SYNTHESIS OF CONJUGATED MONO- AND BIS- ω -DIMETHYLAMINO DERIVATIVES OF SUCCINIMIDES

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Conjugated ω -dimethylamino carbonyl compounds exhibit solvatochromic, thermochromic, and photochromic characteristics and also possess strong fluorescence and generation characteristics [1-4]. In the present work we synthesized conjugated mono- and bis- ω -dimethylamino derivatives of succinimides. The introduction of the succinimide fragment into the polymethine chain seemed of interest in connection with the fact that according to published data [5, 6] the bisalkylidene derivatives of succinimides are used as photochromic materials in holography. The synthesis of the above-mentioned compounds was realized by the condensation of the aminals of conjugated ω -dimethylaminoaldehydes (I) and (III) with succinimides (IV) and (V). When the initial components were briefly heated in a ratio of 2:1 without a solvent or catalyst, the conjugated bis(ω -dimethyl-amino) derivatives of the succinimides (VI-IX) were formed with good yields in the form of stable crystalline substances. The succinimide fragment evidently confers stability onto the polymethine chain containing the terminal Me₂N groups. The known conjugated diamines Me₂N(CH=CH)_nNMe₂, where n = 1, 2 [7], are labile substances. It was only possible to obtain the monodimethylamino derivative of succinimide in the case of (X) by the reaction of equimolar amounts of (I) and (IV) in benzene:



n = 1, R=Ph (VI); n = 2, R=Ph (VII); n = 1, R=H (VIII); n = 2, R=H (IX)

In contrast to (I) and (III), the monodimethylamino derivative (XI) is also only formed from the substituted aminal (II) and the succinimide (IV):



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Fig. 2. The molecular geometry of the bisdimethylaminopropenylidene derivatives of Nphenylsuccinimide (VI).

According to the ¹H and ¹³C NMR spectra (Tables 1 and 2) and the UV spectra (Table 3), compound (XI) only exists in the open-chain dienone form (XI) and does not undergo cyclization to 2-amino-2H-pyran, unlike the series of γ -substituted δ -dimethylaminodienones [1].

The UV spectra of the monodimethylamino derivatives (X) and (XI) (Fig. 1) contain one band, and this is typical of δ -dimethylaminodienones [1]. In the spectra of the bisdimethylamino derivatives (VI-IX) (Fig. 1) there are two strong bands; the narrow short-wave band must be assigned to the Me₂N(CH=CH)_nCH=C-C=O chromophore, where n = 1, 2, and the broad long-

wave band must be assigned to the polymethinediamine fragment $[Me_2N(CH=CH)_nCH=C-]_2$, where

n = 1, 2. The unsaturated diamines $Me_2N(CH=CH)_nNMe_2$ give broad absorption bands at 235 (n = 1) and 292.5 nm (n = 2) [7]. The stereochemistry of the bis(ω -dimethylamino) derivatives of succinimide was studied by x-ray crystallographic analysis (XCA) and ¹H and ¹³C NMR spectroscopy. The geometric parameters obtained by XCA and the conformation of (VI) subsequently made it possible to interpret the data from the ¹H and ¹³C NMR spectra of (VI) unambiguously.*

<u>X-Ray Crystallographic Analysis of (VI)</u>. The monoclinic dark-red crystals of (VI) were obtained by recrystallization from methanol: a = 9.402(1), b = 11.541(1), c = 17.822(2),

^{*}The configuration of (VI) is evidently the same in the solid phase and in solution, since the IR spectra of the crystalline sample and of its solution in chloroform hardly differ at all (Table 3).

