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Abstract

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CHEMISTRY

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THE REACTION OF DIRECT FLUOROVINYLATION*

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The reaction of perfluorovinylation of various elements by the action on their halides of perfluorovinyl organometallic compounds has been investigated rather extensively (1). However, the latter are relatively difficult to obtain, and the method cannot serve preparative purposes. In addition, this method cannot be used to obtain N-fluorovinyl and other derivatives.

More attractive appears to be fluorovinylation by the interaction of fluorinated olefins with metallic derivatives of the elements to be vinylated. An example of such a reaction is perfluorovinylation at the carbon atom, carried out by the action of lithium (magnesium) organic compounds on perfluoro- or perfluorohaloolefins (2,3). Another, less known and little-studied case of a similar reaction is fluorovinylation at oxygen, occurring under the action of fluoroolefins on metal alcoholates (4,5).

These reactions, in contrast to the first, may be regarded as reactions of direct fluorovinylation. Assuming that direct fluorovinylation—the action of fluorinated olefins on metallic derivatives of compounds of various elements—may prove to be a general reaction, we investigated first of all the possibility of obtaining Si- and N-fluorovinyl derivatives. For N-fluorovinyl derivatives, a general preparatively useful method of preparation was developed (6), consisting in the reaction of alkyl- and aryl-substituted lithium amides (and also potassium amides)—derivatives of diethylamine, piperidine, morpholine, methylaniline, and carbazole—with such fluoroolefins as tetrafluoroethylene, chlorotrifluoroethylene, trifluoroethylene, vinylidene fluoride, and hexafluoropropene in media such as ether, tetrahydrofuran, and dioxane.

The starting aliphatic lithium amides were obtained by the action of secondary amines on butyllithium (from dibutylmercury and metallic lithium (7)) or lithium naphthalenide (8); by subsequent reaction with fluoroolefins, compounds I–III, VII, VIII were obtained (see Table 1). Methylanilide and diphenylamide of lithium were obtained by direct metallation of the amines in tetrahydrofuran at elevated temperature; by subsequent reaction with fluoroolefins, IV, V, IX were synthesized. N-Fluorovinyl derivatives of carbazole proved more convenient to obtain starting from potassium carbazole (VI, XIV–XVII).

In attempting to synthesize dialkyl-perfluorovinyl-amines from lithium amides obtained by the usual route ([9])—by the reaction of lithium with an alkyl bromide and then with a secondary amine; consequently, not from the lithium amides themselves, but from their complexes with lithium bromide ([10])—we, somewhat unexpectedly at first glance, isolated N-α-bromofluorovinyl derivatives (X–XIII).

The structures of compounds I-XVII were shown by elemental analysis, determination of the content of readily hydrolyzable halogen, and comparison of the products of their hydrolysis (XXIII-XXV) with fluoroacylamides obtained

Table 1

No.	Substance	Yield, %	b.p., °C/mm Hg	t	n_D^t	d_4^t	MR_D, calc.	MR_D, found	$\nu_{C=C}$, cm^{-1}
I	$(C_2H_5)_2NCF:CF_2$	60–80	87–89/755	23	1.3627	1.0217	33.48	33.31	1803
II	$CH_2(CH_2)_4NCF:CF_2$	70	42–44/35	23	1.4034	1.1306	35.90	35.69	1805
III	$CH_2CH_2O(CH_2)_4NCF:CF_2$	—	34–37/15 (m.p. 75°)	—	—	—	—	—	—
IV	$(CH_3)(C_6H_5)NCF:CF_2$	73	45–46/1	22	1.4775	1.2133	44.18	43.65	1795
V	$(C_6H_5)_2NCF:CF_2$	70	80.5–82/1.4	20	1.5387	1.2374	64.12	63.10	1795
VI	$C_{12}H_8NCF:CF_2$	34	108/1	19	1.5808	1.3406	61.92	61.55	—
VII	$(C_2H_5)_2NCF:CFCF_3$*	25	58.5–59/49	23	1.3680	1.1989	37.62	38.14	1717
VIII	$CH_2(CH_2)_4NCF:CFCF_3$	43	52–53/8	22	1.4081	1.2604	42.13	41.33	1730
IX	$(CH_3)(C_6H_5)NCF:CFCl$	71.5	84–85/3	20	1.5160	1.2589	49.07	48.79	1725
X	$(C_2H_5)_2NCBr:CF_2$	76	39/27	20	1.4345	1.3217	41.27	42.21	1780

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* Reported at the All-Union Conference on the Chemistry and Technology of Organofluorine Compounds (Novosibirsk, June 11–16, 1964).

