[CONTRIBUTION FROM THE DEPARTMENTS OF CHEMISTRY AND CHEMICAL ENGINEERING, UNIVERSITY OF FLORIDA, GAINESVILLE, FLA.]

Fluorocarbon Nitrogen Compounds. VIII. Mono-, Di-, Tri- and Tetra-acyl Derivatives, Oxadiazoles and ω-Bromo Acyl Isocyanates[1]

BY JOHN A. YOUNG, WILLIAM S. DURRELL[2] AND RICHARD D. DRESDNER

RECEIVED NOVEMBER 6, 1961

N,N-Bis-(trifluoromethyl)-amides, $RCON(CF_3)_2$, where R = alkyl or perfluoroalkyl, were made in good yield by the reaction of acyl halides with the mercury derivative of bis-(trifluoromethyl)-amine. Perfluoroacyl amides, $RCONHCOR_F$, were made by reaction of appropriate nitriles with acids, or amides with acid anhydrides or acid halides. Introduction of the second acyl group affected adversely most amide reactions; thus, $CF_3CONHCH_3$ could be added to C_3F_6 while $(CF_3CO)_2NH$ could not, nor did metal derivatives of the latter react with acyl halides. Triacyl compounds could be made in certain cases by reaction of an N-bromoimide and an acyl halide. In the presence of a fluorinated olefin, N-bromoperfluoroglutarimide underwent a free radical rearrangement to 4-bromoperfluorobutyryl isocyanate. A tetrakis-(perfluoroacyl)-hydrazine was made, *via* the mercury derivative of $CF_3CONHNHCOCF_3$, which pyrolyzed readily to give an acid anhydride and a 2,5-bis-(perfluoroalkyl)-oxadiazole. Evidence indicates that a fluorocarbon diacyl diimide $CF_3CON{=}NCOCF_3$ was made by the reaction of ICl with the mercury derivatives of the diacylhydrazine.

This paper describes the preparation and some reactions of several new types of fluorocarbon derivatives containing one or more acylamino groups and generally little or no hydrogen. Physical constants of these compounds are given in Table I and nuclear magnetic resonance assignments in Table II.

The synthesis of organic amides and related compounds usually depends at some crucial point on the nucleophilicity of a nitrogen atom. With fluorocarbon compounds, the powerful inductive effect of fluorine greatly depresses the basicity of the nitrogen atom and thus makes methods based on reaction of a fluorocarbon amine with an acid derivative difficult or impossible (although, of course, fluorocarbon acid derivatives react readily with hydrocarbon amines); furthermore, no primary fluorocarbon amines of the type $R_fCF_2NH_2$ have been reported. Bis-(trifluoromethyl)-amine is too weak a base to react as such with acyl halides[3]; however, N,N-bis(trifluoromethyl)-amides can be made in good yield by the action of acid chlorides on the mercury derivative of the amine, as shown in Eq. 1.

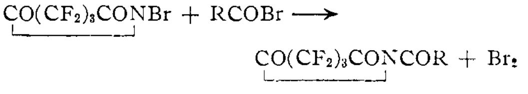
$$(CF_3)_2N{-}Hg{-}N(CF_3)_2 + RCOCl \longrightarrow RCON(CF_3)_2 \quad (1)$$

Although a few such amides have been isolated from electrochemical fluorination products,[4] the method illustrated gives improved yields and allows wide variation on the nature of R, including the use of hydrocarbon as well as of fluorocarbon acid halides. Compounds of the type where R = alkyl have not previously been described. They are not readily attacked by water, showing once again that compounds bearing both fluorinated and fluorine-free groups on nitrogen are apt to be hydrolytically stable as long as the nitrogen is tertiary and fluorine cannot be split off as HF from adjacent atoms.[5]

N-Acylamides, or imides, can be made by reaction of an amide with an acid anhydride,[6] but a purer and more easily isolated product is obtained by reaction of an acid with a nitrile. For instance, $(CF_3CO)_2NH$ made from trifluoroacetamide and trifluoroacetic anhydride was originally reported to be a liquid at room temperature.[6] In our hands, this reaction gave a product melting at about 70°, but the material resulting from reaction of CF_3COOH and CF_3CN gave a melting point of 85°. This imide was very hygroscopic. A fairly detailed study of the acid–nitrile reaction and its mechanism is described in a forthcoming paper; for preparative purposes reaction of equimolar quantities of acid and nitrile for 1–4 hours at 150° in the presence of a few per cent. of H_2SO_4 is recommended.

