.5
C ₆ H ₅	C ₂ F ₅	A	28	58.7	105.2
		B	8	51.9	106.3

^a The chemical shift values are expressed in ϕ (parts per million) values upfield from CCl₃F and the coupling constant values are in cycles per second. ^b A = $\begin{matrix} AR(R) & & Cl \\ & \diagdown & / \\ & C=C & \\ & / & \diagdown \\ XF_2C & & F \end{matrix}$, B = $\begin{matrix} AR(R) & & F \\ & \diagdown & / \\ & C=C & \\ & / & \diagdown \\ XF_2C & & Cl \end{matrix}$. ^c Isomer A or B: aromatic F = +110.0 ϕ .

CF₃, C₂F₅, or Cl) coupling constants ranged from 7 to 13 cps. Both Stone²⁰ and Swalen²¹ have reported coupling constants of 21–24 and 9–12 cps for the respective *cis* and *trans* F,CF_3 coupling constants in α -substituted perfluoropropenes.

Mechanism for Chlorofluoromethylene Ylide Formation from Sodium Dichlorofluoroacetate and Triphenylphosphine.—Several plausible mechanisms can be envisioned to explain the formation of the chlorofluoromethylene ylide from triphenylphosphine and sodium dichlorofluoroacetate. One possibility involves prior decomposition of sodium dichlorofluoroacetate to form chlorofluorocarbene, which then reacts with triphenylphosphine to form the chlorofluoromethylene ylide. In another possibility, sodium dichlorofluoroacetate reacts with triphenylphosphine to form a phosphobetaine salt, such as (C₆H₅)₃P⁺CFCFClO₂⁻, before losing carbon dioxide to form the chlorofluoromethylene ylide. When sodium dichlorofluoroacetate was allowed to decarboxylate in the presence of tetramethylene, a 37% yield of the corresponding chlorofluorocyclopropane adduct was produced. When a similar decarboxylation was carried out in the presence of equimolar amounts of triphenylphosphine and tetramethyl-

ethylene, no cyclopropane adduct was formed. Either triphenylphosphine is a better trapping agent for the chlorofluorocarbene, or triphenylphosphine reacts with the fluorochloroacetate to form the phosphobetaine salt discussed above. To evaluate this former possibility, the chlorofluoromethylene ylide was generated *via* the reaction of dichlorofluoromethane with potassium *t*-butoxide in the presence of equimolar amounts of tetramethylethylene and triphenylphosphine. Subsequently, trifluoroacetophenone was added to the reaction mixture. After work-up, glpc analysis showed a 14% yield of the cyclopropane adduct and a 19% yield of C₆H₅C(CF₃)=CFCl. These results indicate that triphenylphosphine and tetramethylethylene are of comparable ability as trapping agents for the chlorofluorocarbene. Consequently, the absence of cyclopropane formation, when sodium dichlorofluoroacetate was decarboxylated in the presence of equivalent amounts of triphenylphosphine and tetramethylethylene, lends support to the phosphobetaine salt (C₆H₅)₃P⁺CFCFClO₂⁻ as the precursor to the chlorofluoromethylene ylide in the decarboxylation method of ylide generation. Evidence for the formation of similar phosphobetaine salts has been observed by Denney²² in the corresponding hydrocarbon analogs, (C₆H₅)₃P⁺(CH₂)_nCO₂⁻, $n = 2, 3$. These salts could not be isolated in the case where n was equal to 1. Similarly, the analogous fluorinated salt, (C₆H₅)₃P⁺CFCFClO₂⁻, could not be isolated.

Experimental Section

Infrared spectra were recorded on a Perkin-Elmer Model 21 spectrophotometer using a neat film of sample, and calibrated *vs.* a 0.07-mm polystyrene film. Ultraviolet spectra were obtained on a Beckman DK-2A recording spectrophotometer, using both cyclohexane and ethanol as solvents. Proton nmr spectra were obtained on a Varian A-60 spectrometer and are reported in δ values downfield from an internal standard of tetramethylsilane. Fluorine nmr spectra were obtained on a Varian HA-100 spectrometer at 94.1 Mcps and are reported in ϕ values upfield from an internal standard of trichlorofluoromethane. Glpc analyses were obtained on an F & M Model 720 dual column gas chromatograph using helium as a carrier gas. Product yields were determined from comparison of the relative areas under peaks to areas due to external standards of the same compounds. Column A was a 6 ft \times 0.25 in. i.d. copper column packed with 10% w/w silicone rubber supported on 100–120 mesh Gas-Chrom P. Column B was a 6 ft \times 0.25 in. i.d. copper column packed with 10% w/w Carbowax 20M supported on 80–100 mesh Chromosorb P. Column C was a 10 ft \times 0.50 in. i.d. copper column packed with 20% w/w DC-QF-1 fluorosilicone rubber supported on 80–100 mesh Chromosorb P. Carbon and hydrogen analyses were obtained in this laboratory, and fluorine and chlorine analyses were carried out by Schwarzkopf Analytical Laboratories in Woodside, N. Y.

