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TELOMERIZATION OF BUTADIENE AND ISOPRENE WITH SULFONES CONTAINING ACTIVE METHINE AND METHYLENE GROUPS, CATALYZED BY PALLADIUM COMPLEXES

G. A. Tolstikov, O. A. Rozentsvet,
R. V. Kunakova, and N. N. Novitskaya

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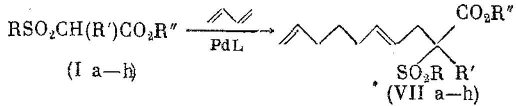
Synthesis involving sulfones have acquired great importance in the chemistry of alkenes in recent years. Special interest lies in sulfones as convenient starting materials for the preparation of polyenes including carotenoids, juvenoids, and other biologically significant compounds [1-5].

In a search for convenient pathways for the synthesis of compounds which hold potential interest as precursors for juvenoids and pheromones, we studied the catalytic telomerization of 1,3-dienes with sulfones. Bisphenylsulfonylmethane as well as esters and amides of arylsulfonylacetic acids react with butadiene to form mono- or bis-2,7-octadienyl derivatives [6-8]. This study was carried out for the reaction of butadiene and isoprene with β-sulfonoesters (I)-(IV), β-ketosulfones (V), and p-toluenesulfonylnitromethane (VI) (Table 1). A $PdCl_2-(Ph_3P)_2-PhONa$ system was used as the catalyst. This system has high activity relative to the telomerization of dienes with β-dicarbonyl compounds [6].

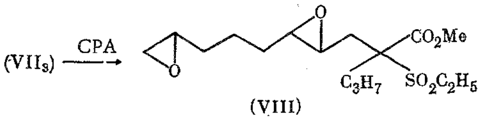
Both aryl- and alkylsulfonoesters readily react with butadiene to yield monoalkylation products (VII) with yields up to 85% (Table 2). Their structure as 2,7-octadienyl derivatives was shown by spectral methods and chemical conversions (Table 3)



(I a—h) (VII a—h)

$R = p\text{-}CH_3C_6H_4$, $R' = H$, $R'' = Me$ (a); $R = p\text{-}CH_3C_6H_4$, $R' = R'' = Me$ (b); $R = Ph$, $R' = Pr$, $R'' = Me$ (c); $R = Et$, $R' = H$, $R'' = Me$ (d); $R = n\text{-}Bu$, $R' = H$, $R'' = Et$ (e); $R =$ втор.Bu, $R' = H$, $R'' = Et$ (f); $R = Et$, $R' = R'' = Me$ (g); $R = Et$, $R' = Pr$, $R'' = Me$ (h).

Sulfonoester (VIIh) upon epoxidation by p-carbomethoxyperbenzoic acid (CPA) yields dioxide (VIII), while its oxidation with atmospheric oxygen by the action of a palladium-copper catalyst according to Clement and Selwitz [10] led to ketoester (IXh). Telomers (VIIa) and (VIIg) are oxidized under analogous conditions to ketoesters (IXa) and (IXg) in almost quantitative yields:



(VIII)

Institute of Chemistry, Bashkir Branch, Academy of Sciences of the USSR, Ufa. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 3, pp. 589-597, March, 1983. Original article submitted March 1, 1982.

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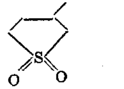
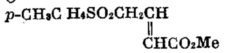
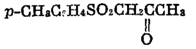
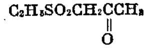
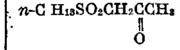
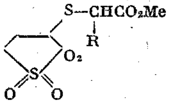
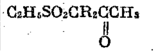
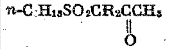
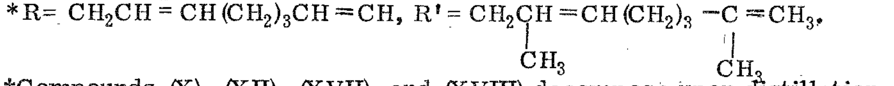
TABLE 1. Characteristics of the Starting Sulfones