The second trifluoroacetyl group strongly decreased the nucleophilic activity of the amide. No base-catalyzed addition of $(CF_3CO)_2NH$ to C_3F_6 could be obtained, although $CF_3CONHCH_3$ gave a 75% yield of its respective adduct. Reaction of the sodium derivative of $CF_3CONHCH_3$ with CF_3COCl gave a fair yield of the N,N-diacyl compound, but no reaction occurred between CF_3COCl and the sodium, mercury or silver derivatives of $(CF_3CO)_2NH$.

Fluorine-containing tertiary amides, $(RCO)_3N$, have not been reported. As mentioned above, they could not be prepared from fluorocarbon secondary amides. Two compounds of this general nature were obtained, however, from an unusual reaction involving N-bromoperfluoroglutarimide and an acyl bromide, as shown in eq. 2. This reaction was successful with benzoyl bromide and perfluoroglutaryl chloride, but since no reaction took place when CF_3COBr or $C_7F_{15}COBr$ was used, it does not seem to be a general method of preparation.[7]



$$\underline{CO(CF_2)_3CONBr} + RCOBr \longrightarrow \underline{CO(CF_2)_3CONCOR} + Br_2 \quad (2)$$

---

[1] This paper was taken in part from the Ph.D. Dissertation of W. S. Durrell, University of Florida, 1961, and was presented at the 140th National Meeting of the American Chemical Society, Chicago, Ill., Sept. 3–8, 1961. The work was supported by the Army Research Office, and this paper may be used in whole or in part for any purposes of the United States Government. For the preceding paper in this series, see *J. Am. Chem. Soc.*, **82**, 4553 (1960).

[2] Present address, Peninsular ChemResearch, Inc., Gainesville, Fla.

[3] J. A. Young, S. N. Tsoukalas and R. D. Dresdner, *J. Am. Chem. Soc.*, **80**, 3604 (1958).

[4] J. A. Young, T. C. Simmons and F. W. Hoffman, *ibid.*, **78**, 5637 (1956).

[5] The adduct of pyrrole and tetrafluoroethylene is hydrolytically stable (D. C. England, L. R. Melby, M. A. Dietrich and R. V. Lindsey, Jr., *ibid.*, **82**, 5116 (1960)), as is the ethylene adduct of $(CF_3)_2NBr$ (unreported work, this Laboratory).

[6] G. H. Smith, U. S. Patent 2,701,814 (1955).

[7] A corresponding reaction with $(CF_3CO)_2NBr$ was not attempted because the N-bromoimide could not be synthesized.

TABLE I

FLUORINE-CONTAINING AMIDE, IMIDE AND ISOCYANATE COMPOUNDS

Compound	B.p., °C. (mm.)	M.p., °C.	Infrared carbonyl assignment, μ[a]	Yield, %
$(CF_3CO)_2NH$	145 (760)	85	5.64, 5.74	80–100[b]
$CF_3CONHCOCH_3$	90 (60)		5.60, 5.79	80–100[b]
$(CF_3CO)_2NCH_3$	118 (760)		5.74	25–30
$CF_3CON(CH_3)CF_2CHFCF_3$	115–116 (760)		5.73	75
$CF_3CON(CF_3)_2$	30 (760)[c]		5.55	80
$CH_3CON(CF_3)_2$	66 (760)		5.60	62
$C_6H_5CON(CF_3)_2$	95 (90)		5.50, 5.77	95
$\underline{CO(CF_2)_3CON}COC_6H_5$	85 (2.5)	39–41	5.56, 5.83	60
$\underline{CO(CF_2)_3CON}CO(CF_2)_3CO\underline{NCO(CF_2)_3CO}$	95–100 (1.5)		5.45, 5.78	28
$(CF_3CO)_4N_2$	108 (760)		5.3, 5.5	95
$CF_3CON{=}NCOCF_3$	6–8 (80)		5.3, 5.5	30–50
$Br(CF_2)_3CONCO$	42 (30)		(4.39), 5.50	100
$Br(CF_2)_3CONH_2$		98–100	5.90	

[a] Infrared spectra were taken on a Perkin–Elmer double beam instrument where bands are reported to three figures, and on a Beckman Infracord where only two figures are given. A 5-cm. cell at a pressure of about 10 mm. was used for gas samples. [b] Paper in preparation. [c] See ref. 4. [d] Purity only *ca.* 80%.

