The Effect of Conformation on the Electronic Absorption Spectrum of the Carboxylate Group[1a,b]

W. D. CLOSSON,[1c] PETER J. ORENSKI,[1d]

Department of Chemistry, Columbia University, New York, New York 10027

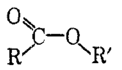
AND BERNARD M. GOLDSCHMIDT

New York University Medical Center, New York, New York 10016

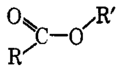
Received April 7, 1967

The energies and intensities of the n → π* transitions of a series of saturated lactones, varying in ring size from 6 to 17 members, have been measured in several solvents. The transition energy of an unstrained carboxylate function constrained to the *s-cis* conformation (as in 6- to 8-membered rings) is found to be about 4 kcal/mole less than that of esters in the *s-trans* conformation. The solvent sensitivity of the n → π* band is also greater for the *s-cis* conformation. Moderate exaltation of the n → π* intensity is observed in hexamethylene adipate and azelate which may be due to transannular interactions between the two *s-trans* carboxylate groups.

The carboxylate ester function, while strongly preferring a roughly planar conformation due to resonance interaction between the ether oxygen and carbonyl group, may exist in either a *s-cis* (Ia) or *s-trans* (Ib) arrangement. The *s-trans* conformation appears to be 3 to 4 kcal/mole more stable than the *s-cis*[2] and is the form usually found in acyclic systems. In cyclic systems (lactones) of 8 or fewer ring members, the *s-cis* conformation is forced on the group and major changes in chemical and physical properties arise. Most of these changes can be traced to a large increase in dipole moment for the *s-cis* ester (the change being from about 1.9 D. for *s-trans* esters[3] to about 4.5 D. for unstrained *s-cis* lactones[2]) and to angle strain in the small ring lactones. The cause of the instability in the *s-cis* arrangement has been attributed both to α,γ-(lone pair)-(lone pair) repulsions[4] and to simple dipole-dipole interactions.[2] Since the nonbonding electrons of the carbonyl oxygen would be intimately involved in either case, it was of interest to examine the conformational effect on the n → π* transition. Previously, we had postulated that this transition might be shifted to lower energy in the *s-cis* conformation but only the strained molecules, propiolactone and butyrolactone, were investigated.[5] Investigation of an extended series of lactones where ring size is changed from small to medium to large would allow correlation of spectral effects with such properties as dipole moment, reactivity, and carboxylate group conformations previously assigned to these compounds.[2] We wish to report here our results on lactones of 6, 7, 8, 9, 10, and 13 ring members and related acyclic esters, as well as the spectra of two dilactones of 14 and 17 ring members.



Ia

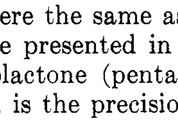


Ib

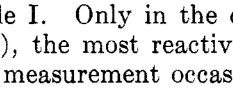
Results and Discussion

The wavelengths of maximum absorption for the low-intensity band were carefully determined for the lactones and several related esters in a series of solvents of different polarities. The techniques of measurement were the same as described previously;[5] the results are presented in Table I. Only in the case of δ-valerolactone (pentanolid), the most reactive ester studied, is the precision of measurement occasionally less than that previously obtained with saturated[5] and α, β-unsaturated esters.[6]

As expected,[5] there is a notable difference in n → π* transition energies of structures Ia and Ib when relatively strainless systems are involved. This is indicated by the abrupt increase (over 3 kcal/mole) in transition energy between the 7- and 8-membered lactones (hexanolid and heptanolid) and the 9-membered octanolid. This is exactly the conformational "turnover point" (suggested by Huisgen and Ott on the basis of dipole moment data)[2] where ring size becomes sufficient to allow the *s-trans* conformation to be the predominant, if not exclusive form. Further increase in ring size results in further increase in transition energy till the 13-membered lactone (dodecanolid) has an n → π* maximum very similar to that of acyclic esters. Hexamethylene adipate and hexamethylene azelate (II and III), 14- and 17-membered dilactones, respectively, have their n → π* maxima at wavelengths indistinguishable from those of acyclic esters of similar structure. It would be expected that these large rings would be flexible enough and free enough from transannular steric interactions to allow their



II



III

---

[1] (a) The Electronic Absorption Spectra of Carboxylate Derivatives. IV. For part III, see W. D. Closson, S. F. Brady, and P. J. Orenski, *J. Org. Chem.*, **30**, 4026 (1965). (b) Supported in part by the Petroleum Research Fund, administered by the American Chemical Society, and by the National Institutes of Health. (c) To whom all correspondence should be addressed at the Department of Chemistry, State University of New York at Albany, Albany, N. Y. 12203. (d) National Institutes of Health Predoctoral Fellow, 1965-1967.

