INVESTIGATIONS INTO SYNTHETIC PHYTOHORMONES.

2. TRIALKYLSILYL ESTERS OF ARYLOXYACETIC ACIDS

M. G. Voronkov, B. O. Shirchin,
N. V. Semenova, and V. M. D'yakov

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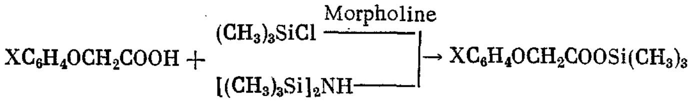
Organosilicon derivatives of ring-substituted aryloxyalkanoic acids (synthetic phytohormones) were unknown until now. We have synthesized the trialkylsilyl esters of some phenoxyacetic acids of formula $XC_6H_4OCH_2COOSiR_3$, where X = H, CH_3, or Cl and R = CH_3 or C_2H_5. The trimethyl esters were prepared according to the reaction scheme given below. Compounds (I) and (II) undergo hydrolysis extremely readily and are thus of no practical interest.



$$XC_6H_4OCH_2COOH + \left.\begin{matrix}(CH_3)_3SiCl \xrightarrow{\text{Morpholine}} \\ [(CH_3)_3Si]_2NH \longrightarrow\end{matrix}\right] \rightarrow XC_6H_4OCH_2COOSi(CH_3)_3$$

(I), (II)

X = H, Alk, Cl

The triethylsilyl esters were synthesized by dehydrocondensation of the aryloxyacetic acids with triethylsilane in the presence of colloidal nickel [1]. The properties of the products are indicated in Table 1.

$$XC_6H_4OCH_2COOH + HSi(C_2H_5)_3 \xrightarrow[-H_2]{Ni} XC_6H_4OCH_2COOSi(C_2H_5)_3$$

(III)—(V)

As was expected, dehydrocondensation of the ring-chlorinated acids is accompanied by partial reduction (due to the chlorine atom), which makes it difficult to isolate the major reaction products and considerably reduces their yield. All of the compounds prepared are colorless liquids with a characteristic odor and are soluble in conventional organic solvents. They are readily hydrolyzed by water. Their structure was confirmed by their PMR and IR spectra. The latter exhibit two bands due to the stretching vibrations of the CO group in the 1720-1750 cm^{-1} region. The vibrations in the 1600-1605, 1495-1500, and 3035-3050 cm^{-1} regions indicate the presence of a benzene ring, and the strong bands in the vicinity of 1090 cm^{-1} characterize the Si—O—C grouping.

EXPERIMENTAL

The IR spectra were obtained from thin films with a UR-20 spectrometer. The PMR spectra were obtained from 20% solutions in CCl_4 with a Tesla BS487C spectrometer (80 MHz) using cyclohexane as internal standard.

Trimethylsilyl p-Chlorophenoxyacetate (I). A mixture of 18.66 g (0.1 mole) of $p\text{-}Cl\cdot C_6H_4OCH_2COOH$ and 8.7 g (0.1 mole) of morpholine in 100 ml of toluene was treated with 10.85 g (0.1 mole) of $(CH_3)_3SiCl$ and boiled for 1 h. After cooling, the precipitated $C_4H_9ON\cdot HCl$ was filtered off, the toluene was distilled off, and the residue was distilled in vacuo.

Triethylsilyl Phenoxyacetate (III). A mixture of 15.2 g (0.1 mole) of $C_6H_5OCH_2COOH$ and 23 g (0.2 mole) of $(C_2H_5)_3SiH$ was boiled in the presence of colloidal nickel (from 0.37 g of $NiCl_2$) [2] until the acid was completely dissolved and H_2 evolution ceased. The reaction mixture was filtered and distilled in vacuo.

