# PREPARATION AND SPECTROSCOPIC STUDIES OF DIALKYLCARBAMOYL–TIN COMPOUNDS

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## SUMMARY

Stable (dimethyl- and diethylcarbamoyl)triphenyltin and (dimethylcarbamoyl)tri-*p*-tolyltin have been synthesized. Their PMR spectra exhibit long-range spin–spin couplings between the $^{117/119}$Sn nuclei and the *N*-alkyl protons. Using the benzene-dilution method and paramagnetic chemical-shift experiments with tris-(dipivaloylmethanato)europium it has been demonstrated that long-range couplings involving the *cis* position relative to the C–N bond are larger in value. IR and UV spectra have also been discussed.

## INTRODUCTION

Many organometallic α-carbonyl compounds of the formula $R_3MC(O)R'$ (M = Si, Ge, Sn, Pb; R, R′ = alkyl, aryl) have been prepared and the electronic interactions of the carbonyl groups with the metal atoms have been investigated[1–4]. However, all organotin α-carbonyl compounds[5] synthesized to date are unstable in air at room temperature and have never been isolated in a pure form. We have attempted the preparation of stable α-carbonyl organotin compounds and in this paper the preparation of stable tin compounds containing the dimethyl- or diethylcarbamoyl group is reported together with a discussion of their PMR, IR and UV spectra in relation to previously reported data for silicon[6] and lead dialkylcarbamoyls[7].

## EXPERIMENTAL

### (Dialkylcarbamoyl)triaryltin

A THF solution of triphenyltinlithium prepared from triphenyltin chloride and lithium metal in THF was slowly added to a nearly equimolar THF solution of dimethylcarbamoyl chloride under a nitrogen atmosphere at −78°. After stirring for 1 h, the solvent was removed and the residue extracted with dichloromethane. The crude product was recrystallized from methanol to give pure (dimethylcarbamoyl)triphenyltin (I); m.p. 139–140°. (Found: C, 59.93; H, 4.78; N, 3.13; mol. wt. in chloroform, 436. $C_{21}H_{21}NOSn$ calcd.: C, 59.75; H, 5.02; N, 3.32%; mol. wt., 422.)

TABLE I

PMR DATA RELATING TO THE PROTONS OF THE $NCH_3$ AND $NCH_2CH_3$ GROUPS IN (DIMETHYL- AND DIETHYLCARBAMOYL)TIN COMPOUNDS IN DICHLOROMETHANE AT $22°$

| Compounds | $\delta(NC\underline{H}_3$ or $NC\underline{H}_2)$ | | $\delta(NCH_2C\underline{H}_3)$ | | $J[^{117/119}Sn{-}C(O)NC\underline{H}_3$ or $-NC\underline{H}_2](Hz)$ | | $J[^{117/119}Sn{-}C(O)NCH_2C\underline{H}_3]$ $(Hz)$ | |
|---|---|---|---|---|---|---|---|---|
| | cis | trans | cis | trans | cis | trans | cis | trans |
| $(C_6H_5)_3SnC(O)N(CH_3)_2$ | 3.00 | 2.96 | | | 5.4 | 3.0 | | |
| $(p\text{-}CH_3\cdot C_6H_4)_3SnC(O)N(CH_3)_2$ | 2.96 | 2.91 | | | 5.3 | 2.3 | | |
| $(C_6H_5)_3SnC(O)N(CH_2CH_3)_2$ | 3.22 | 3.39 | 1.03 | 0.63 | 2.4 | 1.9 | 1.4 | Not observed |
| $Cf.$ | | | | | | | | |
| $(C_6H_5)_3PbC(O)N(CH_3)_2$ | 3.01 (2.98, 2.96)c | 2.96 | | | 11.0a (11, 4)c | 4.2a | | |
| $HC(O)N(CH_3)_2$d | 2.97 | 2.80 | | | 0.3b | 0.6b | | |

a $J[^{207}Pb{-}C(O)NC\underline{H}_3]$. b $J[^1H{-}C(O)NC\underline{H}_3]$. c Ref. 7; in carbon tetrachloride. Complete assignment of the signal was not made. d Ref. 13, in neat liquid.

