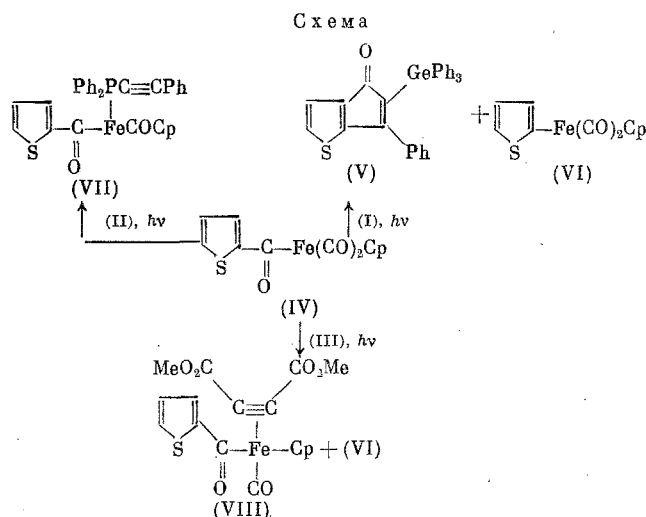


REACTION OF HETEROCYCLIC σ -DERIVATIVES
OF η^5 -CYCLOPENTADIENYLDICARBONYLIRON
WITH ACETYLENES AND THE CRYSTALLINE
AND MOLECULAR STRUCTURE
OF 5-TRIPHENYLGGERMYL-6-PHENYL-4H-CYCLOPENTA[b]-
THIOPHEN-4-ONE

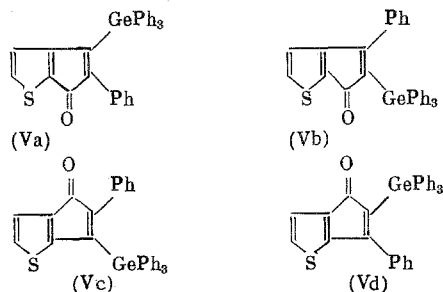
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546.725:547.314:547.733

We studied the photochemical reaction of $\text{Ph}_3\text{GeC}\equiv\text{CPh}$ (I), $\text{Ph}_2\text{PC}\equiv\text{CPh}$ (II), and $\text{MeO}_2\text{CC}\equiv\text{CCO}_2\text{Me}$ (III) with σ -thenoyl complex of η^5 -cyclopentadienyldicarbonyliron (IV) whose properties are typical for heterocyclic σ -derivatives of iron [1] in order to clarify the effect of the acetylene structure and electronic nature of the substituents at the $\text{C}\equiv\text{C}$ bond on the reaction with σ -derivatives of η^5 -cyclopentadienyldicarbonyliron. The reaction of (IV) with acetylenes proceeds by three pathways depending on the nature of the substituents in (I), (II), and (III):



The reaction between (I) and (IV) proceeds analogously to the photochemical reaction of (IV) with toluene [2] which yields cyclization product (V) and the decarbonylated σ -complex (VI). Only one of the four possible structural isomers of (V) was isolated; isomers (Va)-(Vd) may form as a consequence of different orientations of the asymmetric acetylene (I) and different means for the incorporation of the $\text{C}=\text{O}$ group into the ring.



An x-ray diffraction structural study showed that the isomer isolated is 5-triphenylgermyl-6-phenyl-4H-cyclopenta[b]thiophen-4-one (Vd).

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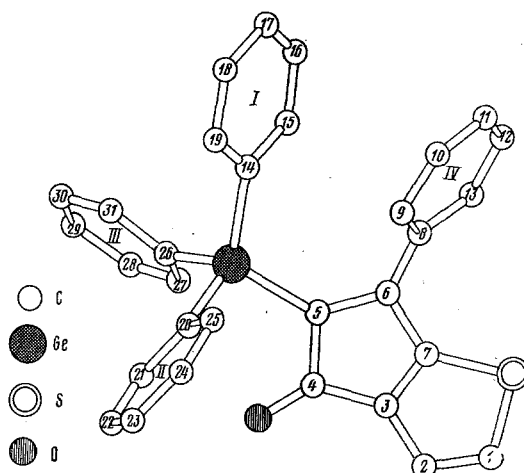


Fig. 1. General view of molecule (Vd) (A) in the crystal and numbering of the atoms.

