Anal. Calcd. for $C_{24}H_{34}O_{14}$: C, 52.8; H, 6.2. Found: C, 53.0; H, 6.3; quant. acetyl analysis showed 3.9 eq. of acetic acid per mole of XI.

Acknowledgments.—The authors express their appreciation to R. A. Paulson, Lorna J. Tregoning and E. R. Deardorff for the microanalyses, and to J. J. Comeford and F. P. Czech for measurements of infrared absorption.

WASHINGTON, D. C.

[CONTRIBUTION FROM THE ROHM & HAAS CO., REDSTONE ARSENAL RESEARCH DIVISION]

Amino-derivatives of 1,2-Dichlorohexafluorocyclopentene-1[1]

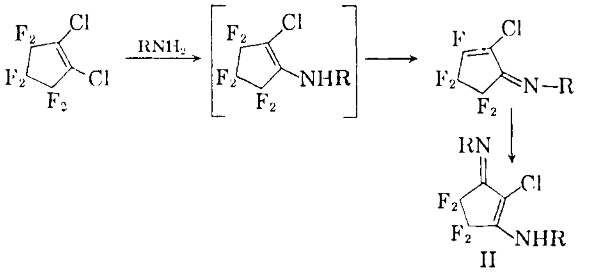
BY CHARLES O. PARKER

RECEIVED SEPTEMBER 11, 1958

1,2-Dichlorohexafluorocyclopentene-1 reacted with secondary aliphatic amines and with sodium azide to give products monosubstituted in the 1-position. With ammonia and primary aliphatic amines, derivatives of 1-amino-2-chloro-3-iminotetrafluorocyclopentene-1 were formed. The latter series of products exhibited amphoteric properties, forming either cationic or anionic salts. The anions underwent alkylation on nitrogen. Both series of amino derivatives were susceptible to acid hydrolysis giving derivatives of 1-amino-2-chloro-3-ketotetrafluorocyclopentene-1.

It is the purpose of this paper to describe the rather facile reactions by which 1,2-dichlorohexafluorocyclopentene-1 (I) is converted into amino derivatives, to describe the chemical and physical properties of these previously unreported compounds and to relate these data to the structural assignments which have been made.

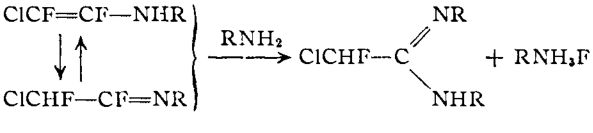
The amino-imines II formed by reaction of I with ammonia and primary aliphatic amines were found to be stable compounds having symmetrical structures. The four fluorine atoms were equivalent and the alkyl hydrogen atoms were equivalent, measured when the compounds were in solution. Further discussion of this feature may be found in the section on n.m.r. spectra. The positions of the ultraviolet absorption maxima of the amino-imines confirmed the presence of conjugated unsaturation in these molecules. These data can be correlated with only one structural arrangement of the amino groups, *i.e.*, the 1,3-positions which flank the remaining chlorine atom. One can construct a fully credible sequence of steps which leads to such a structure. As indicated below this sequence might proceed *via* β-elimination of fluoride ion from the hypothetical monosubstituted product.



II

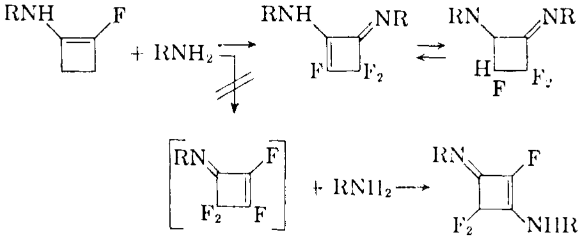
It is evident that structure II by either gain or loss of a proton is converted into ions either of which possesses unique symmetry of structure and charge distribution (see below).

Chlorofluoroölefins and perfluoroölefins (ethylenes) and perfluorocyclobutene also have been reported to form amino-imines by reaction with primary amines.[2] The ethylenes and cyclobutene both have been shown to react with nucleophilic reagents by an addition–elimination process.[2–5] The ethylenic adducts, after loss of hydrogen fluoride, cannot undergo a second stage β-elimination of fluoride ion and consequently attack of a second molecule of amine results in the formation of amidines (1,1-amino-imines). The cyclobutene-



$$\left.\begin{matrix}\text{ClCF=CF—NHR}\\ \downarrow\uparrow\\ \text{ClCHF—CF=NR}\end{matrix}\right\}\xrightarrow{\text{RNH}_2}\text{ClCHF—C}\begin{matrix}\nearrow\!\!\!\!\text{NR}\\ \searrow\text{NHR}\end{matrix}+\text{RNH}_3\text{F}$$

imine intermediates supposedly have a choice between β-elimination of fluoride ion or the postulated second mole addition of amine analogous to the addition of alcohols.[6] If the formation of 1,2-amino-imines is correct as proposed by K. E. Rapp, *et al.*, it would seem that the explanation must involve a much lesser mobility of the double bond in the cyclobutene ring.