PMR Spectra of Compounds (VI-XIV)	6, ppm, in CDCl ₃	$ \begin{array}{ c c c c c c c c c c c c c c c c c c c$	$ \begin{array}{c c c c c c c c c c c c c c c c c c c $	4.94 7.27 6.7 7.38 3.14 & 3.28 1.73 & 2.49 $J_{B,Y} = J_{Y,Y} = J_{Y,Y} = 12$ 7.9 7.22 6.46 6.5-6.74 2.87 1.73 & 2.27 $J_{B,Y} = J_{Y,Y} = 12$ 44 7.8 7.22 6.46 6.5-6.74 3.08 & 3.27 2.27 $J_{B,Y} = J_{Y,Y} = 12$ 45 6.46 6.5-6.74 5.36 7.71 3.08 & 3.27 2.27 $J_{B,Y} = 14; J_{Y,Y} = 12$ 46 6.55 6.5-6.8 2.91 & 2.92 7.14-7.44 $J_{B,Y} = 12, J_{Y,Y} = 12$ 7.13 7.48 7.60 6.5-6.8 2.91 & 2.85 7.25-7.45 79 6.5-6.73 6.97 6.97 6.97 6.97 2.83 & 2.88	nt of the downfield signals to H_{β} and H_{β} ; and of the upfield signals to H_{δ} and H_{δ} ! in XIII) was made on the basis of selective heteronuclear ¹³ C-{ ¹ H} double resonance; in a the signals of the C_{δ} and C_{δ} ' carbons, directly attached to the electronegative N atom, wfield most in the olefinic region [15].	etradeuteromethanol; o \underline{Me}_2 C 0.95 ppm. pm. (bs). H _E ' 5.31 ppm; H _ζ and H _ζ ' (in the region of 6.5-6.8 ppm; with irradiation at a frequency of is observed in the signals in the region of 6.5-6.8 ppm).
Spectra of		H ^a _{b'} H _y	6.94 5.51	7.9 7.9 6.88 5.37 7.13 7.48 6.39 6.5-6.79 6.39	of the dc [, XIII) wa ne signals ield most j (XIII) we (XIII) we	adeuteromei). ¹ 5.31 ppm; observed ir
. The PMR		в ^н В	7.07	7.36 7.14-7.44 6.94 7.17 6.5-6.79	Lifted downf: Make, (VI, XI: S spectra tl ifted downf: MMe, MMe, MMe, MII [14] 0	rum in tetr 3 1.82 ppm. 7.4 ppm (bs .30 ppm, H _E change is (
TABLE 1		Compound	(IV) (IV)	(XIII)b (XIII)b (XIII)b (XIIV)b (XII)d (XII)d (VIII) e (VIII) e (VIII) f	aThe a compount the 13C b b b 0 b 0 b 0 b 0 b 0 b 0 b 0 b 0 b	c_{Spectr} $d_{\delta} Me-C$ $e_{\delta} NH 7$ $e_{\delta} NH 7$ $f_{\delta H_E} 5$. 5.3 a

) _{E1} (1)	+1 H ⁻¹ .	1 Hz)	ı	I								, , ,
Com- pound	cα	cα,	с _в	c _β ,	Ċų	C _V	C	с _ð ,	0—0	NMe2	ųđ	CH2
(X)	108.97		138.12		94,18		152.4		174.09	40.73	133.3. 128.78.	33,07
			(152)		(153)		(164)	, <u> </u>	170.04	(139)	127.68. 126.72	(133 & 7.5)
(IV)	112.5a	111.8 a	131.8 b	137.5 b	95.2 b	99.1 b	152.9 ^a	151.7 ^a	169.6 169.0	40,8		$\begin{array}{c} 133.9. \ 128.5 \\ 126.9 \end{array}$
(IIX)	122.33		140.3		94.63		152.3		197.7	40.88		39,55, 26.58
												24.00 23.7
(IIIX)		119.04		155.58		102.93		164.38	198.35	45.88		39.64(126)
			-	(147 & 5)		(165)		(167)	197.52	(140)		38.18(128)
									,			19.68(129)
(XIV)c		117.3		154.9		102.6		164.5	197.9	46.0(138.7)		53.3
				(148. &4.6)		(164.6)		(167.4)	197.0	38.2(139.6)		51.7(126.7)
p(IX)	107.46		144.39		103.82		153.42		174.53	43.23	133.09: 128.79	34.54
	(t5.5)		(d 148.9)				(d 163.7)		171.12	(q 137.8)	127.74: 126.65	(t135.0 d8.3)
^a The at	signme	nt of t	the sign	nals to C_{α}	or Ca	and to	o C _S or	Co ^t is	arbitra	·y.	e here die e here	

TABLE 2. The ¹³C NMR Spectra of Compounds (VI, X, XII-XIV) in Deuterochloroform, 6, from TMS ± 0.03 ppm

^bThe assignment of the signals to C_{β} and $C_{\beta'}$ and $C_{\gamma'}$ and $C_{\gamma'}$ was made on the basis of selective heteronuclear ¹³C-{¹H} double resonance. ^cThe lines of the carbons of the CMe₂ δ 30.5 and δ 28.6 (q 125.8).

