4. E. Tsuchida, K. Kitamura, and J. Shinohara, J. Polym. Sci., Polym. Chem. Ed., 10, 3639 (1972).
5. B. A. Énglin and R. Kh. Freidlina, Dokl. Akad. Nauk SSSR, 158, No. 4, 922 (1964).
6. N. A. Grigor'ev and A. L. Tumanskaya, Izv. Akad. Nauk SSSR, Ser. Khim., No. 4, 894 (1988).
7. N. A. Grigor'ev and R. Kh. Freidlina, Izv. Akad. Nauk SSSR, Ser. Khim., No. 3, 625 (1980).
8. N. S. Ikonnikov, N. I. Lamova, A. B. Terent'ev, and R. Kh. Freidlina, Izv. Akad. Nauk SSSR, Ser. Khim., No. 12, 2751 (1981).
9. P. Ehrlich and G. A. Mortimer, Advances Polym. Sci., 7, 386 (1970).

REACTIONS OF METHYL TRIFLUOROPYRUVATE WITH FIVE-MEMBERED ELECTRON-RICH HETEROCYCLES

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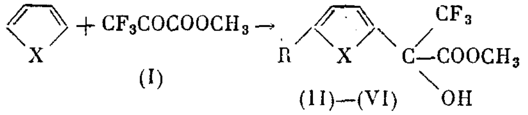
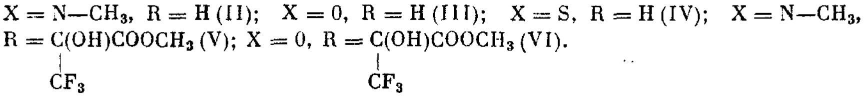
A study was carried out on the reactions of methyl trifluoropyruvate with N-methylpyrrole, furan, and thiophene. Conditions were found for the selective monoalkylation and dialkylation of these heterocycles. The sites of substitution of the heterocycle in the monoalkylation and dialkylation reactions were determined.

The reactions of hexafluoroacetone with N-methylpyrrole, pyrrole, furan, and thiophene lead to the formation of C^2-substituted and C^2,C^4-disubstituted products or their mixtures [1, 2]. Furthermore, in the case of N-methylpyrrole, the C^3-substituted product was also detected [1]. The pyrroles readily undergo these reactions at 20°C, while furan requires moderate heating and thiophene reacts only above 100°C. In the present communication, we examine the analogous reactions for methyl trifluoropyruvate (I).

Ketoester (I) reacts more vigorously with five-membered heterocycles than hexafluoroacetone and forms either C^2-substituted products (II)-(IV) or C^2,C^5-disubstituted products (V) and (VI). The C^3-substituted or C^2,C^4-disubstituted products were not detected





$X = N{-}CH_3,\ R = H\,(II);\ X = 0,\ R = H\,(III);\ X = S,\ R = H\,(IV);\ X = N{-}CH_3,\ R = \underset{\displaystyle CF_3}{C}(OH)COOCH_3\,(V);\ X = 0,\ R = \underset{\displaystyle CF_3}{C}(OH)COOCH_3\,(VI).$

Ketoester (I) reacts especially vigorously with N-methylpyrrole. Mixing the reagents at 20°C without solvent is accompanied by considerable heat evolution and tar formation. However, reaction products were obtained in high yield upon high dilution in a nonpolar solvent. Product (II) is formed selectively only in the case of a five-fold excess of N-methylpyrrole. C^2,C^5-disubstituted (V) was obtained under these conditions (20°C) selectively in the case of a 50% excess of ketoester (I). Mixing equivalent amounts of the reagents leads to a 6:1 mixture of (II) and (V).

The reaction of ketoester (I) with furan is as vigorous as with N-methylpyrrole. The C^2-substitution product, (III), is selectively formed at 20°C, while the formation of the C^2,C^5-disubstituted product, (VI), is observed above 50°C.

Thiophene reacts at a significant rate to form (IV) in CCl_4 at reflux; the yield of (IV) is 20% after 8 h. The alkylation at 20°C proceeds only in the presence of catalytic amounts of $SnCl_4$.

