CONCLUSIONS

1. α-Piperidino- and α-morpholinocrotonaldehydes react with HCl, CF_3COOH, and CCl_3COOH to give enammonium ion salts exclusively.
2. Based on NMR data, at −20°C E forms of the enammonium salts are formed first and gradually isomerized to the corresponding Z forms.
3. The relative rates of hydrolysis of α-piperidino- and α-morpholinocrotonaldehydes, leading to the formation of ethylglyoxal and free amine, were also determined.

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SYNTHESIS AND STRUCTURE OF 2,6-DI(INDANYL)PHENOL

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The aim of this work was the development of a method of preparation of 2,6-di(indanyl)-phenyl (2,6-DIP) by alkylation of phenol with indene in the presence of polyphenoxyalumoxane (PPA) and investigation of the steric and electronic effects of indanyl substituents on the geometry of meso-2,6-di(indanyl)phenol (I).

Synthesis of (I) is brought about by arylcycloalkylation of phenol by indene in the presence of aluminum phenolate [1]. It possesses a number of drawbacks however, viz. solubility in alkylate, hydrolyzability, and impossibility of recovery. We have chosen as catalyst PFA [2] which is a heterogeneous analog of aluminum phenolate and can be prepared by treating tetraethylalumoxane (TEA) [3] or polyisobutylalumoxanes (PIBA) with phenol.

$$R_2Al[OAl(R)]_nOAlR_2 + (n+4)C_6H_5OH \rightarrow (C_6H_5O)_2Al[OAl(OC_6H_5)]_nOAl\cdot(OC_6H_5)_2 + (n+4)RH$$

The mechanism for alkylation of phenol by olefins in the presence of PFA is similar to that proposed for $(PhO)_3Al$ [4].

Di- and tri- indanylphenols (DIP and TIP) are formed by successive alkylation of monoindanylphenols (MIP).

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MIP → DIP → TIP

Under the conditions of the experiment the PPA catalyzed alkylation of phenol by indene gave principally 2,6-DIP with 2-IP, 4-IP, 2,4-DIP, 2,4,6-TIP, and indanylphenyl ether (IPE) as by products in 1-20% yields. The effect of the amount of PPA-10 and PPA-15 used was studied in the range 1.0-10.0% and at temperatures of 80-160°C (Figs. 1a, b). Increase in quantity of catalyst from 1.0-4.5% led to a sharp increase in the yield of 2,6-DIP (~80%). Further increase in concentration causes the yield of 2,6-DIP to fall with an increasing contribution from secondary processes of isomerization and dealkylation—alkylation. The kinetic curves show (Fig. 1c) that decrease in 2-IP is directly related to the increase in formation of 2,6-DIP in the reaction medium. Raising the temperature and the amount of catalyst causes a gradual increase in the yields of 4-IP, 2,4-DIP, and 2,4,6-TIP.

The trisubstituted phenol probably arises via alkylation of 2,4-DIP. Indirect evidence for this proposal arises from its low yield (~5%) under dialkylation conditions (if the synthesis of 2,4,6-TIP is carried out via 2,6-DIP under the conditions used for obtaining (I), the yield of the trisubstituted phenol can be 15-20% and greater).

When the alkylation is carried out with a molar ratio of phenol:indene of 1:3 at 140-150°C the yield of 2,4,6-TIP increases only to 25%. In addition an initial increase in the yield of 2,4-DIP to 36% occurred but it then decreased to 12% with increasing yield of 2,4,6-TIP.

Optimum conditions for synthesizing 2,6-DIP are: 135-140°C, PPA 4.5-5.0%, phenol:indene ratio = 1.0:2.1, and reaction time 120 min. The yield of 2,6-DIP is then 78%.

2,6-Di(indanyl)phenol has two chiral atoms and forms two diastereomers: a racemic pair and a meso form (I). Together with the chromatography laboratory (IPS, Academy of Sciences of the USSR) we have developed a method for the GLC separation of alkylates, containing high boiling diastereomers, which allows separation of 2,6-DIP into the meso form and racemic pair. Repeated recrystallization of 2,6-DIP from isopentane, isooctane, and toluene gave the meso form of 2,6-DIP and its crystalline structure was determined by x-ray analysis (Fig. 2). Hence, alkylation of phenol by indene in the presence of PPA yields 2,6-DIP as a 1:1 mixture of meso-2,6-DIP (I) and the racemic pair.