Succin	imides ()	(X-I/								المعاونين المحاصبين المحاصب والمحادث والمحادث والمحادث والمحادث والمحادث والمحادث والمحادث والمحادث والمحادث
Com-	Initial	Reaction temp., deg	Yield,	Mol. mass			Found/c	alculate	á, 7	λ
pound	reagents (ratio)	C (time, h),solvent	R	(mass spec- trum/	μ ρ . , .	formula	U	Н	N	That is the second s
* (X)	(I) $\underset{(1:1)}{\&}$ (IV)	20 (1) benzene	40	244	465167 (MeOH)	$C_{14}H_{16}N_2O_2$	68.70 68.8	6.82 6.60	<u>11.62</u> <u>11.47</u>	375
(VI) *	$(I) \underbrace{\pounds}_{(2:1)} (IV)$	7080 (0.3)	85	337	218–219 (EtOH)	C20H23N3O2	71.00	6.78 6.87	12.45 12.45	343 (50700) 470 (30500) 485 (29000) plateau 430 (20300)
(III)	$(III) \underbrace{ \& \\ (2:1) \\ (2:1) }$	95-100 (0.3)	77	389	175–176 (CH ₃ CN)	$\mathrm{C}_{24}\mathrm{H}_{27}\mathrm{N}_{3}\mathrm{O}_{2}$	74.17	7.03 6.99	11.13 10.79	412 (78997) 555 (45483) 588 (39700)
(XI) †	$ \begin{pmatrix} \text{(II)} & \xi_{\text{t}} & \text{(IV)} \\ (1:1) & (1:1) \end{pmatrix} $	60-65 (0.5)	64	258	$\frac{189 - 190}{(CHCl_3 + MeOH)}$	$C_{15}H_{18}N_2O_2$	$\frac{70.30}{69.74}$	6.93 7.02	10.41	385 (42000)
(1111)	(I) $\& (V) \\ (2:1)$	80-75 (1.5)	61	261	240 (dec.)	$C_{14}H_{19}N_3O_2$	<u>64.62</u> <u>64.36</u>	7.29	$\frac{15.92}{16.09}$	335 (34400) 440 (plat. (20900)) 475 (27100)
(IX)	$\left \begin{array}{c} (\mathrm{III}) \boldsymbol{\xi}_{-} (\mathrm{V}) \\ (2:1) \end{array} \right $	95-100 (0.3)	32	313	225-227 (dec.)	$C_{18}H_{23}N_{3}O_{2}$				405 (62832) 550 (41126): 580 (38000)
4Th			(A)	vith VR	(U) 1740 m (CO)	1690 s.	1625 s.	1600 s		CO. Ph); (VI) (with

The Characteristics of the Conjugated Mono- and Bis- ω -dimethylamino Derivatives of TABLE 3.

%IR spectrum (v, cm⁻⁺): (X) (with KBr) 1/40 m (CU), 1050 s, 1022 s, 1000 s (cm⁻, CU, FN); (VI) (WI KBr) 1590 s, 1615 m, 1680 m, 1720 w; (in chloroform) 1590 s, 1615 m, 1680 m, 1720 w (Cm⁻C, CO, Ph). +\max, nm (ethanol), 387, c 43, 800; (hexane) 358 (split).

