(6H, $CH_3$), 1.80 m (2H, CH), 2.43-2.71 m (4H, $CH_2$), 7.03-7.34 m (10H, Ph). $^{13}C$ NMR spectrum ($\delta$, ppm): 13.92 ($C^1$), 38.09 d ($C^2$), 41.34 t ($C^3$), 141.36 s ($C^4$), 128.02 d ($C^5$), 128.84 d ($C^6$), 125.51 d ($C^7$). $M^+$ 238.

1,4-Dideutero-threo-2,3-dibenzylbutane (IIId), bp 132-135°C (1 mm). IR spectrum ($\nu$, $cm^{-1}$): 3022, 2943, 2865, 2200, 1605, 1510, 1464, 762, 720. PMR spectrum ($\delta$, ppm): 0.76-0.92 m (4H, $CH_2D$), 1.73-1.86 m (2H, CH), 2.35-2.72 m (4H, $CH_2Ph$), 7.05-7.37 m (10H, Ph). $^{13}C$ NMR spectrum ($\delta$, ppm): 12.83 t ($C^1$), 38.06 d ($C^2$), 41.31 t ($C^3$), 141.48 s ($C^4$), 128.04 d ($C^5$), 128.90 d ($C^6$), 125.53 d ($C^7$). $M^+$ 240.

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# SYNTHESIS OF STERICALLY HINDERED AROMATIC ALDEHYDES


A. P. Yakubov, D. V. Tsyganov, L. I. Belen'kii, and M. M. Krayushkin



UDC 542.91:541.63:547.571



Formylation of mesitylene, durene, and m-xylene derivatives containing electron-donor and electron-acceptor substituents by dichloromethyl methyl ether was studied in the presence of $TiCl_4$. A series of functionally substituted sterically hindered benzaldehydes was prepared from the products of these reactions.


Previously, in studying the formylation of mesitylene by dichloromethyl methyl ether (DCME) in the presence of $AlCl_3$ and $TiCl_4$, we observed an unknown direction of this reaction, leading to the formation of dichloromethyl derivatives [1]. Here we identified among the reaction products not only (dichloromethyl)mesitylene (Ia), but also 2,4,6-trimethyl-3-(dichloromethyl)benzaldehyde (IIa), whose formation was due to the formylation of chloride (Ia) under the reaction conditions. In the present paper, this assumption was confirmed experimentally. In addition to attempting to elucidate the range of use of this reaction, we studied the reaction of DCME in the presence of $TiCl_4$ with substituted mesitylenes and also with durene, m-xylene, and their dichloromethyl-substituted compounds.

From among substituted mesitylenes, we studied the dichloride (Ia), acetylmesitylene (Ie), (chloromethyl)mesitylene (Ib), mesitol (Ic), (trichloromethyl)mesitylene (Id), bis-(chloromethyl)mesitylene (IIIa), and also bis(dichloromethyl)mesitylene (IIIb) and formylmesitylene. The conditions under which formylation of these mesitylene derivatives occurs depend on the electron-acceptor ability of the substituent. Thus, formylation of compounds (Ia-c) occurs at -20°C, whereas less active compounds (Id), (Ie), and (IIIa) are formylated at 40°C, and compound (IIIb), strongly deactivated by two dichloromethyl groups, does not react, even during long-term boiling in methylene chloride, used as a solvent. The products of formylation of compounds (Ia-e) and (IIIa) are the corresponding aldehydes (IIa-e) and (IVa) (Table 1) (see scheme on top of following page).

Because dichloromethyl-substituted compounds are facilely prepared by the reaction of $PCl_5$ with the appropriate aldehydes, the dichloromethyl group can be considered as a unique shielding group, making it possible to carry out the successive introduction of two aldehyde groups into aromatic compounds. Thus, the above-described conversion of dichloride


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Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 7, pp. 1609-1615, July, 1991. Original article submitted June 19, 1990.