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TABLE 1. Properties of Products (II)-(VI)

Compound	Yield, %	Mp, °C	R_f	Found/Calculated, %			Chemical formula
				C	H	N	
(II)	75	35–37	0,52	45,07 45,57	4,24 4,22	6,26 5,91	$C_9H_{10}F_3NO_3$
(III)	85	65–68*	–	42,55 42,86	2,80 3,13	–	$C_8H_7F_3O_4$
(IV)	82	36–38	0,61	39,78 40,00	2,80 2,92	–	$C_8H_7F_3O_3S$
(V)	87†	78–80	0,14	39,45 39,69	3.25 3,31	3,60 3,56	$C_{12}H_{13}F_6NO_6$
(VI)	74	58–60	–	37,35 37,89	2.43 2,63	–	$C_{12}H_{10}F_6O_7$

*Bp at 1 mm Hg.

†Yield using method B.

TABLE 2. ^{13}C NMR Spectra for (II)-(VI) in Acetone-d_6, δ, ppm ($^1J_{C-F}$ = 286 Hz)

Compound	OCH_3	C^2	C^3 and C^4	C^5	CF_3	C=O
(II)*	54,21	124,26	107.37; 111,47	126,74	124.58 q	169,09
(III)	54,24	146.15	111,23; 111,57	144,95	123,91 q	167,61
(IV)	54,38	138,11	123,02; 128,25	128,70	124,03 q	168,45
(V)†	54,47	127,95	110,36	–	124,49 q	168,90
(VI)	54,34	149,35	112,20	–	123,71 q	167,15

*^{13}C NMR chemical shift in N-CH_3 is 35.84 ppm.

†^{13}C NMR chemical shift in N-CH_3 is 33.57 ppm.

Product (III) is a colorless liquid, while (II) and (IV)-(VI) are white crystalline solids.

The structures of (II)-(VI) were established by ^1H and ^{13}C NMR spectroscopy and elemental analysis (Tables 1, 2).

EXPERIMENTAL

The NMR spectra were taken on a Bruker WP-200-SV spectrometer at 200.13 MHz for the PMR spectra and 50.31 MHz for the ^{13}C NMR spectra. The chemical shifts were given relative to TMS as the internal standard. The R_f values were determined on Silufol UV-254 plates with 6:1 CCl_4-acetone as the eluent. The spots were detected using UV light.

2-(α-Carbomethoxy-α-hydroxytrifluoroethyl-N-methylpyrrole (II). A sample of 1.56 g (0.01 mole) ketoester (I) in 10 ml dry CCl_4 was added with stirring to 4.05 g (0.05 mole) N-methylpyrrole in 30 ml dry CCl_4 at 20°C. The mixture was stirred for an additional 1 h. The solvent and excess N-methylpyrrole were distilled off in vacuum and the residue was crystallized from hexane. PMR spectrum in $CDCl_3$ (δ, ppm, J, Hz): 6.51 d.d (1H, H^5, $J_{H^5-H^4}$ = 2.75, $J_{H^5-H^3}$ = 1.75), 6.32 m (1H, H^3), 6.01 d.d (1H, H^4, $J_{H^4-H^3}$ = 3.90, $J_{H^5-H^4}$ = 2.75), 4.23 s (1H, OH), 3.89 s (3H, OCH_3), 3.56 s (3H, N-CH_3).

2-(α-Carbomethoxy-α-hydroxytrifluoroethyl)furan (III). A sample of 7.5 g (0.05 mole) ketoester (I) in 20 ml CCl_4 was added with stirring to 3.40 g (0.05 mole) furan in 20 ml dry CCl_4. The mixture was stirred for 2 h. The volatile compounds were distilled off in vacuum and the solvent was distilled. PMR spectrum in acetone-d_6 (δ, ppm, J, Hz): 7.58 d.d (1H, H^5, $J_{H^5-H^3}$ = 0.75, $J_{H^5-H^5}$ = 1.85), 6.69 d (1H, H^3, $J_{H^3-H^4}$ = 3.50), 6.48 d.d (1H, H^4, $J_{H^4-H^3}$ = 3.50, $J_{H^4-H^3}$ = 1.85), 6.34 br.s (1H, OH), 3.90 s (3H, OCH_3).

