OCH₃), 4.95-5.20 multiplet (2H, CH₂=C), and 5.30 multiplet (1H, CH=C). Found: C 69.2 and H 9.7%. $C_{13}H_{22}O_3$. Calculated: C 69.0 and H 9.8%.

<u>Allyl 3,7-Dimethyl-4(E),9-decadienoate (XII)</u>. The ester (VIII) (0.21 g, 1 mmole) in 20 ml of allyl alcohol was maintained for 5 h at 80°C in the presence of p-Tol.SO₃H. The excess alcohol was removed, and the residue was purified by chromatography on silica gel (G 40/100) with the 9:1 mixture of hexane and ether as the eluent. We obtained 0.14 g (62%) of the ester (XII); 1.4585. The IR spectrum (v, cm⁻¹) was as follows: 930, 1000, 3080 (CH₂=C), 980, 1645, 3030 (trans-CH=CH), 1250, and 1750 (COOR). The PMR spectrum (δ , ppm) was as follows: 0.87 multiplet (3H, CH₃), 1.07 multiplet (3H, CH₃), 1.27 multiplet (1H, CH), 1.61 multiplet (1H, CH), 1.91 multiplet (4H, CH₂=C), 2.35 multiplet (2H, CH₂=CO₂), 4.57 multiplet (2H, OCH₂), 4.75-5.50 multiplet (4H, CH₂=C), and 5.50-6.16 multiplet (4H, CH=C). Found: C 76.0 and H 10.1%. C₁₅H₂₄O₂. Calculated: C 76.2 and H 10.2%.

CONCLUSIONS

The catalytic telomerization of the cis and trans isomers of piperylene with sulfones containing an available hydrogen atom was investigated. The synthesis of compounds having juvenile hormone activity was shown to be possible on the basis of the telomers of piperylene.

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POLYFLUORINATED B-KETOESTERS AND THEIR α-HALOGENATED DERIVATIVES

IN REACTIONS WITH TETRAPHOSPHORUS DECASULFIDE AND 2,4-BIS(4-(METHOXYPHENYL))-2,4-DITHIOXO-P^V,P^V-1,3,2,4-DITHIODIPHOSPHETANE

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On treatment with tetraphosphorus decasulfide (I) in toluene, acetoacetic and α -chloroacetoacetic esters give 5-methyl- (30-40%) and 4-chloro-5-methyl-1,2-dithiolene-3-thiones, respectively [1, 2]. When, instead of (I), 2,4-bis(4-methoxyphenyl)-2,4-dithioxo-PV,PV-1,3,2,4-dithiodiphosphetane (II) with elementary sulfur in toluene is used, the yields of 5-substituted 1,2-dithiolene-3-thiones are increased to 90-95% [3]. There have been no literature reports of the reactions of (I) and (II) with fluorinated β -ketoesters, in which the nucleophilicity of the carbonyl oxygen is considerably reduced. The effect of two halogen atoms in the α position of the β -ketoester on this reaction also remains unclear.

We have examined the reaction of the methyl esters of the fluorinated β -ketoacids (IIIa-d), α -chloro- β -ketoacids (IVa-d), α , α -dibromo- β -ketoacids (Va-d), and α , α -dibromo-acetoacetic ester (Ve) with (I) and (II) in the presence of elementary sulfur.