Molecule (I) has a nonsymmetrical conformation with a cisoid orientation of the $C^{7}-C^{15}$ indanyl group relative to the phenolic ring $C^{1}-C^{6}$ (A) and a transoid orientation for the $C^{16}-C^{24}$ indanyl group, the torsional angles being $C^1C^2C^7C^8$ = 45.9° and $C^1C^6C^{16}C^{17}$ = 132.8°. Steric hindrance between the ortho-substituents and the hydroxy group leads to a significant disturbance to the overall planarity of the molecule (the dihedral angles between the benzene rings being A/B = 77.6° and A/C = 71.6°) and to a notable difference in the corresponding exocyclic valency angles at the atoms of the framework substituents: C^2C^1O 120.8(3) and C^6C^1O 117.1(3), $C^1C^2C^7$ 122.9(3) and $C^3C^2C^7$ 119.4(3), $C^1C^6C^{16}$ 122.5 (3) and $C^5C^6C^{16}$ 119.9(3), $C^2C^7C^8$ 120.3(3) and $C^2C^7C^{15}$ 111.6(3)°. In solution it is also probably the case that rotation of the groups around the $C^{2}-C^{7}$ and $C^{6}-C^{16}$ bonds is strongly hindered, for the indicated reason, leading to the manifestation of the clearly nonsymmetrical conformation seen in the crystal. The bond lengths and valence angles in the individual groups have normal values in line with those found in previously investigated indanes [5-7]. The $C_{(sp^2)}-C_{(sp^3)}$ bonds in the five-membered rings (1.473-1.513 Å) are, as expected, somewhat shorter than the $C_{(sp^3)}-C_{(sp^3)}$ bonds (1.525-1.544 Å) but the endocyclic angles for atoms not contained in the benzene nuclei (101.7-106.1°) are significantly less than the remaining angles in these rings (110.0-112.1°). As for the overwhelming majority of structural investigations of indanyl derivatives (e.g., [6-9]) the five-membered ring has an envelope conformation, the $C^7C^8C^{13}C^{14}$ and $C^{16}C^{17}C^{22}C^{23}$ torsional angles being 0.4 and 0.9° respectively and the displacement of atoms C^{15} and C^{24} from the plane of the remaining ring atoms being 0.409(4) and 0.480(4) Å.

A small difference in the geometrical parameters for the two indanyl groups in (I) was also revealed. Atoms C^7, C^{14}, and C^{15} deviated from the median plane of benzene ring B by 0.058(4), 0.083(5), and −0.295(4) Å and C^{16}, C^{23}, and C^{24} from the plane of ring C by 0.033(3), 0.022(4), and −0.435(4) Å. The deviation of the key C^{16} atom of one of the indanyl groups from the plane of the central benzene ring A is virtually zero [0.001(4) Å] but it is very significant in the case of the corresponding C^7 atom of the other indane group (−0.239(4) Å).

A characteristic distortion of the valence angles is observed in the benzene ring A in good agreement with the known correlations between the geometrical parameters of aromatic