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TABLE 1. Trialkylsilyl Aryloxyacetate Esters $ROCH_2COOSiR'_3$

Compound	R	R'	Yield, %	bp, °C (p, mm. Hg)	n_D^{20}	d_4^{20}	Empirical formula	Found, %				Calculated, %				PMR spectrum, δ, ppm		
								C	H	Si	Cl	C	H	Si	Cl	XC_6H_4O	$O-CH_2-C$	$Si-R_3$
(I)	$4\text{-}ClC_6H_4$	CH_3 *	61,1	150–151 (9)	–	–	$C_{11}H_{15}SiO_3Cl$	50,92	5,50	10,41	13,60	51,05	5,84	10,85	13,70			
(II)	$2,4\text{-}Cl_2C_6H_3$	CH_3	51,8	152–153 (3,5)	1,5128	1,2240	$C_{11}H_{14}SiO_3Cl_2$	45,05	4,61	9,78	24,08	45,06	4,81	9,58	24,18	6,75; 7,07 7,42	4,58	0,32
(III)	C_6H_5	C_2H_5	62	135,5 (2)	1,4915	1,0002	$C_{14}H_{22}SiO_3$	63,00	8,06	10,34	–	63,12	8,32	10,54	–	6,50–7,12	4,46	0,80
(IV)	$2\text{-}CH_3C_6H_4$	C_2H_5	89,3	139 (2)	1,4919	0,9991	$C_{15}H_{24}SiO_3$	64,08	8,47	9,80	–	64,24	8,63	10,01	–	6,50–7,00	4,47	0,80
(V)	$4\text{-}ClC_6H_4$	C_2H_5	32	159 (3)	1,4994	1,0992	$C_{14}H_{21}SiO_3Cl$	55,45	6,90	9,67	11,72	55,89	7,03	9,34	11,78	6,77; 7,17	4,46	0,80

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*Crystalline substance hydrolyzing very easily in air.

CONCLUSIONS

Trialkylsilyl esters of ring-substituted aryloxyacetic acids have been prepared for the first time, and their PMR and IR spectra studied.

LITERATURE CITED

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REACTIONS OF KETO ALCOHOLS WITH ORGANOPHOSPHORUS COMPOUNDS.

8. REACTION OF β-KETO ALCOHOLS WITH AMIDOPHOSPHOROUS ACID CHLORIDES

F. S. Mukhametov, L. V. Stepashkina,
and N. I. Rizpolozhenskii

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Investigations into the properties of γ-ketoalkyl phosphites [1-3] have shown that they have a number of peculiarities; in particular, they are capable of rearranging to dialkyl γ-ketoalkyl phosphonates on heating [2]. In the case of the γ-ketoalkyl esters of thiophosphonous acid, the tendency for the P(III) derivatives to be converted to P(V) derivatives is even more pronounced, and in some cases such conversions occur spontaneously [3]. The compounds prepared from tertiary β-keto alcohols rearrange more rapidly than those prepared from secondary β-keto alcohols, and these in turn rearrange more rapidly than those prepared from primary β-keto alcohols. The question of the influence of the radicals attached to the phosphorus atom on the ability of the γ-keto derivatives of P(III) to undergo rearrangement to P(V) derivatives have never been considered.

In order to study this influence, we first synthesized γ-keto derivatives containing electron-donor radicals, for example R_2N, attached to the P(III) atom. These compounds were synthesized as follows:

$$RR^1PCl + HOR^2R^3CCH_2COCH_3 \xrightarrow[-B\cdot HCl]{+B} \underset{(I)\,-\,(XIII)}{RR^1POR^2R^3CCH_2COCH_3}$$

These experiments resulted in the isolation of products which were identified as γ-keto phosphites on the basis of their IR, ^{1}H NMR, and ^{31}P NMR spectra and their elemental analyses and chemical properties (Table 1).

Thus, the IR spectra of all of the compounds synthesized have a strong absorption band at 1715-1720 cm^{-1}, which is characteristic of an unconjugated C=O group, and do not have a P=O band in the 1200-1300 cm^{-1} region. Their ^{31}P NMR spectra show a single signal between −124 and −138 ppm (see Table 1), which is usual for the amides of P(III) acids [4]. It should be noted that some of the products were unstable. Thus, methyl α,α-dimethyl-γ-ketobutyl diethylamidophosphite (I) becomes viscous on storage for a month. In the IR spectrum of this sample, the C=O band at 1720 cm^{-1} disappeared and was replaced by a C=C band at 1620 cm^{-1} and a C=O band at 1690 cm^{-1}, which are characteristic of mesityl oxide, and by a band at 2350 cm^{-1} due to the vibrations of a P-H bond. It follows that (I) evidently decomposes as follows on storage:

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