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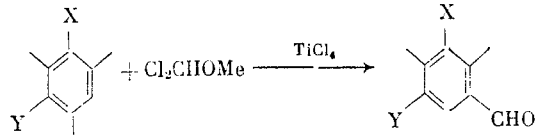
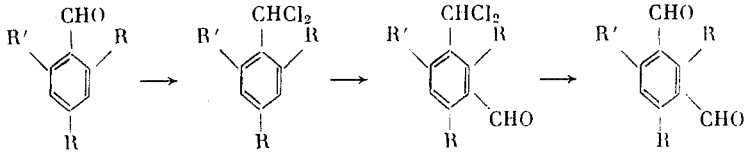



(Ia — e), (IIIa — b) (IIa — e), (IVa)

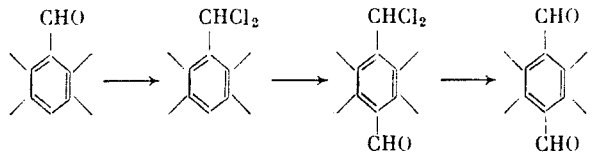
(I), (II): Y = H; X = $CHCl_2$ (a), $CH_2Cl$ (b), OH (c), $CCl_3$ (d), $CH_3CO$ (e); (III), (IV): Y = X = $CH_2Cl$ (a), $CHCl_2$ (b).

(Ia) to dichloromethyl aldehyde (IIa) makes it possible to go from 2,4,6-trimethylbenzaldehyde (Va) via dichloride (Ia) and 3-(dichloromethyl)-2,4,6-trimethylbenzaldehyde (IIa) to 2,4,6-trimethylisophthalaldehyde (VIa). Conversions of 2,4,6-triethylbenzaldehyde (Vb) to 2,4,6-triethylisophthalaldehyde (VIb), 2,4-dimethylbenzaldehyde (Vc) to 2,4-dimethylisophthalaldehyde (VIc), and of 2,3,5,6-tetramethylbenzaldehyde (VII) to 2,3,5,6-tetramethylterephthalaldehyde (VIII) are implemented similarly. In other words, using electrophilic formylation and reversible conversion of formyl to the dichloromethyl group, we can introduce two formyl groups into mesitylene, 1,3,5-triethylbenzene, durene, and m-xylene molecules:




(Va — c) (Ia), (IXb, c) (IIa), (Xb, c) (VIa — c)

R = R' = Me (a); R = R' = Et (b); R = Me, R' = H (c).




(VII) (XI) (XII) (VIII)

However, it was not possible to extend the discussed dialdehyde synthesis route to benzene, toluene, naphthalene, anthracene, and thiophene because of "cross-linking" of the dichloromethyl derivatives under the formylation conditions (in the presence of a Lewis acid). Thus, the possibility of introduction of a formyl group into dichloromethyl derivatives is governed by their containing one or even two shielding methyl groups in ortho positions to the $CHCl_2$ group, which is very similar to the available data concerning the stability of trichloromethylarenes in the presence of Lewis acids [2].

From the above-presented data on the reactions of substituted mesitylenes, the possibility of formylation of ketone (Ie) seemed least obvious. We should note in this regard that our attempt to replace the oxygen atom in compound (Ie) by a chlorine atom for subsequent introduction of the formyl group was unsuccessful because of dehydrochlorination giving 2,4,6-trimethyl-α-chlorostyrene [3]. On the other hand, we were unable to acetylate dichloride (Ia), probably because of the formation of an $ArCHCl^+AlCl_4^-$-type ion pair in which the aromatic ring was deactivated by electrophilic substitution. Direct formylation of ketone (Ie) occurred with high yield, and as previously [1] in other examples, we noted the formation of the product of its (dichloromethyl) substitution (I, X = $CHCl_2$, Y = Ac). Patent [4] describes without experimental details the formylation of acetylmesitylene under conditions close to those that we used. At the same time, our attempt to formylate formylmesitylene (Va) was unsuccessful because of the higher electron-acceptor activity of the formyl group in comparison with the acetyl group. Also of basic interest is the possibility of formylation of (trichloromethyl)mesitylene (Id) that we demonstrated. The presented data indicate that in the presence of Lewis acids DCME is a more active electrophilic agent than the $AcCl \cdot AlCl_3$ complex.