TABLE 1. Bond Lengths

Bond	d, Å		Bond	d, Å	
	molecule A	molecule B		molecule A	molecule B
Ge—C ⁵	1,946(4)	1,958(4)	C ¹³ —C ¹⁸	1,386(6)	1,413(7)
Ge—C ¹⁴	1,941(4)	1,932(5)	C ¹⁴ —C ¹⁵	1,371(6)	1,401(7)
Ge—C ²⁰	1,959(4)	1,969(4)	C ¹⁵ —C ¹⁶	1,392(8)	1,43(1)
Ge—C ²⁶	1,949(4)	1,953(5)	C ¹⁶ —C ¹⁷	1,312(9)	1,31(1)
S—C ¹	1,710(4)	1,707(5)	C ¹⁷ —C ¹⁸	1,39(1)	1,36(1)
S—C ⁷	1,713(5)	1,705(6)	C ¹⁸ —C ¹⁹	1,384(9)	1,385(8)
O—C ⁴	1,217(6)	1,215(6)	C ¹⁹ —C ¹⁴	1,376(8)	1,370(6)
C ¹ —C ²	1,365(8)	1,380(8)	C ²⁰ —C ²¹	1,404(7)	1,392(7)
C ² —C ³	1,436(6)	1,423(7)	C ²¹ —C ²²	1,425(8)	1,390(8)
C ³ —C ⁴	1,486(6)	1,484(7)	C ²² —C ²³	1,36(1)	1,352(9)
C ⁴ —C ⁵	1,504(6)	1,503(7)	C ²³ —C ²⁴	1,359(9)	1,337(8)
C ⁵ —C ⁶	1,360(6)	1,350(6)	C ²⁴ —C ²⁵	1,385(8)	1,422(8)
C ⁶ —C ⁷	1,492(6)	1,485(6)	C ²⁵ —C ²⁶	1,380(7)	1,370(7)
C ⁷ —C ⁸	1,334(6)	1,359(7)	C ²⁶ —C ²⁷	1,364(7)	1,376(8)
C ⁸ —C ⁹	1,452(6)	1,465(6)	C ²⁷ —C ²⁸	1,375(8)	1,356(9)
C ⁸ —C ⁹	1,398(6)	1,385(7)	C ²⁸ —C ²⁹	1,341(8)	1,388(9)
C ⁹ —C ¹⁰	1,391(7)	1,383(8)	C ²⁹ —C ³⁰	1,379(9)	1,37(1)
C ¹⁰ —C ¹¹	1,370(8)	1,355(9)	C ³⁰ —C ³¹	1,392(8)	1,374(9)
C ¹¹ —C ¹²	1,360(8)	1,378(9)	C ³¹ —C ²⁶	1,368(7)	1,381(7)
C ¹¹ —C ¹³	1,373(8)	1,393(8)			

The crystal contains two independent molecules (A) and (B) which are chemically equivalent. The geometrical parameters of these molecules are identical within the error limits. The structure of molecule (A) is shown in Fig. 1. The bond lengths and bond angles are given in Tables 1 and 2.

The germanium atoms have somewhat distorted tetrahedral coordination: The C—Ge—C bond angles vary in the range from 104.0(2)° to 113.3(2)° in molecule A and from 107.9(2)° to 111.0(2)° in molecule B. The Ge—C bond lengths are in the range 1.941(4)–1.959(4) Å in A and 1.932(5)–1.969(4) Å in B and the mean values are 1.948(4) Å in A and 1.954(1) Å in B. These values are close to those found in the structures of tetraphenylgermanium (1.957(5) [3] and 1.954(1) Å [4]), tetrakis(pentafluorophenyl)germanium (1.957(4) Å [5]), and bis-[tri(pentafluorophenyl)germyl]mercury (II) (1.959(9) Å [6]).

The phenyl substituents at the germanium atoms are planar. The dihedral angles between their planes in the two independent molecules differ significantly: The angles between the planes of the phenyl rings in molecule A (see Fig. 1) are 130.0° for I/II, 94.8° for I/III, and 96.4° for II/III, while in molecule B they are 118.9° for I/II, 64.5° for I/III, and 71.4° for II/III. This difference in the angles in the two independent molecules apparently indicates the possibility of rotation of the phenyl rings in a rather broad range. Analysis using a mechanical molecular model for the possible orientations of the C₆F₅ rings in bis[tri(pentafluorophenyl)germyl]mercury [6] which established the presence of a shallow minimum at about 40° for conformational energy relative to the rotation angle (φ) of the C₆F₅ rings about the Ge—C bonds led to an analogous conclusion. This minimum remains shallow even when the orientation of one of the C₆F₅ rings is fixed.

On the other hand, the dihedral angles between planes I and IV in molecules A (24.4°) and B (17.4°) have similar values. The orientation of these rings is restricted by steric interactions. Indeed, the distances