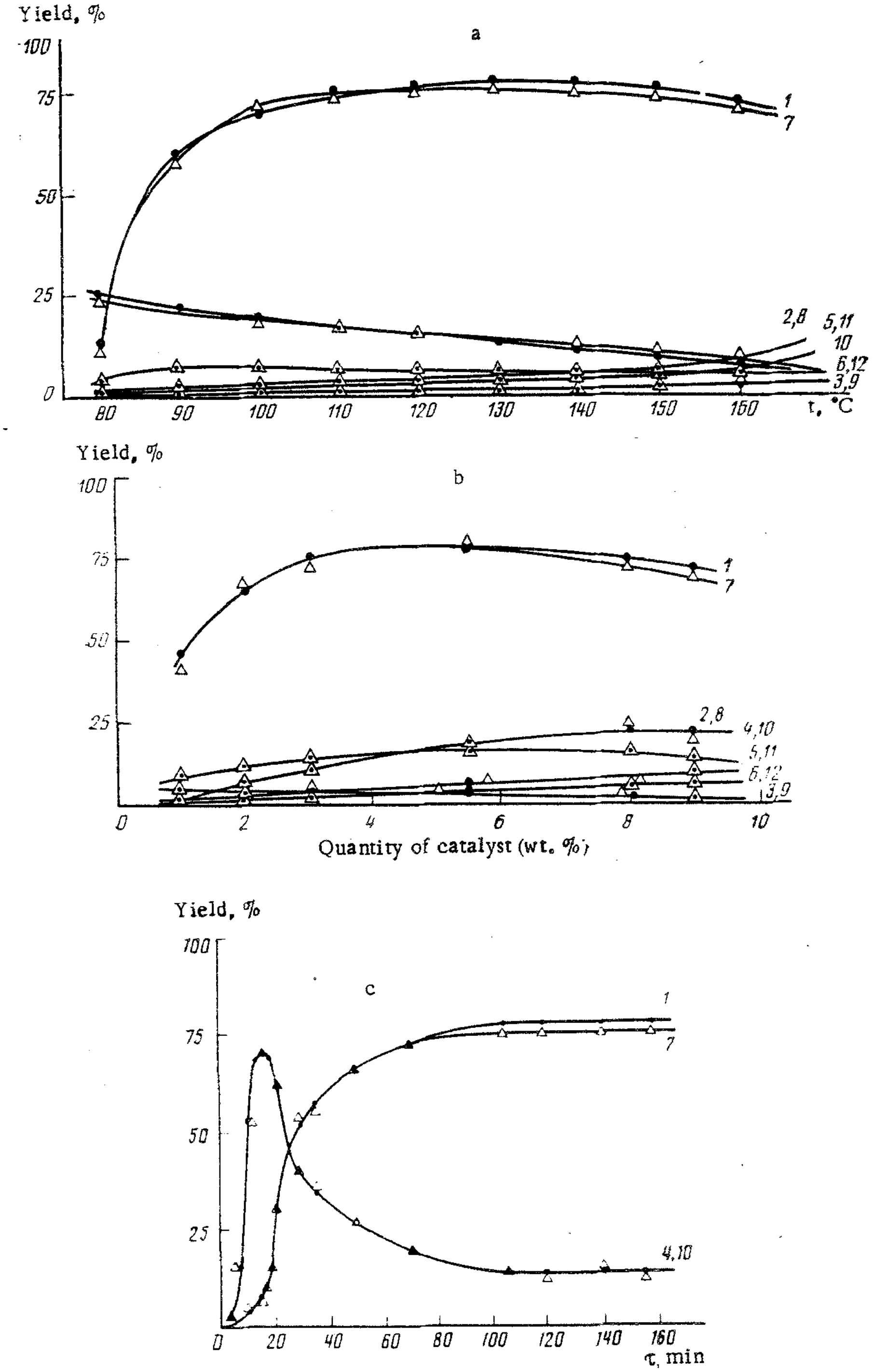

Fig. 1. Dependence of yields of indanylphenols with molar ratio of phenol:indene = 1.0:2.1 [2,6-DIP (1, 7), 2,4-DIP (2, 8), 2,4,6-TIP (3, 9), 2-IP (4, 10), 4-IP (5, 11) IPE (6, 12), PPA-10 (1-6), PPA-15 (7-12)] on: a) temperature (with PPA-10 = PPA-15 = 5.5%; b) catalyst concentration (at 135°C); c) reaction time (at 135°C with PPA-10 = PPA-15 = 5.5%).

nucleus and the substituent electronic effects [10-12]. The negative inductive effect of the hydroxy group and the positive effect of the indanyl groups act in this case in an identical direction and considerably increase the valence angle $C^2C^1C^6$ to 122.1(3)° and decrease $C^1C^2C^3$ to 117.4(3) and $C^1C^6C^5$ to 117.6(3)°.