Chlorine-containing substituents in 2,4,6-trimethyl-3-(chloromethyl)benzaldehyde (IIb), 2,4,6-trimethyl-3-(trichloromethyl)benzaldehyde (IId), and 2,4,6-trimethyl-3,5-bis(chloromethyl)benzaldehyde (IV) are facilely modified under solvolysis conditions, which significantly extends the possibilities of preparation of substituted, sterically shielded aromatic aldehydes. In particular, the reaction of aldehyde (IIb) with ROH in the presence of KOH gives 2,4,6-trimethyl-3-(methoxymethyl)benzaldehyde (XIIIa) and 2,4,6-trimethyl-3-(β-methoxy-

TABLE 1. Synthesized Aromatic Aldehydes[a]

| Compound | Yield, % (hexane)[b] | Mp, °C | Found / Calculated, % C | Found / Calculated, % H | Empirical formula |
|---|---|---|---|---|---|
| (IIb) [1] | 84 | 153–156 | | | |
| (IIc) [14] | 80 | 105–107 | | | |
| (IId)[c] | 95 | | | | |
| (IIe) [4] | 95 | 70–73 | | | |
| (IVa) | 66 | 96–97 | 58.73 / 58.74 | 5.88[d] / 5.75 | $C_{12}H_{14}Cl_2O$ |
| (XIIIa) | 88 | 42–43 | 74.98 / 74.96 | 8.59 / 8.39 | $C_{12}H_{16}O_2$ |
| (XIIIb)[e] | 85 | | 71.45 / 71.15 | 8.60 / 8.53 | $C_{14}H_{20}O_3$ |
| (XIIIc) | 76 | 46–48 | 70.12 / 70.88 | 7.60 / 7.32 | $C_{13}H_{16}O_3$ |
| (XIIId) | 63 | 68–69 | 74.18 / 74.23 | 7.70 / 7.40 | $C_{11}H_{14}O_2$ |
| (XIV) | 95 | 62–65 | 71.47 / 71.15 | 8.51 / 8.57 | $C_{14}H_{22}O_3$ |
| (XVa) | 60 | 58–59 | 70.09 / 69.88 | 6.84 / 6.84 | $C_{12}H_{14}O_3$ |
| (XVb) | 92 | 54–55 | 71.17 / 70.82 | 7.36 / 7.39 | $C_{13}H_{16}O_3$ |
| (XVc) | 35 | 57–58 | 71.84 / 71.77 | 7.61 / 7.74 | $C_{14}H_{18}O_3$ |

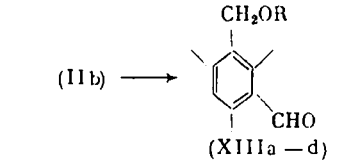
[a]The formylation conditions were 20°C and 0.5 h in the synthesis of compounds (IIb) and (IIc) and 38°C and 2.5, 1, and 2h in the synthesis of (IId), (IIe), and (IVa), respectively.
[b]Compounds (IVa) and (XVb) were recrystallized from benzene, and compounds (IVa) and (XVb) were recrystallized from a mixture of hexane and benzene. [sic].
[c]The oily substance, not purifiable, was characterized by PMR (see Table 2) and mass spectra: $M^+$ 262, 264, 266, 268.
[d]Cl 28.86/28.92.
[e]Bp 155-160°C (0.5 mm), $n_D^{20}$ = 1.5288.

TABLE 2. PMR Spectra of Benzylidene Dichlorides and Dialdehydes

| Compound | δ, ppm[a] 2-Me | 3-Me | 4-Me | 5-Me | 6-Me | —CHO | —CHCl₂ | H² | H⁵ | M+ |
|---|---|---|---|---|---|---|---|---|---|---|
| (IIa) | 2,80 br[b] | – | 2.50 br | – | 2,50 | 10,59 | 7,25 | – | 6,95 | 229, 231, 233 |
| (VIa) | 2,79 | – | 2,58 | – | 2,58 | 10,64 | – | – | 7,02 | |
| (VIb)[c] | 1,30 t | – | 1,23 t | – | 1,23 t | 10,57 | – | – | 7,04 | |
| (VIc) | – | – | 2,70 | – | 2,70 | 10,24 | – | 8,21 | 7,18 | |
| (VIII) | 2,35 | 2,35 | – | 2,35 | 2,35 | 10,62 | – | – | – | |
| (Xc) | – | – | 2,52 | – | 2,64 | 10,23 | 6,92 | 8,19 d | 7,11 d | 215, 217, 219 |
| (XI) | 2,48 | 2,34 br | – | 2,34 br | 2,48 | 10,62 | 7,35 | – | – | 244, 246, 248 |