Atom x O^4 $0.7766(4)$ N^2 $0.7728(4)$ N^3 $1.0361(4)$ O^4 $0.8533(4)$ N^5 $1.4096(5)$	Y 0.0967 (3) 0.2850 (4) -0.2572 (4) 0.4501 (4)	z 0.6639 (2) 0.6305 (2)	Atom	X	Y	7
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	0.0967 (3) 0.2850 (4) -0.2572 (4) 0.4501 (4)	0.6639 (2) 0.6305 (2)				
O ⁴ 0.7766 (4) N ² 0.7728 (4) N ³ 1.0361 (4) O ⁴ 0.8533 (4) N ⁵ 1.4096 (5)	0.0967(3) 0.2850(4) -0.2572(4) 0.4501(4)	0.6639(2) 0.6305(2)				
N ² 0.7728(4) N ³ 1.0361(4) O ⁴ 0.8533(4) N ⁵ 1.4096(5)	$\begin{array}{c} 0.2850(4) \\ -0.2572(4) \\ 0.4501(4) \end{array}$	0.6305(2)	C ¹⁶	0.9221(6)	-0,2779(5)	0.7041(3)
N ³ 1.0361 (4) O ⁴ 0.8533 (4) N ⁵ 1.4096 (5)	-0.2572(4) 0.4501(4)		C ¹⁷	1.2952(5)	0.3071 (5)	0.4809(3)
O ⁴ 0.8533 (4) N ⁵ 1.4096 (5)	0.4501(4)	0.6581(3)	C ¹⁸	0.7015(7)	0,4278(5)	0.7176(3)
N ⁵ 1.4096 (5)		0.5794(2)	C ¹⁹	0.5250(6)	0.2933(6)	0.6550(4)
	0.2636(4)	0.4535(3)	C20	1.1292(7)	-0.3574(5)	0,6456(4)
C ⁶ 1.0536 (6)	-0.1536(5)	0.6271 (3)	C ²¹	1.5121 (7)	0,3437 (8)	0.4239(5)
C ⁷ 1.0819(5)	0.3070(5)	0.5377 (3)	C ²²	0.5956(11)	0.4791 (7)	0.7543(4)
C ⁸ 0.8648 (5)	0.3458(5)	0.5923(3)	C ²³	0.4194(8)	0.3425(9)	0.6925(4)
C ⁹ 0.9696 (5)	-0.579(4)	0.6321(3)	C^{24}	0.4566(11)	0.4359(9)	0.7400(5)
C ¹⁰ 1.1984(5)	0.2443(5)	0.5144(3)	C ²⁵	1,4448 (8)	0.1395(6)	0.4589(4)
C ¹¹ 0.8062 (5)	0.1680(5)	0,6339(3)	H ¹⁰	1.196	0.147	0.522
C ¹² C.9348(5)	0.1504(4)	0.5994(3)	H15	1.097	0.051	0.565
C ¹³ 0.6647 (5)	0.3383(5)	0.6680 (3)	H^7	1.068	0,405	0.524
C ¹⁴ 0.9719(5)	0.2641(4)	0.5722(3)	H17	1.281	0,403	0.483
C ¹⁵ 1,0069 (5)	0.0471(4)	0,5990 (3)	6H	0,879	-0.065	0.665

TABLE 4. The Atomic Coordinates

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 $\beta = 89.99^{\circ}$ (1). Space group P2₁/c, Z = 4. The unit cell parameters and the intensities of 1908 reflections with I \geq 36 were measured on a Hilger-Watts four-circle automatic diffractometer (λ CuK_{α}, graphite monochromator, $\theta/2\theta$ -scan, $\theta \leq 66^{\circ}$).

All the nonhydrogen atoms were localized by the direct method (using the Roentgen-75 program). The structure was refined by the method of least squares in full-matrix anisotropic approximation; the five H atoms were found from the difference F synthesis and were refined by two successive ρ syntheses. The final value of the divergence factor was R = 0.102 for 1764 F (hkl). The atomic coordinates are given in Table 4. A projection of the molecule onto the xy plane is given in Fig. 2. With the exception of the orientation of the phenyl ring the molecule is almost planar (plane I), and the departure of the atoms from this plane is not greater than 0.04 Å. The phenyl ring (plane II) is rotated through 53° in relation to plane I. The planar part of the molecule includes the succinimide ring (0¹, N², 0⁴, C⁸, C¹⁴, C¹¹, C¹²) and the two dimethylaminodiene chains "B" and "A": N³, C¹⁶, C²⁰, C⁶, C⁹, C¹⁵, C¹² and N⁵, C²¹, C²⁵, C¹⁷, C¹⁰, C⁷, C¹⁴.

The chains are characterized by the S-trans arrangement of the α,β - and γ,δ -double bonds and the trans orientation of the H atoms in relation to the γ,δ -double bond; they differ in the arrangement of the H_{\beta} and C_{\gamma} atoms in relation to the α,β -double bond.

