J. Org. Chem. 1988, *53*, 780–782

Enhancement of the Equilibrium Acidities of Carbon Acids by Polyfluoroaryl Substituents

F. G. Bordwell,[*,†] John C. Branca,[†] Joseph E. Bares,[†] and Robert Filler[*,‡]

Departments of Chemistry, Northwestern University, Evanston, Illinois 60208, and Illinois Institute of Technology, Chicago, Illinois 60616

Received July 8, 1987

Acidity measurements in Me_2SO solution have revealed that $C_6F_5CH_2CN$ is 5.9 pK_a units more acidic than $C_6H_5CH_2CN$ due to the large field/inductive effects of the five fluorine atoms. Smaller C_6X_5 substituent differences (ΔpK_a) were observed for parent acids where steric hindrance interfered with effective overlap with the p orbital of the carbanion, as for CH_3CO_2Et (4.4 units), $CH_2(CO_2Et)CN$ (2.9 units), and fluorene (9-position; 3.2 units). The much larger ΔpK_a (8.9) for *p*-$(HC_6F_4)_3CH$ vs $(C_6F_5)_2CH_2$ compared to $(C_6H_5)_3CH$ vs $(C_6H_5)_2CH_2$ (1.9 units) points to more effective carbanion stabilization in the tris(polyfluorophenyl)methanes, which is consistent with the appreciable acid weakening effects observed for the *p*-Me and *p*-MeO groups in (*p*-$MeC_6F_4)_3CH$ and (*p*-$MeOC_6F_4)_3CH$. The 11.8 pK_a unit increase in acidity for 1,2,3,4,5,6,7,8-octafluorofluorene, relative to fluorene, amounts to a 5.9 pK_a unit acidifying effect for the four fluorine atoms in each ring, which matches the effect caused by five fluorine atoms in $C_6F_5CH_2CN$.

An impressive body of experimental evidence has accumulated that demonstrate significant stabilizing effects by fluoro and polyfluoroaryl substituents on carbanions. The evidence includes marked acceleration of the rates of carbanionic rearrangements,[1,2] anomalous reaction chemistry,[3,4] and enhanced hydrocarbon acidities, relative to analogous all-hydrogen systems.[5–7]

In our continuing studies on equilibrium acidities in Me_2SO solution,[8] we have discussed the acidifying effect of replacing one or two of the hydrogen atoms in parent carbon acids such as CH_3CN, CH_3CO_2Et, diphenylmethane, fluorene, and the like by phenyl groups.[9] These studies have now been extended to some polyfluoroaryl substituents. A dramatic exaltation of ion-pair acidities in cyclohexylamine for $(C_6F_5)CH_2$ and $(C_6F_5)_3CH$, relative to the parent $(C_6H_5)_2CH_2$ and $(C_6H_5)_3CH$ carbon acids, has been reported earlier,[7] i.e., replacement of each C_6H_5 group by C_6F_5 increased the acidity by 5–6 p*K* units. The present study confirms and extends these observations.

Fluoro and Polyfluoroaryl Substituent Effects on Acetonitrile, Ethyl Acetate, and Ethyl Cyanoacetate. Examination of Table I shows that *o*-F, *m*-F, and *p*-F atoms change the acidity of $C_6H_5CH_2CN$ by 1.3, 1.75, and −0.5 p*K* unit, respectively. The results indicate that the acid-weakening resonance effect overshadows the acid-strengthening field/inductive effect for *p*-F but not for *o*-F. The acidifying effect of the C_6F_5 moiety in $C_6F_5CH_2CN$, relative to C_6H_5 in $C_6H_5CH_2CN$, is 5.9 p*K* units, which is slightly greater than the sum of the *o*-F, *m*-F, and *p*-F effects (5.6 p*K* units).