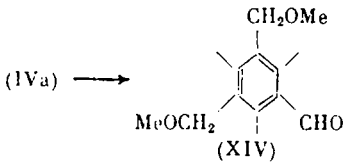
[a]If there is no additional information, the peaks are singlets: here br denotes broadened, t triplet, and d doublet.
[b]See [11].
[c]The spectrum also contains peaks of $C_2H_5$-group methylene protons: 3.18 quartet (2-$CH_2$) and 2.92 quartet (4- and 6-$CH_2$), $J_{Me-CH_2}$ = 7.6 Hz.

ethoxymethyl)benzaldehyde (XIIIb). The reaction of (IIb) with sodium acetate gives acetoxymethyl-substituted aldehyde (XIIIc), the hydrolysis of which gives 2,4,6-trimethyl-3-(hydroxymethyl)benzaldehyde (XIIId). The latter compound can also be obtained directly by hydrolysis of aldehyde (IIb) by an aqueous sodium carbonate solution. Treatment of bis(chloromethyl)benzaldehyde (IVa) with methanol in the presence of alkali gives 3,5-bis(methoxymethyl)mesitylene aldehyde (XIV), and the reaction of (trichloromethyl)-substituted aldehyde (IId) with alcohols in the presence of an acid gives esters of formylmesitylenecarboxylic acids (XVa-c).

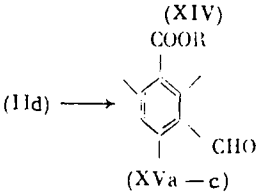



(XIIIa—d)

R = Me (a), $(CH_2)_2OMe$ (b), Ac (c), H (d).




(XIV)




(XVa—c)

R = Me (a), Et (b), *i*-Pr (c).

## EXPERIMENTAL

Chromatographic analyses were carried out on a Model 3700 chromatograph with a flame-ionization detector under linear temperature-programming conditions from 110 to 250°C (rate of 10 deg/min), with an SE-30 column, 5% on Chromosorb R, 2 × 1000 mm, nitrogen carrier gas, and velocity 20 ml/min, with n-heptadecane as the internal standard.

The PMR spectra were recorded on a Bruker WM-250 radiospectrometer (250 MHz) in $CDCl_3$, and the mass spectra were recorded on a Varian MAT CH-6 instrument with direct introduction of the sample into the ion source, ionizing voltage 70 eV, and emission current 100 μA. The IR spectra were recorded on a Perkin-Elmer 577 instrument with a compact containing KBr.

Starting Compounds. Chloromethylmesitylene (Ib) [5], (trichloromethyl)mesitylene (Id) [6], acetylmesitylene (Ie) [7], bis(chloromethyl)mesitylene (IIIa) [8], formylmesitylene (Va) [1], formyltriethylbenzene (Vb) [9], and formyldurene (VII) [9] were obtained by the cited methods [5-9]. Formyl-m-xylene (Vc), with bp 90-93°C (11 mm), was obtained in 95% yield by the method of [1]; see [10] for the literature data. Substituted benzylidene dichlorides were obtained by the reaction of $PCl_5$ with aldehydes (see [1]). Dichloride (Ia) was described in [1], and 2,4,6-triethylbenzylidene dichloride (IXb), with bp 140-143°C (5 mm) and $n_D^{20}$ 1.5380, was obtained in 96% yield. Found, %: C 63.47; H 7.60; Cl 28.87. $C_{13}H_{18}Cl_2$. Calculated, %: C 63.68; H 7.40; Cl 28.92. We obtained 2,4-dimethylbenzylidene dichloride (IXc), with bp 131-135°C (20 mm) and $n_D^{20}$ 1.5481, in 90% yield. Found, %: C 57.11; H 5.41; Cl 37.54. $C_9H_{10}Cl_2$. Calculated, %: C 57.16; H 5.33; Cl 37.5. We obtained 2,3,5,6-tetramethylbenzylidene dichloride (XI), with mp 105-106°C (from hexane), in 95% yield. Found, %: C 60.92; H 6.66; Cl 32.27. $C_{11}H_{14}Cl_2$. Calculated, %: C 60.84; H 6.50; Cl 32.66. Commercial samples of pure-grade mesitol (Ia), DCME, and $TiCl_4$ were used.