Compound	Formula	Mp, °C	Bp, °C (p, mm Hg)	Elemental formula	Found, %			Calculated, %		
					C	H	S	C	H	S
(Ia)	$p\text{-}CH_3C\,H_4SO_2CH_2CO_2Me$	20		$C_{10}H_{12}O_4S$	52,7	5,4	14,2	52,6	5,3	14,1
(Ib)	$p\text{-}CH_3C\,H_4SO_2CH(CH_3)CO_2Me$	52–53		$C_{11}H_{14}O_4S$	54,8	5,9	13,2	54,5	5,8	13,2
(Ic)	$C\,H_5SO_2CH(CH)_3CO_2Me$		180(1)	$C_{12}H_{16}O_4S$	56,6	6,3	13,4	56,2	6,3	12,7
(Id)	$C_2H_5SO_2CH_2CO_2Me$	42–44		$C_5H_{10}O_4S$	36,2	6,1	18,7	36,1	6,1	19,3
(Ie)	$n\text{-}C_4H_9SO_2CH_2Et$		105(1)	$C_8H_{16}O_4S$	46,0	7,8	16,1	46,1	7,7	15,4
(If)	$CH_3CH(C_2H_5)SO_2CH_2CO_2Et$		100(1)	$C_8H_{16}O_4S$	45,7	7,7	16,1	46,1	7,7	15,4
(Ig)	$C_2H_5SO_2CH(CH_3)CO_2Me$	37–38		$C_6H_{12}O_4S$	38,8	6,5	17,9	39,9	6,7	17,8
(Ih)	$C_2H_5SO_2CH(C_3H_7)CO_2Me$		107(1)	$C_8H_{16}O_4S$	45,6	7,6	14,9	46,1	7,7	15,4
(II)	$SO_2(CH_2CO_2Me)_2$	110–112		$C_6H_{10}O_6S$	33,8	4,8	14,9	34,3	4,8	15,3
(III)		104–106		$C_7H_{12}O_6S_2$	32,8	4,5	25,9	32,8	4,7	25,1
(IV)	 $p\text{-}CH_3C\,H_4SO_2CH_2CH{=}CHCO_2Me$	49–51		$C_{12}H_{14}O_4S$	56,1	5,5	12,6	56,6	5,5	12,6
(VII)	 $p\text{-}CH_3C_6H_4SO_2CH_2\underset{\underset{O}{\Vert}}{C}CH_3$	46–47		$C_{10}H_{12}O_3S$	55,4	5,6	15,5	56,6	5,7	15,1
(Vk)	 $C_2H_5SO_2CH_2\underset{\underset{O}{\Vert}}{C}CH_3$		98(1)	$C_5H_{10}O_3S$	39,7	6,8	20,8	39,9	6,7	21,3
(Vl)	 $n\text{-}C\,H_{13}SO_2CH_2\underset{\underset{O}{\Vert}}{C}CH_3$		104(1)	$C_9H_{18}O_3S$	52,2	8,7	15,0	52,3	8,8	15,5
(VI)	$p\text{-}CH_3C_3H_4SO_2CH_2NO_2$ *	109–110		$C_8H_9O_4SN$	44,5	4,2	14,5	44,6	4,2	14,9

*Compound (VI) obtained by the method of Wade et al. [9].