A few reactions of 1,2-dichlorohexafluorocyclopentene-1 (I) with nucleophilic reagents were investigated previously. The results were never published but manufacturers of I at one time cited this work in advertising the chemistry of I.[7] Since it is now evident that some of Latif's work was interpreted incorrectly, a brief account of the

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[1] This research was carried out under Army Ordnance Contract DA-01-021-ORD-5135.

[2] K. E. Rapp, J. T. Barr, C. T. Bahner, J. D. Gibson and R. H. Lafferty, Jr., THIS JOURNAL, **72**, 3616 (1950).

[3] W. T. Miller, Jr., E. F. Fager and P. H. Griswold, *ibid.*, **70**, 431 (1948).

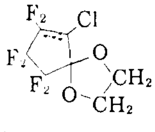
[4] K. E. Rapp, J. T. Barr, R. L. Pruett, C. T. Bahner, J. D. Gibson and R. H. Lafferty, Jr., *ibid.*, **74**, 749 (1952).

[5] W. T. Miller, Jr., and A. H. Fainberg, *ibid.*, **79**, 4164 (1957).

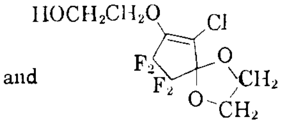
[6] J. D. Park, M. L. Sharrah and J. R. Lacher, *ibid.*, **71**, 2337 (1949).

[7] Hooker Electrochemical Co.

relevant features has been included here.[8] In view of the rather convincing evidence cited above which identified the 1,3-amino-imine derivatives of I as such, and of the chemical evidence presented below which correlated the structures of the hydrolysis products of the 1,3-amino-imines with those of the monosubstituted derivatives, it became apparent that alkoxyl derivatives of I must be 1,3,3-substituted rather than 1,5,5-substituted. Therefore it appears that the ethylene glycol derivatives 8c and 8d most probably have the structures indicated although experimental confirmation has not been sought.

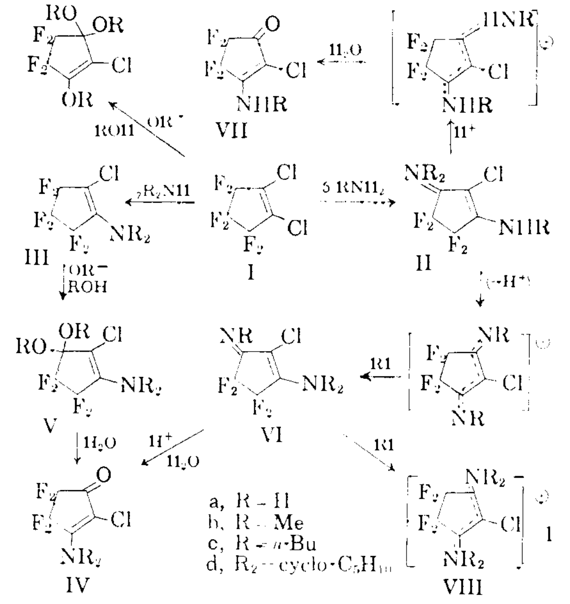


and



The products of reaction of I with ammonia (IIa) and methylamine (IIb) were crystalline solids and only these were examined in any detail. The butylamine derivative IIc was a liquid at room temperature; IIa, IIb and IIc dissolved easily in dilute mineral acid solution and IIa and IIb gave stoichiometric acid titrations. All three could be titrated with perchloric acid in acetic acid solution; IIa dissolved easily in aqueous base, IIb incompletely; none gave definitive titrations with base. All three decomposed gradually in excess alkali solution and the products of decomposition have not been investigated. Hydrochloride salts of IIa and IIb crystallized from chloroform solution when treated with hydrogen chloride. The potassium salt of IIa is the only metal salt of which isolation was attempted; it was stable enough to be manipulated in the open.

The stoichiometry of the preparative reactions of IIa, IIb and IIc was ascertained easily. Five moles of amine were consumed giving two moles of amine hydrofluoride, one mole of amine hydrochloride and one mole of product. The reactions of I with secondary amines in anhydrous non-hydroxylic solvents gave products which were only monosubstituted regardless of how much excess amine was present. These reactions, the relationship and subsequent interconversions of both series of amine derivatives are



Derivatives of three secondary amines were prepared: dimethylamine (IIIb), dibutylamine (IIIc) and piperidine (IIId). The sensitivity of these compounds to moisture was such that the stoppered analytical samples of all three decomposed completely over a period of several months leaving solid residues of the respective ketones IVb, c and d. The direct acid-catalyzed hydrolysis of IIIb to IVb was the only reaction of this series which was performed; ketones IVc and IVd were not worked up for individual identification.

