Hydrolysis of Dimer XI. A solution of 3 mg ($2.3 \cdot 10^{-3}$ mmole) of dimer XI in a mixture of dioxane and 2 N KOH in 80% ethanol was maintained at 20°C for 18 h, after which it was extracted with chloroform (three 30-ml portions). The extract was washed successively with 50 ml of 0.2 N hydrochloric acid and water (three 100-ml portions) and dried with sodium sulfate. The solvent was removed in vacuo, and the residue was separated by preparative TLC on silica gel L 5 × 40 in chloroform—hexane (5:1). The first fraction (V) was collected to give 1 mg (34%) of a product with R_f 0.39 (A). UV spectrum (benzene), λ_{max}: 419, 480, 515, 547, 593, and 552 nm. The second fraction (IX) was collected to give 1 mg (32%) of a product with R_f 0.63 (B). UV spectrum ($CHCl_3$), λ_{max}: 436, 526, 604, and 663 nm.

LITERATURE CITED

1. N. Minami and K. Ichimura, J. Electroanal. Chem., 165, 181 (1984).
2. J. P. Collman, A. O. Chong, C. B. Lameson, R. T. Oakley, E. Rose, E. R. Schitton, and J. A. Ibers, J. Am. Chem. Soc., 103, 516 (1981).
3. M. R. Wasielewski, W. A. Svec, and B. T. Cope, J. Am. Chem. Soc., 100, 1961 (1978).
4. J. A. Anton, J. Kwong, and P. A. Loach, J. Heterocycl. Chem., 13, 717 (1976).
5. R. G. Little, J. Heterocycl. Chem., 15, 203 (1978).
6. D. Jeyakumar and V. Krishnan, Nouv. J. Chim., 7, 697 (1984).
7. G. V. Ponomarev and G. B. Maravin, Khim. Geterotsikl. Soedin., No. 1, 59 (1982).
8. M. Momenteau, R. Loock, E. Bisagni, Rougee, Can. J. Chem., 57, 1804 (1979).
9. I. G. Rish, V. S. Pshezhetskii, K. A. Askarov, and G. V. Ponomarev, Khim. Geterotsikl. Soedin., No. 7, 936 (1985).
10. G. V. Ponomarev and V. G. Yashunskii, USSR Inventor's Certificate No. 458,551; Byull. Izobret., No. 4, 51 (1975).
11. A. M. Shul'ga and G. V. Ponomarev, in: Summaries of Papers Presented at the 3rd All-Union Conference on the Chemistry and Biochemistry of Porphyrins [in Russian], Samarkand (1982), p. 74.

REACTIONS OF INDOLES WITH POLYFLUOROCARBONYL COMPOUNDS

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753.07:541.69

Indoles with different substituents in the 1- and 2-positions of the indole ring react with hexafluoroacetone and methyl trifluoropyruvate to give the 3-alkylated derivatives. The compounds obtained show high fungicidal activity in plants.

Indole (Ia) is known to react [1, 2] with hexafluoroacetone (II) in ether or toluene to give 3-(α-hydroxyhexafluoroisopropyl)indole (IIIa). This reaction is the only example of the C-alkylation of indoles by polyfluorocarbonyl coompounds. We here present some further results of a study of the C-alkylation of indole and 2-methyl, 2-phenyl, and 1-methyl-2-phenylindoles (Ib-d) with hexafluoroacetone (II) and methyl trifluoropyruvate (IV).

The 2-substituted indoles (Ib, c) and the 1,2-disubstituted indole (Id) react with the ketone (II) as readily as indole (Ia) itself. For example, the indole (IIIb) is obtained in chloroform with spontaneous heating of a mixture of 2-methylindole (Ib) and the ketone (II) from —60 to 20°C. Under similar conditions, indoles (Ic, d) react with (II) to give the 3-(α-hydroxyhexafluoroisopropyl)indoles (IIIc, d). All the products were obtained in near-quantitative yields (Table 1).

