Journal of Organometallic Chemistry, 104 (1976) 187—191

FUNCTIONALLY SUBSTITUTED ORGANOTIN COMPOUNDS

V*. BECKMANN REARRANGEMENT OF OXIMES CONTAINING ORGANOTIN SUBSTITUENTS

S.Z. ABBAS and R.C. POLLER*

Chemistry Department, Queen Elizabeth College, Campden Hill Road, London W8 7AH (Great Britain)

(Received July 11th, 1975)

Summary

The structures of the oximes formed from (4-oxopentyl)triphenyltin and (4-oxopentyl)diphenyltin chloride have been determined using IR, PMR and Mössbauer spectroscopy. Beckmann rearrangement of (4-oximinopentyl)diphenyltin chloride with phosphorus pentachloride gave the amide resulting from exchange of *syn* groups. Treatment of the second oxime with phosphorus pentachloride caused other reactions but the *O*-tosyl derivative was rearranged under mild conditions to give a mixture of amides.

Introduction

Few studies have been made of the Beckmann rearrangement of oximes containing organometallic substituents. 4-(Trimethylsilyl)acetophenone oxime rearranged normally [2] but oximes containing an α-cyclopentadienyl group which is π-bonded to a transition metal may give other reactions [3,4]. The present paper which is part of a wider investigation of new methods for the synthesis of functionally substituted organotin compounds describes the Beckmann rearrangement of oximes containing organotin substituents.

Results and discussion

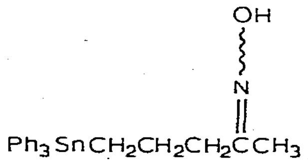
A. Structure of the oximes

The oximes I and II were readily obtained from the corresponding ketones

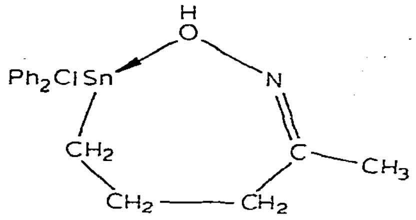
---

* For Part IV see ref. 1.

[1]. Structures were assigned by physical measurements; IR spectra are shown in Table 1.



(I)



(II)

The absence of hydrogen bonding in II is shown by the single sharp ν(O—H, free) band at 3475 cm^{-1} which is unaffected by change in state or by concentration in solution. In contrast I shows broad ν(O—H, assoc.) bands in the solid state at 3240 and 3150 cm^{-1} characteristic of hydrogen bonded oximes [5]. These bands decrease in intensity when the compound is dissolved and a sharp ν(O—H, free) band appears at about 3570 cm^{-1}. Similarly the sharp intense ν(C=N) band in II is in the normal position for ketoximes [6] and is virtually independent of the compound's physical condition. Hydrogen bonding in oximes is usually of the O—H····N type [7] and this gives rise to a weak ν(C=N) band when I is in the solid state, dissociation in solution alters this to a doublet at 1665 and 1640 cm^{-1}.

The PMR spectra are given in Table 2. The sharp signal at τ 4.02 from the proton attached to oxygen in II (in $CDCl_3$ or C_6D_6) is independent of concentration whereas the signal from the corresponding proton in I is a broad resonance at τ 1.32, at lower concentrations, is shifted upfield due to breaking of hydrogen bonds. The large downfield displacement of this resonance for both oximes in perdeuteriodimethylsulphoxide is a consequence of solvation and has been noted by other workers [5].