Convincing proof of the fact that the trimethoxy-derivative was substituted in the 1,3,3-positions rather than the 1,5,5-positions could not be obtained by analysis of its n.m.r. spectrum (see discussion of n.m.r. spectra). It was felt that the 1,3,3-structure would be confirmed if the point of attack of methoxide ion and of water on the monosubstituted amino-derivative IIIb was shown to be in the 3-position. This relationship was demonstrated by synthesizing the ketone IVb, which is the hydrolysis product of the monosubstituted amino-derivative IIIb (and of the ketal Vb), from the 1,3-amino-imine IIb by means of the alkylation and hydrolysis reactions outlined above.

Alkylation of IIb was performed under two different sets of conditions—first by using sodium methoxide in methanol to form the anion of IIb and adding methyl iodide to this solution: then by using sodium hydride suspended in tetrahydrofuran to form the anion of IIb and adding methyl iodide to the filtered tetrahydrofuran solution. The second procedure gave pure VIb while the first procedure gave a mixture of VIb, IVb and VIIb. However, hydrolysis of pure VIb in aqueous mineral acid gave a mixture of IVb and VIIb. This is not unreasonable since the conjugate acid of VIb

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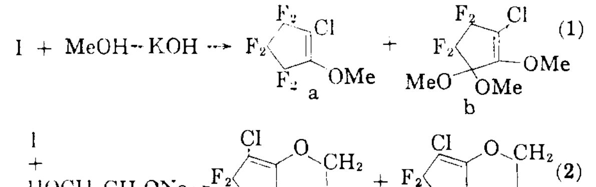
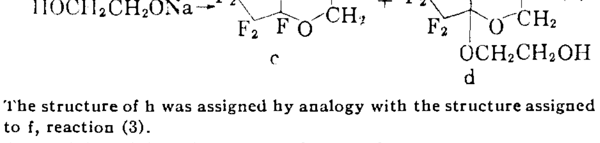
[8] K. A. Latif, Doctoral dissertation to Ohio State University, 1952.





The structure of h was assigned by analogy with the structure assigned to f, reaction (3).

$$CF_3—CCl{=}CCl—CF_3 + MeOH—KOH \longrightarrow$$

$$\underset{e}{CF_3CCl{=}C(OMe)CF_3} + \underset{f}{CF_3CCl{=}C(OMe)CF(OMe)_2} \text{ or }$$

$$\underset{g}{(MeO)_2CFCCl{=}C(OMe)CF_3} \quad (3)$$

The structure f was assigned to the trimethoxy-derivative isolated from reaction 3 in preference to the structure g because from permanganate oxidation of this derivative trifluoroacetic acid was isolated and identified as its amide. Also, considerations of the relative mesomeric contributions to the polarization of the molecule *via* the double bond which might be expected from the methoxy *versus* chloro groups in the intermediate (e) implied that the 4-position, rather than the 1-position should be the more susceptible to further attack by an anion.

has its charge distributed between both nitrogen atoms.

The trimethyl-derivative VIb reacted with methyl iodide to give a product which had properties attributable to a quaternary ammonium iodide VIII. Reasonably diligent efforts to purify this salt were fruitless and consequently no spectroscopic measurements were made on it.

The reaction of I with sodium azide proceeded smoothly and spontaneously in dimethyl sulfoxide solution to give 1-azido-2-chlorohexafluorocyclopentene-1. An orange product, very sensitive to impact, was formed if azide ion was permitted to be present in excess. While the mono-azido derivative was unstable during distillation at temperatures above about 60° and toward storage at room temperature it suffered no measurable decomposition during distillations at lower temperatures and prolonged storage in a refrigerator. When the reactions of IIIb with methoxide ion were being examined, leading to the amino-ketal V, similar reactions of the azido-derivative were carried out. It was found impossible to obtain a pure azido-analog of V. The reaction of the azido-derivative with methoxide ion in methanol proceeded so readily at room temperature that disappearance of methoxide could be followed using phenolphthalein indicator. Examination of this solution revealed that azide ion was being eliminated, leading to a mixture of products of which one almost certainly was the trimethoxy derivative. Consideration of this information suggested that reactions of I and of the azido-derivative with methoxide ion in methanol might very possibly proceed with attack of the second mole of methoxide ion at the already substituted 1-position. Compound I reacting by this mechanism would then yield a 1,1,3-trimethoxy derivative indistinguishable from a 1,3,3-isomer. No reactions which might be expected to test this hypothesis critically have been carried out.

Reactions of I with sodium or potassium cyanide in solvents such as ethanol, methanol, acetonitrile, dimethyl sulfoxide and dimethylformamide proceeded with consumption of many moles of cyanide per mole of I leading to dark colored mixtures from which no other product than unreacted I could be isolated. Reactions of I with sodium nitrite in the same solvents proceeded readily but with no evidence of the formation of a nitro-compound. No products could be isolated. The best deduction that could be made from these efforts was that an unstable nitrite ester was formed initially which decomposed with evolution of volatile fragments (including HF or NOF) and led to water-soluble products.

