br.d (H-C³, J = 6 Hz), 6.68 d (H-C², J = 6 Hz), 9.42 s (1H, CHO). The IIa + IIIa mixture which, according to the GLC data, contains a component with R_t 10.03 min, had an additional signal in its PMR spectrum at δ 6.63 ppm (d, J = 6 Hz) with an integral ascent corresponding to the amount of the component in the mixture. IR spectrum (CCl₄, ν , cm⁻¹): 2704, 1681, 1638 w, 1570, 1450, 1379. UV spectrum (EtOH): λ 316 (ε 21,500). Mass spectrum of the IIa + IIIa mixture: 286 (M⁺. 45.7), 271 (2.0), 268(1.0), 257(1.5), 253(1.0). 243(2.0), 217(6.5), 203(100), 201(4.3), 189(7.5), 175(4.3), 173(4.2), 161(6.4), 147(14.3), 135(27), 134(24), 133(21), 119(23), 105(72), 91(23), 83(69). 69(84), 55(64), 41(96). Mass spectrum of principal component IIa recorded by the GLC-MS method: 286(M⁺, 17), 268(5), 257(7), 253(5), 217(9), 203(100), 189(12), 147(14), 135(11), 134(30), 133(21). 119(24), 105(72), 91(24), 83(30), 69(60), 55(42), 41(66).

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C-ALKYLATION OF INDOLES BY 1,1-BIS(TRIFLUOROMETHYL)-2,2-DI-

CYANOETHYLENE AND 2-TRIFLUOROMETHYL-3, 3-DICYANOACRYLIC

ACID ESTERS

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Indole and its derivatives with various substituents in the 1 and 2 positions of the indole ring react with 1,1-bis(trifluoromethyl)-2,2-dicyanoethylene and 2-trifluoromethyl-3,3-dicyanoacrylic acid esters to give C^3 -alkylation products.

It is known that indoles react with hexafluoroacetone and methyl trifluoropyruvate, as well as with their imines, to give C^3 -substitution products [1-5].

In the present paper we give the results of study of the reactions of indole, 2-methylindole, and 1-methyl-2-phenylindole with 1,1-bis(trifluoromethyl)-2,2-dicyanoethylene (Ia) and methyl (Ib) and ethyl (Ic) 2-trifluoromethyl-3,3-dicyanoacrylates.

The reaction of indole with alkene Ia and 2-trifluoromethyl-3,3-dicyanoacrylic acid esters Ib and Ic in absolute $CHCl_3$ at 20°C for 2 h gives the following C³-substitution products in virtually quantitative yields: 3-[1,1-bis(trifluoromethyl)-2,2-dicyanoethyl]-(IIa),

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TABLE 1. Properties of IIa-c, IIIa-c, and IVb, c

Compound	Yield, %	mp, °C	R _f (eluent)*	Found	i/Calcula	Empirical	
				С	н	N	formula
(Ila)	96	176—178	0,35 (A)	$\frac{50,46}{50,76}$	<u>2,11</u> 2.11	<u>12,79</u> 12.69	C14H7F6N3
(IIÞ)	94	123-125	0,52 (B)	55,89	$\frac{3,07}{3.12}$	<u>13.28</u> 13.08	$C_{15}H_{10}F_8N_8O_2$
(IIc)	98	104-105	0,64 (B)	57,00 57.31	3,87	$\frac{12,50}{12.54}$	$C_{16}H_{12}F_{3}N_{3}O_{2}$
(IIIa)	98	183–185	0,41 (A)	$\frac{52,40}{52,17}$	$\frac{2,46}{2,61}$	<u>12,11</u> 12,17	C15H9 F6N3
(IIIb)	72	105-107	0.73 (B)	57.52 57,31	<u>3,63</u> 3,58	<u>12,91</u> 12,54	$C_{16}H_{12}F_{3}N_{3}O_{2}$
(IIIc)	96	133–135	0,59 (B)	58,11 58,45	$\frac{4,07}{4.01}$	<u>12,28</u> 12,03	$C_{17}II_{14}F_3N_8O_2$
(IVb)	50	202-204	0,59(C)	$\frac{64,08}{64.23}$	$\frac{3,88}{3,89}$	<u>10,51</u> 10,22	C22H16F3N3O2
(IVc)	65	171-173	0,80 (C)	$\frac{64.49}{64.94}$	$\frac{4.36}{4.24}$	<u>10,01</u> 9.88	$C_{23}H_{18}F_{3}N_{3}O_{2}$

*Systems: benzene-acetone (10:1) (A), $CHCl_3$ -acetone (3:1) (B), and $CHCl_3$ -acetone (6:1) (C).

3-(1-methoxycarbonyl-1-trifluoromethyl-2,2-dicyanoethyl)- (IIb), and 3-(1-ethoxycarbonyl-1-trifluoromethyl-2,2-dicyanoethyl)indole (IIc), respectively. Under similar conditoins 3-[1,1-bis(trifluoromethyl)-2,2-dicyanoethyl]- (IIIa), 3-(1-methoxycarbonyl-1-trifluoromethyl-2,2-dicyanoethyl)- (IIIb), and 3-(1-ethoxycarbonyl-1-trifluoromethyl-2,2-dicyanoethyl)-2-methylindole (IIIc) (Table 1) are formed in high yields from 2-methylindole.