In simple oximes such as that of 2-pentanone, ready interconversion of stereoisomers occurs. The PMR in aromatic solvents such as deuteriobenzene shows the protons of the =C—CH_3 methyl group resonating at τ 8.26 (*syn* methyl) and τ 8.34 (*anti* methyl) [8]. That compound II is a single isomer and cannot be readily isomerized is shown by the fact that the signal from the methyl

TABLE 1

INFRARED SPECTRA [a] OF $RPh_2SnCH_2CH_2CH_2C(NOH)CH_3$

R	Phase	ν(OH, free)	ν(OH, assoc)	ν(C=N)
Cl (II)	Nujol	3475s		1651s
Cl (II)	$CHCl_3$ (10%)	3475s		1654s
Cl (II)	$CHCl_3$ (5%)	3475s		1654s
Ph (I)	Nujol		3240b, 3150b	1652w
Ph (I)	$CHCl_3$ (10%)	3570s	3250b, 3110(sh)	1665w, 1640w
Ph (I)	$CHCl_3$ (5%)	3570s	3250b [b]	1665w, 1640w
Ph (I)	CCl_4 (10%)	3575s	3250b, 3110(sh)	1665w, 1640w
Ph (I)	CCl_4 (5%)	3575s	3250b [b], 3110(sh) [b]	1665w, 1640w

[a] cm^{-1}. [b] Reduced in intensity at lower concentration.

TABLE 2

PMR SPECTRA [a] OF $RPh_2SnCH_2CH_2\overset{b}{CH_2}C(=NO\overset{c}{H})\overset{a}{CH_3}$

R	Solvent	H_a (singlet)	H_b (triplet)	H_c [b] (singlet)
Cl (II)	$CDCl_3$	8.15	7.56	4.02
Cl (II)	C_6D_6	8.77	[c]	3.99
Cl (II)	PDMSO [d]	8.30	7.84	−0.22
Ph (I)	$CDCl_3$	8.26	7.77	1.32
Ph (I)	C_6D_6	8.38, 8.50	7.62, 7.98	0.84
Ph (I)	PDMSO [d]	8.35	7.85	−0.13

[a] τ (ppm) values. [b] Signal disappears on treatment with D_2O. [c] Signal obscured. [d] PDMSO perdeuteriodimethylsulphoxide.

group is not split when the solvent is changed from deuteriochloroform to deuteriobenzene. The signals from both the methyl and methylene groups adjacent to the oximino carbon in compound I on the other hand are each split in deuteriobenzene showing the presence of both stereoisomers. (In our preliminary communication [9] the signals due to 2-pentanone oxime are erroneously assigned and the tentative conclusion on the configuration of I is incorrect).

The Mössbauer spectrum of I is a singlet with δ 1.29 mm s^{-1} (cf. tetraphenyltin, δ 1.27 mm s^{-1} [10]). Compound II showed a quadrupole splitting with δ 1.47 mm s^{-1} and Δ 3.34 mm s^{-1}. These figures may be compared with the parameters for (4-oxopentyl)diphenyltin chloride [1] (δ 1.38 mm s^{-1}, Δ 3.30 mm s^{-1}) which was shown to have a trigonal bipyramidal structure with the chlorine and oxygen atoms occupying the axial positions.

B. Beckmann rearrangement

Treatment of the oxime II with phosphorus pentachloride in ether gave a pure crystalline amide. The expected structure arising from the usual *anti* mechanism would be the stannyl *N*-methylbutyramide derivative $Ph_2ClSnCH_2CH_2CH_2CONHCH_3$ (III) whereas the compound isolated was shown to be the *N*-(stannylpropyl)acetamide $Ph_2ClSnCH_2CH_2CH_2NHCOCH_3$ (IV). The IR and PMR spectra of the amide were consistent with the proposed structure, the latter technique allowing a clear choice to be made in favour of IV. The methylene group adjacent to nitrogen appears as a quartet, at τ 6.91, due to coupling with the neighbouring CH_2 and NH groups; treatment with deuterium oxide converted the signal to a triplet at τ 6.91. The methyl group appears as a singlet τ 8.21, unchanged on treatment with D_2O. Thus this Beckmann rearrangement of a ketoxime which is fixed in a known configuration appears to contravene the rule that *anti* groups exchange. However, N—O bond cleavage will be preceded by formation of an intermediate ester containing an N—O—P linkage resulting in cleavage of the O→Sn bond. A change in the configuration at the nitrogen atom could then occur followed by a normal exchange of groups in the *anti* positions.