2-(α-Carbomethoxy-α-hydroxytrifluoroethyl)thiophene (IV). A mixture of 7.50 g (0.05 mole) ketoester (I) and 1.3 g (0.005 mole) $SnCl_4$ in 20 ml CCl_4 was added with stirring to 4.20 g (0.05 mole) thiophene in 20 ml dry CCl_4 at 20°C. The mixture was stirred for 2 h and then poured into 100 ml 5% hydrochloric acid. The organic layer separated, washed with water until pH = 7, and dried over Na_2SO_4. The solvent was distilled off in vacuum and the residue was crystallized from pentane. PMR spectrum in acetone-d_6 (δ, ppm, J, Hz): 7.60 d (1H, H^5, $J_{H^5-H^4}$ = 5.15), 7.29 d (1H, H^3, $J_{H^3-H^4}$ = 3.75), 7.20 d.d (1H, H^4, $J_{H^4-H^3}$ = 3.75, $J_{H^4-H^5}$ = 5.15), 3.96 s (3H, OCH_3).

2,5-Di(α-carbomethoxy-α-hydroxytrifluoroethyl)-N-methylpyrrole (V). A. A sample of 4.68 g (0.03 mole) ketoester (I) in 20 ml CCl_4 was added with stirring to 0.81 g (0.01 mole) N-methylpyrrole in 20 ml dry CCl_4 at 20°C. The mixture was stirred for 2 h. The solvent was distilled off in vacuum and the residue was crystallized from pentane.

B. A sample of 1.56 g (0.01 mole) ketoester (I) in 10 ml CCl_4 was added with stirring to 2.37 g (0.01 mole) (II) in 10 ml dry CCl_4 at 20°C. The mixture was stirred for 1 h. The solvent was distilled off in vacuum and the residue was crystallized from pentane. PMR spectrum in $CDCl_3$ (δ, ppm): 6.31 s (2H, H^3 and H^4), 3.87 s (6H, $2OCH_3$), 3.44 s (3H, $N-CH_3$).

2,5-Di(α-carbomethoxy-α-hydroxytrifluoroethyl)furan (VI). A mixture of 2.24 g (0.01 mole) (III) and 1.56 g ketoester (I) was heated for 5 h at 80°C. The mass was cooled and the product was crystallized from pentane. PMR spectrum in acetone-d_6 (δ, ppm): 6.66 s (2H, H^3 and H^4), 3.83 s (6H, $2OCH_3$).

LITERATURE CITED

1. G. I. Nikishin, V. G. Glukhovtsev, Yu. V. Il'in, and A. V. Ignatenko, Izv. Akad. Nauk SSSR, Ser. Khim., No. 2, 447 (1982).
2. US Patent No. 3,197,480 (1962).

EPR STUDY OF TERTIARY CYCLIC PERFLUORINATED RADICALS: METHYLCYCLOPENTYL AND DECALYL RADICALS

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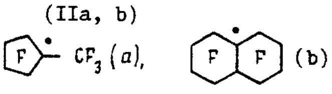
EPR spectroscopy was used to study new cyclic perfluorinated radicals, namely, methylcyclopentyl and decalyl radicals obtained by the photolysis of the corresponding bromides in the presence of dicarboranylmercury. The EPR spectrum of the perfluorocyclopentyl radical shows line broadening, which indicates an insufficiently high rate of inversion of the five-membered ring. The constants for coupling with the β-fluorine atoms in the decalyl radical indicate considerable comparison of the radical site. The motion of the substituents in the decalyl radical is hindered. The much lower dimerization rate constant in comparison with the corresponding acyclic radicals may be related to the stereochemical rigidity of the radical site.

EPR spectroscopy has been used in conjunction with flash photolysis to study the structure and dimerization kinetics of a series of fluorine-containing cumyl [1, 2] and perfluoroalkyl radicals [2, 3]. The steric shielding of the radical site and rate of rotational diffusion of the radicals have the greatest effect on the radical dimerization rate [2]. We investigated the structure and reactivity of cyclic tertiary perfluorinated radicals, in which the motion of the substituents at the radical site is limited on the EPR time scale.

The radicals were generated according to our previous procedure [4]*

$$\underset{\text{(Ia, b)}}{R_F{-}Br} \xrightarrow{HgR_2,\ h\nu} \underset{\text{(IIa, b)}}{R_F^{\bullet}}$$

$R = C_2B_{10}H_{11}$, R_F =



The EPR spectrum of radical (IIa) shown in Fig. 1a has the following coupling constants: $a_{F-\beta}$ (3F) = 17.2 Oe, $a_{F-\beta}$ (4F) = 33.6 Oe, and $a_{F-\gamma}$ (4F) = 2.0 Oe. These values correspond to structure (IIa). The coupling constants with the β-fluorine atoms in the ring are

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*Radicals were not detected upon the irradiation of (Ia) and (Ib) in the absence of HgR_2.

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