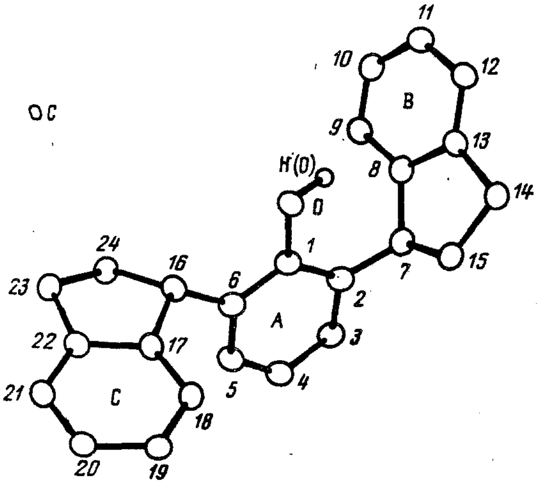

Fig. 2. Structure of the molecule meso-2,6-di(indanyl)phenol.

TABLE 1. Atomic Coordinates

Atom	X	Y	Z	Atom	X	Y	Z
O	0,5695(3)	−0,0737(2)	0,6505(1)	C^{13}	0,3836(5)	0,2148(3)	0,5997(2)
C^{1}	0,6613(4)	−0,1005(3)	0,5918(2)	C^{14}	0,5386(5)	0,2840(3)	0,5959(2)
C^{2}	0,6519(4)	−0,0269(3)	0,5330(2)	C^{15}	0.6647(5)	0,1901(4)	0,5714(2)
C^{3}	0,7425(5)	−0,0619(4)	0,4757(2)	C^{16}	0,7799(5)	−0,2782(3)	0,6586(2)
C^{4}	0,8439(5)	−0,1632(4)	0,4776(2)	C^{17}	0,9525(5)	−0,3074(3)	0,6809(2)
C^{5}	0,8542(5)	−0,2292(3)	0,5367(2)	C^{18}	1.0962(5)	−0,2371(3)	0,6803(2)
C^{6}	0,7656(4)	−0,2002(3)	0,5950(2)	C^{19}	1,2383(5)	−0,2818(4)	0,7053(2)
C^{7}	0,5642(5)	0,0936(3)	0,5327(2)	C^{20}	1,2434(6)	−0,3978(4)	0,7309(2)
C^{8}	0,3945(5)	0,1064(3)	0,5646(2)	C^{21}	1,1108(5)	−0,4685(3)	0,7328(2)
C^{9}	0,2552(5)	0,0318(3)	0,5593(2)	C^{22}	0,9591(5)	−0,4234(3)	0,7073(2)
C^{10}	0,1100(5)	0,0664(4)	0,5901(2)	C^{23}	0,7947(5)	−0,4812(3)	0,7040(2)
C^{11}	0,1028(5)	0,1722(4)	0,6263(2)	C^{24}	0.7029(5)	−0,4041(4)	0.6517(2)
C^{12}	0,2326(6)	0,2461(3)	0,6313(2)	H^{O}	0,493(3)	−0,017(3)	0,638(1)

Despite the presence of an active H atom in the molecule a hydrogen bond is not formed in crystalline (I). The shortest molecular distances $C^{11}...C^{22}$ $(1 - x, 1/2 + y, 1^1/_2 - z)$ 3.448(5), and $C^{11}...C^{21}$ $(1 - x, ^1/_2 + y, 1^1/_2 - z)$ 3.601(5) Å respectively correspond to normal Van der Wall interactions. In CCl_4 solution the hydroxy group of (I) forms an $O-H...\pi$ type intramolecular hydrogen bond with the benzene rign of the indanyl substituent in a cisoid orientation (IR band at $\nu = 3540$ cm^{-1}).

EXPERIMENTAL

Alkylation of Phenol by Indene. Phenol was freshly distilled to mp 41.5°C, bp 178°C/743 mm Hg and contained ≤50 ppm moisture. Indene (coke industry, 94.5% purity) contained trimethylbenzene (0.1%), indane (0.9%), and naphthalene (4.5%), and boiled over a 1°C range. Phenol alkylation by indene was carried out in a glass, four-necked vessel using a 1.0:2.1 molar ratio of phenol:indene at different temperatures, quantities of catalyst, and reaction times.