TABLE II

F^{19} NUCLEAR MAGNETIC RESONANCE SPECTRA[a]

$(CF_3CO)_2NCH_3$			5.57	2 non-equiv. quartets
$CH_3CON(CF_3)_2$			−21.3	Singlet
$C_6H_5CON(CF_3)_2$			−21.5	Singlet
$\underline{CO(CF_2)_3CON}C_6H_5$	a	1	42.1	Triplet
a b	b	2	57.1	Pentet
$\underline{CO(CF_2)_3CON}CO(CF_2)_3CO\underline{NCO(CF_2)_3CO}$	a	2	41.7	Singlet
c d a b	b	1	46.7	Singlet
	c	2	49.0	Triplet
	d	4	55.6	Pentet
$(CF_3CO)_4N_2$		1	−2.1	Singlet
		1	+2.0	Singlet
		1	+4.1	Singlet
		1	+10.6	Singlet
$BrCF_2CF_2CF_2CONCO$	a	1	−14.2	Triple triplet
a b c	b	1	40.1	Triplet
	c	1	38.7	Triplet
$BrCF_2CF_2CF_2CONH_2$	a	1	−15.1	Triple triplet
a b c	b	1	42.1	Triplet
	c	1	42.2	Triplet

[a] Nuclear magnetic resonance spectra were taken on a Varian Associates instrument operating at 60 mc. Chemical shifts are given in p.p.m., high field positive sign, relative to an external standard of CF_3COOH.

Tetraacylated hydrazines have apparently not been previously described in the literature. At least with perfluoroacyl substituents, they seem to be generally accessible in excellent yield by the following series of reactions.

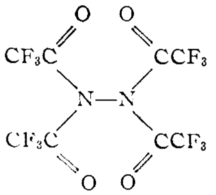
$$R_FCOOEt \xrightarrow{N_2H_4} R_FCONHNH_2 \xrightarrow{(R_FCO)_2O}$$
$$R_FCONHNHCOR_F \xrightarrow{Hg(OAc)_2} (R_FCON)_2Hg \xrightarrow{R_FCOCl} (R_FCO)_4N_2 \quad (3)$$

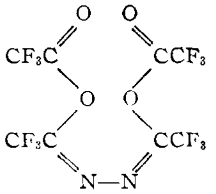
Following this procedure, it was not necessary to isolate the monohydrazide, which is difficult to purify when R = CF_3, and all the steps were virtually quantitative. The mercury derivative was a white, finely divided, amorphous solid, insoluble (except with reaction) in all solvents tested and probably therefore a polymeric rather than a chelated form. If carefully dried, it was very stable thermally, decomposition setting in only above 350° and becoming rapid at 400°. The products were mainly metallic mercury, nitrogen, carbon monoxide and C_2F_6, but a small amount of material boiling at approximately 70° was formed whose infrared spectrum was identical with that of the $(CF_3CO)_4N_2$ pyrolyzate discussed below.

The tetraacyl compound was easily obtained by reaction of the mercurial with CF_3COCl at 50° for eight hours. Of the four acyl groups, two could be removed by reaction with alcohol, giving the diacylhydrazine plus an ester, while three of the four could be titrated with aqueous base to a phenolphthalein end-point.

$$(CF_3CO)_4N_2 + EtOH \longrightarrow 2CF_3COOEt + CF_3CONHNHCOCF_3 \quad (4)$$

The structure of the compound is not rigorously proved, since it could be either the N,N,N′,N′-tetraacylhydrazine I or an imido ester (II).


I


II

Structure I seems the more probable. As can be seen in Table I, all the perfluoroacyl compounds listed, as well as esters such as CF_3COOEt, show carbonyl absorption between 5.5 and 5.9 μ. Structure I would be expected to show only this absorption, while structure II should show in addition to the carbonyl band an absorption due to the $C{=}N{-}N{=}C{-}$ system. For instance, the oxadiazole $CF_3\overbrace{C{=}N{-}N{=}C}^{O}CF_3$ has a moderately strong doublet at 6.2, 6.3μ which can be assigned to that system. The actual spectrum of the tetraacyl compound shows the expected carbonyl doublet at 5.3, 5.5μ, but no absorption in the 6–7 μ region. While it is true that pyrolysis of $(CF_3CO)_4N_2$, as described below, can be more easily rationalized on the basis of structure II, the infrared evidence strongly supports structure I.