Both chains are closed through the succinimide ring into a single conjugated system. In fact, the double bonds C=C (1.369-1.375 Å) and single bonds (1.416-1.427 Å) are significantly delocalized compared with those in trans-1,3-butadiene (1.344 and 1.467 Å) [8] and are close to those observed in the molecules of methyl trans-5-dimethylaminomethoxycarbonylpentadiene-carboxylate [9] and trans-3-acetyl-6-dimethylamino-3,5-hexadien-2-one [10]. The lengths of the C-C bonds in the succinimide ring (1.454; 1.461; 1.465 Å) are also somewhat shorter than the standard value of the $C_{\rm Sp}^2 - C_{\rm Sp}^2$ single bond (1.476 Å). The lengths of the C=O

(1.225, 1.227 Å) and C-N_{sp}² (1.373, 1.376 Å) agree well with the known values for unsubstituted succinimide [11] and its derivatives [12]. The lengths of the $C_{sp}^2 - N_{sp}^2$ bonds in the aminobutadiene fragments (1.338, 1.346 Å) are shorter than the standard value of 1.426 Å, and this is typical of conjugated ω -amino carbonyl compounds [13].

As seen from Fig. 2, with the planar arrangement of the chains and the succinimide ring the H atoms at C¹⁰ and C¹⁵ are sterically hindered. This hindrance is partly reduced during the deformation of the bond angles at C¹² (106, 108, 135°) and C¹⁴ (106, 129, 125°). Nevertheless the intramolecular H¹²...H¹⁴ distance remains greatly shortened (1.85 Å) compared to sums of the van der Waals radii (2.2 Å).

<u>NMR Spectroscopy (Tables 1 and 2).</u>* In the ¹H NMR spectrum of (VI) there are two sets of signals of equal integral intensity for the methine protons. In connection with the XCA data these sets of signals were assigned to the two dimethylaminopropenylidene chains A and B, which differ in the positions of H_{β} and C_{γ} in relation to the α,β -double bond. The set of signals at 5.51 t (H_{γ}), 6.76 d (H_{δ}), and 7.07 d (H_{β}), which corresponds to any AMX first order spectrum, belongs to one chain, as follows from the double resonance experiment; irradiation of H_{γ} at 5.5 ppm leads to coalescence of the components of the doublet at 6.76 ppm and of the doublet at 7.07 ppm. The spin-spin coupling constants ($J_{\beta\gamma} = J_{\gamma\delta} = 12.5 \text{ Hz}$) indicate the trans configuration for the H_{γ} and H_{δ} protons and the S-trans orientation of the α, β and γ , δ double bonds.

The set of signals at 6.94 (H_{β}) , 6.78 dd $(H_{\gamma'})$, and 6.69 d $(H_{\delta'})$ belong to the second chain. The spin-spin coupling constants $(J_{\beta'},\gamma' = 11 \text{ and } J_{\gamma'},\delta' = 12.5 \text{ Hz})$ also indicate the trans configuration for the $H_{\gamma'}$ and $H_{\delta'}$ protons and S-trans orientation for the α' , β' and γ',δ' double bonds.

The largest difference in the chemical shifts of the methine protons in the different chains (\sim 1.3 ppm) is observed for H_Y and H_Y'. The first set of signals must be assigned to chain A, where C_Y and C=O have the trans arrangement with respect to the α , β -double bond and H_Y is distant from the carbonyl group. Such an assignment is confirmed by comparison of the ¹H NMR spectra of the ketone (XII) and the diketone (XIII) (Table 1). In the diketone (XIII) H_Y is oriented toward the C=O bond, and as a result of descreening its signal is \sim 2 ppm downfield compared with H_Y in the ketone (XII).

^{*}The spectra of (XII) and (XIV), which were synthesized earlier [1, 14], and (XIII) are also given in Tables 1 and 2.

In the ¹³C NMR spectrum of (VI) there are also two sets of signals corresponding to chains A and B. The signals at 131.8 and 95.2 ppm were assigned to C_{β} and C_{γ} , while those at 137.5 ppm and 99.1 ppm were assigned to C_{β}' and C_{γ}' on the basis of selective proton decoupling.