Treatment of the oxime I with phosphorus pentachloride gave an unexpected product and it appears that rearrangement was probably accompanied by replacement of a phenyl group by a chlorine atom. The oxime was converted to its *O*-tosyl derivative which was rearranged by passing it, in solution, down an alumina column [11] to give a mixture of the two amides $Ph_3SnCH_2CH_2CH_2NHCOCH_3$ (V) and $Ph_3SnCH_2CH_2CH_2CONHCH_3$ (VI) in a total yield of 81%. As the original oxime was shown to be a mixture of isomers it is reasonable to assume that the tosyl ester is a similar mixture so that on rearrangement both amides are formed.

The PMR spectrum of the mixture showed a quartet at τ 6.76 and a singlet at τ 8.15 (intensity ratio 2/3): treatment with deuterium oxide converted the quartet to a triplet (τ 6.73) but left the singlet unchanged. These signals are due to compound V, the quartet from the methylene group which is joined to both NH and CH_2 groups and the singlet from the methyl group. The spectrum also shows a less intense doublet at τ 7.34 which on treatment with D_2O is converted to a singlet (position unchanged) and this signal is assigned to the CH_3 group in VI. From the integration the relative proportions are 88% V and 12% VI.

Rearrangement of (*O*-tosyl-4-oximinopentyl)triphenyltin was also effected by boiling with 85% aqueous ethanol [12] but the yields were lower and, by crystallisation, it was only possible to obtain V in pure condition.

The IR spectrum of compound V showed a strong ν(C=O, amide I) band at 1632 cm^{-1}. The corresponding band occurs at 1600 cm^{-1} in compound IV which, as an organotin chloride would be expected to have a 5-coordinate structure. In adducts of organotin halides and amides coordination occurs from the amide oxygen to tin [13] and the downfield shift of 32 cm^{-1} on passing from the triphenylstannyl to the chlorodiphenylstannyl compounds confirms this.

Experimental

IR spectra were measured using Perkin—Elmer 325 and Pye Unicam SP 200 spectrophotometers. The PMR spectra were obtained with Perkin—Elmer R-12B and R-10 instruments. The Mössbauer spectrometer has been described previously [14], measurements were made with the samples at 78 K and isomer shifts refer to tin(IV) oxide.

Preparation of the oximes of (4-oxopentyl)triphenyltin and (4-oxopentyl)dipentyltin chloride

A mixture of the ketone (0.07 mol) in hot ethanol (25 ml), hydroxylamine hydrochloride (0.07 mol) in 40% ethanol (20 ml) and 10% aqueous sodium hydroxide (8 ml) was heated on a hot water bath for 0.5 h. Addition of water and extraction with ether gave the oximes. Crude *(4-oximinopentyl)triphenyltin* was obtained in 61% yield, m.p., after crystallisation from mixed light petroleum (b.p. 60-80°C) and benzene (2/1), 74-76°C. (Found: C, 61.35; H, 5.2; N, 2.8. $C_{23}H_{25}NOSn$ calcd.: C, 61.4; H, 5.6; N, 3.1%.) Similarly crude *(4-oximinopentyl)diphenyltinchloride*, 43% yield, was crystallized from the same solvent when it had m.p. 94-97°C. (Found: C, 49.95; H, 5.1; N, 3.4. $C_{17}H_{20}ClONSn$ calcd.: C, 50.0; H, 4.9; N, 3.4%.) Thin layer chromatography showed that each product was homogeneous.

Beckmann rearrangement of (4-oximinopentyl)diphenyltin chloride

A mixture of the oxime (0.90 g) and phosphorus pentachloride (0.45 g) and diethyl ether (60 ml) was placed on a hot water bath for a few minutes.

After cooling, water (30 ml) was added, the mixture warmed for a further 10 min, cooled and filtered. The solid (0.52 g) was crystallised from benzene to give *N-[3-(chlorodiphenylstannyl)propyl]acetamide* (0.21 g), m.p. 149-151°C. (Found: C, 50.2; H, 5.0; N, 3.2. $C_{17}H_{25}ClONSn$ calcd.: C, 50.0; H, 4.9; N, 3.4%.)