Discussion

Nuclear Magnetic Resonance Spectra.—The nuclear magnetic fluorine resonance spectra of several derivatives of 1,2-dichlorohexafluorocyclopentene-1 (I) were measured and the resulting data have been tabulated below. Compounds I and the monoazido derivative have unambiguous structures and therefore assignment of the observed field shift values respectively to the fluorine atoms in the 3–5 and 4 positions may be made with assurance; IIa and IIb (in ethanol solution) showed only one fluorine resonance absorption band (see Table I). Furthermore the proton resonance spectrum of IIb in benzene solution showed only one resonance absorption band for the hydrogen atoms on both methyl groups (field shift × $10^6 = 2.3$, referred to water). The absorption for the amino-hydrogen atom was at 0.0, which is really a necessary condition for equivalence of the methyl groups and nitrogen atoms. (Since the implied high frequency exchange of the amino-hydrogen atoms cannot involve the solvent, benzene, it must be intermolecular. Only one of the amino-imines was checked for molecularity: IIa gave a monomeric molecular weight ebulliometrically in acetone. Admittedly this finding does not exclude the possible existence of dimers in solvents such as benzene at room temperature.) No other structures than those of the hybrid conjugate acid cations[9] of structures IIa and IIb can fulfill this requirement. Thus the consequent values of the field shifts of the adjacent fluorine atoms may be documented. Assignment of the observed field shift values respectively to the 4- and 5-positions of structures IVb and VIb appears to be logical and in accord with the electron density or electronegativity correspondence pattern into which all of the structures thus far mentioned appear to fit. But from the field shift values measured for the trimethoxy derivative one is unable to deduce either that the structure is 1,3,3- or which value is to be assigned to one position or the other. The n.m.r. spectrum of this derivative also showed two additional weak bands indicating the presence of an impurity. The positions of these bands appear to be compatible with field shift values attributable to 1-methoxy-2-chloro-3-ketotetrafluorocyclopentene-1. Since the infrared spectrum of the trimethoxy derivative showed appreciable carbonyl absorption (see Table II), contamination by this ketone has been postulated. The appropriate numbers which appear in Table I rest upon this basis.

TABLE I

FIELD SHIFTS × 10^{6a}

All table values are positive in sign.

Structure	1	3	4	5
I	Cl	36.7	52.7	36.7
IIa	NH	NH	42.5	42.5
IIb	NMe	NMe	38.2	38.2
IVb	NMe_2	O	48.9	37.8
V	NMe_2	$(OMe)_2$	49.8	33.6
VIb	NMe_2	NMe	39.4	33.3
	N_3	37.0	53.0	35.5
	OMe	$(OMe)_2$	49.5	38.0
	OMe	O	48.6	40.8[b]

[a] Field shifts × $10^6 = (H_{\text{cmpd}} - H_{CF_3COOH})/H_{\text{applied}}$. [b] Impurities in $(OMe)_3$.

Infrared Spectra.—Since the compounds reported in this paper are not only new but are dissimilar to any others for which infrared data are available, a tabulation of the principal infrared absorption bands has been prepared for reference purposes (see Table II).

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[9] Or the corresponding conjugate base anions. Since in aqueous ethanol solution these compounds give feebly basic reactions, it must be the cationic form which is dominant.

TABLE II

INFRARED ABSORPTION FREQUENCIES, CM.$^{-1}$

Structure	Position 1	3	NH	N_3	C=N or C=O	C=C
I	Cl	F_2				1631
IIa	NH	NH	3390, 3226		1684	1658, 1603
IIa[a]	NH	NH	3333		1678	1645
IIb	NMe	NMe	3125			1623
IIb[a]	NMe	NMe	3356			1639
IIc	NBu	NBu	3155			1623
IIc[a]	NBu	NBu	. .			1631
IIIb	NMe_2	F_2				1645
IIIc	NBu_2	F_2				1629
IIId	NC_5H_{10}	F_2				1637
IVb	NMe_2	O			1712	1642, 1600
IVb[a]	NMe_2	O			1739	1613
V	NMe_2	$(OMe)_2$				1645
VIb	NMe_2	NMe			1672	1645
VII	NHMe	O	3155		1721	1637,[b] 1608
VII[a]	NHMe	O	3333		1736	1631
	N_3	F_2		2160, 2123		1650
	OMe	$(OMe)_2$			1754[c]	1658, 1618

[a] Solutions in CH_2Cl_2. [b] Shoulder. [c] Probably arises from 1-methoxy-2-chloro-3-keto-derivative as impurity.

The infrared spectra of all the derivatives of I, including I itself, were characterized by having a strong sharp absorption band in the 6 μ region attributable to the carbon–carbon double bond in the cyclopentene ring.

