were taken on a Specord 75-IR spectrometer at from 4000 to 400 cm^{-1} and on a Perkin–Elmer 325 spectrometer at from 450 to 200 cm^{-1} for KBr and CsI pellets and Vaseline mull. The electronic spectra were taken on a Specord UV-VIS spectrophotometer.

The authors thank O. N. Krasochka for a preliminary x-ray diffraction analysis of this complex.

CONCLUSIONS

A platinum(II) complex of chloroanilic acid was synthesized. This complex is isostructural to the analogous palladium complex and has the formula $[Pt(C_6O_4Cl_2)Cl_2]K_2 \cdot H_2O$.

LITERATURE CITED

1. USSR Inventor's Certificate No. 690,006; Byull. Izobret., No. 37 (1979); USSR Inventor's Certificate No. 760,995; Byull. Izobret., No. 39 (1980); USSR Inventor's Certificate No. 773,039; Byull. Izobret., No. 39 (1980).
2. E. G. Chepaikin and M. L. Khidekel', Koordinats. Khim., 4, 644 (1978).
3. A. V. Bulatov, É. N. Izakovich, L. N. Karklin', and M. L. Khidekel', Izv. Akad. Nauk SSSR, Ser. Khim., 2032 (1981).
4. O. N. Krasochka, V. A. Avilov, and L. O. Atovmyan, Zh. Strukt. Khim., 15, 1140 (1974).
5. Handbook for the Synthesis of Platinum-Group Metal Complexes [in Russian], Nauka, Moscow (1964), p. 9.

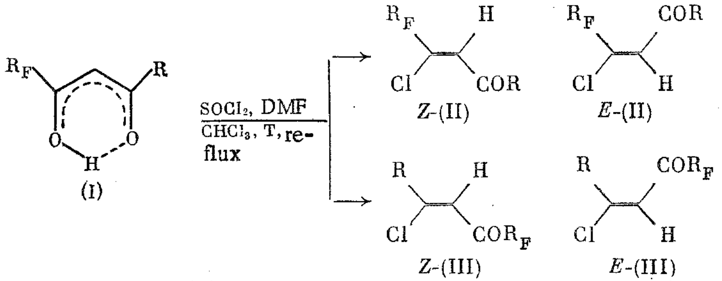
SYNTHESIS AND STRUCTURE OF FLUORINATED β-CHLOROVINYL KETONES

K. I. Pashkevich, M. B. Bobrov, A. Ya. Aizikovich,
and M. N. Rudaya

UDC 542.91:541.6:547.446.5

Symmetrical fluorinated β-diketones react with $SOCl_2$ to form β-chlorovinyl ketones [2, 3] similarly to their hydrocarbon analogs [1]. For unsymmetrically polyfluorinated β-diketones (I) this reaction has not been studied, although the presence of two inequivalent electrophilic sites makes possible the formation of isomeric β-chlorovinyl ketones (II) and (III). In the only study on the substitution of an OH group by chlorine in the enol forms of β-diketones containing a partially fluorinated phenyl group in addition to a perfluoroalkyl substituent, the structures of the products formed were not established [4].

We have investigated the reaction of unsymmetrical polyfluorinated β-diketones (Ia-n) with $SOCl_2$ and the structures of the β-chlorovinyl ketones (II) and (III) formed



$R_F = CF_3$: R = Me(a), CMe_3(b), $CHMe_2$(c), p-C_6H_4X, where X = H(d), OMe(e), Me(f), Cl(g), Br(h), n-Bu(i), $R_F = H(CF_2)_2$: R = Me(j), $CHMe_2$(k), CMe_3(ℓ), Ph (m).

Fluorinated λ-diketones (Ib, c, k, ℓ) which contain bulky alkyl substituents react with $SOCl_2$ in the presence of catalytic amounts of DMF to form only β-chlorovinyl ketones with the chlorine atom in the γ-position to the fluorinated substituent, namely the corresponding

---

Institute of Chemistry, Urals Science Center, Academy of Sciences of the USSR, Sverdlovsk. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 9, pp. 2125-2127, September, 1986. Original article submitted August 8, 1985.

