CONCLUSIONS

3,3-Dicyclopropylcyclopropene was synthesized and its high tendency to undergo quantitative thermal cyclodimerization into 3,3,6,6-tetracyclopropyltricyclo[3,1,0,0^{2,4}] hexane was shown.

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TELOMERIZATION OF ISOBUTYLENE WITH METHYL ESTERS OF PROPIONIC AND ISOBUTYRIC ACIDS

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UDC 66.095.2:547.313.4

Telomerization of isobutylene with methyl chloroacetate is accompanied by the rearrangement of radicals with a 1,5-H-migration and cross-recombination of the telomeric radicals with isobutenyl radicals. Moreover, the dimer of the rearranged radical is formed in a high yield [1]. The present study is on the influence of the nature of the telogen on the course of the telomerization of isobutylene with carboxylic acid esters in the presence of tert-butyl peroxide.

For radical reactions with isobutylene, the allyl cleavage of the chain with the formation of isobutenyl radicals and their cross-recombination with growing radicals is characteristic. This path of the chain cleavage can play a very important role [1]. It is clear that telomerization of isobutylene with methyl isobutyrate proceeds without rearrangement and leads to the formation of two series of compounds, telomers (T_n) and products of cross-recombination of the growing radicals with the isobutenyl radicals (P_m)

$$(CH_3)_2CHCO_2CH_3 \xrightarrow{\text{RO}} (CH_3)_2CCO_2CH_3$$

$$(CH_3)_2CCO_2CH_3 + n(CH_3)_2C=CH_2 \rightarrow [(CH_3)_2CCH_2]_nC(CH_3)_2CO_2CH_3$$

$$(A)$$

$$(A) + DH^* \rightarrow H[(CH_3)_2CCH_2]_nC(CH_3)_2CO_2CH_3(T_n) + D.$$

$$(A) + CH_2C(CH_3) = CH_2 \rightarrow CH_2 = C(CH_3)CH_2[(CH_3)_2CCH_2]_mC(CH_3)_2 \cdot CO_2CH_3(P_m)$$

$$(A) + CH_2C(CH_3) = CH_2 \rightarrow CH_2 = C(CH_3)CH_2[(CH_3)_2CCH_2]_mC(CH_3)_2 \cdot CO_2CH_3(P_m)$$

The yield of unsaturated compounds P_m is commensurable with the number of telomers T_n , and with the increase in the length of the radical chain, the relative yield of the unsaturated products increases by a factor of

*Both the telogen and the monomer can play the role of a hydrogen donor (DH).

Institute of Heteroorganic Compounds, Academy of Sciences of the USSR, Moscow. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 7, pp. 1539-1543, July, 1979. Original article submitted February 20, 1978.

	Formula	Yield,%	PMR spectrum, 5, ppm (referred to TMS)						
Compound		of T ₁ -P ₂	. CH₃O S	(CH ₃) ₂ C S	CH ₃ C=, (CH ₃) ₂ CH	CH ₂ S	Сн ₂ = d		
(I) (T ₁)	(CH _{\$}) ₂ CHCH ₂ C(CH ₅) ₂ CO ₂ CH ₅	18	3,59 (3H)	1,16 (6H)	0,85 d	1,50 (2H)	-		
(II) (P ₀)	CH2=C(CH3)CH3C(CH3)2CO2CH3	8	3,72 (3H)	1,16 (6H)	1,67 5 (3H)	2,34 (2H)	4,83 (2H)		
(III) (T ₂)	CH ₃ _ (CH ₃) ₅ CHCH ₅ CCH ₂ C(CH ₃) ₅ CO ₅ CH ₃ (CH ₃) ₅ CHCH ₅ C	24	3,61 (3H)	1,16 (1) 0,87 (2)	0,92d	1,60 (4H)	- ·		
(IV) (P ₁)	CH _s =C(CH ₂) ⁴ CH ₂ C ³ CH ₃ CH ₃ C(CH ₃) ₂ CO ₄ CH ₃	21	3,59 (3H)	1,20 (1) 0,92 (3)	1,765 (3H)	1,94 (2H) (2) 1,65 (2H) (4)	4,70 (2H)		
(V) (T ₃)	(CH2)2CHCH4[(CH4)2CCH4]2C(CH4)2CO2CH4	13	3,48 (3H)	1,18 (1) 0,98 (2)	0,92 d	1,65 (2H)	-		
(VI) (P ₂)	⁴ CH ₂ =C(CH ₃)CH ₂ [(CH ₃) ₂ CCH ₂] ₂ C(CH ₃) ₂ CO ₂ CH ₂	16	3,68 (3H)	1,15 (1) 0,98 (3)	1,78 s (3H)	$ \begin{vmatrix} 2,00 & (2H) \\ (4) \\ 1,71 \\ 1,29 & (2H) & (2) \end{vmatrix} $	4,85 (2H)		