Catalyst Preparation. Tetraethylalumoxane (TEA, 0.05 mole) in dry toluene (100 ml) was slowly added with stirring over 20 min to phenol (1.0 mole) which had been heated to 80°C in a pure nitrogen atmosphere. The product was further stirred for 60 min at a constant increase in temperature to 130°C. The ether, ethane and toluene evolved were collected in a trap. After cooling to room temperature and addition of dry n-octane (400 ml) the precipitated tetraphenoxyalumoxane (TPA) was filtered off, washed with dry isopentane until phenol was absent in the filtrate, and dried to give TPA (90%). Found, %: C 65.35; H 4.21; Al 11.80. $C_{24}H_{20}O_5Al_2$. Calculated, %: C 65.16; H 4.52; Al 12.22.

Syntheses of PPA-10 and PPA-15, based on PIBA-10 and PIBA-15, were similar and gave PPA-10 (86%). Found, %: C 55.01; H 3.95; Al 18.04. $C_{94}H_{70}O_{25}Al_{12}$.* Calculated, %: C 55.94; H 3.88; Al 17.98. PPA-15 (80%). Found, %: C 54.85; H 3.75; Al 18.06. $C_{114}H_{95}\cdot O_{35}Al_{17}$. Calculated, %: C 55.12; H 3.83; Al 19.04.

GLC analysis was carried out on a Tsvet-530 chromatograph using flame ionization detection and a 25 m × 0.22 mm OV-17 capillary column. The temperature was programmed from 100-305°C at an increase of 5°C/min. The ionization temperature was 330°C, the helium gas carrier velocity 30 ml/min, the flow of hydrogen 28 and of air 280-300 ml/min, the volume of the toluene solution of the sample was 0.05 microliter, the velocity of gas through the column 11 cm/sec, and the sensitivity $2\cdot10^{-10}$ A.

TLC analysis used Silufol UV-254 plates with UV visualization.

^1H and ^{13}C NMR spectra were recorded at 200.13 and 50.29 MHz respectively on a Bruker WP-200 SY instrument. IR specta were recorded on a Perkin Elmer 577 for KBr or as CCl_4 solutions in the range 400-3700 cm^{-1}.

2-Indanylphenol. Yield 16-20%. Found, %: C 85.53; H 6.80; OH 7.92. $C_{15}H_{14}O$. Calculated, %: C 85.71; OH 8.10. IR spectrum (ν, cm^{-1}): 750 (C_{ar}—H), 1220-1240 (C_{ar}—OH), 1350 (COH), 1430, 1470, 1500, 1600 (C_{ar}—C_{ar}), 1450 (CH_2), 3000, 3020, 3050 (C_{ar}—H), 3545, 3612 (C_{ar}—OH).

4-Indanylphenol. Yield 1-4%, mp 92°C. Found, %: C 85.00; H 7.01; OH 7.90. $C_{15}H_{14}O$. Calculated, %: C 85.71; H 6.67; OH 8.10. IR spectrum (ν, cm^{-1}): 820, 830 (C_{ar}—H), 3612 (C_{ar}—OH) (in KBr 3200-3100).

2,4-Di(indanyl)phenol. Yield 2-5%. Found, %: C 88.10; H 7.00; OH 5.50. $C_{24}H_{22}O$. Calculated, %: C 88.34; H 6.75; OH 5.22. IR spectrum (ν, cm^{-1}): 820, 830 (C_{ar}—H), 3540, 3612 (C_{ar}—OH) (in KBr 3300-3500).

Meso-2,6-di(indanyl)phenol (I). Yield 39-40%, mp 112.5-112.7°C. Found, %: C 88.70; H 6.70; OH 5.00. $C_{24}H_{22}O$. Calculated, %: C 88.34; H 6.75; OH 5.22. IR spectrum (ν, cm^{-1}): 750 (C_{ar}—H), 3540 (C_{ar}—OH) (in KBr 3480). PMR spectrum (CCl_4, δ, ppm, J, Hz): 4.44 (H, OH); 6.88 (2H, 3, 5); 6.75 (H, 4): 4.60 (H, 7); 3.11, 2.98 (2H, 14a, b); 2.60, 2.17 (2H, 15a, b); 7.05-7.33 (4H, 9, 10, 11, 12); $J_{3,4} = J_{4,5} = 7.3$; $J_{9-12} = 7.0-7.3$; $J_{14a,b} = 15.5$; $J_{14a,15a}$ $J_{14b,15a} = J_{14b,15b} = J_{15a,7} = J_{15b,7} = 8.7$; $J_{14a,15b} = 4.0$; $J_{15a,15b} = 12.5$. ^{13}C NMR spectrum (δ, ppm): 151.63 (C^1), 130.47 ($C^{2,6}$), 126.69 ($C^{3,5}$), 120.25 (C^4), 34.07 (C^{14}), 31.59 (C^{15}), 46.35 (C^7), 143.88 (C^{16}), 127.38 (C^9), 124.63 or 124.39 (C^{10}), 124.39 or 124.63 (C^{11}), 126.40 (C^{12}), 144.68 (C^{21}).

