cm^{-1} were quantitatively utilized to determine the amounts of *p*- and *m*-cresol, respectively, while bands at 830 and 900 cm^{-1} were used for *p*- and *m*-chlorophenols, respectively. Multiple isomer distribution determinations were done on six cresol mixtures, giving good, reproducible results.

C. **For Chlorinated Products.**—Aryl chloride yields were performed along with phenol yields by glpc (columns A and B). Columns A and C were used to determine the isomeric compositions of the chlorinated hydrocarbons.

D. **For HCl.**—The general procedure was followed except that the reaction flask was continuously purged with nitrogen which was then bubbled through an aqueous sodium hydroxide trap. Titration of aliquots from the trap before and after the reaction gave the amount of acid formed. The yield of HCl produced based on the limiting peroxide reagent was 88% from toluene and 90% from anisole hydroxylations.

Registry No.—Hydrogen peroxide, 7722-84-1; aluminum chloride, 7446-70-0; anisole, 100-66-3; toluene, 108-88-3; chlorobenzene, 108-90-7; *o*-xylene, 95-47-6; mesitylene, 108-67-8; benzene, 71-43-2; nitrobenzene, 98-95-3; cresol, 1319-77-3.

Acknowledgment.—The author thanks the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this work.

Cyclization of N-Substituted Diallylamines to Pyrrolidine Derivatives During the Radical Addition of Perfluoroalkyl Iodides

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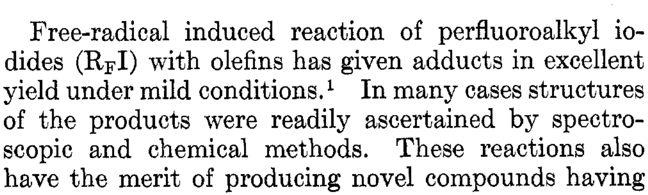
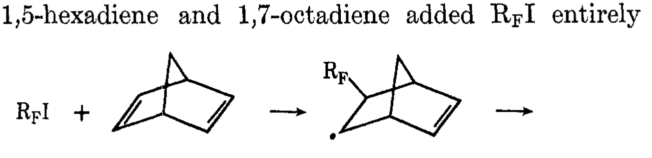
A series of N-substituted diallylamine derivatives, $YN(CH_2CH{=}CH_2)_2$, where Y = CH_3CO, CF_3CO, C_6H_5CO, CN, and $-CH_2CH_2CN$, cyclized during the radical addition of 1-iodoperfluorobutane. The cyclic adducts were shown to possess a 3-iodomethyl-4-(2,2,3,3,4,4,5,5,5-nonafluoropentyl)pyrrolidine structure by spectroscopic and chemical methods. Diallylamine (Y = H) and 1-iodoperfluorobutane, in the presence of a radical generating agent only, gave a polymeric salt in quantitative yield, while 3-diallylaminopropionitrile (Y = CH_2CH_2CN) gave both cyclic adduct and a derived polymeric salt. Cyclopolymers of $YN(CH_2CH{=}CH_2)_2$ synthesized under similar radical conditions have been previously thought to contain six-membered ring repeating units.

Free-radical induced reaction of perfluoroalkyl iodides (R_FI) with olefins has given adducts in excellent yield under mild conditions.[1] In many cases structures of the products were readily ascertained by spectroscopic and chemical methods. These reactions also have the merit of producing novel compounds having unusual physical and chemical properties.[2,3] Addition of R_FI to dienes may also involve rearrangement of the intermediate radical both in cyclic and open-chain forms. Thus, norbornadiene and R_FI gave **1a,b**, while certain 1,6-heptadienes gave **2a,b**.[4] By contrast, 1,5-hexadiene and 1,7-octadiene added R_FI entirely without rearrangement, giving monoadducts **3** and **4** without transfer of the radical to an adjacent center of unsaturation, as would have been expected.[5] This is surprising in view of the reported[6] cyclization of these dienes during addition of CCl_4.



1a, b



2a, b

X, Y = H or $COOC_2H_5$

$$R_FI + CH_2{=}CH(CH_2)_nCH{=}CH_2 \longrightarrow R_FCH_2CHI(CH_2)_nCH{=}CH_2 \quad \mathbf{3},\ n = 2;\ \mathbf{4},\ n = 4$$

One of the most intriguing features of the cyclization of 1,6-heptadienes is the preference for five-membered ring formation.[5–7] Other radical cyclizations[8,9] also show this same preference and it has been ascribed to kinetic control and to steric factors. It was recognized that this feature was inconsistent with cyclopolymerization processes, which generally have been thought to give six-membered ring repeating units.[10,11] N-substituted diallylamines, and *N,N*-diallylamides in particular, have been claimed to give cyclopolymers with piperidine ring units,[12–14] based on chemical[12] and infrared evidence.[13,14] Such polymers are important both from the technical and scientific points of view and merit a careful study of their structures. Identification of these structures by the infrared method is a dif-

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[3] N. O. Brace, *J. Org. Chem.*, **27**, 3027, 3033, 4491 (1962); **28**, 3093 (1963); **32**, 430 (1967).