The presence of a phenyl substituent in the 2 position decreases the reaction rate substantially. Thus, the reaction of 1-methyl-2-phenylindole with 2-trifluoromethyl-3,3-dicyanoacrylic acid esters Ib and Ic is complete after 24 h and leads to 3-(1-methoxycarb-onyl-1-trifluoromethyl-2,2-dicyanoethyl)- (IVb) and 3-(1-ethoxycarbonyl-1-trifluoromethyl-2,2-dicyanoethyl)-1-methyl-2-phenylindole (IVc), respectively.

The positions of the substituents in IIa-c, IIIa-c, and IVb, c were determined by comparison of the ¹³C chemical shifts obtained (Table 2) with the spectra of 3-(α -aminohexafluoroisopropyl)indole [2].

EXPERIMENTAL

The ¹³C NMR spectra were recorded with a Bruker WP-200 SY spectrometer with an operating frequency of 50.31 MHz and tetramethylsilane (TMS) as the internal standard, while the ¹⁹F NMR spectra were recorded with a Perkin-Elmer R-32 spectrometer with an operating frequency of 84.6 MHz and CF₃COOH as the external standard. The R_f values of the compounds obtained are presented for Silufol UV-254 plates with development in UV light.

<u>3-(1-Trifluoromethyl-2,2-dicyanoethyl)indoles IIa-c, IIIa-c, and IVb, c.</u> A 5.05-mmole sample of alkene Ia or 2-trifluoromethyl-3,3-dicyanoacrylic acid ester Ib or Ic was added with stirring to a solution of 5 mmoles of the corresponding indole in 20 ml of absolute

TABLE 2. NMR Spectra of IIa-c, IIIa-c, and IVb, c^{x}

	र्म ₅₁		-13,10 -12,33	-13,56	$^{-12,86}_{-12,88}$	-12,88	-12,89	-12,89	
		CN	108,6	- 8,0	108,7	111,3	111,6	111,6	
	3:1	¹ J _C -F, Hz	122,3 (286,5) 121,8 (279,7)	121,8 (283,1)	122,5 (275,0) 121,9 (279,9)	121,6 (283,3)	121,5 (283,0)	121,5 (281,2)	
		సి	24,1 28,2	28,5	24,3 28,4	28,5	28,8	28,8	
		ů	57,2 58,8	58,2	57,0	58,2	58,8	57,7	
		C'a	127,1 127,3	134,7	134,1 134,6	134.7	136,1	136,1	
		C,	111,7 112,7	111,5	110,5	112,0	111,0	111,0	
6, .ppn		ů	121,9 122,4	121,5	120,9 121,4	121,5	122,6	122.6	
		C²,	120,0 120,5	120,2	119,8 120,2	120,2	121,1	121,2	
		ບໍ່	118.3 118,2	118,2	118,0 118,0	118,2	119,8	119,8	
		C.a	126,6 123,6	125,8	124,9 125,7	125,8	124,7	124,3.	
		ů	97,8 101,7	97,8	93.9 97,7	67,8	98,8	58.9	
		5	136,1 136,4	136,3	135,7 136,2	136.3	141,4	141,5	
	Com-	punod	(11a) (11b)	(IIc)	(1111a) (1111b)	(111c)	(IV b)	(IVc)	

*The spectra were recorded in d_6 -acetone (IVa, Va) and in d_6 -DMSO (the remaining compounds).

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 $CHCl_3$ cooled to -20 °C. The reaction mixture was allowed to stand at 20 °C for 2 h in the case of indole and 2-methylindole or for 24 h in the case of 1-methyl-2-phenylindole. The solvent was evaporated in vacuo, and the residue was crystallized from hexane. The physicochemical characteristics of II-IV are presented in Table 1.

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EFFECT OF AN EXTERNAL MAGNETIC FIELD ON PHOTOLYSIS OF

AQUEOUS SOLUTIONS OF CYCLOHEXANONE

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The effect of an external magnetic field on the ratio of the yields of the basic products of photolysis of aqueous solutions of cyclohexanone was investigated by high-resolution NMR spectroscopy. It was shown that the magnetic field does not significantly affect the yield of the products of the reaction with a 0.2 M concentration of the starting ketone, the yield of 5-hexenal decreases, and the yield of caproic acid and the rate of photolysis increase below 0.02 M. The observed effects are explained by association of cyclohexanone with involvement of the HFI mechanism from the theory of "radical pairs."

Photolysis of solutions of cyclohexanone have been investigated in some detail both by standard kinetic methods [1] and with the effect of chemical polarization of nuclei (CPN) [2]. It was found that α -rupture from the triplet electron state with subsequent recombination or disproportionation of the triplet biradical formed primarily takes place under the effect of light [3]. Disproportionation can take place simultaneously along two paths with formation of unsaturated aldehyde and ketone, which easily yields adducts with a solvent [4]. Based on a study of the field dependences of the CPN effects, it was shown in [5] that the aldehyde and adduct sometimes have different polarization signs and for this reason, using the terminology of the theory of radical pairs, the adduct can be considered as the product of emergence from the "cage."

The dependence of the yield of products of photolysis of aqueous solutions of cyclohexanone on the strength of the external magnetic field predicted by the results of studies of the effects of CPN and the appearance of a magnetic isotope effect (MIE) [6], was investigated.

EXPERIMENTAL

Photolysis of 0.2, 0.02, and 0.002 M solutions in D_2O was investigated. The reaction was conducted at 293 K in 5-mm quartz ampuls using the light from a DRSh-500 lamp passed through a heat filter. The irradiation time was 30 min for the 0.2 and 0.02 M solutions

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