2,4,6-Tri(indanyl)phenol. Yield 5-7%. Found, %: C 89.36; H 7.00; OH 3.63. $C_{33}H_{30}O$. Calculated, %: C 89.59; H 6.79; OH 3.85. IR spectrum (ν, cm^{-1}): 865 (C_{ar}—H), 3550, 3612 (C_{ar}—OH).

X-ray Structural Analysis of (I). Monocrystalline (I) is obtained by successive recrystallization of 2,6-DIP from isopentane, isooctane, and toluene. Colorless, transparent crystals of rhombic (I) had a = 8.079(2), b = 11.138(2), c = 19.491(3) Å, V = 1754.0 $Å^3$, Z = 4, $d_{calc} = 1.242$ g/cm^3, and space group $P2_12_12_1$. Elementary cell parameters and intensities of 973 reflections with $F^2 \geq 5\sigma$ were measured on an Enraf—Nonius CAD4 four circle automatic diffractometer (20°C, λMoK_α, graphite monochromator, scanning rate ratio $\omega:\theta = 1.2:1$, $\theta \leq 24°$).

The structure was solved by a direct method (all nonhydrogen atoms were localized in E-synthesis) and refined by a full matrix least squares method initially isotropically and then in the anisotropic approximation. All H atoms were localized in difference synthesis. Because of the relatively small number of measured reflections (due to the weak reflecting ability of the crystal) the coordinates and temperature factors for the H atoms attached to carbons were not specified in the final refinement stage. Their contribution was introduced by calculation of F_{calc}. The H(O) atom was refined in the isotropic approximation. The final value of the residual factors was R = 0.035, $R_w = 0.048$. All calculations were carried out on a PDP 11/23 PLUS computer using the SDP-PLUS program [13]. The atomic coordinates are given in Table 1.

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*As appears in Russian original — Editor.

CONCLUSIONS

The synthesis and geometry of the sterically hindered meso-2,6-di(indanyl)phenol have been investigated.

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POLYSULFONYLETHENES.

4. REACTIONS OF E-1,2-DI(ORGANYLSULFONYL)DICHLOROETHENES WITH AMINES

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E-1,2-di(organylsulfonyl)dichloroethenes (I) have been previously described [1], however, their activity in nucleophilic vinyl substitution has not been studied. In this work reaction of (I) with primary and secondary aliphatic, alicyclic, and aromatic amines is discussed. It was established that together with aminals of disulfonylketenes (IIa-k), sulfonylchloroacetamides (Va-c) and in some cases disulfonylacetamides (IXa, b). N-monosubstituted 1,2-disulfonylchloroethenes (III), and disulfonylmethane (VIII) are also formed (see Scheme 1).

Reaction of (I) with primary aromatic amines results in products with geminal RSO_2 groups, i.e., N,N-aminals of disulfonylketones (II) in nearly quantitative yield. That is why at first this reaction appeared to be a rearrangement [2]. After more careful investigation of the reaction mixtures it turned out that also sulfonylchloroacetamides (Va-c) can always be isolated in small amounts. Moreover, upon reaction of an equimolar mixture of the two homologous sulfones (Ia) and (Ic) with aniline, together with the expected aminals of di(ethylsulfonyl)- and di(octylsulfonyl)ketenes (IIa) and (IIi) a third product, the aminal of ethyl(octyl)sulfonylketene (IIk), was also isolated in more than 30% yield (Scheme 2). The formation of a mixed aminal refutes the assumption of an intramolecular rearrangement and indicates this reaction to be an intermolecular process.

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