Derivatives monosubstituted in the 1-position showed no other absorption in this region and the frequency of this band was displaced over the range 1630–1650 cm.$^{-1}$ by the groups Cl, NBu_2 < NC_5H_{10} < NMe_2 < N_3. In the three 1-dimethylamino-derivatives (IIIb, V, VIb) the carbon–carbon double bond band appeared at 1645 cm.$^{-1}$. Comparison of methylene chloride solution *vs.* Nujol mull spectra of the solid derivatives IIa, IVb and VII showed a marked lowering of the frequency of the double bond band from 1637–1645 cm.$^{-1}$ in solution to 1600–1608 cm.$^{-1}$ in the mull spectra. The carbonyl bands in the respective ketones underwent an accompanying lowering of frequency. This effect may be correlated with the relaxing of intermolecular forces in the crystal lattice which induce extreme polarization of the nitrogen and oxygen atoms in the 1,3-positions. The absorption bands at 1678 (CH_2Cl_2 solution) and 1672 cm.$^{-1}$ in the spectra of IIa and VIb must be associated with the C=N bonds in the respective molecules. It is curious that analogous bands are missing in the spectra of IIb and IIc. Apparently the Nujol mull spectrum of IIb is really a solution spectrum in Nujol (also obtained from supernatant liquid). Thereby conditions were achieved closely similar to those obtained in measuring the capillary layer spectrum of IIc. Presumably in these very symmetrical molecules the state of conjugation is such that absorption due to the C=N and C=C bonds is blended.

Ultraviolet Spectra.—Comparison of ultraviolet absorption spectra of solutions of IIa, IIb and IIc in ethanol, in 0.1 *N* hydrochloric acid and in 0.1 *N* sodium hydroxide showed in each case a bathochromic shift of absorption maxima in going from ethanol solution to the salt-forming aqueous solutions.

	EtOH		0.1 *N* HCl		0.1 *N* NaOH	
	λ_{max}	ϵ_{max}	λ_{max}	ϵ_{max}	λ_{max}	ϵ_{max}
IIa	278	28,800	291	25,000	303	26,000
IIb	291	43,000	316	48,000	293	40,000
IIc	292	36,000	322	45,000	296	27,000

The relatively high intensities of the absorption maxima in ethanol solution and the observed positions of these maxima require for IIa, IIb and IIc structures which contain a system of conjugated double bonds. The displacement of maxima in the salt-forming aqueous solutions is in agreement with the enhanced conjugation expected for the respective symmetrical ions. The somewhat lower values of ϵ_{max} measured in sodium hydroxide solution may be indicative of partial degradation.

Experimental

Reactions of I with simple aliphatic amines were straightforward and proceeded readily to completion using excess anhydrous amine in non-hydroxylic solvents. Exposure to moisture was avoided, but moisture was not rigorously excluded. In general reactions were mildly exothermic causing reflux of the solvent. Introduction of the amine *via* a bubbling device was found undesirable owing to the formation of much solid which plugged the delivery tube opening, especially if it had a fritted glass terminal. Ammonia was the only amine used which required pressure to promote reaction. The procedure described for the preparation of IIb appeared generally applicable for volatile amines and was modified only by the use of a dropping funnel for addition of liquid amines.

1-Amino-2-chloro-3-iminotetrafluorocyclopentene-1 (IIa).—A 500-ml. low pressure hydrogenation bottle was charged with 50 g. (0.204 mole) of I[10] dissolved in 200 ml. of anhydrous ether (or benzene) and placed in the shaker. The reaction with anhydrous ammonia was conducted using standard hydrogenation procedure. The initial pressure of 35 p.s.i. was continued overnight or until no further pressure drop was registered. Excess ammonia was removed *via* a water aspirator. The ether solution of IIa was filtered to remove salts which were washed with ether. The filtrate and washes were evaporated leaving 34.3 g. (83% yield) of solid residue, m.p. 92-97°. Recrystallization from benzene gave a pure product, m.p. 97-98°. Purified material remained undecomposed indefinitely when kept in an evacuated desiccator containing both solid KOH pellets and sulfuric acid.

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(10) Commercially available from Hooker Electrochemical Co., and from Peninsular Chemical Research Co.

OTHER AMINO-DERIVATIVES OF 1,2-DICHLOROHEXAFLUOROCYCLOPENTENE-1

	Substituent		B.p.			Calculated				Found			
	1	3,3	°C.	Mm.	n_{20D}	C	H	N	Cl	C	H	N	Cl
IIc	NH–Bu	N–Bu	94	0.012	1.5093	49.60	6.04	8.90		49.96	6.51	8.39	
IIIb	NMe_2	F_2	75	15	1.4245	33.14	2.37	5.52		33.39	2.53	5.03	
IIIc	NBu_2	F_2	69	0.2	1.4342			4.15	10.52			4.22	10.35
IIId	NC_5H_{10}	F_2	55	0.3	1.4534								

Anal. Calcd. for $C_5H_3N_2F_4Cl$: C, 29.63; H, 1.48; N, 13.83; Cl, 17.53. Found: C, 29.54; H, 1.91; N, 13.91; Cl, 17.45.

Potassium of Salt of IIa.—Separate cold, concentrated solutions of 2.0 g. (0.01 mole) of IIa and 0.56 g. (0.01 mole) of potassium hydroxide in commercial absolute ethanol were mixed and immediately evaporated to dryness under reduced pressure. The residue was dissolved in a few milliliters of dry acetonitrile. The solution was cooled to 0° and was diluted with anhydrous ether while scratching the walls of the vessel. The white product which crystallized was filtered, washed with anhydrous ether and dried in a vacuum desiccator; equiv. wt. ($HClO_4$ in HOAc) calcd. 240.6, found 242.6.