[2] R. Huisgen and H. Ott, *Tetrahedron*, **6**, 253 (1959).

[3] C. P. Smyth, "Dielectric Behavior and Structure," McGraw-Hill Book Co., Inc., N. Y., New York, 1955, pp. 303-309.

[4] N. L. Owen and N. Sheppard, *Proc. Chem. Soc.* (London), 264 (1963).

[5] W. D. Closson and P. Haug, *J. Am. Chem. Soc.*, **86**, 2384 (1964).

[6] W. D. Closson, S. F. Brady, and P. J. Orenski, *J. Org. Chem.*, **30**, 4026 (1965).

TABLE I

ABSORPTION MAXIMA OF $n \rightarrow \pi^*$ TRANSITIONS OF LACTONES AND ESTERS

Lactone of ring size	Registry No.	λ_{max}, A (ϵ_{max})					
		Isooctane	Acetonitrile	Ethanol	Methanol	80 % aq methanol[a]	TFP[b]
4[c]		2072 (54)	2056 (48)	2045 (52)	2045 (49)	2029 (52)	2014 (50)
5[c]		2140 (25)	2123 (35)	2098 (39)	2078 (40)	2070 (39)	2046 (28)
6	542-28-9	...	2153 (51)	2125 (57)	2138 (55)[d]	...	...
7	502-44-3	2204[e]	2181 (53)	2155 (59)	2145 (63)	2131 (65)	2091 (71)[d]
8	539-87-7	2204 (69)	2180 (58)	2150 (67)	2137 (72)	sh[f]	...
9	5698-29-3	2156 (84)	2138 (86)	2124 (92)	2117 (90)	sh[f]	...
10	6008-27-1	2143 (65)	2132 (65)	2113 (68)	2111 (69)	2094 (71)	sh[f]
13	947-05-7	2135 (55)	2117 (70)	2105 (72)	2103 (71)	2092 (74)	sh[f]
14[g]	13926-69-7	2132 (201)	2106 (210)	...	...	...	2068 (205)
17[h]	13926-70-0	2106 (180)	2092 (194)	...	...	...	2063 (185)
Ester							
n-Pentyl acetate	628-67-7	2109 (60)	2090 (59)	2081 (59)	2075 (57)	2058 (60)	2035 (58)
n-Hexyl acetate	142-92-7	2109 (61)	2090 (59)	2083 (59)	2077 (60)	2063 (60)	2036 (59)
n-Butyl propionate	590-01-2	2120 (63)	2104 (60)	2097 (62)	2090 (60)	2078 (64)	2056 (64)
n-Pentyl propionate	624-54-4	2116 (62)	2101 (62)	2095 (64)	2090 (62)	2074 (65)	2058 (60)
n-Hexyl propionate	2445-76-3	2114 (63)	2098 (61)	2091 (65)	2086 (63)	2075 (61)	2054 (66)
n-Propyl butyrate	105-66-8	2123 (63)	2109 (64)	2102 (66)	2098 (67)	2087 (72)	2067 (71)
n-Pentyl butyrate	540-18-1	2120 (67)	2108 (65)	2101 (68)	2096 (69)	2087 (72)	2067 (73)
Ethyl valerate	539-82-2	2130 (67)	2116 (66)	2108 (67)	2101 (68)	2089 (70)	2068 (72)
n-Propyl valerate	141-06-0	2122 (65)	2111 (66)	2102 (63)	2097 (69)	2087 (68)	2066 (70)
Methyl caproate	106-70-7	2120 (63)	2107 (64)	2099 (67)	2094 (66)	2083 (70)	2062 (75)

[a] Prepared as in ref 5. [b] 2,2,3,3-Tetrafluoropropanol. [c] Data from ref 5. [d] ±6 A. [e] Saturated solution. [f] Shoulder (no distinct maximum). [g] Hexamethylene adipate. [h] Hexamethylene azelate.

carboxylate groups to assume the lowest energy conformations (*s-trans*).