Both the infrared and n.m.r. spectra indicate that $(CF_3CO)_4N_2$ is a rather unusual molecule. In addition to the 5.3 and 5.5μ absorptions in the infrared there are two weak bands at 5.2 and 5.8μ which cannot be dismissed as being due to impurities since the compound was estimated chromatographically to be at least 98% pure. Other strong infrared peaks are present at 7.3, 8.0, 8.3, 8.7, 9.0, 9.3, 11.3 and 13.3μ. With regard to the F^{19} n.m.r. spectrum, structure I would seem to make all fluorines equivalent, predicting a single peak, while structure II should probably give two peaks of equal intensity with closely similar chemical shifts. The actual spectrum shows four separate peaks of identical shape and size, closely but not symmetrically spaced with no fine structure resolvable at 60 mc. Since there is no chance for spin–spin coupling in the molecule, this four-peak spectrum does not furnish much information regarding choice between I and II. The presence of four peaks may be due to double bond character in the C–O and C–N bonds, leading to hindered rotation and the possibility of *cis–trans* isomerism involving the CF_3 groups and the O–C–N–C–O plane. Canonical structures illustrating this possibility can be written; however, hindered rotation should lead to a temperature-dependent n.m.r. spectrum, while no change was actually observed in a spectrum taken at 100°. Comparison of the magnitude of the observed chemical shifts with those of reference compounds was also inconclusive. Trifluoromethyl groups in $CF_3\overbrace{C{=}N{-}N{=}C}^{O}CF_3$, resembling structure I, and in $(CF_3CO)_2O$, resembling structure II, gave chemical shifts of, respectively, +10 and zero p.p.m., both of which values are included in the range of chemical shifts exhibited by the tetraacyl compound.

Pyrolysis of $(CF_3CO)_4N_2$ took place very smoothly at 325° to give trifluoroacetic anhydride and 2,5-bis-(trifluoromethyl)-oxadiazole. Although little effort was made to find optimum conditions, conversions were obtained as high as 89% for the anhydride and 67% for the oxadiazole. The reaction sequence shown in eq. 3, followed by pyrolysis to the oxadiazole, is very similar to the classic ring closure of organic diacyl hydrazines with acetic anhydride to give oxadiazoles, although in the latter case the tetraacyl compounds have not been isolated, and seems to constitute a general route to oxadiazoles bearing perfluoroalkyl substituents in positions 2 and 5.[8]

By oxidation of diacylhydrazines, Cramer[9] has synthesized several diacyldiimides, $RCON{=}NCOR$. It was hoped that an analogous reaction could be applied to $CF_3CONHNHCOCF_3$, but negative results were obtained under a wide variety of conditions on attempted oxidation of either the diacylhydrazine or its mercury derivative, free nitrogen being eliminated very readily. The best results were achieved by reaction of the mercury derivative with iodine monochloride in CCl_4 at about 10–20°. Using continuous fractionation at reduced pressure during the reaction, a product was isolated in approximately 30–50% yield which, although it contained about 20% CCl_4 as estimated both by molecular weight and by infrared spectrum, was a red vapor or blood-red liquid. The color was quickly discharged when the material was exposed to heat or to ultraviolet irradiation, giving only C_2F_6 and noncondensable gases. It seems quite probable that this was actually the diimide, $CF_3CON{=}NCOCF_3$, but the compound was not obtained in pure enough form for characterization. If the identification is correct, it would seem that the fluorocarbon diacyldiimides are even less stable than the hydrocarbon analogs.

The N-bromoamine $(CF_3)_2NBr$ is known to add easily to olefins,[3] including the fairly unreactive C_3F_6. On the other hand, N-bromoperfluoroglutarimide underwent no addition to C_3F_6 or to $CF_2{=}CFCl$ with either peroxide or ultraviolet initiation; however, an interesting rearrangement did occur under these conditions which did not take place in the dark or in the absence of an olefin. Since the necessity of initiation by peroxide or irradiation indicates a free radical mechanism, a parallel was at first inferred between this rearrangement and the reaction of a fluorocarbon imide with silver difluoride,[10] which is thought to proceed by initial abstraction of hydrogen, followed by attack of fluorine on carbonyl carbon to give an acid fluoride and $R_fCON{:}$, the latter rearranging to an isocyanate.

A similar mechanism for the N-bromoimide rearrangement would lead to $BrCO(CF_2)_3N{=}C{=}O$. No labile bromine could be found, however, and the product was eventually identified as 4-bromoperfluorobutyryl isocyanate, $Br(CF_2)_3CON{=}C{=}O$. The fission of a carbon–carbon bond in a fluorocarbon derivative under such mild conditions is re-

---

(8) Since the submission of this paper, compounds of this type have been reported by H. C. Brown, *et al.*, *J. Org. Chem.*, **26**, 4407 (1961), and Chambers and Coffman, *ibid.*, **26**, 4410 (1961).