0568-5230/86/3509-1937$12.50

TABLE 1. Yields, Isomer Ratios, and Elemental Analysis Data for Fluorinated β-Chlorovinyl Ketones

Starting β-diketone	Reaction products								
	Bp, °C* (p, mm Hg)	Yield, %	isomer ratio of			chemical formula	found/calculated, %		
			Z-(II)	Z-(III)	E-(III)		C	H	Cl
(Ib)	169–171	86	–	100	–	$C_8H_{10}ClF_3O$	44,76 44,98	4,66 4,91	16,43 16,60
(Ic)	165–166	52		100		$C_7H_8ClF_3O$	41,89 41,92	3,94 4,02	17,30 17,67
(Id)	92–96 (10)	59	53	33	14	$C_{10}H_6ClF_3O$	51,19 51,37	2,57 2,68	15,11 15,32
(Ie)	90–95 (10)	51	71	18	11	$C_{11}H_8ClF_3O_2$	50,02 49,93	3,46 3,05	13,58 13,40
(If)	70–77 (8)	65	53	36	11	$C_{11}H_8ClF_3O$	53,62 53,14	3,69 3,28	14,21 14,26
(Ig)	80–90 (8)	67	75	21	4	$C_{10}H_5Cl_2F_3O$	44,55 44,64	2,10 1,87	27,01 26,35
(Ih)	107–112 (10)	75	85	12	3	$C_{10}H_5BrClF_3O$	38,26 38,31	1,61 1,61	11,20 11,31
(Ik)	70–71 (15)	57	–	100	–	$C_8H_9ClF_4O$	41,09 40,74	3,96 4,04	15,24 15,59
(Il)	50–51 (10)	71	–	100	–	$C_9H_{11}ClF_4O$	43,83 43,74	4,50 4,54	14,37 14,10
(Im)	135–144 (10)	66	31	50	19	$C_{11}H_7ClF_4O$	49,55 50,04	2,64 3,06	13,29 13,81

*The boiling points for the isomer mixture are given for the aryl-substituted compounds.

†By gas-liquid chromatographic analysis.

TABLE 2. IR and PMR Spectral Data and Dipole Moments for β-Chlorovinyl Ketones (II) and (III)

Compound	PMR spectrum, δ, ppm, CH=	IR spectrum, ν, cm^{-1}		Dipole moment, D	
		C=O	C=C	μ_{calc}	μ_{exp}
Z-(IIIb)	6,9	1730	1600	4,29	4,22
Z-(IIIc)	6,85	1727	1600	4,29	4,08
Z-(IId)	7,62	1680	1600	4,48	4,20
Z-(IIId)	7,35	1720	1590	3,78	3,59
E-(IIId)	7,11	1722	1575	1,28	0,90
Z-(IIe)	7,69	1675	1600	4,74 *	4,82 *
Z-(IIIe)	7,60	1715	1585		
E-(IIIe)	7,22	1720	1580		
Z-(IIf)	7,65	1680	1610		
Z-(IIIf)	7,50	1720	1585	4,25 *	4,27 *
E-(IIIf)	7,32	1722	1570		
Z-(IIg)	7,67	1682	1590	2,50 *	2,35 *
Z-(IIIg)	7,40	1720	1580		
Z-(IIh)	7,60	1680	1600	2,52 *	2,48 *
Z-(IIIh)	7,35	1720	1590		
Z-(IIIk)	7,00	1715	1600		3,27
Z-(IIIl)	7,02	1720	1600		3,39
Z-(IIm)	7,50	1680	1600		3,39
Z-(IIIm)	7,48	1712	1585		3,81
E-(IIIm)	7,29	1710	1575		2,56

*The dipole moments were calculated and determined for the isomer mixtures, whose compositions were determined by gas-liquid chromatographic analysis.

Z-(III) (Table 1). This was established by obtaining β-aminovinyl ketones of known structure from this chloride [5]. β-Diketones (Ia, i, j) with unbranched alkyl substituents react with $SOCl_2$ to form tars, from which the corresponding β-chlorovinyl ketones could not be isolated.

Under the same conditions, β-diketones (Id-h, m) give a mixture of three isomeric β-chlorovinyl ketones, namely the corresponding Z-(II), E- and Z-(III).