The downfield shift of the $C_{\gamma'}$ signal compared with C_{γ} is consistent with the chemical shifts of C_{γ} and $C_{\gamma'}$ in (XII) and (XIII). The assignment of the downfield signals in the ¹H NMR spectra at 7.07 and 6.94 to H_{β} and $H_{\beta'}$ and also those at 6.76 and 6.69 to H_{δ} and $H_{\delta'}$ was confirmed by selective (VIII) decoupling. Comparison of the ¹H NMR spectra of (VII) and (VI) demonstrates the similar stereochemical structure of these compounds. In the ¹H NMR spectra of (VII) and (IX) there are also two sets of signals due to the different configurations of the chains, but the complexity of the spectra does not make it possible to identify all the signals.

It should be noted that the chemical shifts of H_{γ} and H_{γ}' in the ¹H NMR spectra and of C_{γ} and C_{γ}' in the ¹³C spectrum, obtained for the case of (VI), can be used to establish the configuration of the α,β -double bond in the other cyclic δ -aminodienones. Thus, in the mono-dimethylamino derivative (X) (Table 1) and in the cyclic mono- and bis- δ -dimethylamino ketones of types

 $\begin{array}{c} O \\ \parallel \alpha & \beta & \delta \\ \hline & \gamma & NMe_2 \text{ and } Me_2N \\ \hline & \chi & \chi \end{array} \begin{array}{c} O \\ \beta' & \beta' & \alpha' \parallel \alpha & \beta & \delta \\ \hline & \gamma & NMe_2, \\ \hline & \chi & \chi \end{array}$

which were synthesized earlier, the C_{γ} (C_{γ}') atoms have the trans orientation in relation to the CO, since the chemical shifts of H_{γ} (H_{γ}') lie in the region of 4.8-5.5 ppm, while the chemical shifts of C_{γ} (C_{γ}') lie in the region of 94-95.5 ppm.

EXPERIMENTAL

The UV spectra were measured on a Specord UV-VIS instrument. The ¹H NMR spectra were obtained on a Bruker WM-250 instrument (¹H 250, ¹³C 62.89 MHz) with TMS as internal standard.

<u>The Conjugated Mono- and Bis- ω -dimethylamino Derivatives of Succinimides (VI-XI).</u> The reaction conditions, constants, and yields are given in Table 1. After heating (the reaction was monitored by means of the electronic absorption spectra) the reaction mass was evaporated under vacuum, absolute ether or absolute methanol was added to the residue, and the crystalline precipitate was separated and purified by recrystallization.

The diketone (XII) was obtained from (I) and dihydroresorcinol with a yield of 65% by analogy with (XIV) [1]; mp 228-230° C (from absolute methanol). UV spectrum (λ_{max} , ethanol): 280 nm (ϵ 10400) and 410 nm (ϵ 40000).

CONCLUSIONS

1. A series of conjugated mono- and bis- ω -dimethyl-amino derivatives of succinimides were obtained by the condensation of the aminals of conjugated ω -dimethylaminoaldehydes with succinimides.

2. The geometric parameters and conformations of the molecule of the bis- ω -dimethylaminopropenylidene derivative of N-phenylsuccinimide were determined by x-ray crystallographic analysis. It was shown that the dimethylaminopropenylidene chains differ in the configuration of the α,β -double bond.

3. The ¹H and ¹³C NMR spectra of the synthesized compounds were studied. It was shown that the chemical shifts of H_γ and C_γ can be used to determine the configuration of the α,β -double bond in the cyclic δ -aminodienones.

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REACTIONS OF POLYFLUOROCARBONYL COMPOUNDS WITH

POLYPHENOLS

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The general features of the reactions of phenols with hexafluoro-[1-7] and tetrafluoro-dichloroacetone [3] in the presence of Lewis acids and sulfonic acids are well known. We here consider the uncatalyzed reaction of hexafluoroacetone and MeOOCCOCF₃ with di- and trihydroxybenzenes.

It has been found that resorcinol, phloroglucinol, hydroxyhydroquinone, and pyrogallol react in ether, $MeNO_2$, and benzene in the absence of a catalyst at temperatures as low as 20°C with hexafluoroacetone and methyl trifluoropyruvate to give C-alkylation products (Ia, b), (II), (IIIa, b), and (IV). Only pyrocatechol and hydroquinone failed to react even at 100°C.



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