TABLE 2. Bond Angles

Angle	ω , deg		Angle	ω , deg	
	molecule A	molecule B		molecule A	molecule B
C ⁵ GeC ¹⁴	113,3(2)	111,0(2)	C ⁹ C ¹⁰ C ¹¹	120,2(5)	120,8(5)
C ⁵ GeC ²⁰	106,5(2)	108,9(2)	C ¹⁰ C ¹¹ C ¹²	120,4(5)	119,8(6)
C ⁵ GeC ²⁶	111,0(2)	109,9(2)	C ¹¹ C ¹² C ¹³	120,4(5)	120,8(6)
C ¹⁴ GeC ²⁰	112,4(2)	109,4(2)	C ¹² C ¹³ C ⁸	120,8(5)	119,5(5)
C ¹⁴ GeC ²⁶	104,0(2)	110,0(2)	GeC ¹⁴ C ¹⁹	122,8(4)	122,4(4)
GeC ⁵ C ⁴	119,9(3)	119,9(3)	C ¹⁰ C ¹⁴ C ¹⁵	118,1(5)	115,8(5)
GeC ⁵ C ⁶	132,7(3)	131,8(3)	C ¹⁴ C ¹⁵ C ¹⁶	121,4(5)	120,8(5)
C ¹ SC ⁷	91,0(2)	91,2(2)	C ¹⁵ C ¹⁶ C ¹⁷	120,9(6)	118,1(6)
SC ¹ C ²	112,8(4)	113,1(4)	C ¹⁶ C ¹⁷ C ¹⁸	119,0(7)	118,6(8)
C ¹ C ² C ³	110,2(4)	110,2(5)	C ¹⁷ C ¹⁸ C ¹⁹	121,1(8)	123,3(8)
C ² C ³ C ⁷	113,6(4)	113,3(4)	C ¹⁸ C ¹⁹ C ¹⁴	119,5(6)	121,4(7)
C ⁷ C ³ C ⁴	106,7(4)	106,5(4)	GeC ²⁰ C ²¹	120,9(4)	121,6(4)
C ³ C ⁴ O	128,9(4)	126,9(4)	GeC ²⁰ C ²⁵	119,1(4)	119,4(4)
C ³ C ⁴ C ⁵	106,1(3)	106,3(4)	C ²⁵ C ²⁰ C ²¹	119,9(5)	119,0(5)
OC ⁴ C ⁵	125,0(4)	126,7(4)	C ²⁰ C ²¹ C ²²	117,3(5)	120,0(5)
C ⁴ C ⁵ C ⁶	108,2(3)	108,1(4)	C ²¹ C ²² C ²³	121,4(6)	120,9(6)
C ⁵ C ⁶ C ⁷	106,9(3)	108,1(4)	C ²² C ²³ C ²⁴	120,3(7)	119,8(6)
C ⁵ C ⁶ C ⁸	131,1(4)	130,9(4)	C ²³ C ²⁴ C ²⁵	120,2(6)	121,4(6)
C ⁷ C ⁶ C ⁸	121,9(3)	121,0(4)	C ²⁴ C ²⁵ C ²⁰	120,9(5)	118,9(5)
C ⁶ C ⁷ S	135,4(3)	136,7(3)	GeC ²⁶ C ²⁷	126,7(3)	120,2(4)
C ⁶ C ⁷ C ³	112,0(4)	110,9(4)	GeC ²⁶ C ³¹	116,5(4)	122,2(4)
SC ⁷ C ²	112,3(3)	112,2(3)	C ³¹ C ²⁶ C ²⁷	116,4(4)	117,6(5)
C ⁸ C ⁶ C ⁹	121,5(4)	122,3(4)	C ²⁶ C ²⁷ C ²⁸	121,7(5)	122,1(6)
C ⁸ C ⁶ C ¹³	119,9(4)	119,8(4)	C ²⁷ C ²⁸ C ²⁹	121,3(5)	120,3(7)
C ⁸ C ⁶ C ¹⁰	119,6(4)	121,2(5)	C ²⁸ C ²⁹ C ³⁰	119,3(5)	118,0(7)
C ¹³ C ⁶ C ⁹	118,5(4)	117,9(4)	C ²⁹ C ³⁰ C ³¹	118,4(5)	121,4(1)
			C ³⁰ C ³¹ C ²⁶	122,7(5)	120,5(5)

C⁸...C¹⁵ (3.321(7) and 3.270(6) Å), C⁹...C¹⁴ (3.244(6) and 3.178(7) Å), and C⁹...C¹⁵ (3.266(7) and 3.270(6) Å) in A and B, respectively, are shortened relative to twice the van der Waals radius of the carbon atom (3.4 Å) [7]. In addition, deformation is found in the external bond angles at C⁵ and C⁶: angles C⁵C⁶C⁸ (131.1(4)° and 130.9(4)°) are greater than angles C⁷C⁶C⁸ (121.9(3)° and 121.0(4)°), while angles GeC⁵C⁶ (132.7(3)° and 131.8(3)°) are greater than angles GeC⁵C⁴ (119.0(3)° and 119.9(3)°). In the case of such pressure in the "upper" part of the molecule, shortened intramolecular contacts between the oxygen atom and the carbon atoms of phenyl rings II and III are lacking in its "lower" part. On the other hand, the Ge...O distance (3.226(3) Å in A and 3.292(4) Å in B) is less than the sum of the van der Waals radii (3.47 Å) of the germanium atom (1.95 Å [7]) and oxygen atom (1.52 Å [7]).

