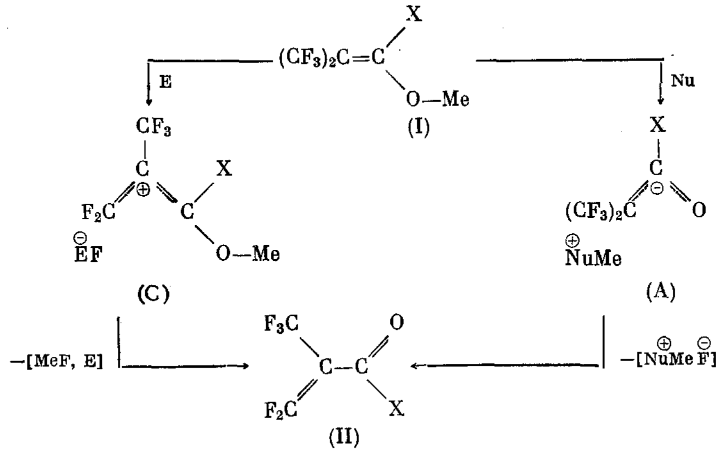
POLYFLUORINATED ANIONS AND CATIONS — INTERMEDIATES IN REACTIONS OF FLUORINE-CONTAINING VINYL ETHERS

V. F. Snegirev, M. V. Galakhov,
V. A. Petrov, K. N. Makarov,
and V. I. Bakhmutov

UDC 542.91:547.361.2'26'161

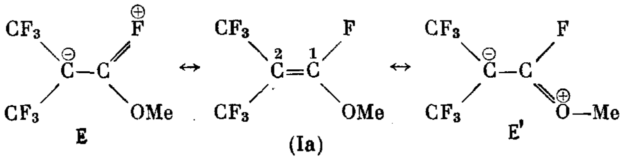
Fluorinated vinyl ethers are convenient starting reagents for the synthesis of fluorine-containing α,β-unsaturated carbonyl compounds. Vinyl ethers are readily transformed by the action of both electrophilic (E) and nucleophilic (Nu) reagents [1-4], so that the formation of intermediate cations and anions, respectively, can be assumed.



(1)

X = F(a), C_2F_5 (b).

In the present work, the particles (A) and (C) are identified by ^{13}C and ^{19}F NMR spectra, and their charge distribution was studied. In Table 1 data are given on the NMR spectra of the initial vinyl ethers (Ia, b) and also of cations (Ca, b) and anions (Aa, b), formed by the action of electrophiles and nucleophiles on ethers (Ia, b) (see the Experimental section). The signals in the NMR spectra were assigned according to the multiplicity, the SSCC values, and the integral intensities, as given in [5]. Figure 1 shows the ^{13}C NMR spectra of vinyl ether (Ia), cation (Ca), and anion (Aa). A comparison of the spectral parameters of the initial olefins (Ia, b) is most interesting. From comparison of the ^{13}C NMR data (see Table 1), it follows that on transition from a substituent with a negative inductive effect only (the C_2F_5 group) to a substituent having an opposite mesomeric effect (the F atom) also, the C^2 signal is shifted considerably to a strong field (33.1 ppm). For the C^1 signal an opposite shift is characteristic, equal to no more than 3.5 ppm. According to [6], these data indicate a higher polarization of the C═C bond in ether (Ia), probably because of increase in the contribution of structure E.



(2)

This conclusion does not contradict the observation of a signal of C^7 (Ia) in a stronger field, compared with the case of (Ib), in which the reverse transfer of the electron density from the O atom is not weakened by the action of the fluorine atom attached to C^1, as in

---

N. A. Nesmeyanov Institute of Heteroorganic Compounds, Academy of Sciences of the USSR, Moscow. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 6, pp. 1318-1325, June, 1986. Original article submitted January 2, 1985.