TABLE 2. Properties of the Unsaturated Sulfones

Compound†	Formula*	Yield, %	Bp, C° (p, mm Hg)	n_D^{20}	Elemental formula	Found, %			Calculated, %		
						C	H	S	C	H	S
(VIIa)	p-$CH_3C H_4SO_2CHRCO_2Me$	80	135 (0,1)	1,5287	$C_{18}H_{24}O_4S$	64,2	7,1	9,5	64,3	7,1	9,5
(VIIb)	p-$CH_3C H_4SO_2C(CH_3)RCO_2Me$	95	183 (0,1)	1,5263	$C_{19}H_{26}O_4S$	65,1	7,4	9,0	65,1	7,5	9,1
(VIIc)	$C_6H_5SO_2C(C_3H_7)RCO_2Me$	85	195 (1)	1,5249	$C_{20}H_{28}O_4S$	66,7	8,4	8,6	65,0	7,7	8,8
(VIId)	$C_2H_5SO_2CHRCO_2Me$	35	120 (1)	1,4882	$C_{13}H_{22}O_4S$	56,7	8,0	11,5	56,9	8,1	11,7
(VIIe)	n-$C_4H_9SO_2CHRCO_2Et$	80	115 (0,1)	1,4887	$C_{16}H_{28}O_4S$	60,7	8,8	9,25	60,7	8,9	10,1
(VIIf)	$CH_3CH(C_2H_5)SO_2CHRCO_2Et$	80	127 (0,1)	1,4306	$C_{16}H_{28}O_4S$	59,4	8,5	10,1	60,7	8,9	10,1
(VIIg)	$C_2H_5SO_2C(CH_3)RCO_2Me$	87	127 (0,065)	1,4886	$C_{14}H_{24}O_4S$	58,6	8,5	10,7	58,3	8,4	11,1
(VIIh)	$C_2H_5SO_2C(C_3H_7)RCO_2Me$	82	132 (0,088)	1,4887	$C_{16}H_{28}O_4S$	60,5	8,8	9,9	60,7	8,9	10,1
(X)	$SO_2(CHRCO_2Me)_2$	55	—	1,4917	$C_{22}H_{34}O_6S$	61,9	8,2	8,4	61,9	8,0	7,5
(XIII)		55	—	1,4835	$C_{15}H_{24}O_6S_2$	59,4	7,7	10,1	59,9	8,0	10,6
(XV)	p-$CH_3C H_4SO_2CHRCCH_3$	91	170 (0,06)	1,5306	$C_{18}H_{24}O_3S$	67,3	7,4	10,4	67,5	7,5	10,0
(XVIk)	 $C_2H_5SO_2CR_2\underset{\underset{O}{\|}}{C}CH_3$	90	175 (0,05)	1,5046	$C_{21}H_{34}O_3S$	68,8	9,3	8,7	68,8	9,3	8,7
(XVIl)	 n-$C H_{13}SO_2CR_2\underset{\underset{O}{\|}}{C}CH_3$	85	210 (0,05)	1,4963	$C_{25}H_{42}O_3$	70,3	10,1	7,4	71,0	10,0	7,5
(XVII)	p-$CH_3C H_4SO_2CR_2NO_2$	75	—	—	$C_{23}H_{33}O_4SN$	66,4	7,5	7,8	66,4	8,1	7,4
(XVIII)	p-$CH_3C H_4SO_2CHRCH{=}CHCO_2Me$	50		1,5261	$C_{20}H_{26}O_4S$	66,3	7,3	9,1	66,3	7,2	8,8
(XIXa)	p-$CH_3C H_4SO_2CHRCO_2Me$	60	159 (0,1)	1,5229	$C_{20}H_{28}O_4S$	64,1	7,5	9,3	64,4	7,1	8,8
(XIXg)	$C_2H_5SO_2C(CH_3)R'CO_2Me$	70	142 (0,054)	1,4919	$C_{16}H_{28}O_4S$	60,6	8,5	10,4	60,7	8,9	10,1
(XIXh)	$C_2H_5SO_2C(C_3H_7)R'CO_2Me$	73	156 (0,088)	1,4898	$C_{18}H_{32}O_4S$	63,0	9,4	9,7	62,8	9,4	9,3



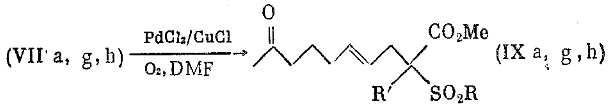
*$R = CH_2CH=CH(CH_2)_3CH=CH$, $R' = CH_2\underset{\underset{CH_3}{|}}{C}H=CH(CH_2)_3-\underset{\underset{CH_3}{|}}{C}=CH_3$.

†Compounds (X), (XII), (XVII), and (XVIII) decompose upon distillation.