Sodium Dichlorofluoroacetate.—Sodium dichlorofluoroacetate was prepared by the careful neutralization of 80 g (0.54 mol) of dichlorofluoroacetic acid in 150 ml of ether with 29 g (0.27 mol) of anhydrous sodium carbonate, with subsequent removal of the ether and water under reduced pressure, then heating overnight at reduced pressure (*ca.* 4 mm or lower) at 50°. Lithium dichlorofluoroacetate was prepared in a similar manner.

Polyfluorinated Ketones.—The polyfluorinated ketones used in this study were prepared by the method of Dishart and Levine.¹² A good example of this type of synthesis is described elsewhere.²³

General Method for the Synthesis of 1-Chlorofluoro Olefins.—The reaction apparatus employed consisted of a three-necked

(20) E. Pitcher and F. G. A. Stone, *Spectrochim. Acta*, **17**, 1244 (1961).
(21) J. D. Swalen and C. A. Reilly, *J. Chem. Phys.*, **34**, 2122 (1961).

(22) D. B. Denney and L. C. Smith, *J. Org. Chem.*, **27**, 2404 (1962).
(23) F. E. Herkes and D. J. Burton, *ibid.*, **32**, 1316 (1967).

round-bottomed flask equipped with a magnetic stirrer, a nitrogen inlet tube, and a reflux condenser equipped with a nitrogen outlet leading to a mercury bubbler and a Dry Ice cooled trap. For small-scale reactions, the pressure-equalized dropping funnel was deleted from the apparatus.

A typical preparative-scale reaction using the synthesis of 2-(*p*-chlorophenyl)-1-chloroperfluoropropene, $p\text{-ClC}_6\text{H}_4\text{C}(\text{CF}_3)=\text{CFCl}$, as an example proceeded as follows. Into a 500-ml three-necked flask, equipped in the manner previously described, were placed 100 ml of triglyme, 80 g (0.3 mol) of triphenylphosphine, and 4.16 g (0.2 mol) of *p*-chlorotrifluoroacetophenone. The reaction mixture was heated to 90° and approximately one-quarter of a solution of 51 g (0.3 mol) of sodium dichlorofluoroacetate in 70 ml of triglyme was added to the reaction mixture. Once the reaction mixture had turned to a dark red or black color, the remaining three-quarters of the solution was added dropwise and the resulting mixture was allowed to stir overnight at 90°. The reaction mixture was then subjected to flash distillation. The distillate was poured into 400 ml of water and the resulting mixture extracted twice with 200-ml portions of ether. The combined ether extracts were washed five times with 200-ml portions of water, dried over anhydrous magnesium sulfate, and diluted to 250 ml with ether. Product yield determined by glpc analysis of the solution on column A indicated a 53% yield of olefin, based on starting ketone, and the absence of starting ketone. If any starting ketone was present it could be readily removed by stirring the ether extract over 100 ml of an aqueous 10% sodium hydroxide solution. The *cis/trans* ratio of product was determined on column B. The configurations of both isomers were determined by the fluorine nmr spectra (see Results and Discussion). Concentration of the ether solution, followed by distillation at reduced pressure yielded 21.5 g (42%) of pure *cis-trans* olefin, bp 88° (15 mm). Pure *cis* and *trans* olefin were obtained by distillation of the *cis-trans* isomer mixture through a 24-in. Nester-Faust Teflon spinning-band column with a reflux ratio of 25:1. Since the lower boiling isomer was still contaminated with about 4% higher boiling isomer after distillation, it was further purified by preparative glpc using column C.

Solvent Study.—The apparatus and general experimental procedure were the same as previously described. A 50-ml three-necked flask was substituted for the 500-ml three-necked flask, and all the reagents were placed in the flask. The reactants were triphenylphosphine, sodium dichlorofluoroacetate, and trifluoroacetophenone in a molar ratio of 1.5:1.5:1, respectively. The rate of decarboxylation and the total amount of carbon dioxide evolved were obtained by collection of the liberated carbon dioxide over water previously saturated with carbon dioxide.