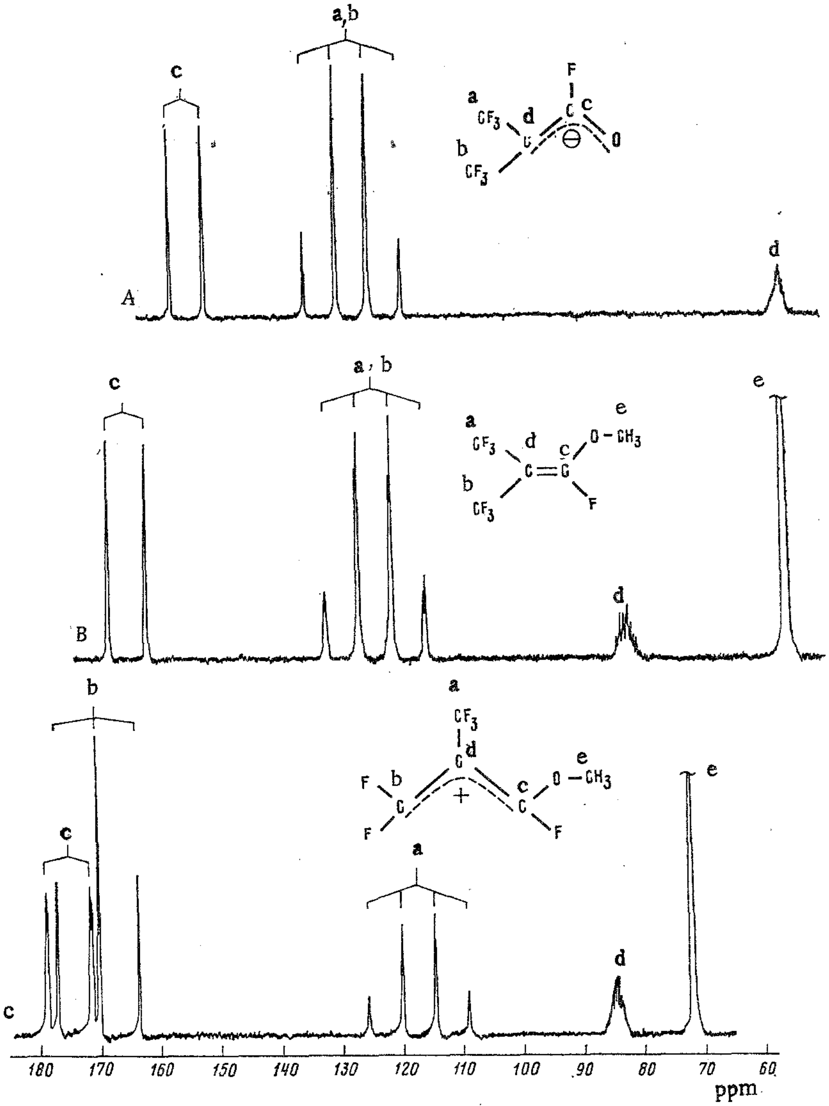
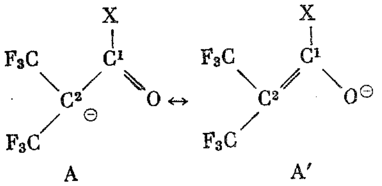


Fig. 1. ^{13}C NMR spectra of: A) anion (Aa); B) ether (Ia); C) cation (Ca).

ether (Ia). The spectral data thus indicate the presence of a higher electron density on the C^2 atom in (Ia). We can therefore expect a higher mobility of the fluorine atoms in the CF_3 groups in ether (Ia). In fact, it was found that when equimolar amounts of ethers (Ia, b) and SbF_5 are mixed, of the two possible cations, only cation (Ca) is recorded, which indicates its higher thermodynamic stability.

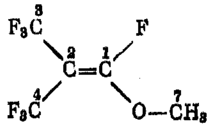
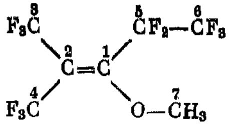
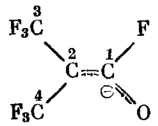
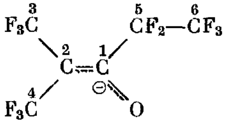
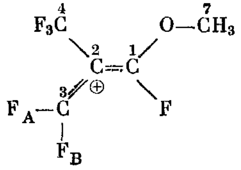
Information on the charge distribution in particles (A) and (C) can be obtained by comparing spectral parameters in the initial vinyl ethers (I). The data in Table 1 show that the formation of anions (Aa, b) is accompanied by a considerable upfield shift of the C^2 signal [$\Delta\delta C^2$ = 24 (a) and 33 (b) ppm] at very low changes in the position of C^1 signals. This result agrees with [7] and indicates the participation of the C^2 atom in the distribution of the negative charge according to Scheme (3) (the negative inductive effect of the two CF_3 groups ensures this participation). An additional argument for the contribution of structure A [see Scheme (3)] is the fact that on transition from ether (Ia) to its anion