The introduction of a para substituent into the phenyl ring leads to an increase in the fraction of isomer (II) without regard to the nature of this substituent. The formation of the E-(II) isomer could not be established in any of the cases studied. This failure is apparently a consequence of the stereospecific course of the reaction at the electrophilic site bound to the fluoroalkyl substituent, in accord with the formation of 1,1,1,5,5,5-hexafluoro-2-chloro-2-penten-4-one exclusively with Z configuration by the reaction of $SOCl_2$ with hexafluoroacetylacetone. The assignment of structural isomers (II) and (III) was made on the basis of the preparation of β-aminovinyl ketones from these isomers, corresponding to compounds of known structure [6] and confirmed by PMR spectroscopy. The methine proton signal δCH= of isomers (II) are shifted downfield and are multiplets due to coupling with the fluorine atoms in the fluoroalkyl group, while this signal is a singlet for isomers (III) (analogous behavior is observed in fluorinated β-aminovinyl ketones [6]). In addition, the νC=O bands for isomers (III) are 30-40 cm^{-1} lower and the νC=C bands for these isomers are 10-20 cm^{-1} lower than the corresponding frequencies of isomers (II). This behavior may also be used for their identification.

The structures of the fluorinated β-chlorovinyl ketone isomers were established by dipole moment measurements (Table 2). As in the case of their hydrocarbon analogs [7], δCH= of the E isomers lie at higher field than for the Z isomers (Δδ = 0.2 ppm), while νC=C is shifted by 15-25 cm^{-1} toward lower frequencies (see Table 2).

EXPERIMENTAL

The IR spectra of (II) and (III) were taken neat on a UR-20 spectrophotometer and the PMR spectra were taken on a Perkin—Elmer R-12B spectrometer for 5% CCl_4 solutions at 35°C with TMS as the internal standard.

The experimental dipole moments were calculated by the Guggenheim—Smith method [8]. The dielectric constants were found using a Tangens-2M permittivity meter in benzene at 25 ± 0.1°C and 1 MHz. The group dipole moments from the monograph of Minkin et al. [9] were used for calculating the dipole moments according to the vector scheme. The gas-liquid chromatographic analysis was carried out on an LKhM-72 chromatograph using a 2-m column packed with 5% SE-30 on Chromaton N-AW-DMCS. The helium gas carrier flow rate was 30 cm^3/min.

β-Chlorovinyl Ketones (IIIb, c, k, ℓ). A sample of 2 ml DMF was added to a solution of 14.3 g (0.12 mole) $SOCl_2$ in 100 ml $CHCl_3$ and then 0.1 mole β-diketone (I) was added slowly. The reaction mixture was heated at reflux until HCl was no longer liberated and poured onto ice. The lower layer was separated, washed twice with cold water and with 10% aqueous $CuOAc_2 \cdot 4H_2O$ to remove (I), and dried over $MgSO_4$. Chloroform was distilled off and the corresponding β-chlorovinyl ketone was distilled.

Analogously prepared β-chlorovinyl ketones (IId-g, n) and (IIId-g, n) were isolated as mixtures of isomers and separated by chromatography on neutral alumina using 1:1 chloroform—hexane as eluant. The fractions were separated in the order: Z-(II), Z-(III), and E-(III).

CONCLUSIONS

1. Unsymmetrical fluorinated β-diketones with bulky alkyl substituents react with $SOCl_2$ to form β-chlorovinyl ketones with Z configuration and the chlorine atom in the γ-position to the fluoroalkyl substituent.

2. Fluorinated β-diketones with aromatic substituents undergo this reaction to give mixtures of isomeric β-chlorovinyl ketones with the chlorine atom in the α- or γ-position to the fluoroalkyl substituent.

LITERATURE CITED

1. N. K. Kochetkov, Usp. Khim., 24, 35 (1955).
2. E. Bauer and H.-P. Müller, Tetrahedron Lett., 533 (1971).
3. K. I. Pashkevich and A. Ya. Aizikovich, Izv. Akad. Nauk SSSR, Ser. Khim., 1908 (1982).
4. K. R. Kumawat, Indian J. Chem., 20B, 759 (1981).
5. K. I. Pashkevich, V. I. Filyakova, Yu. N. Schneider, O. S. Anisimova, I. Ya. Postovskii, and E. F. Kuleshova, Izv. Akad. Nauk SSSR, Ser. Khim., 2087 (1979).