In Figure 1 plots of dipole moment and n $\rightarrow \pi^*$ transition energy *vs.* ring size in lactones are shown. Assuming dipole moment is a sensitive indicator of carboxylate conformation,[2] it is clear from Figure 1 that n $\rightarrow \pi^*$ transition energy is also a convenient tool for determining carboxylate conformation in medium rings. It can also be seen that angle strain in small-ring lactones, which results in only a modest decrease in dipole moment, is related to an enormous increase in n $\rightarrow \pi^*$ transition energy. As discussed previously,[5] these effects are probably a complex result of rehybridization of the atoms in the small ring and not simply due to the "dampening" of ester resonance.

The free-energy difference between strainless *s-cis* and *s-trans* conformations has been estimated, from saponification rates of 7- and 14-ring lactones, to be 3.8 kcal/mole.[2] Interestingly, we find a difference in n $\rightarrow \pi^*$ transition energies (isooctane) between the 7- and 13-ring lactones of 4.2 kcal/mole, a remarkably close number. This suggests that a major portion of the potential energy difference between the two conformations is expressed as destabilization of the nonbonding electrons of the carbonyl oxygen. A more precise estimate of the amount of destabilization of the n-level electrons is not possible at present since this would involve the differences in energy of the "Franck–Condon" singlet π^* states for the *s-cis* and *s-trans* conformations. The higher end absorption present in the spectra of unstrained *s-cis* lactones does suggest that the $\pi \rightarrow \pi^*$ transition energy may be less than that for *s-trans* esters, but this could also be due to an increase in intensity of the allowed band in the *cis* case. At present, the coincidence of the spectral energy shift and the enthalpy of activation difference for saponification rates must be regarded as just that.

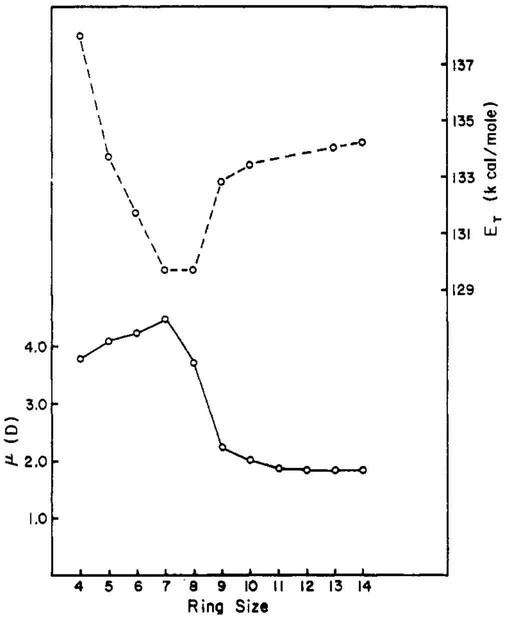


Figure 1.—Variation of dipole moment (lower plot) and n $\rightarrow \pi^*$ transition energy (isooctane) (upper plot), with lactone ring size. Dipole moment data are from ref 2. The value of E_{T} for the 14-ring lactone is that of hexamethylene adipate; the value of E_{T} for the 6-ring lactone in isooctane was estimated from the value in acetonitrile assuming a solvent shift half-way between that of the 5- and 7-ring lactones.

The sensitivity of the n $\rightarrow \pi^*$ transition of lactones to solvent polarity also appears to be a strong function of conformation. In Table II are shown dipole moment data and the difference in transition energies between methanol and isooctane [E_{T}(MeOH) − E_{T}(isooctane)] for the lactones and related esters. This latter figure should be a rough measure of solvent sensitivity; more precise measurements were not possible for many of the lactones because of their limited solubilities in many solvents and the serious overlap of their $\pi \rightarrow \pi^*$ and n $\rightarrow \pi^*$ bands in solvents of high polarity.

TABLE II

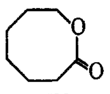
SOLVENT SENSITIVITIES OF LACTONES AND RELATED ESTERS

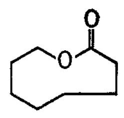
Lactone of ring size	Dipole moment, D.[a]	E_T(MeOH) − E_T(*i*-oct) (kcal/mole)	m^b
4	3.8	1.82[c]	0.119[c]
5	4.09	3.98[c]	0.183[c]
6	4.22	...	...
7	4.45	3.57	0.152
8	3.70	4.06	0.177
9	2.25	2.44	0.104
10	2.01	2.02	0.095
13	1.86	2.04	0.091
Acyclic esters[d]			
7-carbon		1.85	0.078
8-carbon		1.76	0.076
9-carbon		1.68	0.071

[a] Data from ref 2. [b] From relationship $E_T = mZ + b$, where Z is solvent polarity constant. See ref 9. [c] Data from ref 5. [d] Average of the data for the esters in Table I.