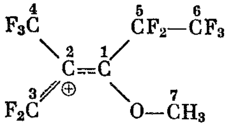
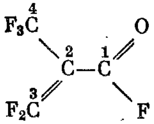
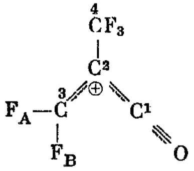
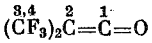


(3)

(Aa), the ^{19}F signal at C^1 is sharply shifted downfield ($\Delta\delta F^1$ = 69.2 ppm). In fact, Table 1

TABLE 1. Spectral Parameters ($\delta^{19}F$ and $\delta^{13}C$, ppm; $J_{^{13}C-^{19}F}$, Hz)

Compound		Parameter	Position of C and F nuclei						
			1	2	3	4	5	6	7
	(Ia)	$\delta^{13}C$	162,9	82,1	122,8	122,6	—	—	56,8
		^1J	306,7d	—	267,9	268,0	—	—	^3J=13,4 d
		^2J	—	26,8 d, 34,3 hept	—	—	—	—	—
		$\delta^{19}F$	−9,8	—	−19,9	−19,1	—	—	—
	(Ib)	$\delta^{13}C$	159,4	115,2	120,3	120,8	110,0	118,2	64,9
		^1J	—	—	280,5 g	280,5 g	169,4 t	293,0 g	—
		^2J	27,7t	27,2 hept	—	—	38,9 g	36,0 t	—
		$\delta^{19}F$	—	—	−20,9	−17,5	36,6	4,4	—
	(Aa)	$\delta^{13}C$	157,1	58,1	129,4	129,1	—	—	—
		^1J	291,8d	—	263,5 g	263,5g	—	—	—
		^2J	—	13,4d, 37,2 hept	—	—	—	—	—
		$\delta^{19}F$	−79,0	—	−29,0	−27,7	—	—	—
	(Ab)	$\delta^{13}C$	167,5	82,0	128,4	127,9	110,8	120,3	—
		^1J	—	—	279,4 g	274,7g	282,5 t	279,9 g	—
		^2J	23,8 t	28,3 hept	—	—	34,0 g	37,8 t	—
		$\delta^{19}F$	—	—	−29,6	−24,2	38,2	2,6	—
	(Ca)	$\delta^{13}C$	175,2	84,6	170,4	117,6	—	—	71,86
		^1J	363,2 d	—	339,4 t	276,9 g	—	—	^3J=9,1d
		^2J	—	41,7g, 28,3 t, 19,4d	—	—	—	—	—
		$\delta^{19}F$	−102,6	—	−70,1 (A) −67,1 (B)	−19,8	—	—	—

	(Cb)	$\delta^{13}C$ ^1J ^2J $\delta^{19}F$	203,6 — 34,7 t —	93,1 — 43,0 g, 15,3 t —	168,3 340,6 t — −64,4 †	117,6 284,7 g — −22,8	108,4 283,3 g 44,4 g 34,1	115,8 295,6 g 33,3 t 1,1	82,8 — — —
	(IIa)	$\delta^{13}C$ ^1J $\delta^{19}F$	148,4 338,6 d −114,2	83,6 — —	163,6 320,6 t −16,5	119,6 265,4 g −26,2	— — —	— — —	— — —
	(Cc)	$\delta^{13}C$ ^1J ^2J $\delta^{19}F$	147,3 — — —	138,0 — 45,2 g, 49,1 d, 10,1 d —	176,6 346,1 t — −93,6 (A) ‡ −83,0 (C)	116,0 281,3 g — −26,4	— — — —	— — — —	— — — —
 $\overset{3,4}{(CF_3)_2}\overset{2}{C}=\overset{1}{C}=O$	(III)	$\delta^{13}C$ ^1J ^2J	181,8 — —	157,9 — 43,2 hept	123,6 269,5 g —	123,6 269,5 g —	— — —	— — —	— — —

*At −70°C, Z, E isomers are observed with respect to $C^1 \doteq C^2$ bond.