(9) R. Cramer, *J. Am. Chem. Soc.*, **79**, 6215 (1957).

(10) J. A. Young, W. S. Durrell and R. D. Dresdner, *ibid.*, **82**, 4553 (1960).

markable, but the reaction is unmistakably similar to the rearrangement of N-bromosuccinimide, reported several years ago to proceed under comparable conditions.[11,12] The mechanism of these reactions has not been elucidated, but may possibly resemble that proposed quite recently for the free radical rearrangement of cyclopropanols.[13]

Experimental

Reaction of Acyl Halides with $[(CF_3)_2N]_2Hg$.—About 0.2 mole of the mercurial[3] and 0.4–0.6 mole of the appropriate acid chloride were sealed in glass and allowed to warm to room temperature. A short heating period at 40° initially employed was found to be unnecessary. Distillation then gave the amides.

N,N-Bis-(trifluoromethyl)-trifluoroacetamide was identified by comparison of an infrared spectrum with that of a known sample.[4]

N,N-Bis-(trifluoromethyl)-acetamide: *Anal.* Calcd. for $C_9F_6H_3NO$: mol. wt., 195; N, 7.22. Found: mol. wt., 194; N, 7.41.

N,N-Bis-(trifluoromethyl)-benzamide: *Anal.* Calcd. for $C_9F_6H_5NO$: N, 5.40. Found: N, 5.72.

Synthesis of Imides.—The acid–nitrile and amide–anhydride reactions are described in detail in a forthcoming paper.

N-Acetyltrifluoroacetamide: *Anal.* Calcd. for $C_4F_8H_4NO_2$: C, 31.0; H, 2.6; N, 9.0. Found: C, 31.2; H, 2.8; N, 8.6.

N-Methyl-N-trifluoroacetyltrifluoroacetamide.—To a slurry of 0.1 g. atom of sodium sand in 300 ml. of tetrahydrofuran, 13.7 g. (0.1 mole) of $CF_3CONHCH_3$ dissolved in a small amount of tetrahydrofuran was added with stiring and cooling. Then 13.2 g. (0.1 mole) of CF_3COCl was condensed into the cooled solution, which was stirred overnight and finally brought to reflux. Filtration and fractionation gave 5.0 g. of $(CF_3CO)_2NCH_3$. The secondary amide was also prepared (3 g.) by fractionating a mixture of 0.05 mole each of pyridine, CF_8COCl and $CF_3CONHCH_3$, after reaction overnight at room temperature.

Anal. Calcd. for $C_5F_6H_3NO_2$: C, 26.9; H, 1.3; N, 6.3. Found: C, 27.2; H, 1.5; N, 6.0.

N-Benzoylperfluoroglutarimide.—Thirteen grams (0.043 mole) of N-bromoperfluoroglutarimide and 7.5 g. (0.043 mole) of benzoyl bromide were mixed and heated at 90° at about 45 mm. pressure for 4 hours. Fractionation gave 8 g. of the hygroscopic tertiary amide. The n.m.r. spectrum showed that the perfluoroglutarimide ring was still intact.

Anal. Calcd. for $C_{12}F_6H_5NO_3$: N, 4.3. Found: N, 4.5.

N,N,N′,N′-Bis-(perfluoroglutaryl)-perfluoroglutardiamide.—Twenty-one grams (0.07 mole) of N-bromoperfluoroglutarimide and 9 g. (0.033 mole) of perfluoroglutaryl chloride were heated together at 100° for 3 days, with a slight vacuum maintained. Vacuum fractionation gave 6 g. of $\underbrace{CO(CF_2)_3CON}CO(CF_2)_3CO\underbrace{NCO(CF_2)_3CO}$. The n.m.r. spectrum showed two cyclic perfluoroglutarimido rings and one linear perfluoroglutaryl group.

Anal. Calcd. for $C_{15}F_{18}N_2O_6$: N, 4.3. Found: N, 4.7.