The short contacts between the carbon atoms of phenyl rings I and IV may be eliminated by some rotation about the Ge-C¹⁴ bond. Such a rotation would lead to equalization of the exocyclic bond angles at C⁵ and, thus, to a lengthening of the Ge...O distance. A simple geometric construction shows that when angles GeC⁵C⁴ and GeC⁵C⁶ are equal, the Ge...O distance would increase to about 3.4 Å, i.e., would be equal to the sum of the van der Waals radii. The reason for the absence of such a rotation about the Ge-C⁵ bond apparently cannot be a "retarding effect" of phenyl rings II and III since, as discussed above, the orientation of these rings may vary in a relatively broad range, which, in principle, should permit these rings to adjust to the geometric and steric requirements of the remainder of the molecule. These features of the molecular geometry may apparently be attributed to weak intramolecular secondary Ge...O bonds.

The oxygen atom is located above the face of the tetrahedron at the germanium atom formed by C⁵, C²⁰, and C²⁶ and the inequality found for the exocyclic bond angles at C⁵ leads not only to approximation of the Ge and O atoms but also to a position of the oxygen atom closer to the extrapolation of the line defined by the C¹⁴-Ge bond (the O...Ge-C¹⁴ angle is 160.4° in A and 156.6° in B) than when the angles at C⁵ are not distorted. A geometrical analysis shows that when the exocyclic bond angles for C⁵ are equal and there is coplanarity of the Ge-C¹⁴ bond to the plane of the cyclopentadienyl fragment, the O...Ge-C¹⁴ angle is 152°. If we exclude the condition of coplanarity, this angle will be even smaller. The position of the oxygen heteroatom found in the structure of (Vd) relative to the tetrahedron at the germanium atom is characteristic for weak secondary bonds in Sn and Pb derivatives [8]; it is a model for the initial stages of nucleophilic substitution at M atoms by the S_N2 mechanism [9].

Although the formation of secondary bonds for the germanium atom and its organic derivatives is less characteristic than for tin and lead atoms, there are examples in the literature, in which the germanium atom has fivefold or even trigonal-bipyramidal coordination. The germathrane structures are such examples [10-12]. By analogy with tin and lead derivatives, we may assume that germathranes are models for the intermediate stage of nucleophilic substitution at the Ge atom, while molecule (Vd) is a model for the initial stage of this reaction.

TABLE 3. UV Spectral Data for Indenone Heteroanalogs in CH₂Cl₂

Compound	Structural formula	Color	UV spectrum: $\lambda_{\max}$, nm (log ϵ)
(Vd)		Red	265(4,52), 463(3,55)
(IX)		"	267(4,67), 448(3,44)
(X)		"	267(4,47), 470(3,66)
(XI)		"	259(4,59), 263(4,58), 464(3,88)
(XII)		Dark violet	267(4,40), 510(3,10)

Phenyl group IV is twisted from the plane of the cyclopentadienyl fragment by 53.0° in A and 48.8° in B as a result of steric strain. Thus, the conjugation between these fragments is disrupted in (Vd). The C⁶-C⁸ bond lengths (1.452(6) Å in A and 1.465(6) Å in B) are close to the standard value for the length of the C_{sp²}-C_{sp²} single bond (1.476 Å [13]). The double bonds are localized in the planar cyclopentadienyl ring: The shortest are C⁵-C⁶ (1.360(6) and 1.350(6) Å) and C³-C⁷ (1.334(6) and 1.359(7) Å in A and B) are only slightly longer than the standard length of the C=C double bond (1.333 Å [13]). The other bond lengths in this ring C⁶-C⁷ (1.492(6) and 1.485(6) Å), C⁴-C⁵ (1.504(6) and 1.503(7) Å), and C³-C⁴ (1.486(6) and 1.484(7) Å in A and B, respectively) also are somewhat longer than the standard value (1.476 Å). The C=O bond has standard length (0.217(6) and 1.215(6) Å). The thiophene ring is planar and coplanar to the cyclopentadienyl ring condensed to it. The S-C bond lengths in molecules A and B are in the range from 1.705(6) to 1.713(5) Å, which are identical to those found for thiophene [14] and its derivatives [15]. The C-C bond lengths in the thiophene fragment of (Vd) as in thiophene itself alternate: C¹-C² is 1.315(8) and 1.380(8) Å, C³-C⁷ is 1.334(6) and 1.359(7) Å, C²-C³ is 1.436(6) and 1.423(7) Å in A and B, respectively. The short C-C bond lengths in thiophene are 1.370 Å and the longer C-C bond lengths are 1.423 Å.