Table I. Effect of Fluorine and Polyfluoro Substituents on the Acidities of Acetonitrile, Ethyl Acetate, and Their Derivatives in Me_2SO Solution at 25 °C

acid	pK_a[a]	ΔpK_a[b]	ΔpK_a[b]	ΔpK_a[b]
CH_3CN	31.3	(0.0)		
$C_6H_5CH_2CN$	21.7	9.8	(0.0)	
o-$FC_6H_4CH_2CN$	20.4		1.3	
m-$FC_6H_4CH_2CN$	19.95		1.75	
p-$FC_6H_4CH_2CN$	22.2		−0.50	
$C_6F_5CH_2CN$	15.8	15.7	5.9	
$(C_6H_5)_2CHCN$	17.5		4.5	(0.0)
$(C_6F_5)_2CHCN$	7.95	23.8	14.05	9.55
$CH_2(CO_2Me)CN$	12.8			
$CH_2(CO_2Et)CN$	13.1			(0.0)
$C_6H_5CH(CO_2Et)CN$	8.0			5.4
$C_6F_5CH(CO_2Et)CN$	5.1			8.3
CH_3CO_2Et	~30	(0.0)		
$C_6H_5CH_2CO_2Et$	22.65	~7.5		
$(C_6H_5)_2CHCO_2Et$	21.9	~8.3	(0.0)	
$(C_6F_5)_2CHCO_2Et$	13.1	~17.1	8.8	

[a] Measured as previously described[8] in Me_2SO using two or more indicators or standard acids. [b] Statistically corrected for the number of acidic hydrogen atoms, where appropriate.

The acidifying effect brought about by substituting a C_6F_5 function for a hydrogen atom in CH_3CN is 15.8 pK_a units (21.6 kcal/mol) as compared to 9.8 pK_a units for C_6H_5. (This and subsequent ΔpK_a comparisons are statistically corrected for the number of acidic hydrogen atoms present.) The difference of 5.9 pK_a units represents the sum of the field/inductive effects of the five fluorine atoms. Substitution of two C_6F_5 functions for hydrogen atoms in CH_3CN increases the acidity by 23.8 pK_a units (Table I). The attenuation of the acidifying effect of the second C_6F_5 function from 15.7 to 8 pK_a units (52%) is expected by analogy with the attenuation of the effect of the second C_6H_5 function from 9.8 to 4.5 pK_a units (45%). The ΔpK_a of 8.3 for $C_6F_5CH(CO_2Et)CN$ vs $CH_2(CO_2Et)CN$ is much smaller than that between $C_6F_5CH_2CN$ and CH_3CN (15.8), partly because steric hindrance in the anion, caused by the presence of the CO_2Et function, prevents effective overlap of the carbanion p orbital with the π-system in the C_6F_5 function and partly because of the resonance saturation effect.[10] The larger attenuation

---

[†] Northwestern University.

[‡] Illinois Institute of Technology.

(1) Chambers, R. D.; Clark, M.; Spring, D. J. *J. Chem. Soc., Perkin Trans. 1* **1972**, 2464.

(2) Chambers, R. D.; Clark, M. *J. Chem. Soc., Perkin Trans. 1* **1972**, *1*, 2469.

(3) Filler, R. *Fluorine Chemistry Reviews*; Tarrant, P., Ed.; Marcel Dekker: New York, 1977; Vol. 8, p 1.

(4) Filler, R.; Fiebig, A. E.; Pelister, M. Y. *J. Org. Chem.* **1980**, *45*, 1290.

(5) (a) Streitwieser, A., Jr.; Hudson, J. A.; Mares, F. *J. Am. Chem. Soc.* **1968**, *90*, 648; (b) **1968**, *90*, 244. (c) Streitwieser, A. Jr.; Scannon, P. J.; Niemeyer, H. M. *Ibid.* **1972**, *94*, 7936.

(6) Vanier (Vanier, N. R. Ph.D. Dissertation, Northwestern University, 1976) has shown that α-fluorine atoms exert acid-strengthening effects relative to α-H or α-Me in FCH_2SO_2Ph, FCH_2COPh, and 9-fluorofluorene.

(7) Filler, R.; Wang, C. S. *J. Chem. Soc. D* **1968**, 287.

(8) Matthews, W. S.; Bares, J. E.; Bartmess, J. E.; Bordwell, F. G.; Cornforth, F. J.; Drucker, G. E.; Margolin, Z.; McCallum, R. J.; McCollum, G. J.; Vanier, N. R. *J. Am. Chem. Soc.* **1975**, *97*, 7006. Bordwell, F. G.; Branca, J. C.; Hughes, D. L.; Olmstead, W. N. *J. Org. Chem.* **1980**, *45*, 3306.

(9) Bordwell, F. G.; Bares, J. E.; Bartmess, J. E.; McCollum, G. J.; Van der Puy, M.; Vanier, N. R.; Matthews, W. S. *J. Org. Chem.* **1977**, *42*, 321.