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		Empirical formula		$C_4H_2F_2S_3$	$\mathrm{C}_{5}\mathrm{H}_{2}\mathrm{F}_{4}\mathrm{S}_{3}$	$C_4HF_3S_3$	C7HF9S3	$C_4HCIF_2S_3$	$C_4HClF_4S_3$	$C_4HBrF_2S_3$	$C_5HBrF_4S_3$	$C_4H_3BrS_3$
			s	$\frac{52,82}{52,21}$	40,85 41,06	47,33 47,57	$\frac{27,16}{27,23}$	<u>44,04</u> <u>43,98</u>	35,80 35,80	36,24 36,55	$\frac{30.40}{30.72}$	$\frac{12,12}{42,34}$
			Æ	$\frac{20,39}{20,62}$	$\frac{32,50}{32,44}$	$\frac{28,40}{28,18}$	48,90 48,68	$\frac{17,28}{17,37}$	28,30 28,28	<u>14,47</u> <u>14,44</u>	$\frac{24,47}{24,27}$	I
	1c. %		CI		I	I.	J	$\frac{15,96}{16,21}$	$\frac{12,93}{13,19}$	1	l	1
	Found/ca		ų		I	I	, 	1	1	$\frac{30,18}{30,27}$	$\frac{26,11}{25,82}$	34,82 35,17
			н	$\frac{1,14}{1.09}$	1,11 0,86	0,50 0,50	0,38 0,29	0.65 0.46	$0.58 \\ 0.40$	$0,82 \\ 0,48$	$0.42 \\ 0.32$	<u>1,60</u> <u>1,33</u>
S S S S			υ	25,82 26,08	$\frac{25,41}{25,63}$	$\frac{23,52}{23,76}$	23,51 23,80	$\frac{22,23}{21,97}$	<u>22,05</u> 22,35	$\frac{17,92}{18,26}$	$\frac{19,12}{19,18}$	$\frac{21,41}{21,15}$
niones	%	lca1	(II)	74	76	80	72	66	15	30,5	8.5	
sne-3-tl	Yield,	Empiri	(I)	58	21,5	32,5	26	28,5	I	14	I	16
)ithiole		0	ر ط	28-29	31-32	• 1	45-46	41-43	51-53	34-35	62-64	
R-1,2-I		÷	4	н	н	Н	Н	CI	ច	Br	Br	Br
4-X-5-R		f	¥	HCF ₂	$H(CF_2)_2$	CF ₃	C₄F9	HCF_2	$H(CF_2)_2$	HCF_2	$H(CF_2)_2$	CH _s
TABLE 1.			Compound	(Vla)	- (VIb)	(Vlc) *	(MId)	(VIIIa)	(dIIIb)	(Xa)	(Xb)	(Xe) *

*Low-melting compounds distill with decomposition.

ł

TABLE 2. IR and PMR Spectral Parameters for R

Com~	X	R .	IR sp V, cm	ectra,	PMR spe ppth (J,	¹⁹ F NMR spectra, δ, ppm (J, Hz)			
pound			C—C	s—s	CH=	H(CF ₂) _n	CF3	CF2	HCF_2
(V <u>I</u> a)	н	HCF ₂	1520	540	7,21	6,66; (53 5)	-	-	52,3;
(VIÞ)	H	H(CF ₂) ₂	1520	570	7,15	6,03;	-	54,6	35,8;
(VJc) (VId)	H H	CF3 C4F9	1550 1520	525 570	7,34 7,32	(33,0; 4,0) - -	93,0 80,8	56,3; 40,0; 36 1	(33,0)
(VIIIª)	- Cl	HCF_2	4510	525	~~	6,86; (53.0)	-	-	48,5;
(VIIIb)	Cl	$H(CF_2)_2$	1505	535	-	6,46;		51,5	26,9;
(Xa)	Br	HCF ₂	1590	550	<u> </u>	(35,0; 4,7) 6,84;			(33,0) 48,0;
(Xb)	Br	$H(CF_2)_2$	1590	540		(51,0) 6,42;	_	50,5	(51,0) 27,4;
(Xe)	Br	CH3	1520 1305	520	2,5(CH ₃)	(20,8; 4,4) —	_	-	(50,8)

The β -ketoesters (III) on boiling with a 2.4-fold excess of (I) in toluene yield, like their hydrocarbon analogs, 5-fluoroalkyl-1,2-dithiolene-3-thiones (VI) (Table 1), but in lower yields (20-35%):



Replacement of (I) by (II) increases the yields of (VI) to 70-80%.

The IR spectra of (VI) (Table 2) show absorption at 1505-1590 and 530-570 cm⁻¹, attributed to the C-C and S=S vibrations of the ring [4]. Absorption for the thione group (1110-1190 cm⁻¹) is difficult to identify as a result of superimposition of C-F absorption. In the PMR spectra (Table 2), signals are seen for the proton in the 4 position (δ 7.15-7.35 ppm) and for the terminal proton of the fluoroalkyl radicals (δ 6.03-6.66 ppm) for (VIa, b). The ¹⁹F NMR spectra (Table 2) correspond to the structures of the fluoroalkyl radicals.

The presence of the thione group in (VI) was confirmed by the formation of salts (VII) on reaction with $CuCl_2$ in boiling acetone, which is also characteristic of fluorine-free 1,2-dithiolene-3-thiones [5].