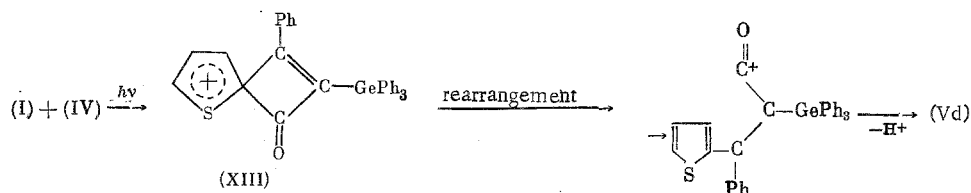
Comparison of the UV spectral data for the germyl-substituted thiaindenone (Vd) and of previously prepared thiaindenone (IX) and oxaindenones (X) and (XI) [2] showed that these compounds have absorption maxima in the visible range which are similar in position and intensity (Table 3). All these compounds, including (Vd), are red. On the other hand, the UV spectrum of the violet thiaindenone (XII) obtained by the irradiation of (IV) with toluene [2] features an absorption maximum in the visible region which is significantly shifted toward longer wavelengths ($\Delta\lambda$ 50-60 nm). These differences in the UV spectra may result from structural features of the compounds studied, specifically, the C=O group in the indenone ring in (Vd) and (IX)-(XI) is at C⁴ in (Vd), (IX), and (X) and at C¹ in tricyclic oxaindenone (XI) which are the furthest positions from the heteroatom in these molecules, while the C=O group in (XII) is at C⁶ which is the closest position to the sulfur atom. The greater conjugation of the C=O group with the heteroatom in (XII) apparently produces a bathochromic shift of the absorption maximum in the visible region (see Table 3).

Migration of the C=O group to C⁴ in (Vd) may be a result of rearrangement of an intermediate spirocyclic complex (XIII)

TABLE 4. ^{31}P NMR Spectra of Phosphorus-Containing Heterocyclic σ -Derivatives of Iron in CH_2Cl_2

Compound	Structural formula	δ , ppm
(VII)		57,03
(II)	$\text{Ph}_3\text{P}\cdot\text{C}\equiv\text{CPh}$	-33,71
(XIV)		74,25
(XV)		76,80
-	PPh_3	-5,9 *

*According to Koslapoff [19].



We note that such a rearrangement was found in the formation of indenones upon the condensation of aroyl chlorides with 3-hexyne in the presence of AlCl_3 [16].

The other physicochemical and spectral indices of (Vd) are analogous to those described previously for indenone heteroanalogs [2] (see Experimental).

The replacement of the Ph_3Ge group by Ph_2P leads to a change in the direction of the reaction scheme above). The coordination of (II) with the iron atom through the phosphorus free electron pair occurs with the formation of complex (VII) and the $\text{C}\equiv\text{C}$ bond of ligand (II) does not participate in the reaction. The IR spectrum of (VII) has a band at 1943 cm^{-1} corresponding to the stretching vibrations of the terminal $\text{C}\equiv\text{O}$ group and a band for the ketone $\text{C}=\text{O}$ group at 1565 cm^{-1} . The positions of the $\nu\text{C}\equiv\text{O}$ and $\nu\text{C}=\text{O}$ bands are analogous to those for the corresponding groups in the triphenylphosphine heterocyclic σ -complexes of iron [1]. The IR spectrum of (VII) also contains a band at 2165 cm^{-1} which corresponds to stretching vibrations of the uncoordinated $\text{C}\equiv\text{C}$ bond of the acetylenic ligand ($\nu\text{C}\equiv\text{C}$ of free acetylene (II) is found at 2170 cm^{-1} [17]).

The ^{31}P NMR spectra of (II) and (VII) (Table 4) shows a significant difference in the position of the phosphorus atom signal which appears about 90 ppm upfield for (VII) relative to (II). An analogous shift due to a change in the electronic state of the phosphorus atom is also noted in the ^{31}P NMR spectrum of triphenylphosphine derivatives of σ -thienyl (XIV) and σ -thenoyl (XV) complexes of iron for the conversion of PPh_3 from the free to the coordinated state. The replacement a PPh_3 phenyl group by a phenylethynyl group produces an upfield shift of the phosphorus atom signal by 20-25 ppm both in the spectrum of the free ligand (II) and in the spectrum of σ -complex (VII) (see Table 4). We should note that the replacement of a phenyl group by an ethynyl group causes an analogous effect in the ^{13}C NMR spectrum in the case of ferrocenyl derivatives [18]. Thus, the spectral data indicate coordination of acetylene (II) with the Fe atom through the phosphorus free electron pair and not through the $\text{C}\equiv\text{C}$ bond.

The introduction of acetylene (III) which contains electron-withdrawing CO_2Me groups in the reaction with (IV) leads to the formation of an unstable product (VIII) which, in our opinion, contains a π -bonded acetylenic

TABLE 5. Atomic Coordinates ($\times 10^4$, Ge $\times 10^5$)