0022-3263/88/1953-0780$01.50/0

Table II. Acidities of Polyfluorinated Diphenylmethane, Triphenylmethanes, and Fluorenes

acid	pK_a[a]	ΔpK_a[b]	ΔpK_a[b]	ΔpK_a[b]
$(C_6H_5)_2CH_2$	32.2	(0.0)		
$(C_6F_5)_2CH_2$	22.0	10.2		
$(C_6H_5)_3CH$	30.6	(0.0)		
$(p\text{-}HC_6F_4)_3CH$	13.4	17.2	(0.0)	
$(p\text{-}MeC_6F_4)_3CH$	15.9	14.7	−2.5	
$(p\text{-}MeOC_6F_4)_3CH$	16.2	14.4	−2.8	
fluorene	22.6	(0.0)		
9-(C_6H_5)fluorene	17.9	5.0	(0.0)	
9-(C_6F_5)fluorene	14.7	8.2	3.2	
2-F-fluorene	21.0	1.6		
3-F-fluorene	22.07	0.53		
1,2,3,4,5,6,7,8-octafluorofluorene	10.8	11.8		
9-(CO_2Me)fluorene	10.35	12.55		(0.0)
9-(CO_2Et)-1,2,3,4,5,6,7,8-octafluorofluorene	6.1	16.8		4.25

[a] Measured as previously described[8] in Me_2SO using two or more indicators or standard acids. [b] Statistically corrected for the number of acidic hydrogen atoms where appropriate.

observed for $C_6H_5CH(CO_2Et)CN$ vs $CH_2(CO_2Et)CN$ (ΔpK_a = 5.4) than for $C_6F_5CH(CO_2Et)CN$ vs $CH_2(CO_2Et)CN$ (ΔpK_a = 8.3) is expected in view of the much smaller contribution from the field/inductive effect.

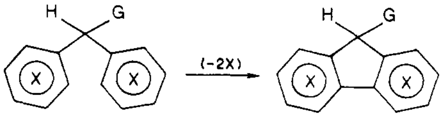
The effect of replacement of one, and then two, α-hydrogen atom in CH_3CO_2Et by C_6H_5 is estimated to increase the acidity by at least 7.5 and 8.3 pK_a units, respectively. The much smaller effect of the second phenyl group (0.8 pK_a unit) than for the change from $C_6H_5CH_2CN$ to $(C_6H_5)_2CHCN$ (4.5 pK_a units) indicates that the CO_2Et function is imposing relatively severe steric constraints on the overlap of one, or both, of the phenyl groups in the $(C_6H_5)_2CCO_2Et^-$ anion. (Steric hindrance to approach of the electrophile to this carbanion has been shown to lead marked retardation of rates of S_N2 reactions with $PhCH_2Cl$.[11]) The ΔpK_a of 8.8 pK_a units between $(C_6F_5)_2CHCO_2Et$ and $(C_6H_5)_2CHCO_2Et$ is comparable to the ΔpK_a of 9.55 for $(C_6F_5)_2CHCN$ vs $(C_6H_5)_2CHCN$ (Table I).

Polyfluoro Effects in Diphenylmethanes, Triphenylmethanes, and Fluorenes. The acidity data for these compounds are summarized in Table II.

The ΔpK_a for $(C_6F_5)_2CH_2$ vs $(C_6H_5)_2CH_2$ reported in Table II is 10.2 units, 1 unit larger than the ΔpK_a of 9.55 observed between $(C_6F_5)_2CHCN$ and $(C_6H_5)_2CHCN$, which probably reflects the lesser steric effect for H vs CN. A similar comparison of ΔpK_a for $(C_6F_5)_3CH$ and $(C_6H_5)_3CH$ was frustrated by the low solubility of the polyfluoro compound. The ΔpK_a of 17.2 observed for $(p\text{-}HC_6F_4)_3CH$ vs $(C_6H_5)_3CH$ must be close to the mark, however,[12] since the effect of p-F is not much different from that of p-H (Table I). The average effect of a C_6F_5 substituent vs C_6H_5 in $(C_6X_5)_3CH$ is then 5–6 pK_a units, i.e., as large as or larger than that between $(C_6F_5)_2CH_2$ and $(C_6H_5)_2CH_2$. The difference in acidity between $(p\text{-}HC_6F_4)_3CH$ and $(C_6F_5)_2CH_2$ is 8.9 pK_a units, compared to only 1.9 units between $(C_6H_5)_3CH$ and $(C_6H_5)_2CH_2$. Both of these comparisons are consistent with a large field/inductive effect for C_6F_5, as was brought out from the data in Table I. The 3.2 pK_a unit larger effect for substitution of C_6F_5 vs C_6H_5 for a hydrogen atom at the 9-position of fluorene (Table II) provides a further example.