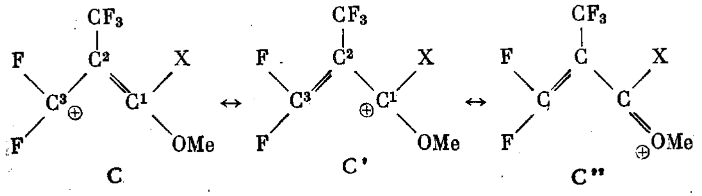
†AB system with $\Delta\delta_{A-B} \approx 0.8$ ppm and $^2J_{A-B} = 168$ Hz.

**$^2J_{A-B} = 176.4$, $^2J_{F_A-CF_3} = {}^4J_{F_B-CF_3} = 10.2$ Hz.

shows that the F^1 signal in the spectrum of compound (IIa), which models structure A [see Scheme (3)], is observed in a weak field (−114 ppm). The contribution of structure A' in the case of anions (Aa, b) is confirmed by the nonequivalency of the CF_3 groups (according to the ^{19}F NMR spectra), indicating their slow rotation in the NMR time scale around the $C^1 = C^2$ bond. According to the δC^2 values of the anions studied [58.1 and 82.0 ppm for (Aa) and (Ab), respectively], the highest contribution of structure A [see Scheme (3)] should be expected for anion (Aa) with X = F. This agrees well with the chemical properties of these anions. Thus, (Aa) is readily alkylated at the C^2 atom and acylated with the elimination of the fluorine atom from the CF_3 group. In contrast, (Ab) does not undergo alkylation, even under rigid conditions, and its acylation proceeds mainly at the O atom (see the Experimental Section).

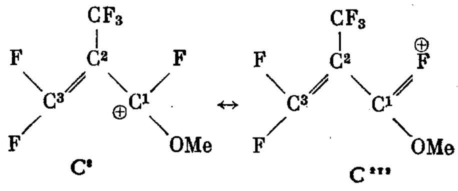
We shall now consider the spectral changes that occur on transition from ethers (Ia, b) to their cations (Ca, b), formed by the action of SbF_5 (see the Experimental section). Table 1 shows that the generation of (Ca) is accompanied by a shift of 12.3 and 47.6 ppm of the C^1 and C^3 signals, respectively, to the weak field. The position of the C^2 signal thus practically does not change. The downfield shift is also characteristic of the ^{19}F signals at C^1 and C^3, with simultaneous increase in the SSCC $^1J_{^{13}C-^{19}F}$ to 363 (C^1) and 339 (C^3) Hz. A similar situation is observed on transition from (Ib) to (Cb). In the cations studied the charge is therefore distributed on the C^1 and C^3 atoms [structures C and C' in Scheme (4)], which agrees with the generally accepted concepts on the delocalization of charge in allyl cations [8].

Table 1 shows that on transition from (Ia, b) to (Ca, b), the chemical shift at C^7 increases considerably [$\Delta\delta C^7$ = 15.1 and 17.9 ppm for (Ca) and (Cb)].



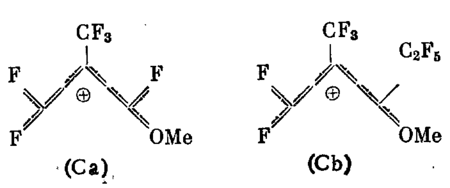
(4)

which indicates the participation of the O atom also in the charge delocalization [structure C" in Scheme (4)]. By comparing the spectral parameters of (Ca) and (Cb), we can understand the difference in the charge distribution of the cations studied. Table 1 shows that the δC^3 for (Ca) and (Cb) practically do not differ. At the same time, the δC^1 for (Cb) exceeds the δC^1 for (Ca) by 28.4 ppm, which indicates an increase in the charge on the C^1 atom on transition from (Ca) to (Cb). It is possible that this indicates the participation of the F atom at C^1 also in the delocalization of the positive charge due to reverse transfer of the electron density



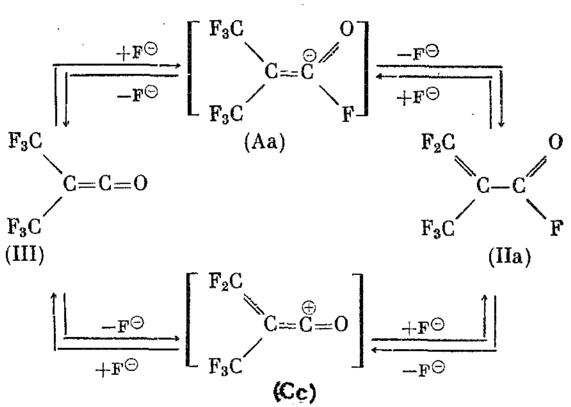
(5)

Thus, cations (Ca) and (Cb) differ, as in the first case the charge is delocalized on three F atoms, and in the second on two only [see Scheme (6) (participation of the MeO group in the delocalization of the charge in (C) was discussed above)].