Atom	Molecule A			Molecule B		
	X	Y	Z	X	Y	Z
Ge	29122(4)	41828(3)	71678(3)	19574(5)	98742(3)	21387(3)
S	6333(1)	7140(1)	6110(1)	5666(1)	12687(1)	1032(1)
O	5971(3)	4475(2)	7000(2)	1091(3)	11527(2)	1773(2)
C ¹	7779(4)	6964(3)	6183(3)	4652(5)	13395(3)	1044(3)
C ²	7700(4)	6208(3)	6395(3)	3370(5)	13093(3)	1282(3)
C ³	6403(3)	5774(3)	6506(3)	3248(4)	12263(3)	1449(3)
C ⁴	5620(4)	5027(3)	6805(3)	2243(4)	11550(3)	1668(3)
C ⁵	4255(3)	5067(3)	6816(2)	2937(4)	10846(3)	1710(3)
C ⁶	4236(3)	5776(3)	6569(2)	4212(4)	11094(3)	1500(2)
C ⁷	5591(4)	6193(2)	6373(2)	4396(4)	11984(3)	1354(2)
C ⁸	3173(4)	6156(2)	6522(2)	5317(4)	10629(3)	1392(3)
C ⁹	2090(4)	6411(3)	7233(3)	5406(5)	9659(3)	907(3)
C ¹⁰	1098(4)	6780(3)	7162(3)	6448(6)	9233(4)	828(3)
C ¹¹	1177(5)	6883(3)	6397(4)	7407(5)	9754(4)	1231(4)
C ¹²	2233(5)	6642(4)	5706(4)	7351(5)	10721(4)	1721(4)
C ¹³	3231(4)	6289(3)	5765(3)	6324(5)	11173(3)	1804(3)
C ¹⁴	1264(4)	4210(3)	6980(3)	3072(4)	9258(3)	2375(3)
C ¹⁵	1221(4)	4162(3)	6173(3)	3936(5)	9782(3)	2912(3)
C ¹⁶	58(5)	4117(4)	5979(4)	4754(6)	9362(4)	3075(4)
C ¹⁷	-1037(5)	4112(5)	6563(4)	4691(8)	8341(5)	2692(6)
C ¹⁸	-1024(5)	4168(7)	7391(5)	3899(7)	7859(4)	2174(6)
C ¹⁹	118(5)	4193(5)	7592(4)	3106(6)	8278(4)	1999(5)
C ²⁰	2824(4)	4497(3)	8418(3)	668(4)	10485(3)	3247(3)
C ²¹	2118(5)	5239(4)	9109(2)	885(5)	10738(4)	4081(3)
C ²²	2174(7)	5462(5)	9995(4)	-38(6)	11183(4)	4849(3)
C ²³	2879(7)	4974(5)	10166(4)	-1163(6)	11359(4)	4800(4)
C ²⁴	3555(6)	4258(5)	9487(4)	-1389(5)	11116(4)	4004(4)
C ²⁵	3529(5)	4018(4)	8615(3)	-478(5)	10654(3)	3199(3)
C ²⁶	3322(4)	2868(3)	6442(3)	1042(4)	8930(3)	1259(3)
C ²⁷	4412(5)	2569(3)	5792(3)	155(6)	8249(4)	1464(4)
C ²⁸	4578(5)	1617(4)	5297(4)	-487(6)	7571(4)	869(5)
C ²⁹	3646(6)	941(3)	5402(3)	-277(6)	7553(4)	25(4)
C ³⁰	2503(6)	1206(3)	6025(4)	580(7)	8244(5)	-179(4)
C ³¹	2365(5)	2174(3)	6529(4)	1284(5)	8913(4)	419(3)

ligand. The proposed structure for (VIII) is in accord with the IR and mass spectra. The band at 1975 cm^{-1} in the IR spectrum of (VIII) corresponds to stretching vibrations of the terminal carbonyl group and the strong band at 1710 cm^{-1} apparently corresponds to the stretching vibrations of the coordinated $\text{C}\equiv\text{C}$ bond of the acetylenic ligand. The less intense band at 1725 cm^{-1} corresponds to the stretching vibrations of the ester carbonyl group and the band at 1520 cm^{-1} corresponds to stretching vibrations of the ketone carbonyl group. The strong shift of the $\nu\text{C}\equiv\text{C}$ band towards lower frequencies upon conversion of the acetylenic ligand from the free to the coordinated state is characteristic for π -acetylenic complexes of transition metals [20]. The appearance of the stretching band for the ketone carbonyl group also at very low frequencies is typical for acyl ion σ -complexes [1]. The mass spectrum of (VIII) has a low-intensity molecular ion peak (m/z 402). The fragmentation proceeds with the consecutive splitting of the terminal and acyl CO groups and then the π -acetylenic ligand. The further decomposition of (VIII) by the action of electron impact is characteristic for iron-containing heterocyclic σ -derivatives [21].

Attempts to effect intramolecular cyclization of complex (VIII) were unsuccessful.

EXPERIMENTAL

X-Ray Diffraction Structural Analysis of (Vd). Crystals of (Vd) ($\text{C}_{31}\text{H}_{22}\text{GeOS}$) are triclinic with $a=10.956(2)$, $b=15.678(4)$, $c=17.194(4)$ Å, $\alpha=116.03(1)^\circ$, $\beta=72.34(1)^\circ$, $\gamma=102.16(2)^\circ$, $V=2518(1)$ Å³, $d_{\text{calc}}=1.33\text{ g/cm}^3$, $Z=4$, sp. gr. $\text{P}\bar{1}$.