Anal. Calcd. for $C_5H_2N_2F_4ClK$: C, 24.95; H, 0.83; N, 11.64. Found: C, 24.81; H, 0.91; N, 11.85.

1-Methylamino-2-chloro-3-methyliminotetrafluorocyclopentene-1 (IIb).—A solution of 50 g. (0.204 mole) of I in 400 ml. of anhydrous ether was placed in a 1-l. three-necked creased flask equipped with a Trubore stirrer and two 250-ml. cold finger condensers. The gas connection of one condenser led to a methylamine cylinder and the other to a drying tube. Both condensers were charged with acetone and Dry Ice which was replenished frequently. Methylamine was admitted intermittently over the stirred mixture so as to maintain visible refluxing. The mixture remained warm from 2 to 3 hours after which no further addition of methylamine was required. Stirring was stopped and the Dry Ice in the condensers and excess methylamine were allowed to evaporate into the hood overnight. Product was worked up as described for IIa. The crude solid residue was dissolved *in situ* in hot ligroin. The yield of recrystallized IIb was 40 g. (85%), m p. 87–89°. Further recrystallization gave a m.p. 88–89°.

Anal. Calcd. for $C_7H_7N_2F_4Cl$: C, 36.52; H, 3.04; N, 12.17. Found: C, 36.42; H, 3.04; N, 11.35.

1-Dimethylamino-2-chloro-3-ketotetrafluorocyclopentene-1 (IVb).—This ketone never was prepared by deliberate acid or alkaline hydrolysis of V in such a way as to determine optimum conditions. It was encountered as a byproduct in the preparation of V (IIIb + methoxide in methanol, water washed), as the major product from acid hydrolysis of VIb (minor product, VII), as the result of heating IIIb under reflux in methanol solution and as the product of extended storage decomposition of IIIb. In order to avoid etching of glassware a recommended procedure would be to subject IIIb to dissolution in aqueous alcohol containing a slightly acid buffer until precipitated product gave a melting point near 61–63°; IVb was nearly insoluble in water, dilute aqueous acid and alkali. It crystallized well from cyclohexane-benzene mixtures.

Anal. Calcd. for $C_7H_6ONF_4Cl$: C, 36.29; H, 2.59; N, 6.05. Found: C, 36.59; H, 3.05; N, 6.01.

1-Dimethylamino-2-chloro-3,3-dimethoxytetrafluorocyclopentene-1 (V).—A solution of 1.84 g. (0.08 mole) of sodium metal in 70 ml. of anhydrous methanol was prepared in a three-necked flask equipped with a dropping funnel, stirrer and reflux condenser protected with a drying tube. Ten grams (0.04 mole) of 1-dimethylamino-2-chlorohexafluorocyclopentene-1 (IIIb) was added to this solution *via* the dropping funnel. The resulting solution was heated under reflux overnight, allowed to cool, poured into ice-water and extracted with four portions of ether. The combined ether extracts were dried, solvent was evaporated and the residue was distilled under reduced pressure using conventional Metroware apparatus. Two fractions were collected and there was an appreciable semi-solid residue: (1) 0.6 g., b.p. 73–88° (4 mm.), $n^{20}D$ 1.4267; (2) 3.7 g., b.p. 89–98° (4 mm.), $n^{20}D$ 1.4491. Fraction 2 was redistilled through a Holtzman column collecting three fractions: (2a) b.p. 84–85° (1 mm.), $n^{20}D$ 1.4409; (2b) 85° (1 mm.), $n^{20}D$ 1.4490; (2c) 85–86° (1.0–1.3 mm.), $n^{20}D$ 1.4509. Fraction 2b was submitted for analysis and for infrared and n.m.r. measurements.

Anal. Calcd. for $C_9H_{12}O_2NF_4Cl$: C, 38.93; H, 4.36; N, 5.05. Found: C, 39.31; H, 4.44; N, 4.53.

The residue from the first distillation was recrystallized from a mixture of toluene and cyclohexane giving crystalline IVb, m.p. 61.5–63.5°.