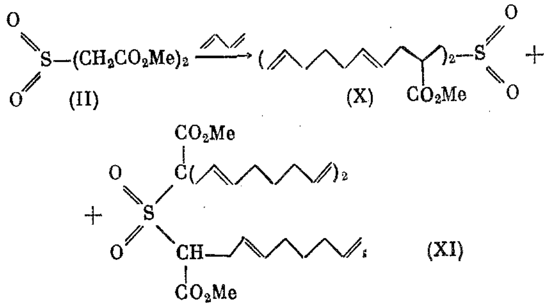
TABLE 3. Spectral Characteristics of Unsaturated Sulfones*

Compound	IR spectrum, ν, cm^{-1}						PMR spectrum (δ, ppm)									
	SO_2	CO_2CH_3; $C=O$	C_6H_5	$CH=CH_2$	$CH=CH$	CH_3, $CH_3C=$	CH_2	CH_2C	CH_3 C_5H_4	$SO_2-CH_2C=$	CH_2-SO_2	CH_3O $CH_3C=O$	CH SO_2	$CH_2=$ $CH=CH$	$C=CH$ $CH=$	C_6H_4
(Va)	1150, 1330	1250, 1745	730, 770, 1590, 3010	920, 1005, 3080	975, 1640 3030	–	1,37 m	1,83m	2,37 s	2,58 m		3,58 s	3,88 m	4,80 m	5,30 m	7,50 m
(VIIb)	1150, 1330	1240, 1740	730, 770, 1590, 3010	920, 1005, 3030	975, 1640, 3030	1,21 m	1,35 m	1,85m	2,37 s	2,53 m	–	3,57 s	3,85 m	4,83 m	5,30 m	7,50 m
(VIIc)	1155, 1320	1250, 1740	730, 770, 1580, 3010	925, 1005, 3080	980, 1645, 3030	0,95 m	1,45 m	1,85 m		2,70 m	–	3,51 s	–	4,76 m	5,40 m	7,50 m
(VIId)	1140, 1320	1230, 1740	–	920, 1005, 3080	975, 1640, 3080	–	1,4 m	1,86m		2,60 d	3,07 m	3,63 s	3,70 s	4,66 m	5,28 m	–
(VIIe)	1135, 1325	1240, 1735	–	920, 1005, 3080	975, 1640, 3030	0,83 m 1,18 m	1,28 m	1,83m		2,65 d	–	4,40 (CH_2CO)	3,75 m	4,80 m	5,20 m	–
(VIIf)	1140, 1330	1240, 1740	–	920, 1005, 3080	975, 1640, 3080	0,96 t 1,2 t	1,36 m	1,83m		2,65 d		4,41 s (CH_2CO)	3,75 m	4,80 m	5,20 m	–
(VIIg)	1145, 1310	1250, 1735	–	920, 1000, 3080	975, 1640, 3030	1,5 m	1,30 m	1,96 m		2,50 d	3,13 m	3,70 s	–	4,80 m	5,30 m	–
(VIIh)	1140, 1315	1230, 1735	–	920, 1005, 3080	975, 1640, 3030	0,88 m 1,25 t	1,36 m 1,52 m	1,83 m		2,63 d	3,00 q	3,70 s	–	4,81 m	5,40 m	–
(X)	1145, 1340	1250, 1745	–	925, 1005, 3080	975, 1645, 3010	–	1,4 m	1,91 m		2,75 m	–	3,75 s	4,15 m	4,76 m	5,46 m	–
(XIII)	1150, 1320	1245, 1740	–	925, 1000, 3080	990, 1660, 3020	–	1,35 m	1,96m		2,78 m	3,42 m	3,76 s	4,20 m	4,90 m	5,48 m	–
(XV)	1150, 1320	1720 ($C=O$)	710, 780, 1590, 3010	920, 1000, 3080	975, 1640, 3030	–	1,20 m	1,85m	2,40 s	–	–	2,26 s (CH_3-CO)	3,85 m	4,70 m	5,20 m	7,50 m
(XVIk)	1135, 1315	1710 ($C=O$)	–	920, 1000, 3080	975, 1645, 3030	1,83 t	1,51 m	1,98m	–	2,80 m		2,26 s ($CH_3C=O$)	–	4,88 m	5,40 m	–
(XVIl)	1145, 1325	1710 ($C=O$)	–	920, 1000, 3080	975, 1640, 3030	0,80 m	1,21 m	1,86m	–	2,70 m		2,26 s (CH_3-CO)	–	4,66 m	5,30 m	–
(XIXa)	1125, 1315	1250, 1740		890, 3080	840, 1640, 3030	1,25 (CH_3) 1,48 s 1,60 ($CH_3C=$)		1,76 m	2,36 s	2,58 m		3,55 s	3,20 m	4,58 m	5,08 m	7,50 m
(XIXg)	1145, 1315	1250, 1730	–	890, 3080	840, 1640, 3030	1,43 s (CH_3) 1,60 ($CH_5C=$)	1,28 m	1,88m	–	2,45 m	3,13 m	3,68 s	–	4,56 m	5,16 m	–
(XIXh)	1130, 1315	1240, 1735	–	890, 3080	840, 1640, 3030	0,86 m 1,38 s ($CH_3C=$) 1,55 s ($CH_3C=$)	1,23 m	1,75m	–	2,60 m	3,06 m	3,66 s	–	4,51 m	5,16 m	–