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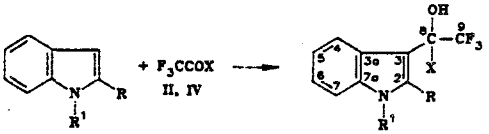
TABLE 1. Properties of Compounds Obtained

Compound	T_{mp}, °C	R_f	Found, %				Empirical formula	Calculated, %				Yield, %
			C	H	F	N		C	H	F	N	
IIIb	84	0,53	48,1	2,8	38,1	4,4	$C_{12}H_9F_6NO$	48,5	4,7	38,4	3,0	89
IIIc	144—146	0,71	57,1	3,4	31,5	4,1	$C_{17}H_{11}F_6NO$	56,8	3,9	31,8	3,1	91
IIId	160—162	0,83	57,6	3,8	30,2	4,0	$C_{18}H_{13}F_6NO$	57,9	3,8	30,6	3,5	88
Va	94—96	0,40	52,5	3,2	20,4	5,0	$C_{12}H_{10}F_3NO_2$	52,8	5,1	20,4	3,7	81
Vb	90—92	0,47	54,0	4,2	19,7	5,0	$C_{13}H_{12}F_3NO_3$	54,4	4,9	19,9	4,2	86
Vc	187—189	0,53	61,5	3,8	16,0	4,4	$C_{18}H_{14}F_3NO_3$	61,9	4,0	16,3	4,0	91
Vd	116—118	0,87	62,4	4,9	15,6	4,1	$C_{19}H_{16}F_3NO_3$	62,8	3,9	15,7	4,4	93

TABLE 2. NMR Spectra of Indoles (IIIb-d) and (Va-d)

Compound	^{19}F and ^{13}C NMR chemical shifts, ppm (acetone)									$^1J_{C-F}$, Hz
	^{19}F	^{13}C								
		2	3	3a	4, 5, 6	7	7a	8	9	
IIIb	−2,37	137,9	101,4	127,7	120,6, 121,3, 121,8	111,5	136,1	79,0	124,4	289,0
IIIc	−2,24	140,8	102,6	126,8	121,1, 122,4, 122,9	112,1	136,9	79,1	124,6	297,3
IIId	−2,30	142,0	102,9	126,3	121,1, 122,6, 122,8	110,6	137,7	79,0	124,4	289,3
Va	−1,44	137,6	109,5	125,6	120,6, 121,5, 122,8	112,5	126,2	78,1	125,1	287,1
Vb	−1,28	136,3	104,8	127,9	120,2, 120,3, 121,6	111,3	135,9	78,6	125,6	286,8
Vc	−1,67	138,8	106,7	128,2	120,6, 122,8, 123,1	111,8	136,6	78,7	130,1	287,0
Vd	−1,88	140,1	106,9	127,3	120,6, 122,7, 123,1	110,2	137,3	78,6	125,6	288,7

The ketoester (IV) reacts with indoles (Ia-d) similarly to (II), to give exclusively the 3-alkylated products. The corresponding 3-(α-hydroxy-α-methoxycarbonyltrifluoroethyl)-indoles (Va-d) were also obtained in high yields (Table 1).



Ia-d IIIa-d; Va-d

II, III X=CF_3; IV, V X=$COOCH_3$; I, III, V a R=R¹=H; b R=CH_3, R¹=H; c R=C_6H_5, R¹=H; d R=C_6H_5, R¹=CH_3

These results show that the presence of a bulky substituent in the 2-position of indole has little effect on the course of and optimum conditions for the C-alkylation of indoles by polyfluorocarbonyl compounds.

The position of the substituent in (IIIb-d) and (Va-d) was established by comparison of the ^{13}C chemical shifts (Table 2) with those for 3-(α-aminohexafluoroisopropyl)indole [3].

According to the patent literature, indoles containing alkyl and aryl substituents in the 2- and 3-positions possess a wide spectrum of fungicidal activity [4]. The activity of the indoles (IIIb-d) and (Va-d) was determined on artificially-infected wheat in the greenhouse. The test results showed that all the compounds examined possessed clearly apparent fungicidal activity against the causative agents of brown rust and powdery mildew of wheat. The most active compounds in these tests were (IIIb) and (Va, b) (70-90% inhibition), but they were, however, less active than the commercial fungicide Benlate.