TABLE 1. Telomerization of Isobutylene with Methyl Isobutyrate

2.5. Thus, the conclusion that they are formed by disproportionation of the growing radicals is not very probable. The compounds T_1 and P_m (m = 0-2) were isolated in the form of narrow fractions (90-95%), while T_2 and T_3 were isolated as individual compounds (see experimental part). The structure of all the isolated compounds was confirmed by PMR spectra (Table 1), with well identifiable signals (singlets and a doublet). Compounds P_1 and P_2 are readily hydrogenated with conversion into T_2 and T_3 , respectively. This also confirms their structure as unsaturated analogs of the main series of the telomers. In the reaction, up to 20% (based on the sum of T_1-P_2) of hydrocarbons are also formed, which were identified by elementary analysis (C 83.72%, H 14.12%) and by PMR spectral data.

In the telomerization of isobutylene with methyl propionate, the telomeric radicals (B_p) can, in principle, be rearranged with 1,3- (p = 1)- or 1,5- (p = 2)-migration of the hydrogen atom

$$\begin{array}{c} [(CH_3)_2CCH_2]_pCH(CH_3)CO_2CH_3^{\dagger} \rightarrow H[(CH_3)_2CCH_2]_pC(CH_3)CO_2CH_3 \\ (B_p) & (F_p) \end{array}$$

$$(2)$$

In the study of the composition of the telomers fraction containing up to three monomeric units per molecule, presence of the following compounds was observed:

 $H[(CH_3)_2CCH_2]_pCH(CH_3)CO_2CH_3, (T_p), (p = 1, 2)$

and

 $H[(CH_3)_2CCH_2]_PC(CH_3)CO_2CH_3, \quad (P_k')(k=2)$ $| CH_2C(CH_3)=CH_2$

The absence of appreciable amounts of product P'_1 (p = 1) or its saturated analog shows that radical B_1 (scheme 2) does not isomerize with 1,3-H-migration, while the 1,5-H-migration in radical B_2 proceeds to a high extent, as evident from the ratio of yields of telomers T_2 and P'_2 (Table 2). Thus, under our conditions, the rearranged radical F_2 (see scheme 2) is mainly captured in the form of product P'_2 due to cross-recombination with the isobutenyl radicals. The telomers fraction studied also contains four hydrocarbon compounds (total yield ~25% of the sum of identified products), and two nonidentified compounds (total yield ~3-5%) with group signals in the PMR spectrum (TMS) at 3.65 ppm (CH₃O), and, possibly, 4.78 ppm (CH₂=). The structure of telomers T_1 , T_2 , and P'_2 was confirmed by the values of chemical shifts and multiplicity of signals in the ¹³C NMR spectra (see Table 2) run with and without suppression of the interaction with protons, and by their comparison with previously studied reference compounds [2]. For compound P'_2 , the most characteristic are three signals, singlets from the quaternary C atoms [atoms 2,4, compound (III), Table 2], and the trigonal atom (atom 9, in the same compound), present under very different conditions of screening.

Comparison of the results shows that the chain transfer to the telogen by sterically hindered growing radicals $(CH_3)_2\dot{C}CH_2[(CH_3)_2CCH_2]_nCR(CH_3)CO_2CH_3(E_n)$ is very dependent on the structure of the telogen. In the case of methyl propionate, for the nonrearranged radicals E_n (n = 0, 1; R = H), the chain transfer proceeds