One would expect that the large increase in dipole moment on going to the *s-cis* conformation would result in a greater interaction with polar solvents. For example, it has been suggested that the hydrogen bond strength between methanol and the carbonyl oxygen of an unstrained *cis* lactone is about twice that for the corresponding hydrogen bond involving an acyclic *trans* ester.[7] If, as suggested by several sources,[8] the blue shift of n → π^* transitions on going from hydrocarbon to hydroxylic solvents is about equal to the strength of the hydrogen bond formed, the data in Table II are quite reasonable. It can be seen that the solvent sensitivities [measured either by E_T (MeOH) − E_T (*i*-oct) or by m[9]] fall in two groups, 3.5 to 4.0 kcal/mole for the *s-cis* lactones (except for propiolactone whose pecularities have been discussed previously[5]), and 1.7 to 2.0 kcal/mole for transoid lactones and esters, in quite good agreement with available hydrogen-bond-strength data.[7] A definite but smaller difference also exists between the cyclic and acyclic transoid cases, since the n → π^* transitions of the lactones are a few tenths of a kilocalorie more sensitive to the shift from isooctane to methanol than are those of the esters. This is probably due to a greater steric hindrance to solvation in the acyclic cases, since solvent sensitivity does decrease slightly with increasing chain length of the ester. The effect may be envisaged as a tendency of the long hydrocarbon chains to "clump" in polar solvents and decrease the ability of solvent to approach a central carbonyl group. The slightly greater solvent shifts of acetate esters, where the carboxylate function is near the end of the chain, compared with those of the other acyclic esters in Table I support this explanation. Kosower has observed a similar low solvent sensitivity of the n → π^* transition of a large-ring cyclic ketone (cyclopentadecanone) and has advanced a similar explanation.[10] The somewhat more rigid transoid lactones should be less prone to show this effect.

The cases of heptanolid (IV) and octanolid (V) are worthy of special comment. The transition energy (isooctane) of IV is identical with that of hexanolid and the solvent sensitivity of its transition (Table II) is also high; yet it has a lower dipole moment than any of the other *cis* lactones. Models suggest that nonbonded steric interactions involving the carbonyl group may be considerable even in the *cis* conformation of IV, which could lead to a lower than normal transition energy.[5,6] Part of the change in E_T with solvent polarity may be due to a change in the fraction of *trans* conformer, which has been suggested to be present in small amounts.[2] The rather high (for a *trans* lactone) solvent sensitivity of V may also be a reflection of the small amount of *cis* conformer claimed to be present.[2]


IV


V

The large-ring dilactones, II and III, have n → π^* transitions of rather high molar absorptivities. It is about 35% higher than that of acyclic adipate diesters in the case of II,[11] and probably similarly heightened in the case of III. This is clearly outside experimental error. While calculation of the oscillator strength (*f*) for these transitions was not carried out (see Experimental Section), the great similarities of band shape for the n → π^* transitions of all of these esters and lactones suggests exaltation due to transannular interaction between the carboxylate functions of the dilactones. (Dodecanolid, a 13-ring monolactone, shows a normal $\epsilon_{\max}$.)

Experimental Section[13]

Solvents.—All solvents were of at least Spectrograde quality. The 2,2,3,3-tetrafluoropropanol was purified by the method of Kosower and Huang.[10]

Materials.—The acyclic esters were prepared by standard methods and their purity checked by gas chromatography before use. The lactones were prepared by Baeyer–Villiger oxidation of the appropriate ketones after the method of Sanger and Duckworth.[2,14] Their properties are given below.

Pentanolid (valerolactone, 5-hydroxypentanoic acid lactone) has bp 90° (4.5 mm) (lit.[15] bp 88° (4 mm)), n^{21}_{D} 1.4509 (lit. n^{20}_{D} 1.4613, 1.4600,[14] n^{20}_{D} 1.4868,[16] n^{20}_{D} 1.4503[15]). The wide range of published refractive indices probably indicates different degrees of polymerization of the samples used. Our own sample showed n^{21}_{D} 1.4564 and traces of polymer after 2-week storage at −5°. We therefore regard the spectroscopic measurements made with this lactone as the least reliable.

Hexanolid (6-hydroxyhexanoic acid lactone) has bp 87–89° (2 mm) (lit.[17] bp 98–99° (2 mm)), n^{24}_{D} 1.4582, n^{22}_{D} 1.4597 (lit. n^{24}_{D} 1.4608,[17] n^{22}_{D} 1.4611[15]).