In contrast to the reaction of α -chloroacetoacetic ester with (I), which gives 4-chloro-5-methyl-1,2-dithiolene-3-thione [2], fluorinated α -chloro- β -ketoesters (IVa-d) react with (I) and (II) in different ways, giving products which differ depending on the fluoroalkyl substituent. For example, β -ketoesters (IVa, b), with a terminal hydrogen atom in the fluoroalkyl substituent, give with (II) a mixture of compounds (VIa, b) and 4-chloroTABLE 3. Salts $\mathbf{R}_{\mathbf{F}} \xrightarrow{|} \mathbf{S} - \mathbf{CuCl}^+ \mathbf{Cl}^-$

pu	B		p.)	%		Found	/calc.	Empirical .	V, cm ⁻¹		
Compou	тњ	x	mp, °C (decom	Yield,	С	н	Cl	F	s		s s
(VIJa)	HCF2	н	233-236	89	$\frac{15,35}{15,07}$	$\frac{0,90}{0,63}$	21,95	10,95	29,95	$C_4H_2Cl_2F_2S_3Cu$	1300, 1520
(VIIb)	$\mathrm{H}\left(\mathrm{CF}_{2}\right)_{2}$	н	229-231	90	$\frac{16,35}{16,29}$	$\frac{0.83}{0.55}$	<u>19,12</u> 19,23	21,00	$\frac{26,09}{26,09}$	C ₅ H ₂ Cl ₂ F ₄ S ₃ Cu	1305, 1505
(VIIc)	CF₃	н	225-228	90	$\frac{14,44}{14,27}$	$\frac{0,46}{0,30}$	$\frac{20,90}{21,06}$	$\frac{17,2}{16,93}$	$\frac{28,62}{28,57}$	C4HCl2F3S3Cu	1210
(VI1d)	C ₄ F ₉	н	221-223	92	$\frac{17,22}{17,24}$	$\frac{0,52}{0,21}$	$\frac{14,8}{14,54}$	35,03 35,26	$\frac{19,34}{19,72}$	C7HCl₂F9S3Cu	1300
(IXa)	HCF ₂	Cl	219-221	94	<u>14,11</u> 13,60	$\frac{0,37}{0,29}$	$\frac{29,72}{30,12}$	11,00 10,76	$\frac{27,55}{27,24}$	C₄HCl₃F₂S₃Cu	1320, 1495

5-fluoroalkyl-1,2-dithiolene-3-thiones (VIIIa, b) (Tables 1 and 2) in 75-86% yields. As the length of R_F is increased from HCF₂ to H(CF₂)₂, the yield of halo compounds (VIII) falls from 66 to 15%, whereas the α -chloro- β -ketoesters (IVc, d) with perfluoro substituents give only chlorine-free products (VIc-d):



The structures of (VIIIa, b) were confirmed by their IR and ¹H and ¹⁹F NMR spectra (Table 2), which were similar to those of (VIa, b) except that no signals were present for a proton in the 4 position. The presence of the thione group in (VIIIa) was confirmed by the formation of the salt (IXa) (Table 3) on reaction with $CuCl_2$.



The methyl esters of the fluorinated α, α -dibromo- β -ketoacids (Va, b), which have a terminal hydrogen atom in the fluoroalkyl radical, react with (I) and (II) to give mixtures of (VIa, b) and 4-bromo-5-fluoroalkyl-1,2-dithiolene-3-thiones (Xa, b) (Tables 1 and 2) in 35-40% yields [when (II) is used], and (Vc, d), which have perfluoroalkyl substituents, give the bromine-free 5-fluoroalkyl-1,2-dithiolene-3-thiones (VIc, d) in 34-38% yields. The α, α -dibromoacetoacetic ester (Ve) reacts with (I) to give only 4-bromo-5-methyl-1,2-dithiolene-3-thione (Xe) (Tables 1 and 2) in 16% yield, the product resulting from the elimination of two bromine atoms (5-methyl-1,2-dithiolene-3-thione) being absent from the reaction mixture. In this series of compounds (V), as in the case of compounds (IV), increasing the length of R_F and its extent of fluorination results in an increase in the yields of nonhalogenated 5-fluoroalkyl-1,2-dithiolene-3-thiones (VI), indicating that the lability of the halogens in the α position of β -ketoesters increases with increasing electron-acceptor properties of R_F. The structures of (Xa, b, e) were confirmed by their IR and NMR spectra (Tables 1 and 2).