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TABLE I

NMR SPECTRAL PARAMETERS OF N-SUBSTITUTED DIALLYLAMINES, $YN(CH_2CH{=}CH_2)_2$

		Chemical shift and coupling constants for group						
		$CH_2{=}$		$=CH-$	$(CH_2)_2N$		Y protons	
Compd	Y	δ	J, Hz	δ	δ	J, Hz	δ	J, Hz
5	H	4.7	m	5.4 m	3.75	5	1.7	8[a]
6	CH_3CO	5.1	m	5.6 m	3.85	7	1.98	s
7	CF_3CO	5.1	m	5.6 m	3.95	7		
8	C_6H_5CO	5.1	m	5.6 m	3.95	7	7.35	m
9	CH_2CH_2CN	5.15	15, 5	5.6 m	3.15	7	2.66	7
10	CN	5.3	14, 4	5.7 m	3.62	6		

[a] The sample was run neat and also with added D_2O, which caused this resonance to disappear.

TABLE II

PREPARATION OF ADDUCTS FROM $YN(CH_2CH{=}CH_2)_2$ AND 1-IODOPERFLUOROBUTANE AT 70°, 16 HR

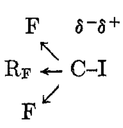
Reactants				Adducts							
							Analyses				
							Calcd, %		Found, %		
Compd	$YN(CH_2CH{=}CH_2)_2$, mol × 10^3	R_FI,[a] mol × 10^3	ABN,[a] mol × 10^3	Compd	Conversion, %[b]	Yield, %[b]	C	H	C	H
5	50.0	100	0.912		100[c]	...[d]	27.10	2.48	27.19[d]	2.60[d]
6	75.0	125	1.50	**11**	78	94				
6	100	200	1.53	**11**	100	100	29.71	2.70	29.90	2.91
7	50.0	100	0.912	**12**	87	100	26.73	1.87	26.97	1.90
8	50.0	100	1.82	**13**	93	~98[c]	37.31	2.76	39.32[c]	3.03[c]
9	50.0	100	1.93	**14**	100[d]	...[d]	31.50	2.85	31.76	2.91
10[e]	50.0	100	0.93	**15**[e]	98	98				

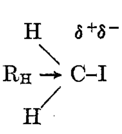
[a] R_FI was 1-iodoperfluorobutane, ABN was azobisisobutyronitrile. [b] Conversion calculated from moles of products/moles of limiting reactant; yield from moles of limiting reactant used up. [c] Viscous, high-boiling oil not readily purified for analysis. [d] See Experimental Section. [e] See ref 7.

ficult procedure, however, and will be discussed elsewhere.[15]

The approach taken here was to prepare cyclization products from R_FI and N-substituted diallylamines, or *N,N*-diallylamides under conditions identical with those previously used for cyclopolymerization. Identification of these cyclic products was expected to have considerable bearing on the problem of polymer structure.

It was also of interest to determine the behavior of diallylamine with R_FI under free-radical conditions, since it has been reported[13] that this amine failed to cyclopolymerize. 1-Iodoperfluorobutane, as a typical perfluoroalkyl iodide, would not be expected to react with diallylamine *as a base*, since the fluorine atoms shield the carbon atom from nucleophilic attack and inductively polarize the C–I bond opposite to that found in ordinary alkyl iodides.[16] An ethanol solution





of potassium hydroxide, however, gives C_4F_9H, by attack at the positive iodine.[16]

$$OH^- + I\text{-}(CF_2)_3CF_3 \longrightarrow HOI + {}^-(CF_2)_3CF_3 \xrightarrow{ROH} CH(CF_2)_3CF_3$$

Results and Discussion

N-Substituted diallylamines and *N,N*-diallylamides were prepared from diallylamine (**5**) by standard procedures. Infrared spectra and nmr spectra of these compounds were useful in ascertaining structures of their reaction products. Some nmr data of $YN(CH_2CH{=}CH_2)_2$ (where Y = H, CH_3CO, CF_3CO, C_6H_5CO, CH_2CH_2CN, and CN) are recorded in Table I, and infrared data are given in the Experimental Section.

A doublet characteristic of the $(CH_2)_2N$ group appeared in nmr spectra of $YN(CH_2CH{=}CH_2)_2$ at δ 2.75–3.95. A complex quartet from protons of CH_2CH_2CN was found at δ 2.66. The chemical shift of $(CH_2)_2N$ protons thus was dependent on the electron-withdrawing nature of the Y group, being greatest for CF_3CO and C_6H_5CO and least for H.

Reaction of 1-iodoperfluorobutane (R_FI) with $YN(CH_2CH{=}CH_2)_2$ under free-radical conditions occurred readily at 70°, using azo initiator (Table II). The adducts were obtained in nearly quantitative yields, and with **6** at a higher efficiency with 2 mol of R_FI to **6** than at a 1.67:1 reactant ratio. It was previously shown for **10** that a 2:1 reactant ratio was optimum.[7] These results show that efficient radical cyclization is characteristic for this entire group of diallylamine derivatives in spite of the anticipated retardation through allylic abstraction reactions. Conversion of adducts to derivatives for determination of structure is shown in Chart I. In each instance reduction by zinc gave a product having a methyl group attached to the pyrrolidine ring.