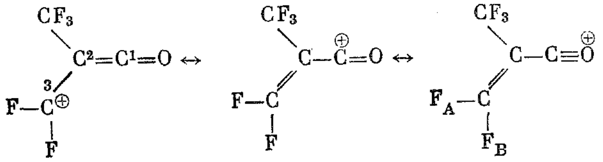
(6)

In the study of a mixture of ether (Ia) with excess SbF_5, it was found that when the sample is heated above ∿20°C, a gas (possibly, MeF) is evolved, and additional signals appear in the ^{19}F and ^{13}C NMR spectra. It is known [2] that when catalytic amounts of SbF_5 act on ether (Ia), besides the evolution of MeF, perfluoromethacrylyl fluoride (IIa) is formed [see Scheme (1)]. However, the spectral characteristics of the new compounds — the acid fluoride (IIa) and its isomeric bis(trifluoromethyl) ketene (III) — are entirely different. Previously [9], in a study of the isomerization of ketene (III) into acid fluoride (IIa) by catalytic amounts of both nucleophilic and electrophilic reagents, it was assumed that mesomeric ions are formed at the intermediate stage. By addition of the F^- anion, the mesomeric carbanion (Aa) is generated. Its structure and spectral characteristics have been discussed above. In contrast, in isomerization by the action of Lewis acids ($ZnCl_2$, BF_3) it was assumed that the F^- anion splits off with the formation of a mesomeric cabanion (Cc). The isomerizations are reversible, and as a result equilibrium mixtures of ∿60% of ketene (III) and ∿40% of acid fluoride (IIa) are formed:



(7)

As we used excess amounts of SbF_5, and not catalytic, it can be assumed that the corresponding cation (Cc) is formed from (IIa) due to splitting of the F^- anion from the C(O)F group. We unequivocally confirmed this supposition by the identity of the ^{13}C and ^{19}F NMR spectra of the new compound obtained from a solution of ether (Ia) in SbF_5 and solutions of acid fluoride (IIa) or ketene (III) in SbF_5. In turn, this proves that in all these cases, one and the same intermediate acylium cation (Cc)* is formed. Information on the charge distribution in cation (Cc) can be obtained by comparing the spectral parameters of this cation and two of its predecessors (IIa) and (III). Table 1 shows that on transition from ketene (III) to cation (Cc), the ^1C and ^3C signals are shifted by 34.5 and 53 ppm to the strong and weak fields, respectively. The C^1 signal of cation (Cc) lies in the a region characteristic of the acylium cations [10]. On transition from acid fluoride (IIa) to cation (Cc), a small downfield shift of 13 ppm of the C^1 signal of the carbonyl group is observed, possibly due to a change in the hybridization of this atom from sp^2 to sp level. From the data obtained, cation (Cc) can be described by resonance structures, represented in the following scheme:



(8)

It should be noted that for this cation an unusual SSCC relationship $^4J_{F_A\text{-}CF_3} = {}^4J_{F_B\text{-}CF_3}$ = 10.2 Hz is observed, despite the different relative orientation of the interacting nuclei ($\Delta\delta F_A - F_B$ = 10.6 ppm). This effect is apparently the result of the complex angular dependence of SSCC on $^{19}F-^{19}F$.

EXPERIMENTAL

The $^{13}C-\{^1H\}$ NMR spectra were recorded on a Bruker WP-200SY spectrometer (50.3 MHz) with the main pulse duration of 8 μsec (40°C) and overall relaxational delay (AQ + PD) of 2 sec at ∿20°C. In all cases, the scanning width was 10 kHz at a memory volume of 16 K per spectrum. In separate cases, a mathematical narrowing of lines was used. The ^{19}F NMR spectra were recorded on a Perkin-Elmer R-32 spectrometer (84.6 MHz). The chemical shifts were measured with reference to TMS and CF_3COOH, used as external standards.

---

*On formation of stable perfluorinated mesomeric acylium cations, homologs of (Cc), see [4].