Anal. Calcd for $C_6H_{10}O_2$: C, 63.16; H, 8.77. Found: C, 63.15; H, 8.44.

Heptanolid (7-hydroxyheptanoic acid lactone) has bp 83–85° (10.5 mm) (lit.[2] bp 80–82 (10.5 mm)), n^{24}_{D} 1.4673, n^{22}_{D} 1.4680.

---

(7) S. Searles, M. Tamres, and G. N. Barrow, *J. Am. Chem. Soc.*, **75**, 71(1953).

(8) (a) H. H. Jaffé and M. Orchin, "Theory and Applications of Ultraviolet Spectroscopy," John Wiley and Sons, Inc., New York, N. Y., 1962, p 187 and references cited thereon. (b) M. Ito, K. Inuzuka, and S. Imanishi, *J. Chem. Phys.*, **31**, 1694 (1959).

(9) E. M. Kosower, *J. Am. Chem. Soc.*, **80**, 3261 (1958).

(10) E. M. Kosower and G. S. Wu, *ibid.*, **83**, 3142 (1961).

(11) Simple dialkyl adipate esters have molar absorptivities of about 130 in isooctane; hexamethylene diacetate has a maximum molar absorptivity of 117 in the same solvent.[12]

(12) P. J. Orenski, Ph.D. Thesis, Columbia University, 1967.

(13) We wish to thank Mrs. Hansa Menon for making some of the preliminary spectroscopic measurements, and Dr. E. O. Langerak, of the Organic Chemicals Department, E. I. du Pont de Nemours and Co. for a generous gift of 2,2,3,3-tetrafluoropropanol.

(14) W. F. Sanger and A. Duckworth, *J. Am. Chem. Soc.*, **77**, 188 (1955).

(15) I. Heilbron, *et al.*, Ed., "Dictionary of Organic Compounds," Vol. 5, Oxford University Press, New York, N. Y., 1965, p 2997.

(16) D. D. Coffman, *J. Am. Chem. Soc.*, **57**, 1981 (1935).

(17) F. J. van Natta, J. W. Hill, and W. H. Carothers, *ibid.*, **56**, 455 (1934).

Anal. Calcd for $C_7H_{12}O_2$: C, 65.63; H, 9.38. Found: C, 65.63; H, 9.50.

Octanolid (8-hydroxyoctanoic acid lactone) has bp 76–76.5° (13.5 mm) (lit.[2] bp 72–73° (10.5 mm)), n^{26}_D 1.4580, n^{22}_D 1.4595.

Anal. Calcd for $C_8H_{14}O_2$: C, 67.61; H, 9.86. Found: C, 67.39; H, 9.95.

Nonanolid (9-hydroxynonanoic acid lactone) has bp 92° (12 mm) (lit.[2] bp 86–87° (10.5 mm)), n^{26}_D 1.4652, n^{24}_D 1.4660, n^{21}_D 1.4673.

Anal. Calcd for $C_9H_{16}O_2$: C, 69.23; H, 10.26. Found: C, 69.12; H, 10.38.

Dodecanolid (12-hydroxydodecanoic acid lactone) has bp 119–120° (5 mm) (lit.[2] bp 130° (10.5 mm)), n^{23}_D 1.4698, n^{20}_D 1.4709.

Anal. Calcd for $C_{12}H_{22}O_2$: C, 72.73; H, 11.11. Found: C, 72.35; H, 11.19.

Hexamethylene adipate was prepared after the general procedure of Spanagel and Carothers.[18] Chromatographing the product twice on Florosil gave mp 68–70° (lit.[18] mp 70°).

Anal. Calcd for $C_{12}H_{20}O_4$: C, 63.14; H, 8.83. Found: C, 62.95; H, 8.71.

Hexamethylene azelate was prepared in similar fashion,[18] mp (after chromatography on Florosil) 54–56° (lit.[18] mp 59°).

Anal. Calcd for $C_{15}H_{26}O_4$: C, 66.64; H, 9.69. Found: C, 66.75; H, 9.85.