The infrared spectrum of **18** (Y = CF_3CO) showed the rocking frequencies for CH_3–C at 1450 and 1380 cm^{-1}; in **17** the 1380-cm^{-1} band appeared as a shoulder on the stronger 1350-cm^{-1} band. Dehydrohalogenation of **11** gave a single compound **16**, mp 59°, having an exocyclic methylene group. Infrared showed ν_{CH_2} = 3090, $\nu_{C=O}$ and $\nu_{C=C}$ at 1650, and $\gamma_{CH_2=}$ at 905 cm^{-1}; bands at 935 and 970 cm^{-1} and weak overtone bands at 1810 and 1940 cm^{-1} previously cited for similar exocyclic compounds were also present.[5] Catalytic hydrogenation of **16** then afforded the same *cis* and *trans* methyl-substituted pyrrolidine **17** obtained by zinc reduction of **11**. Gas chromatography confirmed product purity and identity.

The viscous product **13** (Y = C_6H_5CO) was difficult

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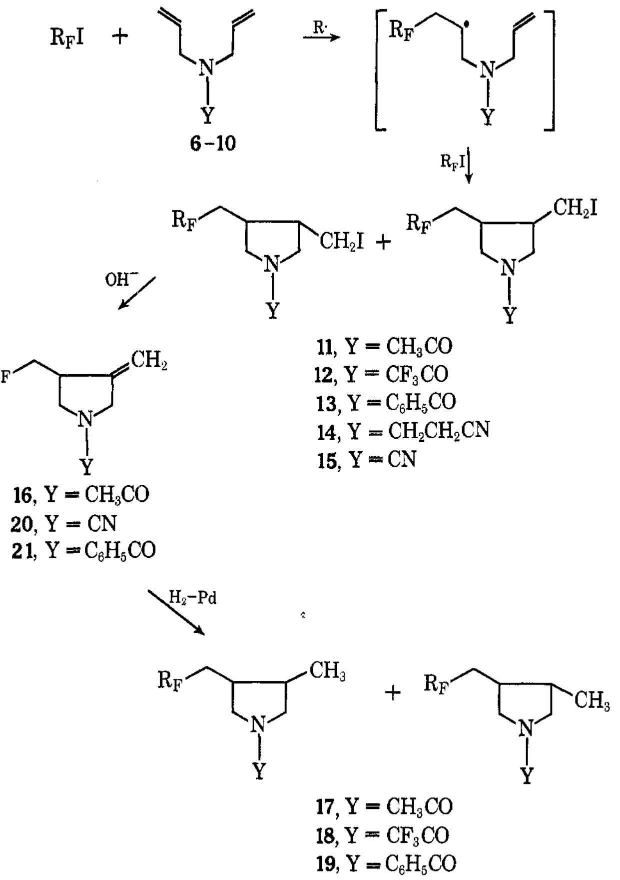
(15) N. O. Brace, unpublished work.

(16) R. E. Banks, "Fluorocarbons and Their Derivatives," Oldbourne Press, London, 1964, p 56.

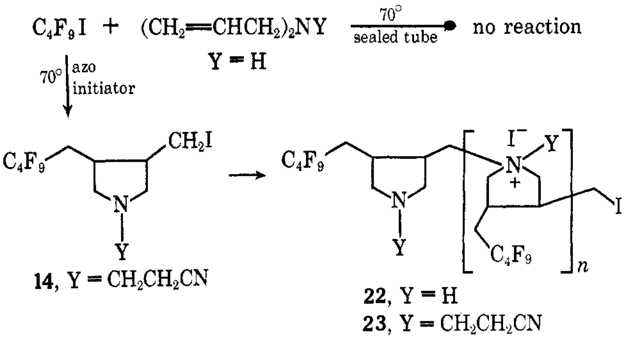
CHART I



to purify and was converted to methyl derivative **19** and methylene derivative **21** for identification. The Y = CF_3CO compounds (**7**, **12** and **18**) were of special interest, since the strong electron-withdrawing group might have been expected to modify the reactivity of the intermediate allylamino radical. The absence of CH_3CO also was desired to facilitate ir and nmr spectroscopic analysis. Cyclic polymerization[15] of **7** occurred readily under conditions used for **6**, **8**, **9**, and **10**.

1-Iodoperfluorobutane and Diallylamine (5).—Reaction of C_4F_9I and **5** in an evacuated, sealed tube from which air was carefully removed did not occur at 70°. All the starting materials were recovered. A similar result was obtained by refluxing C_4F_9I and piperidine for several hours. This behavior is consistent with the known absence of nucleophilic attack on perfluoroalkyl iodides.[16] Once addition of C_4F_9I to the unsaturated linkage has occurred, however, the carbon–iodine bond will no longer be shielded and subsequent S$_N$2 displacement may take place. Thus, reaction of C_4F_9I with diallylamine (**5**) under *radical* conditions gave polymeric salt **22** as a dark red gum in quantitative yield (Chart II). **22** was soluble in acetone or alcohol and insoluble in CCl_4, water, or aqueous acid or base, but reacted readily with alcoholic silver nitrate solution. The infrared spectrum of **22** showed NH stretching bands, CH bands at 1440 and 1350, and bands (1025, 950, 880, 730, and 530 cm^{-1}) in the fingerprint region which were also found in several of the cyclic adducts **11–15**. There was no evidence for unsaturation. Elementary analysis of **22** confirmed its composition and showed from the ratio of "ionic iodine" to total iodine, an approximate value of 3.5 for n in the general formula **22**.