Replacements of p-H in $(p\text{-}HC_6F_4)_3CH$ by MeO and by Me lead to acid-weakening effects of 2.8 and 2.5 pK_a units, respectively. The calculated two-point Hammett ρ values are about 3.5 and 5, respectively. These sizable ρ values are consistent with the large stabilizing effects indicated for $(p\text{-}HC_6F_4)_3C^-$ anions, relative to $(C_6H_5)_3C^-$ anions.

Scheme I. Acidity Effects on Conversions of Diphenylmethanes to Fluorenes



1 2

X	G	pK_a(1)	pK_a(2)	ΔpK_a
H	H	32.2	22.6	9.6
F	H	22.0	10.8	11.2
H	CO_2Et	21.9	10.35 (CO_2Me)	11.6
F	CO_2Et	13.1	6.1	7.0

Substitution of a fluorine atom for hydrogen in the 2-position (meta) of fluorene causes a 1.6 pK_a unit acidity increase, compared to a 0.53 unit increase at the 3-position (para). Substitution of fluorine atoms into the 1, 2, 3, 4, 5, 6, 7, and 8 positions increases the acidity by 11.8 pK_a units, which corresponds reasonably well to the effect calculated (10.1 units) by assuming that the effects in the 2, 4, 5, and 7 positions are equivalent and additive (4 × 1.6 = 6.4), that the effects in the 3 and 6 positions are equivalent and additive (2 × 0.53), and that the effects in the 1 and 8 positions are equivalent to the ortho effects in $o\text{-}FC_6H_4CH_2CN$ (Table I) and additive (2 × 1.3).

The effect on the acidity of enforcing coplanarity of the benzene rings in diphenylmethanes, $(C_6X_5)_2CHG$, by eliding two ortho X atoms (X = H or F) to form a fluorene ring is shown for two systems in Scheme I.

Part of the large ΔpK_a's shown in Scheme I, which average about 10 pK_a units, is caused by the enforced coplanarity of the rings and part by the aromaticity of the fluorenide ions, which are 14 π-electron systems.

Experimental Section

Acidity measurements were carried out at Northwestern University as previously described.[8]

Synthesis of polyfluoroarenes was carried out at Illinois Institute of Technology as described in the sections that follow.

(Pentafluorophenyl)acetonitrile, $C_6F_5CH_2CN$, bp 105 °C (8 Torr), $n^{25}{}_D$ 1.4370, was prepared by the reaction of hexafluorobenzene with ethyl cyanoacetate in the presence of K_2CO_3, followed by acid hydrolysis of the resulting ethyl cyano(pentafluorophenyl)acetate, $C_6F_5CH(CN)CO_2C_2H_5$, mp 38–38.5 °C.[13] (Proton and fluorine magnetic resonance data for both compounds are available in ref 13.)

Bis(pentafluorophenyl)acetonitrile, $(C_6F_5)_2CHCN$, bp 120–124 °C (2.8 Torr), mp 65 °C subl, was prepared by reaction of C_6F_6 with $C_6F_5CH_2CN$ in the presence of sodium hydride in DMF.[4,14]

Ethyl bis(pentafluorophenyl)acetate, $(C_6H_5)_2CHCO_2C_2H_5$, was obtained by acid-catalyzed ethanolysis (H_2SO_4) of $(C_6F_5)_2CHCN$, bp 108–110 °C (3.5 Torr).[4]

The preparation and properties of ethyl 9-octafluorofluorenecarboxylate, mp 75–76 °C) and octafluorofluorene (mp 113.5–115 °C) are described in ref 15.

---

(10) Bordwell, F. G.; McCollum, G. J. *J. Org. Chem.* **1976**, *41*, 2391.

(11) Bordwell, F. G.; Hughes, D. L. *J. Org. Chem.* **1983**, *48*, 2216.

(12) Kulkarni, S. V.; Schure, R.; Filler, R. *J. Am. Chem. Soc.* **1973**, *95*, 1859.

(13) Filler, R.; Woods, S. M. *Org. Synth.* **1977**, *57*, 80.