These results, in conjunction with the findings reported in [1, 2], show that the reaction of (I) and (II) with β -ketoesters is not regiospecific, but takes place at two nonequivalent reaction centers, viz., the oxygen atoms of the carbonyl and ester groups, followed by ring closure to 1,2-dithiolene-3-thiones. The formation of halogen-free 5-substituted 1,2-dithiolene-3-thiones (VI) from α -halo- and α, α -dihalo- β -ketoesters (IV) and (V), and of 4-bromo-5-substituted 1,2-dithiolene-3-thiones (Xa, b, e) from α, α -dibromo- β -ketoesters (Va, b, d) may be due to the presence in the reaction mixture of trivalent phosphorus compounds, which undergo the Perkov reaction either with the original α -halo- β -ketoester (IV) or (V), or with the 4-halo-1,2-dithiolene-3-thione (VIII) or (IX). This assumption is con-



firmed by the observation that on treatment with Ph_3P and H_2S in toluene, (IV) and (V) are converted into (III), whereas under these conditions (VIII) and (X) do not give 5-fluoroalkyl-1,2-dithiolene-3-thiones (VI). In the absence of Ph_3P , H_2S does not reduce halogen in the α position.

EXPERIMENTAL

The IR spectra were obtained on a Specord IR-75 spectrophotometer as pastes in Vaseline oil or layers, and the ¹H and ¹⁹F NMR spectra on a Tesla BS-567A (100 MHz for ¹H), and 93.1 MHz for(¹⁹F), with an internal standard of TMS (¹H) or C_6F_6 (¹⁹F), in CDCl₃ or CCl₄.

GLC analysis for the β -ketoesters (III) was carried out on an LKhM-72 chromatograph: carrier gas helium, katharometer detector, 2 m × 4 mm steel column packed with Chromaton N-AW-DMCS with 5% silicone SE-30, temperature 170°C. The fluoroalkylated α -chloro- (IV) and α, α dibromo- β -ketoesters (V) were obtained as described in [6], and the α, α -dibromoacetoacetic ester (Ve) as described in [7].

4-X-5-R-1,2-Dithiolene-3-thiones. To a suspension of 0.12 mole of (I) or (II) and 0.1 mole of sulfur in 60 ml of toluene was added dropwise with stirring at the boil 0.05 mole of the β -ketoester (III)-(V), and the mixture was boiled for 7-12 h. The reaction mixture was then cooled to 20°C, kept for 3-4 h, and filtered; the toluene was distilled off; and the residue was chromatographed on a silica gel column (hexane-chloroform, 3:1). The red band was isolated, the solvent removed, and the residue recrystallized from hexane. When the reaction was carried out with β -ketoesters (IVa, b) and (Va, b), the eluent was hexane-benzene-chloroform, 20:10:3. Products (VI), (VIII), and (X) were obtained (see Table 1 and 2).

<u>Salts (VII) and (IX)</u>. To $6 \cdot 10^{-3}$ mole of CuCl₂ · 2H₂O in 25 ml of acetone was added dropwise with stirring at the boil a solution of $5 \cdot 10^{-5}$ mole of (VI) or (VIII) in 5 ml of acetone. The mixture was cooled, and the precipitated solid was filtered off and the acetone removed. The residue was combined with the solid and recrystallized from DMSO. Salts (VII) and (IX) were obtained (Table 3).

Reaction of α -Halogenated β -Ketoesters (IV) and (V) with Triphenylphosphine and Hydrogen Sulfide. To a suspension of 6 mmoles of triphenylphosphine in 10 ml of toluene was added with stirring 3 mmoles of the α -halo- β -ketoester (IV) or (V). The mixture was brought to the boil, a stream of hydrogen sulfide was passed through for 2 h, then it was cooled and filtered. The products (β -ketoesters (III)) were determined by GLC by comparison with authentic samples.