1-Dimethylamino-2-chloro-3-(methylimino)-tetrafluorocyclopentene-1 (VIb).—One hundred milliliters of tetrahydrofuran was distilled from sodium hydride into a three necked flask equipped with a dropping funnel, stirrer and reflux condenser protected with a drying tube. One and six-tenths grams (0.064 mole) of sodium hydride was added to the tetrahydrofuran and this suspension was stirred at room temperature while a solution of 14.7 g. (0.064 mole) of 1-methylamino-2-chloro-3-(methylimino)-tetrafluorocyclopentene-1 (IIb) in 20 ml. of similarly dried tetrahydrofuran was added to it dropwise. The exothermic reaction proceeded spontaneously, with gas evolution, dissolution of the sodium hydride and darkening of the reaction mixture. When gas evolution ceased the solution was filtered quickly to remove residual particles of sodium hydride and was replaced in the reaction flask. Addition of 23 g. (0.16 mole) of methyl iodide to the reaction mixture *via* the dropping funnel caused a rather strong exotherm, slight lightening of color and precipitation of sodium iodide. After 30 minutes the solution tested neutral. The solution was filtered to remove sodium iodide, evaporated and the viscous residue diluted with methylene chloride. Precipitated sodium iodide was removed again by filtration. Solvent was evaporated and the residue distilled under reduced pressure: (1) 1.1 g., b.p. 54–56° (0.15 mm.), $n^{20}D$ 1.5305; (2) 6.0 g., b.p. 56–60° (0.15–0.30 mm.), $n^{20}D$ 1.5308. Both fractions were colorless and completely soluble in dilute mineral acid solution.

Anal. Calcd. for $C_8H_9N_2ClF_4$: C, 39.26; H, 3.68; N, 11.45. Found: C, 39.21; H, 3.81; N, 11.19.

Quaternary Salt from 1-Dimethylamino-2-chloro-3-(methylimino)-tetrafluorocyclopentene-1 (VIb).—Three grams (0.012 mole) of VIb was dissolved in 6.5 ml. (excess) of methyl iodide by dropwise addition, cooling the solution in an ice-bath. The solution at once acquired an orange-red coloration. It was heated to gentle reflux of the methyl iodide overnight. The entire reaction mixture then consisted of a mass of yellow orange crystals. The product was suspended in carbon tetrachloride, filtered and washed with fresh solvent. The orange colored product weighed 3.5 g. (76% yield), m.p. 146–152°. It dissolved easily in chloroform, ethylene dichloride and more polar solvents at room temperature giving a red solution. It was insoluble in carbon tetrachloride, benzene and less polar solvents. Attempts to effect recrystallization from solvent mixtures failed. The product dissolved in water giving a pale yellow solution and left some red colored matter undissolved. The filtered solution was neutral and contained iodide ions. Water was evaporated at 0° under vacuum leaving a yellow liquid which did not crystallize after 24 hours under vacuum. The product was not investigated further.

Acid Hydrolysis of 1-Dimethylamino-2-chloro-3-methyliminotetrafluorocyclopentene-1 (VIb).—Five grams (0.02 mole) of VIb was suspended in 20 ml. of water. The suspension was stirred and cooled in an ice-bath while 2.0 g. (0.02 mole) of sulfuric acid was added to it dropwise, giving a clear, colorless solution. After standing at room temperature for two days the reaction mixture was cooled to 0°, the crystals which had formed were collected on a filter, washed with a little cold water and dried. The weight of mixed ketones was 2.6 g., m.p. 50–57°. This material was suspended in 20 ml. of 3 *N* sodium hydroxide solution. The insoluble portion was triturated very thoroughly and was filtered, washing the collected product with cold water until the wash liquor was neutral. The insoluble portion after drying and recrystallization from benzene–cyclohexane solution, melted at 61–63°, and gave no depression in melting point in admixture with authentic IVb. The recovered weight was 1.0 g. The sodium hydroxide solution filtrate (above) was first acidified with dilute hydrochloric acid and then neutralized by addition of sodium bicarbonate. The precipitated product was filtered, dried and recrystallized from benzene, giving 0.1 g., m.p. 140.5–142.5°. This material gave no depression in melting point in admixture with authentic VII.

1-Methylamino-2-chloro-3-ketotetrafluorocyclopentene-1 (VII) also never was prepared by deliberate acid or alkaline hydrolysis of IIb in such a way as to determine optimum conditions. It was encountered as a by-product from attempts to alkylate IIb with methyl iodide using sodium ethoxide in ethanol to generate the anion of IIb and as the minor product from acid hydrolysis of VIb. A recommended procedure for its preparation would be to subject IIb to aqueous acid hydrolysis until VII crystallized from the reaction mixture in satisfactory yield; VII was soluble in dilute alkaline solution and sparingly soluble in cold water or dilute acid solution. It crystallized well from benzene solution, m.p. 141–142°.

Anal. Calcd. for $C_6H_4ONF_4Cl$: C, 33.10; H, 1.84; N, 6.44; Cl, 16.32; F, 34.94. Found: C, 33.52; H, 2.38; N, 6.73; Cl, 16.97; F, 35.3.