(14) Vlasov, V. M.; Yakobson, G. G. *Zh. Org. Khim.* **1973**, *9*, 1024; *Chem. Abstr.* **1973**, *79*, 52902.

(15) See ref 4.

Bis(pentafluorophenyl)methane, $(C_6F_5)_2CH_2$, mp 59.5–60.5 °C, was prepared by Friedel–Crafts alkylation of C_6F_5H with CH_2Cl_2.[15] PMR: $\delta = 5.9$ (quintet), $J_{HF} = 0.7$ Hz.

(p-$MeC_6H_4)_3CH$ and (p-$MeOC_6F_4)_3CH$ were prepared by either alkylation of p-MeC_6F_4H and p-$MeOC_6F_4$, respectively, with $CHCl_3$[7,16] or by reaction of the corresponding triarylmethanol[12] with phosphorus tribromide.[16]

Tris(2,3,5,6-tetrafluorophenyl)methane.[17] A solution of 5.00 g (8.87 mmol) of tris(4-chloro-2,3,5,6-tetrafluorophenyl)methane[15,18] in 250 mL of anhydrous ether, under a nitrogen atmosphere, was cooled in a dry ice–acetone bath. Thirty milliliters (0.311 g, 48.6 mmol of n-BuLi) of a 15.25% solution of n-butyllithium in hexane was added over a period of 40 min. The reaction mixture immediately turned an intense yellow-green. After an additional hour of stirring in the cold, 100 mL of 6 N hydrochloric acid was added to the cloudy yellow reaction mixture and the cooling bath was removed. The reaction mixture was allowed to warm overnight. The almost colorless layers were separated and the aqueous layer was extracted with three portions of ether. The combined ethereal layers were washed with water three times, dried over anhydrous magnesium sulfate, and evaporated in vacuo to give a white solid. Three crystallizations from Skellysolve B gave 1.71 g (41.9%) of product, mp 124–126 °C: IR (CCl_4) 3075 (w, aromatic C-H), 1648, 1627, and 1610 (w, aromatic C=C), 1507 (vs, aromatic ring), and 986 cm^{-1} (w, C-F); ^1H NMR (CCl_4) δ 6.37 (s, 1 H) and 7.10 (m, 3 H, Ar). Anal. Calcd for $C_{19}H_4F_{12}$: C, 49.59; H, 0.88. Found: C, 49.37; H, 0.80.

9-(Pentafluorophenyl)fluorene was prepared by reduction of 9-(pentafluorophenyl)-9-fluorenol, as described in the following procedures (ref 20).

9-(Pentafluorophenyl)fluorenol. A well-stirred solution of 12.35 g (50.01 mmol) of bromopentafluorobenzene in 250 mL of anhydrous ethyl ether was cooled in a dry ice–acetone bath under a nitrogen atmosphere. A 15.13% solution of n-butyllithium in hexane (31.2 mL, 3.20 g, 50.0 mmol) was added over 15 min. The colorless solution was stirred in the cold for 1 h before 8.11 g (45.0 mmol) of 9-fluorenone in 100 mL of ether was added over 37 min. The reaction was stirred for an additional hour before the dry ice–acetone bath was replaced with a dry ice–carbon tetrachloride bath. After an additional 3 h, 100 mL of 6 N hydrochloric acid was added to the lime green solution and the cold bath was removed. The layers were separated and the aqueous layer was extracted 3 times with ether. The combined ethereal layers were washed 3 times with water, dried over anhydrous magnesium sulfate, and evaporated in vacuo to give a yellow oil. The oil was allowed to stand and was seeded with powdered dry ice and scratched to give a crude yellow solid. Two crystallizations from Skellysolve B, using Darco G-60 charcoal, gave 7.14 g (45.5%) of product as white plates, mp 92.5–95 °C. Two additional crystallizations from Skellysolve B gave 5.82 g (37.1%) as white plates, mp 94.5–96.5 °C (sealed capillary): IR (CCl_4) 3599 (m, free OH), ca. 3500–3320 (w, br, bonded OH), 1651 (m, Ar C=C), 1523 and 1488 (vs, aromatic ring), 1451 (s, aromatic ring), and 993 cm^{-1} (vs, C—F); NMR ($CDCl_3$) δ 2.95 (s, 1, OH) and ca. 7.40 (complex multiplet, 8, Ar H). Anal. Calcd for $C_{19}H_9OF_5$: C, 65.53; H, 2.60. Found: C, 65.05; H, 2.52.