The unit cell parameters and intensities of 7112 independent reflections with $F > 2\sigma$ were measured on an automatic four-circle Hilger Watts diffractometer with $\lambda\text{CuK}\alpha$ radiation, graphite monochromator, $\theta/2\theta$ scanning, $2\theta_{\text{max}}=128^\circ$. Absorption was not taken into account ($\mu(\text{CuK}\alpha)=26.9\text{ cm}^{-1}$).

The structure was deciphered by the heavy atom method and refined by the method of least squares in the anisotropic full-matrix approximation. All the hydrogen atoms in their geometrically calculated positions with fixed coordinates and isotropic temperature factors $B_{\text{iso}}=8.0\text{ Å}^2$ were included in the final refinement stage. The final refinement led to $R=0.0486$ ($R_w=0.0798$) for 6673 reflection with $F > 5\sigma$. The coordinates of all the atoms are given in Table 5. The temperature factor tables may be obtained from the authors.

The photochemical reaction was carried out in a Schlenk tube in an inert atmosphere cooled with a water flow. A PRK-4 200-W quartz lamp was used with emission maximum at 365 nm. The IR spectra were taken on

a UR-20 spectrometer in CH_2Cl_2 . The mass spectra were taken on an MS-30 mass spectrometer with a DS-50 data treatment system at 30°C inlet temperature and 180°C source temperature. The ionizing voltage was 70 V. The $^{31}\text{P}-\{\text{H}\}$ NMR spectra were taken on a Bruker-90 spectrometer at 36.43 MHz using 85% H_3PO_4 as the standard. The UV spectra were taken on a Perkin-Elmer 402 spectrophotometer. Type L silica gel (160–250 μm) was used for chromatography.

5-Triphenylgermyl-6-phenyl-4H-cyclopenta[b]thiophen-4-one (V). A solution of 0.29 g (1 mmole) (IV) and 0.4 g (1 mmole) (I) in 100 ml benzene was irradiated for 4 h. After solvent removal, the residue was subjected to column chromatography with petroleum ether– CH_2Cl_2 eluent with gradual increase in the CH_2Cl_2 content. The yellow first zone yielded 0.04 g (16%) decarbonylated σ -complex (VI) identified by thin-layer chromatography on Silufol and IR spectroscopy. The dark red second zone yielded 0.26 g (51%) red crystalline (V) with mp 190–191°C (hexane). Found: C 72.33; H 3.96; Ge 14.41%. $\text{C}_{31}\text{H}_{22}\text{GeOS}$. Calculated: C 72.23; H 4.27; Ge 14.10%. IR spectrum: 1708 cm^{-1} ($\nu\text{C}=\text{O}$). Mass spectrum: 512 (M) $^{+}$, 484 ($\text{M}-\text{CO}$) $^{+}$, 435 ($\text{M}-\text{Ph}$) $^{+}$, 407 ($\text{M}-\text{CO}-\text{Ph}$) $^{+}$, 301 (Ph_3Ge) $^{+}$, 288 ($\text{M}-\text{Ph}_3-\text{Ge}$) $^{+}$.

σ -Thenoyl- η^5 -cyclopentadienyl (phenylethynyldiphenylphosphine) (monocarbonyl)iron (VII). A solution of 0.51 g (1.77 mmole) (IV) and 0.6 g (2.1 mmoles) (II) in 120 ml benzene was irradiated for 5 h. After column chromatography of the reaction mixture with petroleum ether– CH_2Cl_2 eluent we obtained 0.42 g (43%) (VII) with mp 163–165°C (from 10:1 petroleum ether– Et_2O). Found: C 68.29; H 4.23; P 5.39%. $\text{C}_{31}\text{H}_{23}\text{FeOPS}$. Calculated: C 68.14; H 4.24; P 5.67%. IR spectrum (νCO): 2165, 1943, 1565 cm^{-1} . Mass spectrum ($\text{L}=\text{Ph}_2\text{PC}\equiv\text{CPh}$): 286 (L) $^{+}$, 260 ($\text{M}-\text{L}$) $^{+}$, 232 ($\text{M}-\text{CO}-\text{L}$) $^{+}$, 204 ($\text{M}-\text{L}-\text{Fe}$) $^{+}$, 186 [$(\text{C}_5\text{H}_5)_2\text{Fe}$] $^{+}$, 178 (Ph_2C_2) $^{+}$, 121 ($\text{C}_5\text{H}_5\text{Fe}$) $^{-}$, 111 ($\text{C}_4\text{H}_3\text{SCO}$) $^{+}$, 89 (PhC_2) $^{+}$, 83 ($\text{C}_4\text{H}_3\text{S}$) $^{+}$, 56 (Fe) $^{+}$.