1-Azido-2-chlorohexafluorocyclopentene-1.—A solution of 47.5 g. (0.73 mole) of sodium azide in 600 ml. of warm dimethyl sulfoxide was placed in a steam-jacketed dropping funnel (to prevent crystallization) and was added to a stirred suspension of 170 g. (0.695 mole) of 1,2-dichlorohexafluorocyclopentene-1 in 700 ml. of dimethyl sulfoxide over a period of 3.5 hours. The reaction temperature stayed between 28–36° without external cooling. Immediately after completion of addition a test for azide ion with ferric chloride was negative. (A second molar equivalent of sodium azide readily may be consumed in such a reaction mixture. The product, considerably more orange colored than the monoazido compound described above, detonated with great violence upon the only occasion when its distillation was attempted. An undistilled sample of this material was found to have an impact sensitivity of one inch/1 kg. weight *vs.* cyclotrimethylene trinitramine = 12 inches.) The solution was poured into two liters of ice and water (to compensate for the considerable heat of solution of dimethyl sulfoxide). The lower layer was separated, washed again with water, giving 146 g. of crude product. This was dried over Drierite, keeping the product in the refrigerator. The product was distilled at 46 mm. pressure. After a small forerun, b.p. 37–48°, nearly the entire remainder was collected in one fraction, b.p. 48–50°, n^{20}_{D} 1.4135, wt. 122.6 g., 48.8% yield. This material could be kept indefinitely without noticeable decomposition when stored in the refrigerator. Samples stored at room temperature developed pressure within a day or two. A redistillation attempted at 75° head temperature was interrupted by excessive rise in pressure. Distillations at 45–50° never have given trouble.

Anal. Calcd. for $C_5N_3F_6Cl$: C, 23.86; N, 16.70; Cl, 14.11. Found: C, 24.13; N, 15.24; Cl, 13.63.

1,3,3-Trimethoxy-2-chlorotetrafluorocyclopentene-1.—A solution of 13.8 g. (0.6 mole) of sodium metal in 300 ml. of absolute methanol was prepared in a 1-liter three-necked flask equipped with a stirrer, dropping funnel and reflux condenser protected with a drying tube. Forty-nine grams (0.2 mole) of 1,2-dichlorohexafluorocyclopentene-1 was added to the stirred sodium methoxide solution at a rate sufficient to cause brisk refluxing. Precipitation of sodium halides was observed at once. The reaction mixture was heated for an additional 3 hours and allowed to stand overnight. Precipitated solids were removed by filtration and the filtrate was mixed with 1.5 liters of water. The mixture was extracted with two 200-ml. portions of ether. The combined ether extracts were washed twice with equal volumes of water and dried with magnesium sulfate. Solvent was evaporated and the residue distilled at 6.4 mm. giving: (1) 0.8 g., b.p. 78–80°; (2) 36.0 g., b.p. 80–81° (68% yield); and 3.4 g. of residue. Fraction 2 was redistilled at 5.8 mm. giving a small forerun and 33.7 g., b.p. 80–81°, n^{20}_{D} 1.4225. The infrared spectrum of this material showed contamination by a small amount of carbonyl-containing compound (see Discussion). It would appear probable that such contamination might be reduced by avoiding the aqueous extraction step in the work-up procedure.

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HUNTSVILLE, ALA.

[CONTRIBUTION FROM THE DEPARTMENT OF AGRICULTURAL CHEMISTRY, NORTH DAKOTA AGRICULTURAL COLLEGE]

The Glucosides of Flaxseed. II. Linocaffein[1]

BY HAROLD J. KLOSTERMAN AND ROBERT Z. MUGGLI

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A second crystalline glucoside obtained by the alkaline methanolysis of the complex polymer present in flaxseed hulls is shown to be methyl 4-β-D-glucopyranosylcaffeate (I). The structure of I, which is designated *linocaffein*, has been established by degradation and synthesis.

An earlier paper[2] described the isolation of a brown, amorphous, gum-like substance from the hull of flaxseed. Alkaline methanolysis of this gum was shown to give rise to the methyl esters of β-hydroxy-β-methylglutaric acid,[3] 4-glucosyloxycinnamic acid (linocinnamarin),[2] together with a mixture of unknown glucosides and phenolic constituents. One of these glucosidic components is shown herein to be methyl 4-β-D-glucopyranosylcaffeate (I) and it has been named linocaffein.

Caffeic acid has been isolated from a wide variety of plant materials. It is found either free or combined in an unknown manner. Various investigators have suggested that caffeic acid also occurs in nature as the glucoside, although this had not been previously substantiated.

The yellow glucosidic mixture which remained after the isolation of the β-hydroxy-β-methylglutaric acid[3] was examined for phenolic glucosides by partition chromatography using an ammoniacal butanol–ethanol–water mixture as the partitioning liquid. The dried chromatogram was sprayed with the bis-diazotized benzidine reagent used by Linstedt[4] in the detection of phenolic compounds to give a series of brown colored spots and one deep pink

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(1) Presented before the Division of Carbohydrate Chemistry at the 132nd National American Chemical Society Meeting, New York, N. Y., September, 1957. Published by permission of the Director, North Dakota Agricultural Experiment Station.

(2) H. J. Klosterman, F. Smith and C. O. Clagett, THIS JOURNAL, **77**, 420 (1955).

(3) H. J. Klosterman and F. Smith, *ibid.*, **76**, 1229 (1954).

(4) G. Linstedt, *Acta Chem. Scand.*, **4**, 448 (1950).