Spectroscopic Measurement.—All spectra were measured with a Cary recording spectrophotometer, Model 14, using matched 0.1-cm quartz cells. The details of the technique have been described previously.[5] The precision of measurement was at least ±5 A, and usually ±3 A, except where otherwise noted. Molar absorptivities were reproducible to at least ±5%. The oscillator strengths (f) of a few of the $n \rightarrow \pi^*$ transitions in isooctane were determined by a method described before.[19] The values follow: heptanolid, $f = 0.0019$; nonanolid, $f = 0.0019$; dodecanolid, $f = 0.0018$. These are very similar to the value previously found for *n*-butyl acetate in methanol (0.0017).[5] The values of f determined by this technique are probably in error by no more than 5% due to overlap of the weak band by the nearby allowed transition. Only a single smooth maximum in the $n \rightarrow \pi^*$ region was observed in each case.

---

[18] E. W. Spanagel and W. H. Carothers, *ibid.*, **57**, 939 (1935).

[19] Reference 5, footnote 13.

The Reactions of Sodium Pentafluorophenolate with Substituted Pentafluorobenzenes

RALPH J. DE PASQUALE AND CHRIST TAMBORSKI

Polymer Branch, Air Force Materials Laboratory, Wright-Patterson Air Force Base, Ohio

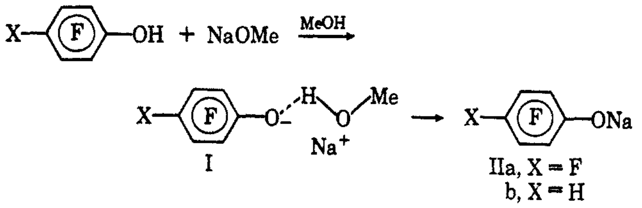
Received April 10, 1967

Sodium pentafluorophenolate was prepared by proton exchange using NaOMe–MeOH. This salt was freed from residual methanol and treated with a series of substituted pentafluorobenzenes (C_6F_5R, R = CF_3, CO_2Et, C_6F_5, Br, Cl, F, and H) using N,N-dimethylacetamide (DMAC) as solvent. The major product arising from displacement of fluorine *para* to the substituent was a fluorinated diphenyl ether. For some substituents (Cl, Br, and H), displacement of *o*-fluorine was competitive but minor. Mixtures of triphenyl ethers were occasionally observed. The relative reaction rates of these pentafluorobenzenes with sodium pentafluorophenoxide were measured in DMAC at 106°. These values when plotted against Hammett's substituent constant σ_p gave a reasonably straight line. From the slope, the σ_p of a pentafluorophenyl group can be estimated at +0.4. The halide ion mobilities were qualitatively measured as F > Cl or Br which is consistent with a two-step addition–elimination mechanism where the first step is rate determining.

In the past, the use of pentafluorophenoxide as a nucleophile has received limited attention.[1,2] Using aprotic conditions, we have found that this nucleophile reacts with a variety of substituted pentafluorobenzenes producing fair to excellent yields of the expected ethers.

Results[3a]

Reactions.—Pentafluorophenol and 4-hydrotetrafluorophenol were treated with cold NaOMe–MeOH. Removal of the solvent at reduced pressure left the salts as methanolates (I). Since the presence of alcohol would be detrimental to the salts' nucleophilic properties from both steric and electronic considerations, it was removed by heating in a vacuum oven. These salts were then treated with a series of substituted pentafluorobenzenes (see Table I).



SNAr reactions of charged anions with neutral substrates generally proceed faster in dipolar aprotic solvents than in protic solvents of similar dielectric constants.[3b] In our work dimethylformamide (DMF) and dimethylacetamide (DMAC) were used as the reaction media.

4-Bromononafluorodiphenyl ether (III) was the first of the series of fluorinated ethers prepared by the reaction between pentafluorophenolate and a substituted pentafluorobenzene. Experiments varying reaction parameters were carried out in order to obtain optimum yields of the desired ether (see Table II).

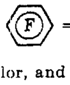
In DMF, incorporation of a solvent fragment into the perfluoroaromatic nucleus competed with the formation of III. The formation of this side product 4-N,N-dimethylaminobromotetrafluorobenzene (IV) was base catalyzed since it was produced faster and in higher yields in the presence of sodium pentafluorophenolate.

---

[1] W. J. Pummer and L. A. Wall, *J. Res. Natl. Bur. Std.*, **68A**, 277 (1964).

[2] E. S. Blake, G. A. Richardson, and J. A. Webster, Air Force Materials Laboratory Technical Report, RTD-TDR-63-4186.

[3] (a) For purposes of clarity and economy of space, the following symbol is employed. Only the substituents other than fluorine are indicated.



= C_6F_6

(b) R. A. Raphael, E. C. Taylor, and H. Wynberg, *Advan. Org. Chem.*, **5**, 9 (1965).