σ -(2-Thenoyl- η^5 -cyclopentadienyl- η^2 -dicarbomethoxyacetylene)carbonyliron (VIII). A solution of 0.75 g (2.6 mmole) (IV) and 0.4 g (2.6 mmole) (III) in 120 ml benzene was irradiated for 5 h. After solvent removal, the reaction mixture was subjected to column chromatography in an argon stream. Fraction 1 using 15:1 petroleum ether– Et_2O eluent yielded 0.08 g (12%) (VI) and fraction 2 using 10:1 petroleum ether– Et_2O eluent yielded 0.15 g unreacted (IV). Fraction 3 using 1:1 petroleum ether– CH_2Cl_2 yielded 0.56 g (53%) dark green (VIII) as an oil. IR spectrum (νCO): 1975, 1710, 1525 cm^{-1} . Mass spectrum [$\text{L}=\text{MeO}_2\text{CC}\equiv\text{CCO}_2\text{Me}$]: 402 (M) $^{+}$, 374 ($\text{M}-\text{CO}$) $^{+}$, 346 ($\text{M}-2\text{CO}$) $^{+}$, 204 ($\text{M}-2\text{CO}-\text{L}$) $^{+}$, 186 [$(\text{C}_5\text{H}_5)_2\text{Fe}$] $^{+}$, 142 (L) $^{+}$, 121 ($\text{C}_5\text{H}_5\text{Fe}$) $^{+}$, 111 ($\text{C}_4\text{H}_3\text{COS}$) $^{+}$, 93 ($\text{C}_3\text{H}_3\text{Fe}$) $^{+}$, 83 ($\text{C}_4\text{H}_3\text{S}$) $^{+}$, 56 (Fe) $^{+}$.

CONCLUSIONS

1. The reaction of σ -thenoyl- η^5 -cyclopentadienyldicarbonyliron with acetylenes may proceed by three different pathways depending on the acetylene structure: 1) formation of indenone heteroanalogs due to cyclization of the σ -ligand and acetylene (tolane, 1-triphenylgermyl-2-phenylacetylene), 2) replacement of a carbonyl group by an n-donor ligand in the case of an n-donor atom in the acetylene (2-phenylethynyldiphenylphosphine), and 3) formation of a π -acetylenic complex (dicarbomethoxyacetylene).

2. X-ray diffraction structural analysis showed that the product of the reaction of σ -thenoyl- η^5 -cyclopentadienyldicarbonyliron with 1-triphenylgermyl-2-phenylacetylene is 5-triphenylgermyl-6-phenyl-4H-cyclopenta[b]thiophen-4-one.

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SYNTHESIS OF POLYSACCHARIDES

COMMUNICATION 13. SYNTHESIS OF 1,3-GLUCAN

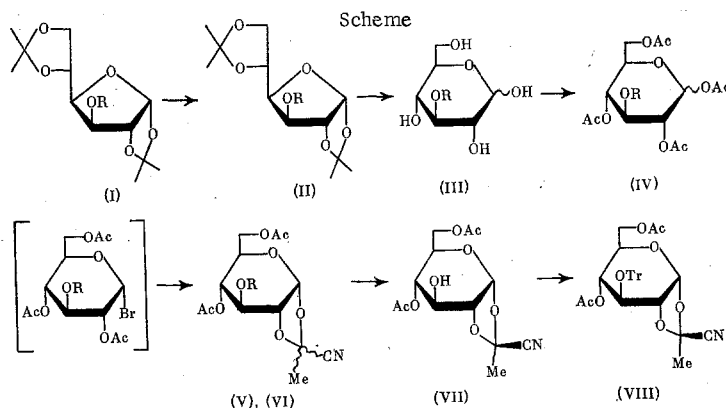
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Our method for the synthesis of regular polysaccharides based on the polycondensation of O-trityl ethers of 1,2-cyanoethylidene derivatives of mono- and oligosaccharides is the first procedure which permits the preparation of a series of regular homo- and heteropolysaccharides, in which the repeating units are linked by 1,2-trans glycoside bonds [1].

In an attempt to expand this approach and determine the limits of its applicability, we undertook the synthesis of glucan with a β -1,3-bond; polysaccharides of this type are common in nature [2]. Most of the polysaccharides which have been synthesized belong to the 1,6-type, in which the repeating glycoside bond contains a primary alcoholic hydroxyl [1]. On the other hand, a method is known for the synthesis of α -1,3- [3] and α -1,4-rhamnan [4] which demonstrates the applicability of this approach for the preparation of polysaccharides with a bond involving a secondary alcoholic hydroxyl. An attempt to further expand the limits of this method in this direction was the basis for the synthesis described below.

The factor hindering the expansion of this method in the indicated direction was the preparation of a monomer with the desired structure, in this case, 3-O-trityl-4,6-di-O-acetyl-1,2-cyanoethylidene-glucopyranose (VIII). The lack of methods for the selective tritylation of secondary hydroxyls in sugars and the impossibility of introducing the cyanoethylidene group after introduction of the trityl group excluded the use of the simple scheme for the synthesis of monomers which had been used.



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