When a similar reaction was attempted with (4-oximinopentyl)triphenyltin a crude product m.p. 110-120°C, which could not be purified, was obtained. (Found: C, 47.0; H, 4.7; N, 3.2%.)

Preparation and rearrangement of [O-(toluene-p-sulphonyl)-4-oximinopentyl]-triphenyltin

Solutions of (4-oximinopentyl)triphenyltin (6.00 g) in dry pyridine (15 ml) and toluene-*p*-sulphonyl chloride (2.66 g) in the same solvent (10 ml) both at 0°C were mixed and stirred. The mixture was kept at 0°C for 14 h, poured on to ice-water and extracted with dichloromethane. The organic layer, after washing with water and aqueous cadmium chloride solution to remove pyridine, gave the required *tosyl derivative* as a white solid (3.00 g) m.p. 94-96°C (dec.). (Found: C, 59.8; H, 5.3; N, 2.2. $C_{30}H_{31}NO_3SSn$ calcd.: C, 59.6; H, 5.2; N, 2.3%.)

This compound (0.50 g) in benzene (5 ml) was added to a column of alumina (Brockmann activity I, neutral, 12.5 g) in hexane. Elution with a mixture of benzene and chloroform gave the mixed amides (0.30 g). The IR spectrum was consistent with this product being a mixture of compounds V and VI, details of the NMR spectrum are given in the discussion. (Found: C, 61.1; H, 5.6; N, 3.2. $C_{23}H_{25}NOSn$ calcd.: C, 61.4; H, 5.6; N, 3.1%.)

A solution of the tosyl derivative (2.00 g) in 85% ethanol (20 ml) was heated on a hot water bath for 20 min. After cooling, ether (150 ml) was added and the organic layer, after washing with aqueous sodium hydrogen carbonate and water, gave a crude product which yielded, on crystallisation from light petroleum (b.p. 60-80°C)/benzene (3/1), *N*-[3-triphenylstannyl)propyl]acetamide (0.21 g) m.p. 102-104°C (lit. [15] m.p. 95-98°C). (Found: C, 61.5; H, 6.1; N, 3.3. $C_{23}H_{25}NOSn$ calcd.: C, 61.4; H, 5.6; N, 3.1%.)

References

1 S.Z. Abbas and R.C. Poller, J. Chem. Soc., Dalton Trans., (1974) 1769.
2 R.G. Neville, J. Org. Chem., 24 (1959) 870.
3 E. Cuingnet et M. Tauterat-Adalberon, Bull. Soc. Chim. Fr., (1965) 3728.
4 H. Patin, Tetrahedron Lett., (1974) 2893.
5 D.S. Jackson, J. Chem. Soc. B, (1969) 785.
6 S.F. Dyke, A.J. Floyd, M. Sainsbury and R.S. Theobald, Organic Spectroscopy, Penguin Books Ltd., London, 1971, p. 88.
7 H. Sauvaitre and J. Deschamps, Tetrahedron Lett., (1967) 1761.
8 G.J. Karabatsos, R.A. Taller and F.M. Vane, J. Amer. Chem. Soc., 85 (1963) 2326.
9 S.Z. Abbas and R.C. Poller, J. Organometal. Chem., 55 (1973) C9.
10 R.V. Parish and R.H. Platt, Chem. Commun., (1968) 1118.
11 J.C. Craig and A.R. Naik, J. Amer. Chem. Soc., 84 (1962) 3410.
12 H.P. Fisher and C.A. Grob, Helv. Chim. Acta,47 (1964) 564.
13 E.L. Muetterties, J. Amer. Chem. Soc., 82 (1960) 1082.
14 R.C. Poller and J.N.R. Ruddick, J. Chem. Soc., A, (1969) 2273.
15 G.J.M. van der Kerk and J.G. Noltes, J. Appl. Chem., 9 (1959) 106.