TABLE 2.	Telomerization	of Iso	butylene	with	Methyl	Propionate
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Compound	Formula	Yield, % of the sum of T ₁ -P ₂	Found/calculated,"		¹³ C NMR spectrum ^{\$} , ppm (referred to TMS)				
			G	н	coo	G	СН	CH3	CH2
(I) (T ₁)	(CH ₃) ₂ CHCH ₂ CH(CH ₅)CO ₂ CH ₂	23 *	-	_	175,4	-	43,0(2) 25,8(4)	22,4(5) 17,4(3') 50,7(1.1)	37,1
(II) (T ₂)	(CH ₄) ₅ CHCH ₂ C(CH ₅) ₂ CH ₂ CH(CH ₆)CO ₂ CH ₃	₃₄ †	71,53 72,00	<u>12,18</u> 12,00	176,4	33,7	35,2(2) 23,9(6)	27,1 27,2(5') 25,4(7) 20,2(3') 50,6(1.1)	51,3(5) 46,4(3)
(III) (P ₂ ')	$\begin{array}{cccccc} 7 & 6 & 5 & 4 & 5' & 3 & 2 & 3' & 1 & 1.1 \\ (CH_{3})_{2}CHCH_{2}C(CH_{3})_{2}CH_{2}C(CH_{3})_{3}CO_{3}CH_{3} \\ & CH_{2}C(CH_{3})=CH_{2} \\ & CH_{2}C(CH_{3})=CH_{2} \\ & 8 & 9 & 10' & 10 \end{array}$	43 ‡	75,17 75,59	<u>11,51</u> 11,81	176,5	131,3 (9) 45,1 (2) 35,0 (4)	23,4	27,0 28,7 (5') 25,7 (7) 23,9 (10') 21,3 (3') 50,6 (1.1)	115,0 (10) 54,0 (8) 53,0 (3) 51,6 (5)

*Isolated in the form of a 95% fraction with an admixture of hydrocarbons. Found: C 67.89; H 11.82. Calculated; C 66.66; H 11.11%. $\label{eq:relation} \begin{array}{c} ^{\dagger} \, n_D^{\ 20} \ 1.4277; \ d_4^{\ 20} \ 0.8693. \\ ^{\ddagger} \, n_D^{\ 20} \ 1.4527; \ d_4^{\ 20} \ 0.9016. \end{array}$

mainly with the formation of telomers of the (T_p) series, while in the reaction with methyl isobutyrate, where the C-H bond is screened by two CH_3 groups, the chain transfer is hindered, and the cross-recombination reaction with isobutenyl radicals, competing with it proceeds to a considerable extent.

An important role in the direction of the course of the processes studied is also played by the polar properties of the growing radicals and the telogens. The nucleophilic nonrearranged radicals E_n transfer the chain to the electrophilic telogen, and this transfer apparently proceeds to methyl propionate rather more readily than to the less electrophilic methyl isobuty rate. At the same time, the electrophilic rearranged radical F_{2} (see scheme 2) not only does not participate in the chain transfer with the electrophilic telogen, as observed in other cases also [3], but also does not grow. We explain this last fact by unfavorable combination of steric factors: at the growth stage, the branched radical would have to react with a branched monomer.

EXPERIMENTAL

The GLC analysis was carried out on the "Tswett 4-67" apparatus; a 2000 \times 3 mm column; chromosorb W SKTFT-50 (15%); helium, katharometer; 110-115°C; preparative GLC; PAKhV-02; a 2600-10 mm column; N-AW SKTFT-50 chromatone (20%); helium, katharometer; 110-190°C.

The PMR spectra were run on the "Perkin-Elmer R-20" spectrometers, internal standard - TMS; ¹³C NMR spectra - on "Bruker Physik HX-90," internal standard - CCl₄.

Telomerization of Isobutylene with Methyl Isobutyrate. The experiments were carried out in a 0.5-liter stainless steel autoclave. Into a preliminarily cooled and N_2 -purged autoclave, 200 g of methyl isobutyrate, 9 g of tert-butyl peroxide and 100 ml of isobutylene were charged, and the mixture was heated for 4 h at 135°C. After distillation of the initial ester from the products of five batches, a mixture of telomers (67 g) was obtained (6.7% based on ester used). The yield of the light fraction, including telomers T_1-T_3 , was 43 g (65% of mixture of products). By distillation on a column, the light fraction was divided into narrow fractions of telomers (control by GLC and PMR), which were additionally purified by preparative GLC (see Table 1). T_1 [compound (I)]. Found: C 69.38; H 11.87%. $C_9H_{18}O_2$. Calculated: C 68.35; H 11.39%. T₂ [compound (III)]: n_{10}^{20} 1.4359; d_4^{20} 0.8834. Found: C 72.58; H 11.92%. $C_{13}H_{26}O_2$. Calculated: C 72.90; H 12.15%. T_3 [compound (V)]: n_D^{20} 1.4508; d_4^{20} 0.8995. Found: C 75.62; H 12.40%. $C_{17}H_{34}O_2$. Calculated: C 75.60; H 12.56%. The yields of the individual reaction products are given from the data of GLC-analysis of a typical experiment on separation into fractions.