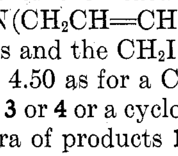
CHART II



1-Iodoperfluorobutane and 3-Diallylaminopropionitrile, 9.—In **9** the *tertiary* amine function was readily quaternized. The cyclic adduct **14** was thus able to react further with another molecule of **14** to give a polymeric salt of postulated structure **23**. About half of the product was isolated as the free amine **14** and the remainder was obtained as a brittle brown solid **23** which reacted readily with silver nitrate solution. **14** did not react with silver nitrate under these conditions. During the distillation of **14** some decomposition occurred and the hydrogen iodide released formed salt from part of **14**. This complication made an estimate of n in general formula **23** of doubtful value.

Nmr Spectroscopy.—That cyclization to pyrrolidine derivatives had occurred was also evident from the nmr spectra of the reaction products. The olefinic bands of $YN(CH_2CH{=}CH_2)_2$ at δ 4.9–6.0 were absent in most cases and the CH_2I protons appeared at δ 3.25 and not at δ 4.50 as for a CHI group of an olefinic adduct such as **3** or **4** or a cyclohexane derivative.[4]

The spectra of products **11–15** were very similar, although not well defined. Conversion to methylene- and methyl-substituted pyrrolidines (Chart I) was very helpful in deducing structures from nmr spectra. The exocyclic methylene in **16** gave a doublet at δ 5.1, J = 7 Hz, with additional splitting of 2 Hz by a ring proton; another doublet appeared at δ 4.1, 2 protons, J = 9 Hz, ascribed to the C-2 methylene because of the inductive effect of the double bond and because the C-2 protons are isolated. The CH_3CO group gave a singlet at δ 1.95 and $-CH_2CF_2$ a triplet at δ 2.4, J_{HF} = 20 Hz, with additional 7 Hz splitting by the methinyl proton. The remaining proton resonances were more complex, but the C-4 methinyl proton resonance appeared at δ 3.7 and the C-5 methylene protons as a multiplet centered at δ 3.2. The spectrum of **16** bore a striking resemblance to that of **20** (Y = CN) previously isolated.[7] The formation of **16** from a piperidine-ring cyclic adduct **24** could not have occurred without unusual rearrangement. The nmr spectra of **17–19** showed the methyl group on C-3 at about δ 1.0 in each case (J = 7 Hz, with additional 2 Hz splitting). Since cis and trans isomers were formed in unequal amount having different chemical shifts for the methyl group, the expected doublets overlapped, giving the appearance of a triplet. The in-



(Y = CH_3CO)

24

ner peak of the doublet at higher field was the higher of the two. The remaining resonances (except for CH_3CO or C_6H_5CO) were not well defined, although they appeared to have the anticipated chemical shifts.

Had cyclization given a piperidine derivative **24**, reduction would have formed a product without a ring methyl and the number of methylene protons would have been greater than found in **17–19**.

Experimental Section

Source of Materials and Methods.—Diallylamine from Aldrich Chemical Co. was distilled, bp 109.5–110°, $n^{25}\mathrm{D}$ 1.4374. 1-Iodoperfluorobutane (**25**) was a gift from Thiokol Chemical Co. and was distilled in a 30-in. platinum spinning-band column (column A), bp 67°, $n^{25}\mathrm{D}$ 1.3250. Other reagents were the best commercial grade available. Infrared spectra were recorded using a Perkin-Elmer Model 337 grating spectrophotometer. Nmr spectra were obtained on a Varian A-60 spectrometer.

N,*N*-**Diallylacetamide** (**6**),[13,14] bp 98–100° (13 mm), $n^{25}\mathrm{D}$ 1.4684 was distilled in column A;[17] glpc analysis on an 8-ft FFAP column (15% on Chromosorb WA, 185°, 20-psi helium pressure) gave one peak at 13.5 min; ir (KBr plates) $\nu_{\mathrm{CH_2=C}}$ 3080, ν_{CH} 3000, 2975, 2925, $\nu_{\mathrm{C=O}}$ and $\nu_{\mathrm{C=C}}$ 1650, $\delta_{\mathrm{COCH_3}}$ 1470, 1360, $\gamma_{\mathrm{CH=CH_2}}$ 985 and 925 cm^{-1}.

N,*N*-**Diallylbenzamide** (**8**),[13,14] bp 101° (0.25 mm), $n^{25}\mathrm{D}$ 1.5380, was obtained in 92% yield from reaction of **5**, benzoyl chloride, and sodium hydroxide solution at 15–25°:[17] ir (KBr plates) ν_{CH} 3080, 3050, 3020, 3000, 2980, 2920, $\nu_{\mathrm{C=O}}$ 1640, $\nu_{\mathrm{C=C}}$ 1600, 1580, δ_{CH} 1495, 1450, 1410, 1265; bands at 1210, 1185, 1150, 1110, 1075, 1000, 980, 925, 790, 725, 700, 645, and 550 cm^{-1}.