6. K. I. Pashkevich, V. I. Filyakova, and I. Ya. Postovskii, Izv. Akad. Nauk SSSR, Ser. Khim., 2346 (1981).
7. H. Martens, B. Hoornaert, and S. Toppet, Tetrahedron, 29, 4241 (1973).
8. E. A. Guggenheim and V. W. Smith, Trans. Faraday Soc., 45, 714 (1949).
9. V. I. Minkin, O. A. Osipov, and Yu. A. Zhdanov, Dipole Moments in Organic Chemistry [in Russian], Khimiya, Moscow (1968), p. 77.

SYNTHESIS OF SPIRO-o-CARBORANYLENECYCLOPHOSPHAZENES

V. V. Korshak, N. I. Bekasova, and M. P. Prigozhina

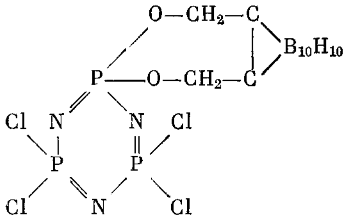
UDC 542.91:547.1'127'118

Carborane-containing cyclophosphazenes and cyclophosphazene polymers hold interest since the thermal stability of polyphosphazenes is significantly enhanced upon the introduction of carborane fragments [1, 2].

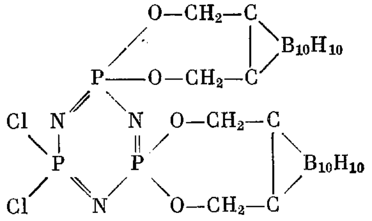
Spiro-o-carboranylenecyclophosphazenes, synthesized by the reactions of bis(hydroxymethyl)-o-carborane with hexachlorocyclophosphazene, were selected as the monomers for the preparation of linear and cyclic polymers.

In this reaction, we would expect the ready formation of spiro compounds since the IR spectrum of a dilute solution of bis(hydroxymethyl)-o-carborane shows a band in the vicinity of 3600 cm^{-1} for intramolecular hydrogen bonds between the hydroxyl groups [3] and, furthermore, a series of cyclic derivatives of this diol is known [4].

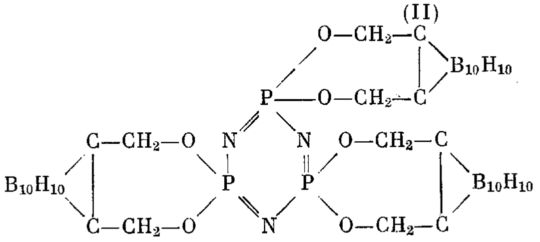
The reactions of bis(hydroxymethyl)-o-carborane with hexachlorocyclophosphazene for 6 h at 50°C in benzene in the presence of triethylamine as the HCl acceptor gave the previous unknown spiro-o-carboranylenecyclophosphazenes (I)-(III)



(I)



(II)



(III)

When the ratio of the starting reagents is 1:1, 80% (I) is formed with a trace of (II), which was separated by column chromatography. When the carborane—phosphazene ratio is 3:1, we obtained 90% (II) and 10% (III). Products (I)-(III) are white, high-melting powders. Products (I) and (II) are readily soluble in organic solvents, while (III) forms only dilute solutions in N-methylpyrrolidone and THF. The IR spectra of these spiro-o-carboranylenecyclophosphazenes show strong bands at 2600 cm^{-1} for the carborane B—H bond and at 1200-1400 cm^{-1} for the phosphazene ring P—N bond. The IR spectra of (I) and (II) have bands at 520 and 620 cm^{-1} for the phosphazene ring P—Cl bond, which are lacking in the IR spectrum of (III). In addition, the spectra of all three of these compounds lack the band at 3200 cm^{-1} corresponding to the OH group found with high intensity in the spectrum of starting bis(hydroxymethyl)-

---

A. N. Nesmeyanov Institute of Heteroorganic Compounds, Academy of Sciences of the USSR, Moscow. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 9, pp. 2128-2129, September, 1986. Original article submitted September 17, 1985.

0568-5230/86/3509-1940$12.50