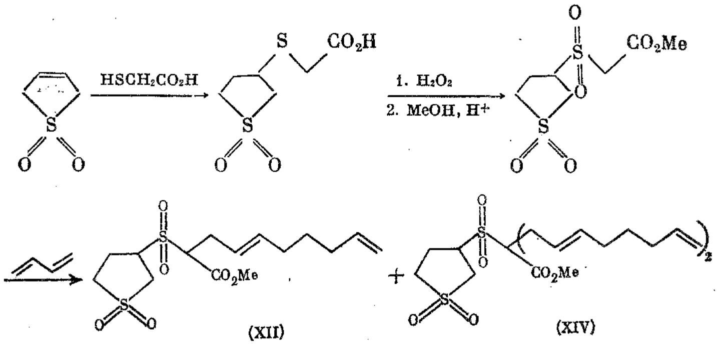
*The spectra of (IV) and (VII) are given in the experimental.



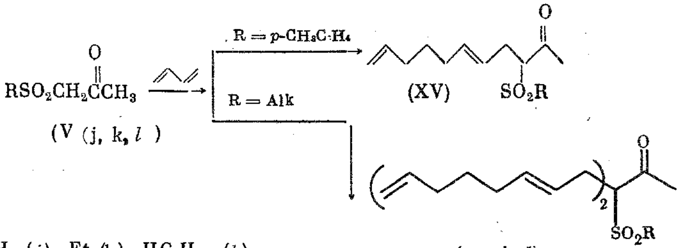
The reaction of ester (II) with butadiene led to two compounds, one of which is a symmetrical telomer (X). The PMR spectrum of (X) is in full accord with this structure. This spectrum displays a narrow singlet at δ 3.75 ppm (CH_3-O), triplet at 2.75 ppm ($CH_2-C=$), multiplet at δ 4.15 ppm ($CH-SO_2$) and a group of olefin proton signals at 4.70–5.80 ppm in 6 : 4 : 2 : 10 intensity ratio. The PMR spectrum of the second compound has two methoxyl proton signals of equal intensity at δ 3.67 and 3.70 ppm. The ratio of the methoxy and olefin protons is 6 : 15. There are two signals at 2.60–2.75 ppm which correspond to six allyl protons. The multiplet centered at 4.70 ppm corresponds in intensity to one $CH-SO_2$ proton. Hence, the second telomerization product (XI) is formed as a result of the participation of six butadiene molecules in the reaction



Sulfone (III) obtained by the addition of thioglycolic acid to 3-sulfolene with subsequent oxidation of adduct (XII) by hydrogen peroxide reacts with excess butadiene to give an 85% mixture of mono- and bis-octadienyl derivatives (XII) and (XIII) in 6 : 4 ratio