N,*N*-**Diallyltrifluoroacetamide** (**7**).[18]—To a well-stirred solution of **5** (97.0 g, 1.00 mol) in 200 ml of dichloromethane, protected from the atmosphere by a slow stream of nitrogen, redistilled trifluoroacetic anhydride (105 g, 0.500 mol) was added dropwise at 0–5° over a 4-hr period. After 0.5 hr of additional stirring the mixture was poured into 100 ml of water, rinsed with 25 ml of water, and dried ($MgSO_4$). **7** distilled, bp 87–88° (38 mm), $n^{25}\mathrm{D}$ 1.4110, 84.7 g (88%); a residue (40.3 g) of crystalline diallylammonium trifluoroacetate remained. The cold trap contained an additional 6.7 g of **7** (94.5% total). **7** was redistilled in column A, bp 67–68.5° (13 mm), $n^{25}\mathrm{D}$ 1.4105. Glpc analysis [FFAP column, 185° (20 psi)] gave a single peak at 3.0 min; ir $\nu_{\mathrm{CH_2=CH}}$ 3080, 3020, $\nu_{\mathrm{CH_2}}$ 2990, 2930, 2880, $\nu_{\mathrm{C=O}}$ 1700, $\nu_{\mathrm{C=C}}$ 1650, δ_{CH} 1520, 1480, 1460, 1425, 1315, 1290, ν_{CF} 1220–1120; bands at 1000–990, 930, 790, 760, 715, 660, 610, 550, and 530 cm^{-1}.

Anal. Calcd for $C_8H_{10}F_3NO$: C, 49.74; H, 5.22. Found: C, 49.63; H, 5.28.

3-Diallylaminopropionitrile (**9**).[13,14,18]—**5** (13.0 g, 0.134 mol) and acrylonitrile (12.0 g, 0.226 mol), kept at 50–60° for 15 hr and distilled gave **9**, bp 108–109° (13 mm), $n^{25}\mathrm{D}$ 1.4619, 17.0 g, 84%); in succeeding preparations conversions varied from 47–53%; ir $\nu_{\mathrm{CH_2=CH}}$ 3070, 3000, 1650, $\nu_{\mathrm{C\equiv N}}$ 2250, $\gamma_{\mathrm{CH_2=CH}}$ 1000 and 928 cm^{-1}.

N-**Acetyl-3-iodomethyl-4-(2,2,3,3,4,4,5,5,5-nonafluoropentyl)-pyrrolidine** (**11**).—**6** (18.92 g, 0.100 mol), **25** (69.0 g, 0.200 mol), and azobisisobutyronitrile (ABN, 0.262 g, 0.00153 mol) were charged to a Fischer–Porter aerosol pressure tube, cooled to −78°, evacuated, and filled with nitrogen three times. The tube was evacuated to 0.2 mm, sealed, and placed in a thermostated oil bath at 70° for 17 hr. The viscous amber liquid was transferrred to a flask and excess **25** was distilled into a −78° trap (32.0 g, 93% recovery); the reaction product was heated to 80° (12 mm). The adduct **11**, 49.0 g (100% conversion), showed little absorption for olefinic protons in its ir or nmr spectra. A 3.5-ml aliquot was sublimed at 110° (0.10 mm): $n^{25}\mathrm{D}$ 1.4495; ir (KBr plates) ν_{CH} 3000, 2980, 2960, 2880, $\nu_{\mathrm{C=O}}$ 1650, δ_{CH} 1450, 1420, 1350, ν_{CF} 1250–1200, 1140; bands at 1020, 930, 905, 880 (s), 735, 600, and 530 cm^{-1}.

N-**Trifluoroacetyl-3-iodomethyl-4-(2,2,3,3,4,4,5,5,5-nonafluoropentyl)pyrrolidine** (**12**).—In similar fashion **12** was obtained from **7** as a viscous oil: bp 117° (0.25 mm), $n^{25}\mathrm{D}$ 1.4250; 23.4 g (87%); ir (KBr plates) ν_{CH} 2950, 2880, $\nu_{\mathrm{C=O}}$ 1690, δ_{CH} 1450, 1350, ν_{CF} 1300–1100; bands at 1025, 990, 948, 930, 910, 880, 850, 760, 740, and 720 cm^{-1}; glpc, using 6-ft QF-1 column [10% on Chromosorb WA, 185° (20 psi helium)] gave 27.5% at 9.7 min, 72.5% at 15.0 min, and *ca.* 1% of **7** at 0.9 min; nmr (CCl_4) δ 1.5–3.5 (multiplets, six protons of CH_2R_F, CH_2I, CHCH), 3.5–4.5 [four protons, overlapping doublets of $(CH_2)_2N$].