Reaction of Triphenylphosphine, Sodium Dichlorofluoroacetate, and Tetramethylethylene in Triglyme at 70°.—A mixture consisting of 6.4 g (0.037 mol) of sodium dichlorofluoroacetate, 9.8 g (0.037 mol) of triphenylphosphine, and 3.1 g (0.037 mol) of tetramethylethylene in 20 ml of triglyme was heated at 70° until carbon dioxide evolution had ceased. Flash distillation of the volatile material into a Dry Ice cooled receiver, followed by glpc analysis of the distillate on column A showed

the absence of any cyclopropane derivative. From the reaction, 3.0 g (97%) of the tetramethylethylene was recovered.

A control reaction consisting of a solution of 25 g (0.3 mol) of tetramethylethylene and 34 g (0.2 mol) of sodium dichlorofluoroacetate in 100 ml of triglyme heated overnight at 70° gave the corresponding chlorofluorocyclopropane adduct in a 37% yield. The proton nmr spectrum of the compound showed a doublet at δ 1.13 ($J_{\text{F,CF}_3} = 2.0$ cps).²⁴

Anal. Calcd for $\text{C}_7\text{H}_{12}\text{ClF}$: C, 55.81; H, 7.97. Found: C, 55.74; H, 7.69.

A third reaction was carried out consisting of 50 ml of dry diethyl ether, 9.8 g (0.037 mol) of triphenylphosphine, 4.3 g (0.037 mol) of potassium *t*-butoxide, and 3.4 g (0.040 mol) of tetramethylethylene. The resulting mixture was cooled in an ice bath and 5.0 g (0.040 mol) of dichlorofluoromethane was added. Then 4.0 g (0.025 mole) of trifluoroacetophenone was added. Flash distillation of the volatile material into a Dry Ice cooled receiver, followed by glpc analysis of the distillate on column A showed a 14% yield of the cyclopropane adduct and a 19% yield of $\text{C}_6\text{H}_5\text{C}(\text{CF}_3)=\text{CFCl}$.

Preparation of the Chlorofluoromethylene Ylide via Triphenylphosphine, Dichlorofluoromethane, and Potassium *t*-Butoxide.—The reaction apparatus employed consisted of a 100-ml three-necked round-bottomed flask equipped with a nitrogen inlet, magnetic stirrer, rubber septum, and a Dry Ice condenser fitted with an inlet near the bottom for the introduction of condensable gases and an outlet at the top leading to a mercury bubbler, and a Dry Ice cooled trap.

Into the reaction apparatus were placed 65 ml of heptane, 4.3 g (0.038 mol) of potassium *t*-butoxide, and 9.8 g (0.037 mol) of triphenylphosphine. The resulting slurry was cooled in an ice bath, a slow flow of nitrogen started, and 5 g (0.040 mol) of dichlorofluoromethane was added *via* the gas inlet at the bottom of the Dry Ice condenser. When the gas came into contact with the Dry Ice cooled cold finger in the center of the condenser, it liquified and dripped into the reaction mixture in much the same fashion as a liquid added from a dropping funnel. As the dichlorofluoromethane was added, the color of the reaction mixture turned from yellow to orange to brown. Ten minutes after all of the dichlorofluoromethane was added, 4 g (0.025 mol) of trifluoroacetophenone was added. The resulting mixture was stirred overnight at room temperature, then flash distilled into a Dry Ice cooled receiver at a reduced pressure of 4 mm (or lower if possible) and an oil-bath temperature of 130°. Glpc analysis of the distillate on column A showed a 31% yield of $\text{C}_6\text{H}_5\text{C}(\text{CF}_3)=\text{CFCl}$. When the amount of solvent was increased to 100 ml, and the amounts of triphenylphosphine, potassium *t*-butoxide, and dichlorofluoromethane were doubled, the yield of $\text{C}_6\text{H}_5\text{C}(\text{CF}_3)=\text{CFCl}$ was increased to 55%.

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(24) Reported for 1-chlorofluorotetramethylcyclopropane, doublet at δ 1.13 ($J_{\text{F,CH}_3} = 2.0$ cps): R. A. Moss and R. Gerstl, *Tetrahedron*, **23**, 2549 (1967).