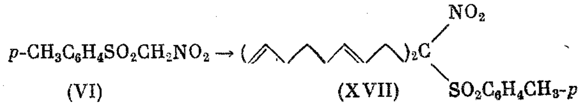
We should note that bis-octadienyl compounds are formed in all cases, in which the reacting sulfone has a methylene group. It is impossible to prevent the accumulation of the exhaustive alkylation product even by limitation of the amount of butadiene introduced. Nevertheless, the yields of the bis-octadienyl derivatives in the presence of excess butadiene differ considerably and depend on the C–H acidity of the starting sulfone. In particular, the marked dependence of the reactivity on C–H acidity is seen in the reactivity of the ketosulfones. Thus, less acidic p-tolylsulfonylacetone (VII) gives almost exclusively sulfonoketone (XV) while alkylsulfonylacetones (Vk, l) react with four butadiene molecules to give ketones (XVIk, l). Nitrosulfone (VI) which has high



$R = p\text{-}CH_3C_6H_4$ (j), Et (k), HC_6H_{13} (l).

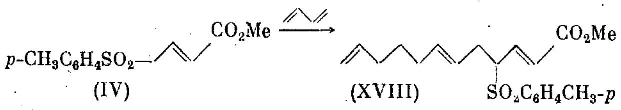
(XVI k, l)

C–H acidity also forms the bis-octadienylation product (XVII)



We should stress that the reaction cannot be stopped at the monotelomer even when using only two molar equivalents of butadiene.

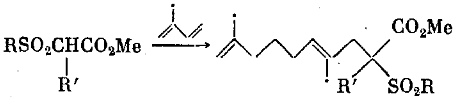
In order to obtain higher sulfones containing several double bonds, we carried out the reaction of butadiene with sulfonoester (IV) which, according to its PMR spectrum, consists of 85% E-isomer. The telomer obtained was shown by spectroscopy and elemental analysis to be the methyl ester of 4-p-tolylsulfonyl-2,6-(E)-11-dodecatriene-1-carboxylic acid (XVIII). Product (XVIII) is not formed in yields above 50%.



(IV) (XVIII)

Thus, the IR spectrum of (XVIII) has bands at 1150, 1320, 1240, and 1720 cm^{-1} which are characteristic of the SO_2 and CO_2CH_3 groups. The E-alkene has bands at 980, 1640, and 3030 cm^{-1} while bands are found at 920, 1000, and 3080 cm^{-1} for the vinyl group. The PMR spectrum displays a multiplet at 1.27 ppm for the CH_2 group. The six allylic protons are found at 2.01 ppm. The singlet at 2.2 ppm corresponds to the CH_3 group attached to the aromatic ring. The single proton at the carbon bonded to the SO_2 group gives a multiplet at 3.56 ppm. The adjacent singlet at 3.58 ppm belongs to the methoxyl protons. Signals for the olefinic protons are found at 4.50-5.30 ppm. The ratio of the intensities of the olefinic and methoxyl protons is 7 : 3. Thus, the vinylog effect is evident in the catalyzed telomerization reaction.

The telomerization of isoprene was studied for sulfones (Ia), (Ig), and (Ih) and (II). Although the yields of the unsaturated sulfonoesters are somewhat lower than those for the case of butadiene, they are quite satisfactory (60-70%). Thus, (Ia) yields 60% (XIXa). The yields of (XIXg) and (XIXh) are 70 and 73%, respectively.



(Ia, g, h) (XIXa, g, h)

Tests of unsaturated sulfones (VIIa, c, e-h) and (X) for juvenile action showed a slight effect relative to pupae of the meal worm (Tenebrio molitor) and bee moth (Galleria melonella).

EXPERIMENTAL

The IR spectra were taken on a UR-20 spectrometer neat or in a Vaseline mull. The PMR spectra were taken on a Tesla BS-487B spectrometer in $CDCl_3$ with HMDS internal standard. The gas-liquid chromatographic analysis was carried out on a Chrom-4 chromatograph with a flame ionization detector on a 1.5-m SE-30 column using helium as the carrier gas.

Polymerization-grade samples of butadiene and isoprene were used. The $PdCl_2-(Ph_3P)_2$ complex was prepared according to Hata et al. [6]. The starting sulfones were prepared either by the reaction of the sodium salts of the sulfinic acids with a halogen-containing compound according to Ashley [11] and Kuchin [12] or by oxidation of sulfides with H_2O_2 in acetic acid [13]. The physical constants of the starting sulfones are given in Table 1.