1-Methoxyperfluoro-2-methyl-1-propene (Ia) and 3-methoxyperfluoro-2-methyl-2-pentene (Ib) were obtained according to [11] and [12]. Tetraethylammonium perfluoro-2-methyl-1-propenol-1-ate (Aa) and tetraethylammonium perfluoro-2-methyl-2-pentenol-3-ate (Ab) were obtained according to [1] and [13].

Preparation of Methoxy-Containing Polyfluoroalkenyl Carbonium Ions (Ca) and (Cb). A 0.6-g portion (3 mmoles) of SbF_5 was added dropwise, with stirring (0°C), to 0.3 g (1 mmole) of 1-methoxyperfluoro-2-methyl-1-propene (Ia) or 3-methoxyperfluoro-2-methyl-2-pentene (Ib), and the mixture was then soldered in an ampule.

Preparation of Acylium Cation (Cc). A 0.6-g portion (3 mmoles) of SbF_5 was added dropwise, with stirring (0°C), to 0.2 g (1 mmole; of perfluoromethacrylyl fluoride (IIa) or bis(trifluoromethyl) ketene (III), and the mixture was soldered into an ampule.

3-Benzoyloxyperfluoro-2-methyl-2-pentene (IV). A solution of 2.8 g (0.02 mole) of benzoyl chloride in 10 ml of absolute MeCN was added to a solution of potassium perfluoro-2-methyl-2-pentenol-3-ate [1], obtained from 6.3 g (0.2 mole) of (Ib) and 3.5 g (0.02 mole) of KI in 15 ml of absolute MeCN. After 3 h, distillation of the filtrate gave 4.2 g (52%) of (IV), bp 43-45°C (2 mm). IR spectrum (ν, cm^{-1}): 1665 (C=C), 1755 (C=O). ^{19}F NMR spectrum: -20.7 q. q. t (CF_3^1), -16.6 q (CF_3^2), 4.2 q (CF_3^3), 36.7 q (CF_2) (cf. [14]).

CONCLUSIONS

1. The existence of polyfluorinated cations as intermediates in reactions of polyfluorine-containing vinyl ethers with electrophilic reagents has been proved.

2. ^{13}C and ^{19}F NMR parameters were obtained of cations and anions formed from 1-methoxyperfluoro-2-methyl-1-propene and 3-methoxyperfluoro-2-methyl-2-pentene.

3. Perfluorinated acylium cation was obtained from the first time and was identified by ^{13}C and ^{19}F NMR methods.

LITERATURE CITED

1. V. F. Snegirev, K. N. Makarov, and I. L. Knunyants, J. Fluor. Chem., 17, 441 (1980).
2. I. L. Knunyants, Yo. G. Abduganiev, E. M. Roklin, P. O. Okulevich, and N. I. Karpushina, Tetrahedron, 29, 595 (1973).
3. D. G. Anderson, D. C. England, and A. S. Millian, U. S. Patent No. 4357282 (1982); Chem. Abstr., 98, 34222n (1983).
4. V. F. Snegirev, L. L. Gervits, and K. N. Makarov, Izv. Akad. Nauk SSSR, Ser. Khim., 2765 (1983).
5. J. W. Emsley, Z. Phillips, and E. Wrey, Fluorine Constants, Pergamon Press, New York (1977), p. 766.
6. G. C. Levy and G. L. Nelson, Carbon-13 Nuclear Magnetic Resonance for Organic Chemists, Wiley (1972).
7. R. Bates, S. Brenner, C. Cole, E. Davidson, G. Forsythe, D. McCombs, and A. J. Roth, J. Am. Chem. Soc., 95, 926 (1973).
8. J. B. Stothers, Carbon-13 NMR Spectroscopy, Academic Press (1972), p. 38.
9. E. M. Rokhlin, E. G. Abduganiev, and Y. Utebaev, Usp. Khim., 45, 1174 (1976).
10. G. Olah and A. M. White, J. Am. Chem. Soc., 91, 5801 (1969).
11. I. L. Knunyants, L. S. German, and B. L. Dyatkin, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, 1353 (1956).
12. N. Ishikawa and A. Nagashima, Bull. Chem. Soc. Jpn., 49, 502 (1976).
13. S. G. Kocharyan, E. M. Rokhlin, and I. L. Knunyants, Izv. Akad. Nauk SSSR, Ser. Khim., 846 (1968).
14. S. Yanagida, Y. Nōji, and M. Okahara, Tetrahedron Lett., 2337 (1977).