No.	Substance	Yield, %	b.p., °C/mm Hg	t	n_D^t	d_4^t	MR_D, calc.	MR_D, found	$\nu_{C=C}$, cm^{-1}
XI	$(C_2H_5)_2NCBr:CFCl$	31	36/3	20	1.4715	1.3812	46.15	46.67	1680
XII	$CH_2(CH_2)_4NCBr:CF_2$	41	39–49.5/6	20	1.4700	1.4247	43.68	44.27	1760
XIII	$CH_2(CH_2)_4NCBr:CFCl$	–	69–75/5,5.5	23.5	1.4940	–	–	–	–
XIV	$C_{12}H_8NCF:CFH$	48.5	148–152/2 (m.p. 47°)	–	–	–	–	–	–
XV	$C_{12}H_8NCF:CH_2$	51	126–128/2	20	1.6307	1.1881	63.31	61.96	–
XVI	$C_{12}H_8NCF:CHCF_3$	–	110–117/1.5 (m.p. 43°)	–	–	–	–	–	–
XVII	$C_{12}H_8NCF:CFCl$	49	145–146/2	20	1.6150	1.3336	65.73	64.03	1735
XVIII	$CH_2(CH_2)_4NCF_2CF_2H$	–	70–71/54	20	1.3932	1.2289	36.35	35.97	–
XIX	$CH_2(CH_2)_4NCF_2CFClH$	–	56–57/7	20	1.4290	1.2890	41.13	40.35	–
XX	$(CH_3)(C_6H_5)NCF_2CF_2H$	41	53–54/0.7	21	1.4482	1.2837	44.63	43.23	–
XXI	$(C_2H_5)_2NCF_2CFHCF_3$	36	38–39/20	24	1.2160	1.2127	40.37	39.12	–
XXII	$CH_2(CH_2)_4NCF_2CFHCF_3$	–	35.5–36/4	22	1.3767	1.3064	41.39	41.32	–
XXIII	$CH_2(CH_2)_4NCOCF_2H$	–	73–75/2	20	1.4479	1.2158	36.11	35.93	–
XXIV	$C_{12}H_8NCOCFH_2$	–	(m.p. 139°)	–	–	–	–	–	–
XXV	$CH_2(CH_2)_4NCOCFClH$	–	(m.p. 34.8–35.6°)	–	–	–	–	–	–
XXVI	$(C_2H_5)_2NCOCF_2Br$	–	54–56/1.5	20	1.4433	1.4573	41.45	41.88	–

No.	Substance	Yield, %	b.p., °C/mm Hg	t	n_D^t	d_4^t	MR_D, calc.	MR_D, found	$\nu_{C=C}$, cm^{-1}
XXVII	$(CH_3)(C_6H_5)NCFBrCF_2Br$	–	90–91/1	20	1.5340	1.6980	62.75	63.46	–
XXVIII	$(CH_3)(C_6H_5)NCOCF_2Br$	–	(m.p. 138°)	–	–	–	–	–	–
XXIX	$(CH_3)(C_6H_5)NCOCFClBr$	–	(m.p. 36°)	–	–	–	–	–	–
XXX	$(C_6H_5)_3SiCF:CF_2$	18	(m.p. 73–74°)	–	–	–	–	–	–

* Literature data (^{16}); b.p. 55–59°/49, n_D^{20} 1.3715.

by hydrolysis of the corresponding saturated products of addition of free amines to fluoroolefins ($^{11-13}$); in part, such addition products were obtained by us for the first time (XVIII–XX and XXII). In individual cases, bromination products (XXVII) or products of their hydrolysis (XXVI, XXVIII, XXIX) were obtained. Finally, molecular weights and molecular refractions were determined, and infrared absorption spectra and NMR spectra were examined.

The formation of α-brominated fluorovinyl derivatives led to the discovery of an interesting and unusual reaction—the facile exchange of the α-vinyl halogen, including fluorine, for example, for other halogens and, in general, for nucleophilic groups; the hydrolysis reaction should also be included here. The following regularity was established: on passing from aliphatic fluorovinylamines through partially arylated ones to fully arylated ones and then to carbazole, the ability to exchange the α-halogen and, in particular, the ability to undergo hydrolysis gradually decreases, disappearing completely for the carbazole derivatives (the exception was α,β-difluorovinylcarbazole XIV, which under severe hydrolysis conditions gives monofluoroacetylcarbazole XXIV).

A possible explanation for this should be sought in the fact that the unshared pair of electrons of nitrogen in the aliphatic derivatives is displaced by the α-halogen atom, especially fluorine (p,σ-conjugation), to such an extent that a carbonium ion readily arises. As aromatic rings accumulate, the pair of p-electrons of nitrogen becomes involved in ever greater conjugation with the rings.

(π,p-conjugation); the degree of this participation in conjugation in the case when the nitrogen atom itself becomes a member of the aromatic ring (carbazole) is such that even the influence of fluorine becomes insufficient, and the α-halogen bond with carbon acquires the reactivity characteristic of an ordinary vinyl halide.

In the reaction of triphenylsilyllithium [14] with tetrafluoroethylene in tetrahydrofuran (80°, 28 h), along with the previously known [15] 1,2-bis-triphenylsilyl-difluoroethylene as the main reaction product (yield 54%), we succeeded in isolating trifluorovinyl-triphenylsilane XXX (yield 18%).

N. I. Gazieva, L. F. Osipova, V. V. Smolyanitskaya, O. P. Solovova, and E. N. Fogelzang took part in the experimental work.

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Note: Figure translations are in progress. See original paper for figures.