General Method for the Telomerization of 1,3-Dienes with Sulfones. A sample of 0.01 mole sulfone in 4 ml benzene and 0.03 mole butadiene were placed in a steel autoclave cooled to −20°C. Then, samples of 0.05 mmoles $PdCl_2-(Ph_3P)_2$ and 5 mmoles PhONa were added. The contents of the autoclave were stirred at 85°C for 16 h in the experiments with butadiene and 18-20 h with isoprene. The solvent was evaporated and the reaction products subjected to chromatography on 150 g G40/100 silica gel with 7 : 3 hexane−ethyl acetate as eluent. The physicochemical constants and spectral characteristics of the telomers are given in Tables 2 and 3.

3-(2-Carbomethoxymethanesulfonyl)sulfolane (III). A sample of 9.2 g (0.1 mole) thioglycolic acid was added dropwise with stirring at 20°C to a mixture of 11.8 g (0.1 mole) 3-sulfolene and 3.8 g (0.2 mole) NaOH in 80 ml water. The reaction mass was heated for 4 h at 65°C. The solution was neutralized with the calculated amount of HCl. Water was evaporated in vacuum and the residue was dried by azeotropic distillation with isopropyl alcohol to yield 19 g (90%) sulfide (XII) as an oil. A sample of 21-ml H_2O_2 was gradually added to a solution of this product in 60 ml glacial acetic acid and heated for 1 h at 100°C. Acetic acid was distilled off and the residue was crystallized from methanol to yield 16 g (80%) sulfone (III). IR spectrum (ν, cm^{-1}): 1130, 1320 (SO_2), 1240, 1740 (CO_2CH_3). PMR spectrum (δ, ppm): 2.82 m (2H, CCH_2C), 3.33 m (5H, $2HC_2$, CH), 3.90 s (3H, OCH_3), 4.35 s (2H, CH_2CO).

Methyl Ester of 2-Ethylsulfonyl-4,9-epoxy-2-propyldecane-1-carboxylic Acid (VIII) [14]. A sample of 3.7 g (0.015 mole) 68% p-carbomethoxyperbenzoic acid was added with stirring to a solution of 1.58 g (0.05 mole) sulfone (VIIh) in 20 ml dry CCl_4 and heated for 5 h at 65°C. The reaction mass was washed with saturated aq. $Na_2S_2O_5$ and water and dried over $MgSO_4$. After solvent removal, the products were subjected to chromatography on 100 g alumina with 7 : 3 hexane–ethyl acetate eluent to yield 0.5 g (50%) dioxide (VIII) with n_D^{20} 1.4872. IR spectrum (ν, cm^{-1}): 1150, 1320 (SO_2), 850, 1250, 3050 ($\underset{O}{C-C}$), 1235, 1740 (CO_2CH_3). PMR spectrum (δ, ppm): 0.9 t (3H, CH_3), 1.13 t (3H, CH_3), 1.27 m (4H, CH_2), 1.48 m (4H, CH_2), 1.88 m (6H, $CH_2-\overset{O}{C-C}$), 2.58 m (2H, $\overset{O}{HC-CH}$), 2.90 m (3H, $\overset{O}{H_2C-CH}$), 3.67 s (3H, OCH_3). Found: C, 55.0; H 8.2%. Calculated for $C_{10}H_{28}O_6S$: C, 55.1; H, 8.1%.

Methyl Ester of 2-Ethylsulfonyl-4-(E)-2-propyl-9-oxadecene-1-carboxylic Acid (IXg) with bp 110°C (0.1 mm) and n_D^{20} 1.4892 was obtained in 90% yield. IR spectrum (ν, cm^{-1}): 1150, 1320 (SO_2), 1245, 1740 (CO_2CH_3), 1710 (C = O), 975, 1650, 3030 (trans-CH = CH). PMR spectrum (δ, ppm): 1.38 t (3H, CH_3), 1.40 m (4H, CH_2), 1.58 t (3H, CH_3), 1.83 m (2H, $CH_2C=$), 2.12 s (3H, $CH_3C=O$), 2.48 m (4H, $CH_2C=O$, CH_2) 3.23 m (4H, CH_2SO_2, $CH_2C=O$), 3.78 s (3H, OCH_3), 5.45 m (2H, CH = CH). Found: C, 57.6; H, 8.2; S, 10.1%. Calculated for $C_{16}H_{28}O_5S$: C, 57.8; H, 8.3; S, 9.7%.