EXPERIMENTAL

^{13}C NMR and ^{19}F NMR spectra were obtained on a Bruker WP-200 spectrometer (200.13 and 188.31 MHz), internal standard TMS (^{13}C), external standard CF_3COOH (^{19}F). The R_f values of the compounds are given for Silufol UV-254 plates in the system CCl_4–acetone (3:1), visualized in UV.

3-(α-Hydroxyhexafluoroisopropyl)indoles (IIIb-d) (Table 1). In a glass ampul was placed a solution of 50 mmole of the appropriate indole in 50 ml of dry chloroform, cooled to −60°C, hexafluoroacetone (9.1 g, 55 mmole) condensed in, sealed, and kept for 1 h at 20°C. The ampul was cooled to −60°C, opened, the solvent removed under reduced pressure, and the residue crystallized from CCl_4.

3-(α-Hydroxy-α-methoxycarbonyltrifluoroethyl)indoles (Va-d). To a solution of 50 mmole of the appropriate indole in 80 ml of dry chloroform was added dropwise at 0°C with stirring 8.1 g (52 mmole) of methyl trifluoropyruvate. The cooling was removed, and the mixture stirred for 1 h at 20°C, the solvent removed under reduced pressure, and the residue crystallized from CCl_4 (Table 1).

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. E. E. Gilbert, J. Heterocycl. Chem., 6, 483 (1969).
3. A. V. Fokin, N. D. Chkanikov, V. L. Vershinin, A. F. Kolomiets, and M. V. Galakhov, Izv. Akad. Nauk SSSR, Ser. Khim., No. 6, 1364 (1985).
4. Kuraray Co. Ltd., Jpn. Pat. No. 81135404; Chem. Abstr., 96, 81337 (1982).

THERMAL AND PHOTOSTABILITY OF 5',7'-DIALKOXY-5,6'-DINITRO-1,3,3-TRIMETHYLSPIRO(INDOLIN-2,2'-[2H]CHROMENES)

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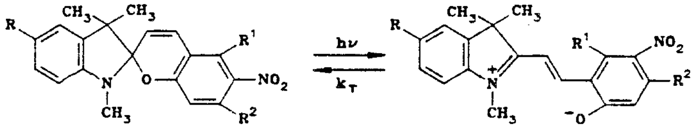
Some photochromic indoline spiropyrans have been synthesized and their thermal and photostability examined in films and in solution. Introduction of the NO_2 group into the indoline moiety of the molecule stabilizes the spiropyran form in solution and in films, but blocking the NO_2 group in the pyran moiety by adjacent alkoxy groups enhances the light stability of the compounds.

The photochromism of spiropyrans, consisting of reversible changes in color on exposure to light as a result of the conversion of the colorless spiropyran form (A) to the colored merocyanine form (B) is of interest in view of possible practical applications [1].



I-VA

I-VB

I $R=NO_2$, $R^1=R^2=OCH_3$; II $R=NO_2$, $R^1=R^2=OC_2H_5$; III $R=H$, $R^1=R^2=OCH_3$; IV $R=NO_2$, $R^1=R^2=H$; V $R=R^1=R^2=H$

In most of the known spiropyrans, the merocyanine forms absorb at 560-630 nm, only a few photomerocyanines absorbing at shorter wavelengths [2, 3]. The latter compounds include 5',7'-dialkoxy-6'-nitro-1,3,3-trimethylspiropyrans, which are deeply colored under normal conditions as a result of the existence of a thermodynamic equilibrium between forms A and B. Continuing earlier investigations [3, 4], we have examined the possibility of stabilizing form A in 5',7'-dialkoxy-6'nitro-1,3,3-trimethylspiropyrans by introducing the electron-acceptor nitro-group into the indoline moiety of the molecule, and also the light stability of such pyrans.

The compounds chosen for study were the spiropyrans (I) and (II). They were obtained in the usual way, by condensing the methylene bases with the appropriately substituted salicyladehydes. The properties of the spiropyrans (I) and (II) were compared with those of the known compounds (III-V). For solutions and films at 20°C there were obtained, as

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