N-**2-Cyanoethyl-3-iodomethyl-4-(2,2,3,3,4,4,5,5,5-nonafluoropentyl)pyrrolidine** (**14**).—**25** (34.6 g, 0.100 mol), **9** (7.50 g, 0.0500 mol), and ABN (0.3192 g, 0.00200 mol), kept at 70° for 17 hr as above, gave a brown, viscous residue (24.8 g, 100% conversion) after the volatile starting materials were removed (C_4F_9I, 15.23 g, $n^{25}\mathrm{D}$ 1.3225). A 2.7-g aliquot was sublimed as above with **11**, giving 1.30 g of viscous oil (**14**) at 121° (0.20 mm), $n^{25}\mathrm{D}$ 1.4360; similarly 19.6 g gave 9.45 g of **14** and 0.60 g of volatile trap liquid ($n^{25}\mathrm{D}$ 1.3980) having an odor of acrylonitrile. The brittle brown solid residue (**23**, 14.8 g) was soluble in acetone or alcohol and insoluble in CCl_4 or water, and reacted immediately with alcoholic silver nitrate solution to precipitate silver iodide. **14** gave no immediate reaction: ir ν_{CH} 2940, 2800, $\nu_{\mathrm{C\equiv N}}$ 2250, δ_{CH} 1480, 1420, 1380, 1345, ν_{CF} 1260–1200, 1140; bands at 1020, 930, 880, 850, 730, 600, 530 cm^{-1}; nmr δ 1.9–3.2 (overlapping multiplets, 12 protons, CH_2CH_2CN, ring protons, R_FCH_2, CH_2I), 3.3 (doublet, J = 7 Hz, two protons, CH_2N). The four-line, 5-Hz splitting pattern of CH_2CH_2CN seen in **9** was also present in **14**.

Elemental analysis of **23** showed that it was a polymeric salt, and that an excess of HI was present. In view of the decomposition noted above, and the difficulties inherent in purification of such a material, further investigation was not undertaken.

Anal. Calcd for $C_{13}H_{14}F_9N_2I$: C, 31.36; H, 2.83; I, 25.49. Found (**23**): C, 27.79; H, 2.57; I, 33.36, I^-, 28.06.

Addition of 1-Iodoperfluorobutane (**25**) **to Diallylamine** (**5**).—**25** (34.5 g, 0.100 mol), **5** (4.85 g, 0.0500 mol), and ABN (0.150 g, 0.912 mmol) heated at 70° for 18 hr as above gave a viscous, dark red liquid. Unreacted starting material was removed by distillation from the reaction tube under reduced pressure. The dark red gum (**22**) (22.0 g, 100% conversion) which remained dissolved in acetone or alcohol but was insoluble in water, in aqueous acid or base, and in CCl_4. A film cast on KBr plates from a warm CCl_4 slurry showed ir ν_{NH} 3400, ν_{CH} 2940 superimposed on broad R_2NH^+ band at 2800–2400, δ_{CH} 1440, 1350, ν_{CF} 1230, 1140; bands at 1020, 950, 910, 880 (s), 730, 650, 600, and 530 cm^{-1}. **22** was a polymeric salt. **25** and **5** treated as above without ABN initiator gave back only starting materials by distillation in column A under reduced pressure at 70° pot temperature.

Anal. Calcd for $C_{10}H_{11}F_9NI$: C, 27.10; H, 2.48; F, 38.59; I, 28.60. Found: C, 27.19; H, 2.60; F, 38.43; I, 28.46; I^-, 22.08.

N-**Acetyl-3-methylene-4-(2,2,3,3,4,4,5,5,5-nonafluoropentyl)-pyrrolidine** (**16**).[17]—To **11** (26.1 g, 0.0536 mol) in 60 ml of 90% aqueous ethanol was added while stirring at 40° a solution of KOH (3.50 g, 0.062 mol) in 60 ml of 90% ethanol and the solution was refluxed for 5.25 hr at 65–70°. The mixture was poured into water (130 ml), extracted with benzene (25 ml, three times), rinsed with 10 ml of water, and dried ($MgSO_4$). **16** distilled, bp 130–131° (3 mm), solid mp 46–48°, 17.1 g (89% conversion), leaving a residue of 2.8 g. Recrystallization twice from ligroin (bp 60°, 6 ml to 1 g) afforded pure **16**: mp 59°; ir (CCl_4, 10%) ν_{CH} 3070, 2980, 2940, 2900, 2880, 2850, $\nu_{\mathrm{C=O}}$ 1650, δ_{CH} 1420, 1380, 1350; ν_{CF} 1250–1200, 1130; bands at 1070, 1050, 1020, 975, 900, 880, 855, 725, 710, and 600 cm^{-1}; nmr (CCl_4) δ 1.95 (s, 3 protons, CH_3CO), 2.4 (t, two protons, J = 20 Hz, CH_2R_F), 3.2 (distorted quartet, two protons, J = 7 Hz, $\mathbf{CH_2}CH$), 3.7 (multiplet, one proton, $CH_2\mathbf{CH}$), 4.1 (d, two protons, J = 9 Hz, $N\mathbf{CH_2}C{=}CH_2$), 5.1 (d, two protons, J = 6 Hz, with additional 2 Hz splitting, $CH_2{=}C$); glpc analysis [8-ft FFAP column, 180° (30 psi)] gave one peak at 14.0 min.