(Dichloromethyl)formylmesitylene (IIa). To a solution of 15.38 g (80.1 mmoles) of $TiCl_4$ in 65 ml of $CH_2Cl_2$ was added a mixture of 4.12 g (20.27 mmoles) of (dichloromethyl)-mesitylene (Ia) and 4.56 g (40.54 mmoles) of DCME in 60 ml of $CH_2Cl_2$. The obtained mixture was stirred for 0.5 h at 20°C and poured onto ice. The organic layer was separated, and the aqueous layer was extracted with $CHCl_3$ (2 × 30 ml). The organic extracts were combined and washed with HCl-acidified water (2 × 200 ml). After the solvent was driven off, we obtained (IIa) (95% purity, GLC). The PMR spectrum is given in Table 2. We obtained similarly compounds (IIb-e), (IVa), (Xc), and (XII) (see Tables 1-3). It was not possible to re-

TABLE 3. PMR Spectra of Aldehydes

| Compound | δ, ppm* | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | 2-Me | 4-Me | 6-Me | $H_{Ar}$ | CHO | $CH_2$ | OMe | Additional peaks |
| (IId) | 2,90 | 2.50 | 2.75 | 6,97 | 10,57 | – | — | |
| (IVa) | 2,61 | 2.61 | 2.61 | – | 10,60 | 4.70 | — | |
| (XIIIa) | 2,62 | 2.41 | 2.55 | 6,96 | 10,61 | 4,48 | 3,43 | |
| (XIIIb) | 2,63 | 2,43 | 2.53 | 6,95 | 10,60 | 4,60 | 3,38 | 3,66 ($-CH_2CH_2-$) |
| (XIIIc) | 2,60 | 2.41 | 2,55 | 6.96 | 10,59 | 5.21 | 2,07 | |
| (XIIId) | 2,68 | 2.46 | 2.55 | 6,96 | 10,60 | 4,78 | — | 1,60 (OH) |
| (XIV) | 2.53 | 2.48 | 2.53 | – | 10,61 | 4.51 | 3,44 | |
| (XVa) | 2.59 | 2,30 | 2.53 | 6,95 | 10,58 | – | 3,94 | |
| (XVb) | 2,58 | 2.31 | 2.54 | 6,97 | 10,58 | 4.42 q | — | 1,40 t (Me) |
| (XVc) | 2,58 | 2.30 | 2.52 | 6,95 | 10.58 | – | — | 5.31 m (CH), 1,38 d (Me) |

*If there is no additional information, the peaks are singlets; here q denotes quartet, t triplet, m multiplet, and d doublet.

cover compound (Xb) in a form acceptable for PMR and mass spectroscopy, and it was hydrolyzed without additional purification.

2,4,6-Trimethylisophthalaldehyde (VIa). (Dichloromethyl)formylmesitylene (IIa) was dissolved in 50 ml of HCl-acidified ethanol and boiled for 1 h.* The reaction material was poured into water (300 ml) and extracted with $CHCl_3$ (2 × 50 ml). After removal of the solvent, we obtained 3.3 g (93%) of dialdehyde (VIa) [1, 10] with mp 87-89°C (from hexane).

We obtained similarly the previously described 2,4-dimethylisophthalaldehyde (VIc) with mp 100-106°C (hexane–benzene, 5:1) in 68% yield [11] and 2,3,5,6-tetramethylterephthalaldehyde (VIII) with 179-182°C (in a sealed capillary) in 76% yield [12, 13] and also synthesized for the first time 2,4,6-triethylisophthalaldehyde (VIb) with bp 132-134°C (0.2 mm) in 69% yield, which was identified as the dioxime with mp 122-123.5°C. Found, %: N 10.96. $C_{14}H_{20}N_2O_2$. Calculated, %: N 11.28.

Methoxymethylformylmesitylene (XIIIa). To a solution of 21.7 g (110.4 mmoles) of chloromethylformylmesitylene (IIb) in 100 ml of MeOH was added portionwise 5.92 g (148 mmoles) of NaOH, and the whole was boiled with a reflux condenser for 3 h. After the MeOH was driven off, the reaction material was diluted with 200 ml of $CHCl_3$ and washed with water (2 × 200 ml). After removal of the solvent and distillation of the residue in vacuo (150-153°C, 10 mm), we obtained 18.64 g of compound (XIIIa). (β-Methoxyethoxymethyl)formylmesitylene (XIIIb) was similarly obtained (see Tables 1 and 3).