Hydrogenation of unsaturated compounds P_1 and P_2 (see Fig. 1) was carried out in a long-necked hydrogenation flask over a Pd/BaSO₄ catalyst (5%) in CH₃OH at 20°C, until no more H₂ was adsorbed. By hydrogenating 4.5 g of the P₁ and T₂ mixture containing, according to GLC analysis, 60% of P₁ (2.7 g), followed by fractional distillation, 3.6 g of T_2 were obtained (purity control by GLC and PMR). Similarly, from a mixture of 1.4 g of P_2 and T_3 , containing, according to GLC, 65% of P_2 (0.9 g), 1 g of T_3 was obtained.

<u>Telomerization of Isobutylene with Methyl Propionate.</u> The experiments were carried out and materials were processed as described above. In the experiments, 200 g of methyl propionate, 9 g of tert-butyl peroxide and 100 g of isobutylene were used. From four batches, 69 g (8.7% based on ester used) of the telomers mixture were obtained. The yield of the fraction containing T_1 - P'_2 was 45 g (56% of the sum of products). The yields and properties of compounds obtained are given in Table 2. Hydrocarbon fractions were also isolated from the reaction mixture. Found: 84.45; H 15.84%.

CONCLUSIONS

1. Telomerization of isobutylene with methyl isobutyrate leads to the formation of telomers $H[(CH_3)_2-CCH_2]_nC(CH_3)_2CO_2CH_3$ and the products of the cross-recombination of the growing radicals with isobutenyl radicals $CH_2 = C(CH_3)CH_2[(CH_3)_2CCH_2]_mC(CH_3)_2CO_2CH_3$.

2. The telomerization of isobutylene with methyl propionate is accompanied by rearrangement of the radicals with 1,5-migration of the hydrogen atom. The nonrearranged radicals are captured mainly by chain transfer, while the rearranged radical, by cross-recombination with isobutenyl radicals.

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THE Fe(CO)₅ INITIATED REDUCTION OF

POLYCHLOROALKANES OF THE CCl₃CH₂CHXY TYPE

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Reactions are known of radical addition [1], telomerization [2], and reduction of compounds containing the CCl_3 group [3-5], which are accompanied by rearrangement of the polychloroalkyl radicals in the liquid phase with 1,4-[3], 1,5-[1-5], and 1,6-migration of the hydrogen atom according to the scheme

 $\dot{\text{CCl}}_2$ --(C)_n--CH₂R \rightarrow HCCl₂--(C)_n- $\dot{\text{CHR}}$

An interesting feature of these unusual rearrangements is the isomerization of the more stable radicals into less stable, but more reactive radicals. Rearrangements of this type are rare, and have been little studied.

As a continuation of these investigations in the present work we studied the behavior of the $CCl_2CH_2CH_2CH_2CI$ (A), $CCl_2CH_2CHClCH_3$ (B), and $CCl_2CH_2CH_2CH_3$ (C) radicals. These radicals were selected as models for studying a possible unusual rearrangement with 1,3-migration of the hydrogen atom. Radicals (A), (B), and (C) were generated by reducing $CCl_3CH_2CH_2CI$ (I), $CCl_3CH_2CHClCH_3$ (II), and $CCl_3CH_2CH_2CH_3$ (III), respectively, by the action of the $Fe(CO)_5 - i-C_3H_7OH$ system and relative reducing systems. The reduction of (I) by the $Fe(CO)_5 - i-C_3H_7OH$ and other reducing systems has been described in [6]. The formation of radicals (A) during the reaction of (I) with the $Fe(CO)_5 - DMFA$ system was confirmed by EPR using spin traps [7]. The reduction of (II) and (III) is of particular interest as a route for synthesis of compounds of the $HCCl_2CH_2CHXY$ type.

The reduction of (I)-(III) was carried out in stainless steel autoclaves and glass ampules (Table 1); in all cases the main products of the reduction are compounds with a dichloromethyl group of the $HCCl_2CH_2CHXY$ type, where X = H, Y = Cl (IV); X = CH₃, Y = Cl (VIII), and X = CH₃, Y = H (XI). Compounds were also formed which usually accompany the reduction of polychloroalkanes by the Fe(CO)₅ + i-C₃H₇OH system [6], and are adducts of the initial polychloroalkanes with propylene (dehydration of isopropanol) – XYCHCH₂CCl₂CH₂CHCl-CH₃ (V), (IX), (XII) and recombination products of radicals XYCHCH₂CCl₂ with dechlorination – compounds (VI),

Institute of Heteroorganic Compounds, Academy of Sciences of the USSR, Moscow. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 7, pp. 1543-1548, July, 1979. Original article submitted February 20, 1978.