9-(Pentafluorophenyl)fluorene by Reduction of 9-(Pentafluorophenyl)fluorenol. A mixture of 3.52 g (10.1 mmol) of 9-(pentafluorophenyl)fluorenol, 100 mL of glacial acetic acid, and 80 mL of concentrated hydrochloric acid was warmed with stirring overnight. The mixture was then heated under reflux and 9.48 g (0.145 g-atom) of mossy zinc metal was added in small pieces. After about 2 h of reflux, an additional 4.00 g (0.0613 g-atom) of zinc dust was slowly added. After an additional 5 h of reflux, the reaction mixture was cooled and filtered. The collected solid was dried and dissolved in ether, and the ethereal solution was filtered and evaporated in vacuo to give 2.33 g (69.6%) of crude product. Two crystallizations from methanol–water gave 1.34 g (40.0%) of pure product, mp 164–166 °C: IR (CCl_4) 1649 (w, aromatic C=C), 1529 (s, aromatic ring), 1503 (vs, aromatic ring), 1004 and 980 cm^{-1} (w,—C-F); NMR ($CDCl_3$) δ 7.50 (complex multiplet, 8, aromatic H) and 5.41 (s, 1 H). Anal. Calcd for $C_{19}H_9F_5$: C, 68.68; H, 2.73. Found: C, 68.46; H, 2.59.

Acknowledgment. The research at Northwestern was supported by the National Science Foundation.

Registry No. CH_3CN, 75-05-8; $C_6H_5CH_2CN$, 140-29-4; o-$FC_6H_4CH_2CN$, 326-62-5; m-$FC_6H_4CH_2CN$, 501-00-8; p-$FC_6H_4CH_2CN$, 459-22-3; $C_6F_5CH_2CN$, 653-30-5; $(C_6H_5)_2CHCN$, 86-29-3; $(C_6F_5)_2CHCN$, 42238-34-6; $CH_2(CO_2Me)CN$, 105-34-0; $CH_2(CO_2Et)CN$, 105-56-6; $C_6H_5CH(CO_2Et)CN$, 4553-07-5; $C_6F_5CH(CO_2Et)CN$, 2340-87-6; CH_3CO_2Et, 141-78-6; $C_6H_5CH_2CO_2Et$, 101-97-3; $(C_6H_5)_2CHCO_2Et$, 3468-99-3; $(C_6F_5)_2CHCO_2Et$, 42238-45-9; $(C_6H_5)_2CH_2$, 101-81-5; $(C_6F_5)_2CH_2$, 5736-46-9; $(C_6H_5)_3CH$, 519-73-3; (p-$HC_6F_4)_3CH$, 112320-05-5; (p-$MeC_6F_4)_3CH$, 18681-67-9; (p-$MeOC_6F_4)_3CH$, 17547-31-8; fluorene, 86-73-7; 9-(C_6H_5)fluorene, 789-24-2; 9-(C_6F_5)fluorene, 73482-93-6; 2-F-fluorene, 343-43-1; 3-F-fluorene, 343-40-8; 1,2,3,4,5,6,7,8-octafluorofluorene, 27053-34-5; 9-(CO_2Me)fluorene, 3002-30-0; 9-(CO_2Et)-1,2,3,4,5,6,7,8-octafluorofluorene, 27053-33-4; tris(4-chloro-2,3,5,6-tetrafluorophenyl)methane, 20020-06-8; bromopentafluorobenzene, 344-04-7; 9-fluorenone, 486-25-9; 9-(pentafluorophenyl)fluorenol, 73475-35-1.

---

(16) Beckert, W. F.; Lowe, J. U., Jr. *J. Org. Chem.* **1967**, *32*, 582.

(17) See ref 7.

(18) Wang, C. S. Ph.D. Thesis, Illinois Institute of Technology, June, 1967.

(19) Kulkarni, S. V.; Schure, R.; Filler, R. *J. Am. Chem. Soc.* **1973**, *95*, 1859.

(20) Fiebig, A. E. Ph.D. Thesis, Illinois Institute of Technology, May, 1971.

(21) Gerasimova, T. N.; Barkhash, V. A.; Vorozhtsov, N. N., Jr. *J. Gen. Chem. USSR* **1968** *38*(3), 510.