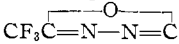
Tetrakis-(trifluoroacetyl)-hydrazine.—A solution of 180 g. (1.26 moles) of ethyl trifluoroacetate in 200 ml. of absolute ethanol was stirred and 45 g. (1.40 moles) of anhydrous hyhydrazine in 150 ml. of absolute ethanol added dropwise with intermittent cooling. After standing overnight, alcohol was removed under a water-pump vacuum at room temperature until the sirupy residue began to crystallize. Trifluoroacetic acid, 200 g., was then added to dissolve most of the monohydrazide and 420 g. (2.0 moles) of $(CF_3CO)_2O$ added with stirring, under an ice-water-cooled reflux condenser. As reaction took place, the solution first became clear, with subsequent crystallization of the diacyl compound. After the reaction had stood overnight, trifluoroacetic acid and excess anhydride were removed (under vacuum toward the last). The crude diacylhydrazine was then recrystallized from about 2 l. of dry toluene and dried to give 290 g. of $CF_3CONHNCOCF_3$, m.p. 175–176°.

The mercury derivative was prepared by dissolving 33 g. (0.15 mole) of $CF_3CONHNHCOCF_3$ in 250 ml. of water and adding 43 g. (0.15 mole) of mercuric acetate in 150 ml. of water, acidified slightly with acetic acid. The very insoluble but extremely finely divided precipitate was filtered at 50° or so to decrease viscosity, through a medium grade sintered glass filter, left overnight on a clay plate, then vacuum dried for several hours at room temperature. Application of heat before drying was completed resulted in some decomposition.

Anal. Calcd. for $C_4F_6HgN_2O_2$: Hg, 47.5. Found: Hg, 47.9.

Trifluoroacetyl chloride (38 g., 0.29 mole) and 50 g. of a fluorocarbon solvent boiling at about 50° were condensed into a pressure vessel containing 57 g. (0.14 mole) of thoroughly dried $(CF_3CON)_2Hg$. After sealing, the vessel was rocked for 14 hours at 50°. Volatiles were then removed by pumping and fractionated to give the product, 53 g. $(CF_3CO)_4N_2$.

Anal. Calcd. for $C_8F_{12}N_2O_4$: C, 23.1; F, 54.8; N, 6.7; neut. equiv., 138. Found: C, 23.4; F, 55.2; N, 5.9; neut. equiv., 138.

2,5-Bis-(trifluoromethyl)-oxadiazole.—Eighteen grams (0.043 mole) of $(CF_3CO)_4N_2$ was dropped into a vertical Pyrex column packed with glass helices and heated to 325 ± 5°, over a period of 18 minutes. The exit vapors were condensed in cold traps and subsequently fractionated to give 8 g. (89%) of $(CF_3CO)_2O$, identified by boiling point, molecular weight and infrared spectrum, and 6 g. (67%) of  $CF_3\overbrace{C{=}N{-}N{=}C}^{O}CF_3$, identified by molecular weight and comparison of its infrared spectrum with that of an authentic specimen.

Below 275°, little pyrolysis took place; at 400°, products resembling those from the pyrolysis of trifluoroacetic anhydride, that is, CF_3COF, COF_2 and $(-CF_2-)n$, were found.

Bis-(trifluoroacetyl)-diimide.—To a flask fitted with stirrer, dropping funnel and a good fractionating column was added 13.0 g. (0.031 mole) of $(CF_3CON)_2Hg$ and 100 ml. of carefully dried carbon tetrachloride. Reflux was established at 80 mm. pressure, and 9.0 g. (0.055 mole) of dry iodine monochloride in 50 ml. of dry CCl_4 was added at such a rate that little or no unreacted ICl solidified on the cold finger of the condenser, which was kept at about −40°. The reflux temperature dropped gradually from 16 to 6° and vapor was taken off slowly into a cold trap as long as the reflux was dark red and the reflux temperature did not exceed 8°. The product so obtained was estimated to contain about 17% CCl_4 both by molecular weight measurements (mol. wt.: $(CF_3CON)_2$, 222; CCl_4, 154; product, 210) and by estimation of CCl_4 content from the intensity of the 12.6 μ line in the infrared. Short exposure of samples sealed in glass to either ultraviolet exposure or to a temperature of 100° discharged the red color completely, leaving as the only condensable material a colorless gas or solid subliming at low pressures and showing bands attributable only to C_2F_6 in its infrared spectrum.

N-Methyl-N-(2-H-perfluoropropyl)-trifluoroacetamide.—An excess of methylamine was bubbled into ethyl trifluoroacetate at room temperature. Fractionation then gave $CF_3CONHCH_3$ in about 80% yield.

Anal. Calcd. for $C_3F_3H_4NO$: C, 28.4; H, 3.2; N, 11.0. Found: C, 28.6; H, 3.4; N, 10.9.