Methyl Ester of 2-Ethylsulfonyl-4-(E)-2-methyl-9-oxodecene-1-carboxylic Acid (IXa). With bp 104°C (0.1 mm) and n_D^{20} 1.4869 was obtained in 90% yield. IR spectrum (ν, cm^{-1}): 1150, 1320 (SO_2), 1245, 1740 (CO_2CH_3), 1710 (C = O), 975, 1650, 3030 (trans-CH = CH). PMR spectrum (δ, ppm): 1.45 m (3H, CH_3), 1.53 m (2H, CH_2), 1.63 m (3H, $CH_3C=O$), 1.83 m (2H, $CH_2C=$), 2.17 s (CH_3-CO_2), 2.46 m (4H, CH_2CCO), 3.25 m (4H, CH_2SO_2), 3.86 s (3H, OCH_3), 5.5 m (2H, CH = CH). Found: C, 55.0; H, 8.0, S, 10.5%. Calculated for $C_{14}H_{24}O_5S$: C, 55.2; H, 7.9; S, 10.5%.

1-p-Tolylsulfonyl-bis(2-trans-7-octadienyl)nitromethane (XVII). IR spectrum (ν, cm^{-1}): 1150, 1320 (SO_2), 1565 (NO_2), 920, 1000, 3080 ($CH=CH_2$), 980, 1640, 3030 (trans-CH = CH), 710, 1590, 3010 (C_6H_4). PMR spectrum (δ, ppm): 1.33 m (4H, CH_2), 1.91 m (8H, $CH_2C=$), 2.35 s ($CH_3C_6H_4$), 3.03 m (4H, CCH_2C), 4.75 m (4H, $=CH_2$), 5.47 m (6H, CH = CH, CH =), 7.5 m (4H, C_6H_4).

Methyl Ester of 2-p-tolylsulfonyl-4-(E)-9-oxodecene-1-carboxylic Acid (XVIII). A volume of 25 ml O_2 was passed over 1 h through a solution of 0.09 g (5.1 mmoles) $PdCl_2$ and 0.5 g (52.6 mmoles) CuCl in 5 ml DMF and 0.7 ml H_2O. Then, 1.68 g (5 mmoles) sulfone (VIIa) was added to the prepared catalyst and stirred for 6 h until 70 ml O_2 was taken up. The mixture was treated with 10 ml 3 N HCl and extracted with CH_2Cl_2. The extract was dried over $MgSO_4$. After removal of the solvent, vacuum distillation gave 1.5 g (90%) ketone (XVIII) with bp 142°C (0.1 mm) and n_D^{20} 1.5287. IR spectrum (ν, cm^{-1}): 1150, 1320 (SO_2), 1245, 1740 (CO_2CH_3), 1715 (C (C = O), 730, 820, 1600, 3100 (C_6H_4), 975, 1650, 3030 (trans-CH = CH). PMR spectrum (δ, ppm): 1.37 m (2H, CH_2), 1.83 m (4H, $CH_2C=$), 2.02 s (3H, $CH_3C=O$), 2.21 m (2H, $CH_2C=O$), 2.38 s (3H, $CH_3C_6H_4$), 3.58 s (3H, OCH_3), 3.88 m ($CHSO_2$), 5.30 m (2H, CH = CH), 7.50 m (4H, C_6H_4). Found: C, 61.4; H, 6.9; S, 9.4%. Calculated for $C_{18}H_{24}O_4S$: C, 61.3; H 6.9; S, 9.1%.

CONCLUSIONS

A study was carried out on the telomerization of butadiene and isoprene with β-sulfonoesters, β-ketoesters, and β-nitrosulfones catalyzed by palladium catalysts. Independently of the reagent ratios, nitrosulfones and ketosulfones predominantly form dialkylation products. The reaction in the case of sulfonoesters may be stopped at the stage of monooctadienylation.

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