Acetoxymethylformylmesitylene (XIIIc). A mixture of 3.97 g (20.2 mmoles) of chloromethyl aldehyde (IIb) and 3.20 g (40.4 mmoles) of $CH_3COONa$ in 20 ml of glacial $CH_3COOH$ was boiled with stirring for 4 h. After the $CH_3COOH$ was driven off, the obtained residue was dissolved in 100 ml of $CHCl_3$ and washed with a 1% KOH solution (100 ml) and water (100 ml). The solvent was driven off, and 3.37 g of compound (XIIIc) with bp 156-159°C (0.5 mm) was obtained by distillation of the residue in vacuo (see Tables 1 and 3).

(Hydroxymethyl)formylmesitylene (XIIId). To a solution of 1.49 g (6.77 mmoles) of (XIIIc) in 50 ml of $C_2H_5OH$ was added a solution of 1.20 g (30 mmoles) of NaOH in 5 ml of water. The reaction material was stirred for 1 h at 20°C, diluted with 300 ml of water, and extracted with $CHCl_3$ (3 × 300 ml). The extract was washed with water (50 ml). After the solvent was driven off and the residue was recrystallized from hexane, we obtained 1.01 g of (XIIId) (see Tables 1 and 2).

Ethyl 2,4,6-Trimethyl-3-formylbenzoate (XVb). We dissolved 37.5 g of trichloromethylformylmesitylene (IId) in 350 ml of $C_2H_5OH$, added 20 ml of concentrated HCl, and boiled the whole with a reflux condenser for 4 h. After the solvent was driven off, the reaction material was diluted with 200 ml of $CHCl_3$ and washed with water (2 × 100 ml), after which the $CHCl_3$ was driven off. Distillation of the residue gave 28.75 g of the product (XVb).

*In the case of compounds (VIb) and (VIII) the solvent was n-butanol, and the boiling time was 15-25 h.

Compounds (XVa) and (XVc) were similarly obtained (see Tables 1-3).

(Dichloromethyl)acetylmesitylene (I, X = $CHCl_2$, Y = Ac). To a solution of 1.0 g (5.20 mmoles) of acetylformylmesitylene (IIe) in 50 ml of $CH_2Cl_2$ was added 2.1 g (10.4 mmoles) of $PCl_5$ at 20°C with stirring. The reaction material was stirred for 2 h and poured into water, and the organic layer was separated and washed with water (3 × 50 ml). After the solvent was driven off and the residue was recrystallized from hexane, we obtained 0.92 g (72%) of compound (I, X = $CHCl_2$, Y = Ac) with mp 110-113°C. Found, %: C 58.75; H 5.87; Cl 28.38. $C_{12}H_{14}Cl_2O$. Calculated, %: C 58.79; H 5.57; Cl 28.92. PMR spectrum (δ, ppm): 2.60 (2-$CH_3$), 2.21 (4-$CH_3$), 2.50 (6-$CH_3$), 7.21 (-$CHCl_2$), 6.92 ($H_{arom}$).

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# FLUORINATION OF ANIONIC σ-COMPLEXES BY CESIUM FLUOROXYSULFATE


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UDC 542.944+546.16:541.49−128.2:547.546'161



Anionic σ-complexes and related structures react with cesium fluoroxysulfate to give predominantly the C-fluoro derivatives: fluoronitrocyclohexadienes or substituted fluoronitrobenzenes. Oxidation or degradation of a complex to form substituted nitrobenzenes is also possible. The balance between all these processes is determined by the structure of the original complex.


The formation, stability, and structure of anionic σ-complexes (AC) have been the subject of numerous articles and reviews (see [1-3], for example). Less well studied are the reactions of AC with electrophiles, halogenation for example, and the related possibilities of using AC in synthesis [4, 5].

Unlike chlorination and bromination, fluorination of AC has not yet been studied. This is quite understandable in view of the lability of most AC and the corrosive nature of most electrophilic fluorinating agents.

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Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 7, pp. 1615-1619, July, 1991. Original article submitted August 29, 1990.




0568-5230/91/4007-1432$12.50