Four grams (0.17 g. atom) of sodium metal was heated with 168 g. of $CF_3CONHCH_3$ until it had dissolved. This solution was treated with 40 g. (0.25 mole) of $CF_3CF{=}CF_2$ in a rocking autoclave at 80° for 40 hours. On cooling and venting of the autoclave no olefin was recovered. Fractionation gave 52 g. of adduct, $n^{28}D$ 1.3170. The complex n.m.r. peak for the lone proton indicated that the direction of addition was that shown in the formula $CF_3CON(CH_3)CF_2CHFCF_3$.

4-Bromoperfluorobutyryl Isocyanate.—Fifteen grams (0.05 mole) of N-bromoperfluoroglutarimide and 5 g. (0.03 mole) of $CF_3CF{=}CF_2$ were sealed in glass and left in direct sunlight for 4 days, although there was no apparent further change after the first day. Fractionation of the product resulted in recovery of all the olefin and a quantitative yield of $Br(CF_2)_3CONCO$. The acyl isocyanate reacted almost explosively with water, but the solution gave no test for Br^-. Reaction of the same quantities of reactants with 1 g. of

---

(11) H. W. Johnson and D. E. Bublitz, *J. Am. Chem. Soc.*, **79**, 753 (1957); **80**, 3150 (1958).

(12) J. C. Martin and P. D. Bartlett, *ibid.*, **79**, 2533 (1957).

(13) C. H. dePuy, G. M. Dappen and J. W. Hausser, *ibid.*, **83**, 3156 (1961).

benzoyl peroxide at 100° gave comparable results, and quantitative rearrangement was also obtained when C_3F_6 was replaced by $CF_2{=}CFCl$ and the mixture exposed to sunlight. Substitution of $(CF_3CO)_2O$ for the olefin or exposure of the N-bromoimide alone to sunlight gave a little free bromine but recovery of most of the bromoimide, with no rearranged product.

Because of the extreme reactivity of the acyl isocyanate, it was identified by indirect methods, as follows.

A small sample of the isocyanate was allowed to stand 2 weeks in an ether solution of benzyl alcohol. Evaporation of the solvent left a solid which on recrystallization from cyclohexane melted at 76.5 to 78.5°.

Anal. Calcd. for $BrC_{12}F_6H_8NO_3$: C, 35.2; H, 2.0; N, 3.4. Found: C, 35.7; H, 2.3; N, 3.0.

The white solid formed on reaction of the acyl isocyanate with water, after washing and recrystallization from benzene, melted at 98 to 100°.

Anal. Calcd. for $BrC_4F_6H_2NO$: Br, 29.2; N, 5.1. Found: Br, 26.9[14]; N, 5.0.

Acknowledgments.—The authors are indebted to Dr. Wallace Brey for interpretation of the n.m.r. spectra, and to Dr. Henry C. Brown for a comparison infrared spectrum of 2,5-bis-(trifluoromethyl)-oxadiazole.

[14] Although the bromine value for this compound is low, it is felt that the complete body of evidence strongly supports the proposed structure for the rearranged product.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, PURDUE UNIVERSITY, LAFAYETTE, IND.]

Stereochemistry of the Diels–Alder Reaction. III. Fluorinated *trans*-Olefinic Acids as Dienophiles

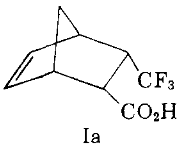
BY H. P. BRAENDLIN, A. Z. ZIELINSKI[1] AND E. T. MCBEE

RECEIVED JUNE 29, 1961

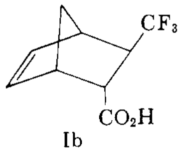
Adducts between cyclopentadiene and acids of the general formula *trans*-$R_fCH{=}CHCO_2H$ were prepared. Bromination in chloroform was shown to be a good adduct isomer determination method, revealing a consistent carboxy-*exo* to carboxy-*endo* relationship of 2:1. In some instances of adduct hydration, skeletal rearrangement was observed.