CONCLUSIONS

1. Fluoroalkylated β -ketoesters react with tetraphosphorus decasulfide and 2,4-bis(4-methoxyphenyl)-2,4-dithioxo-PV,PV-1,3,2,4-dithiodiphosphetane to give 5-fluoroalkyl-1,2-dithiolene-3-thiones. In these reactions, fluoroalkylated α -chloro- β -ketoesters in which $R_F = H(CF_2)_n$ (n = 1, 2) give mixtures of 5-fluoroalkyl-1,2-dithiolene-3-thiones and 4-chloro-5-fluoroalkyl-1,2-dithiolene-3-thiones, but when $R = CF_3$ or C_4F_9 , only the first of these are formed.

2. α, α -Dibromoacetoacetic ester gives 4-bromo-5-methyl-1,2-dithiolene-3-thione, whereas fluoroalkylated α, α -dibromo- β -ketoesters in which $R_F = H(CF_2)_2$ (n = 1, 2) give mixtures of 1,2-dithiolene-3-thiones either unsubstituted or monosubstituted with bromine in the 4 position, or when $R_F = CF_3$ or C_4F_9 , only the bromine-free compounds.

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FLUOROINDENES. COMMUNICATION 8.* SYNTHESIS OF POLYFLUOROINDENES CONTAINING CHLORINE IN THE AROMATIC RING, BY DEHALOGENATION OF THE PRODUCTS OF REACTION OF 1-CHLORONONAFLUOROINDAN WITH LiC1

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We have previously generated a series of polyfluoroindenyl cations bearing substituents in the five-membered ring [2]. Ions containing substituents other than fluorine in the sixmembered ring are not known. The unavailability of such ions does not permit the unambiguous assignment of the signals for the fluorine atoms, and the analysis of the ¹⁹F NMR spectra of these species, which hinders the examination of their electronic structure. The precursors of the polyfluoroindenyl cations are the corresponding indenes [2]. Polyfluoroindenes containing one or two hydrogen atoms in the aromatic ring have been described [3]. However, these indenes, together with other indenes with substituents in the aromatic ring, cannot

*For communication 7, see [1]. †Deceased.

TABLE 1. ¹⁹F NMR Spectra of Polyfluorochloroindans



Compound	ð, ppm *										
	F^{1}_{α}	F_{α}^{2}	F_{β}^2	$F^3_{\alpha,\beta}$	F4	\mathbf{F}^{5}	\mathbf{F}^{6}	F?	$J_{2\alpha,2\beta}$		
(II) † (III) (IV) (V) (VI) (VII) (VIII) (IX) (XII)	51,1 50,0 50,9 49,5 57,0 51,4 56,3-54,3 50,2	34,2 34,4 34,6 34,3 35,2 34,5 35,2 35,2 44,2	$\begin{array}{c} 41,2\\ 41,3\\ 41,3\\ 42,7\\ 41,8\\ 42,7\\ 41,8\\ 42,4\\ 41,6\\ 44,2\\ \end{array}$	$55,3 \\ 55,0 \\ 55,0 \\ 55,3 \\ 56,4 \\ 56,3-54,3 \\ 56,3-54,3 \\ 56,3-54,3 \\ 54,9 \\ 54,9 \\ 54,9 \\ 54,9 \\ 55,3-54,3 \\ 54,9 \\ 54,9 \\ 55,3-54,3 \\ 54,9 \\ 55,3-54,3 \\ 54,9 \\ 55,3-54,3 \\ 54,9 \\ 55,3-54,3 \\ 54,9 \\ 55,3-54,3 \\ 54,9 \\ 55,3-54,3 \\ 54,9 \\ 55,3-54,3 \\ 54,9 \\ 55,3-54,3 \\ 54,9 \\ 55,3-54,3 \\ 54,9 \\ 55,3-54,3 \\ 54,9 \\ 55,3-54,3 \\ 54,9 \\ 55,3-54,3 \\ 54,9 \\ 55,3-54,3 \\ 54,9 \\ 55,3-54,3 \\ 54,9 \\ 55,3-54,3 \\ 54,9 \\ 54,$	24,4 45,6 22,5 47,3 33,5 20,0 34,3 45,9 46,7	18,0 39,5 (3,2) 26,0 (3,2)	19,3 40,7 27,3 (3,2) (3,2)	24,4 22,9 46,3 47,9 20,6 34,3 46,7 34,8 48,5	241 232 232 232 231 231 230 230		

*The chemical shifts of the signals for the dimethylamino group in the ¹H NMR spectra are given in parentheses. +The spectrum of (II) has been given in [9].

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