Anal. Calcd for $C_{12}H_{12}F_9NO$: C, 40.34; H, 3.39. Found: C, 40.37; H, 3.47.

N-**Benzoyl-3-methylene-4-(2,2,3,3,4,4,5,5,5-nonafluoropentyl)-pyrrolidine** (**21**).—Similarly, **13** (5.7 g, 0.0104 mol) gave crude **21** (2.3 g, 53%), bp 111–116° (0.15 mm), mp 31–42°. Recrystallization from 10 ml of ligroin (bp 60–80°) gave pure **21**: mp 65–66.5°; ir (CCl_4) $\nu_{\mathrm{CH_2=}}$ 3080, ν_{ArH} 3060, 3020, ν_{CH} 2980, 2960, 2930, 2850, $\nu_{\mathrm{C=O,C=CH_2}}$ 1640; bands at 1020, 890, 880, 850, 710, 690, and 660 cm^{-1}; nmr (CCl_4) δ 4.2, (s, two protons, $N\mathbf{CH_2}$-$C{=}CH_2$), 5.1 (d, J = 7 Hz with 2-Hz additional splitting, two protons, $C{=}CH_2$), 7.45 (s, five protons, C_6H_5).

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(17) Assistance by Mr. W. D. Beutel is gratefully acknowledged.

(18) Assistance by Miss Grace Woo is gratefully acknowledged.

Anal. Calcd for $C_{17}H_{14}F_9NO$: C, 48.69; H, 3.36. Found: C, 48.08; H, 3.40.

cis- **and** ***trans-N*****-Acetyl-3-methyl-4-(2,2,3,3,4,4,5,5,5-nonafluoropentyl)pyrrolidine (17).**—**11** (14.5 g, 0.0300 mol), ether (50 ml), and acetic acid (glacial, 50 ml) were stirred by a magnet as zinc dust (5.0 g, 0.076 g-atom) was added in portions at 55°.[19] Exothermic reaction began immediately and continued for 0.5 hr; the cloudy white suspension was heated by means of a bath for 4 hr at reflux temperature (58°). The product was worked up by the literature procedure[19] and distilled, bp 102° (0.45 mm), $n^{25}{}_D$ 1.3728, 9.2 g, 86%. A viscous oil residue, 1.0 g, remained: glpc analysis [8-ft FFAP column, 180° (30 psi)] gave 2.5% at 8.3 min, and 97.5% at 16.2 min; ir (KBr plates) ν_{CH} 2960, 2880, $\nu_{C=O}$ 1650, δ_{CH} 1470, 1440, 1420, 1380, 1350, ν_{CF} 1300–1200, 1140; bands at 1090, 1060, 1025, 985, 970, 930, 910, 885, 855, 730, 715, 690, 660, 620, 600, and 530 cm^{-1}; nmr (CCl_4) δ 1.00 (two doublets overlapped, three protons, $J = 7$ Hz, with 2-Hz additional splitting, CH_3CH, cis and trans), 1.9 (s, four protons, CH_3CO and $CHCH_2$), 2.25 (2.1–2.9) (t, three protons, $J = 20$ Hz, CH_2R_F and $CHCH_2$), 3.0–4.0 (4.5 protons, CH_2NCH_2); the methinyl protons were obscured by the other resonances.

Anal. Calcd for $C_{12}H_{14}F_9NO$: C, 40.11; H, 3.93. Found: C, 40.23; H, 3.96.

Hydrogenation of *N*-Acetyl-3-methylene-4-(2,2,3,3,4,4,5,5,5-nonafluoropentyl)pyrrolidine (16) to *cis-* and *trans-N*-Acetyl-3-methyl-4-(2,2,3,3,4,4,5,5,5-nonafluoropentyl)pyrrolidine (17).—**16** (7.14 g, 0.020 mol), 35 ml of 95% ethanol, and 0.10 g of 10% palladium on carbon were shaken in a Parr hydrogenator at 45 psi hydrogen pressure for 24 hr. **17** was recovered, bp 145–152° (12 mm), $n^{25}{}_D$ 1.3913, 6.0 g, 84%. Spectra (nmr and ir) and glpc analysis showed that none of **16** remained in the sample of **17**.

Preparation of *N*-Trifluoroacetyl-3-methyl-4-(2,2,3,3,4,4,5,5,5-nonafluoropentyl)pyrrolidine (18) by Zinc Reduction of *N*-Trifluoroacetyl-3-iodomethyl-4-(2,2,3,3,4,4,5,5,5-nonafluoropentyl)-pyrrolidine (12).—As with **17**, zinc reduction of **12** (10.8 g, 0.0200 mol) gave **18**, bp 89–92° (0.40 mm), $n^{25}{}_D$ 1.3680, 76%, and a viscous residue (1.1 g): ir (KBr plates) ν_{CH} 2960, 2880, $\nu_{C=O}$ 1770, δ_{CH} 1460, 1440, 1385, 1350, ν_{CF} 1250–1140; bands at 1060, 1025, 985, 940, 932, 910, 882, 855, 760, 738, 730, 720, 595, and 530 cm^{-1}; nmr δ 1.1 (2 d, three protons, $J = 7$ Hz, CH_3C), 2.5–3.0 (m, four protons, CH_2R_F, CH), 3.0–4.2 [3.9 protons, m, $(CH_2)_2N$]; glpc analysis [8-ft FFAP column, 180° (20 psi)] gave two peaks at 5 min, not resolved.