The steric course of the Diels–Alder reaction between a cyclic conjugated diene and a dienophile was stipulated by Alder and Stein to result in the product with maximum overlap of double bonds.[2] This was extended by Alder and Windemuth to include the formation of products wherein maximum overlap of unshared electron pairs is observed.[3] Thus, dienophiles carrying an electronegative substituent near the olefinic linkage were said to react with cyclic conjugated dienes to give predominantly the adduct with the substituent in the *endo* position of close proximity to the double bond formed by the diene portion of the molecule. However, exceptions to this rule are being observed with increasing frequency. Not only have *cis*-α,β-disubstituted ethylenes, such as maleic anhydride, been known for some time to give both *endo* and *exo* products,[3,4] but also in *trans*-olefin addition both substituents have been found to vie for the *endo* position to give mixed adducts.[5] In most cases of such mixed addition of *trans*-α,β-disubstituted ethylenes to a cyclic conjugated diene both substituents carried double bonds, *i.e.*, two π-electron systems were in competition. Recently, however, also *trans* substituents lacking π-electrons, such as trifluoromethyl[5e] and halogen,[5f] have been observed to exert considerable *endo* direction. Finally, studies with acrylic compounds[5f,6] have revealed that, at least in these systems, two α-substituents can compete with each other for the *endo* position even if one substituent is not electronegative. Thus, acrylonitrile, acrylamide and methacrylic compounds give cyclopentadiene adducts with large percentages of the isomers having hydrogen or methyl *endo*.

Since the mechanism of the Diels–Alder reaction is still obscure, the driving forces behind these anomalies are also unexplained. It is possible that the behaviors of the three groups of ethylenic dienophiles, *cis*- and *trans*-α,β- and α,α-disubstituted ethylenes, differ essentially. Whereas α-methyl may compete with α-carboxy for the *endo* position, *trans*-β-methyl appears to be unable to do so: *trans*-crotonyl chloride adds to cyclopentadiene with the methyl group exclusively *exo*[7]; *trans*-4,4,4-trifluorocrotonic acid, on the other hand, gives an adduct mixture (I) which was indicated to have a carboxy-*exo* (Ia) to carboxy-*endo* (Ib) ratio of 2:1.[5e]



Ia



Ib

It has now been found that this ratio is not only reproducible but applies also to cyclopentadiene adducts of other fluorinated acids of the formula $R_fCH{=}CHCO_2H$. The compounds $C_3F_7CH{=}C$-

---

[1] Present address: Politechnike Szczecinska, Wydzial Chemiczny, Szczecin, Poland.

[2] K. Alder and G. Stein, *Angew. Chem.*, **50**, 510 (1937).

[3] K. Alder and E. Windemuth, *Ber.*, **71**, 1939 (1938).

[4] (a) A. Wassermann, *J. Chem. Soc.*, 1511 (1935); 612 (1942); *Trans. Faraday Soc.*, **34**, 128 (1938); **35**, 841 (1939); (b) K. Alder, *et al.*, *Ann.*, **525**, 247 (1936); **566**, 1, 58 (1950); (c) H. Kwart and I. Burchuk, *J. Am. Chem. Soc.*, **74**, 3094 (1952); (d) D. Craig, *et al.*, *ibid.*, **73**, 4889 (1951); **76**, 4060 (1954); (e) J. A. Berson, *et al.*, *ibid.*, **75**, 1721 (1953); **78**, 6049 (1956).

[5] (a) C. S. Rondestvedt and J. C. Wygant, *J. Org. Chem.*, **17**, 975 (1952); *J. Am. Chem. Soc.*, **73**, 5785 (1951); (b) C. D. VerNooy and C. S. Rondestvedt, *ibid.*, **77**, 3583 (1955); C. S. Rondestvedt and C. D. VerNooy, *ibid.*, **77**, 4878 (1955); (d) F. Winternits, M. Mousseron and G. Rouzier, *Bull. soc. chim. France*, 170 (1955); (e) E. T. McBee, C. G. Hsu and C. W. Roberts, *J. Am. Chem. Soc.*, **78**, 3389 (1956); (f) K. Alder, R. Hartmann and W. Roth, *Ann.*, **613**, 6 (1958).

[6] (a) J. S. Meek and W. B. Trapp, *J. Am. Chem. Soc.*, **79**, 3909 (1957); (b) W. R. Boehme, E. Schipper, W. G. Scharpf and J. Nichols, *ibid.*, **80**, 5488 (1958); (c) K. Alder, K. Heimbach and R. Reubke, *Ber.*, **91**, 1516 (1958); (d) M. Schwarz and M. Maienthal, *J. Org. Chem.*, **25**, 499 (1960); (e) J. A. Berson *et al.*, *J. Am. Chem. Soc.*, **82**, 5501 (1960); *Tetrahedron Letters*, **No. 4**, 131 (1961).

[7] K. Alder and G. Stein, *Ann.*, **514**, 197 (1934).