Anal. Calcd for $C_{12}H_{11}F_{12}NO$: C, 34.56; H, 2.70. Found: C, 34.81; H, 2.71.

cis- **and** ***trans-N*****-Benzoyl-3-methyl-4-(2,2,3,3,4,4,5,5,5-nonafluoropentyl)pyrrolidine (19).**—**13** (18.0 g, 0.0330 mol) by similar zinc reduction gave **19** (10.0 g, 86%), bp 138–139° (0.25 mm), $n^{25}{}_D$ 1.4581, and a residue (2.6 g): ir $\nu_{CH=}$ 3080, 3050, ν_{CH} 2960, 2935, 2870, $\nu_{C=C(Ar)}$ 1710, $\nu_{C=O}$ 1640, δ_{CH} 1499, 1475, 1450, 1420, 1380, 1350; bands at 1140, 1075, 1055, 1025, 980, 930, 905, 880 (s), 850, 790, 730 (s), 720 (s), 670, 660, 650, 595, and 530 cm^{-1}; nmr (CCl_4) δ 0.9 (t, poorly resolved, 2.7 protons, $J = 7$ Hz, cis and trans (CH_3CH), 1.9–2.9 (t, 3.7 protons, $J = 19$ Hz, CH_2R_F and CH- ring), 2.9–3.9 [m, four protons, $(CH_2)_2N$], 5.2 (m, 0.2 protons, $CH_2{=}CH$ impurity), 7.4 (s, five protons, C_6H_5). Some 4% of **13** appeared to be present in the sample.

Anal. Calcd for $C_{17}H_{16}F_9NO$: C, 53.26; H, 4.20. Found: C, 53.10; H, 4.25.

Registry No.—**5,** 124-02-7; **6,** 6296-61-3; **7,** 14618-49-6; **8,** 10283-70-2; **9,** 31164-08-6; **10,** 538-08-9; **11,** 31164-10-0; **12,** 31164-11-1; **14,** 31164-12-2; **16,** 31164-13-3; ***cis*-17,** 31164-14-4; ***trans*-17,** 31164-15-5; **18,** 31164-16-6; ***cis*-19,** 31164-17-7; ***trans*-19,** 31164-18-8; **21,** 31164-19-9; **22,** 31153-74-9.

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Cyclopentenone Synthesis by Directed Cyclization

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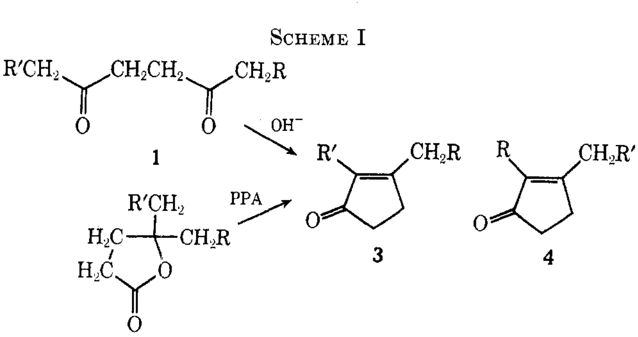
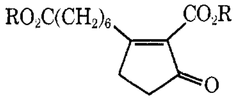
A procedure is described for the synthesis of 3-substituted 2-carbomethoxycyclopentenones **3** ($R' = CO_2CH_3$). An attempt to prepare such a compound (**5**, $R = CH_2CH_3$) by the polyphosphoric acid catalyzed rearrangement of the γ lactone **9** was unsuccessful. A satisfactory route to **5** ($R = CH_3$) was the base-catalyzed cyclization of the appropriate diketone **17**, obtained by ring opening the 5-substituted 2-furanacetic ester **15**. Novel dimeric products were obtained on application of the procedure to 5-methyl-2-furanacetic ester.

Two important methods of cyclopentenone synthesis, base-catalyzed cyclization of γ diketones[1] and polyphosphoric acid rearrangement of γ lactones[2] (Scheme I), suffer from the limitation that, except for the special cases of **1** ($R = H$) or ($R = R'$) and **2** ($R = H$) or ($R = R'$), the result is a difficultly separable mixture of cyclopentenones **3** and **4**.[3] That such difficulties are still encountered in the synthesis of a desired cyclopentenone was commented upon recently.[4]

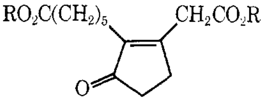
SCHEME I



We became interested in the synthesis of cyclopentenones, as they are intermediates in the route we have chosen to the prostaglandins.[5] More particularly we were desirous of obtaining access to **5** ($R = CH_3$), which would be a useful starting material.



5



6

Allylic oxidation[5,6] would enable the additional oxygen function to be introduced, and the carbomethoxy

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