(Dimethylcarbamoyl)tri-*p*-tolyltin (II) and (diethylcarbamoyl)triphenyltin (III) were prepared from tri-*p*-tolyltinlithium and dimethylcarbamoyl chloride and from triphenyltinlithium and diethylcarbamoyl chloride in THF, respectively, using essentially the same procedure as described above. (II); m.p. 141–143°. (Found: C, 62.01; H, 5.70; N, 2.78; mol. wt. in chloroform 496. $C_{24}H_{27}NOSn$ calcd.: C, 62.01; H, 5.86; N, 3.02 %; mol. wt., 464.) (III); m.p. 82–84° (Found: C, 61.22; H, 5.56; N, 3.03; mol. wt. in chloroform, 488. $C_{23}H_{25}NOSn$ calcd.: C, 61.37; H, 5.60; N, 3.11 %; mol. wt., 450.)

(Dimethylcarbamoyl)triphenyllead was also prepared in a similar way; m.p. 138–140° (lit.[7] 142–145°). (Found: C, 49.62; H, 4.27; N, 2.93. $C_{21}H_{21}NOPb$ calcd.: C, 49.40; H, 4.15; N, 2.74%.)

*Physical measurements*

PMR spectra were recorded on a Japan Electron Optics JNM-3H-60 model spectrometer at 60 MHz or on a JNM-PS-100 model spectrometer at 100 MHz, both equipped with a variable temperature probe and a temperature controller, tetramethylsilane being used as an internal standard. IR spectra were recorded on a Hitachi 225 spectrophotometer either as Nujol mulls or in solution. UV spectra were measured using a Hitachi 124 spectrophotometer with 1 cm and 1 mm quartz cells at room temperature.

Molecular weights were determined in chloroform using a Hitachi–Perkin–Elmer 115 vapor pressure osmometer.

RESULTS AND DISCUSSION

Two types of proton signals corresponding to $NCH_3$ and $NCH_2CH_3$ groups are observed in the PMR spectra of the (dialkylcarbamoyl)tin compounds in dichloromethane at room temperature due to restricted rotation around the partially double-bonded C(O)–N bond. Each of these signals exhibits satellites due to long-range spin–spin couplings with $^{117/119}$Sn nuclei. Although the coupling constants were found to be small, their relative magnitudes were consistent with those previously reported for the $NCH_3$ protons and the $^{207}$Pb atom of (dimethylcarbamoyl)triphenyllead[7]. These results are summarized in Table 1.

In order to assign the two kinds of *N*-alkyl signals the benzene-dilution method was used. The $NCH_3$ proton chemical shifts of (I) in dichloromethane solution are plotted in Fig. 1 relative to the amounts of benzene in the system. The initial low-field $NCH_3$ signal experiences a greater shift to higher field than the initially high-field signal as the proportion of benzene is increased. If the preferred arrangement of a benzene molecule toward amides is taken to be as depicted in (A), where the negatively charged carbonyl oxygen tends to be some distance removed from the center of the benzene ring[8], the originally low-field signal which moves to a higher field under the
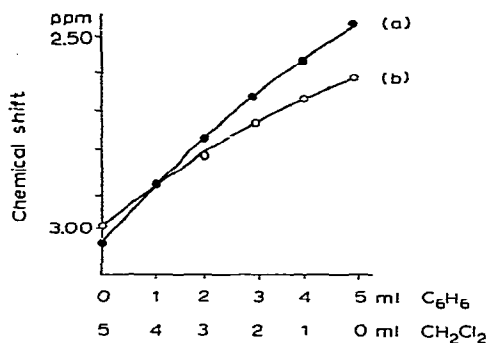


(A)
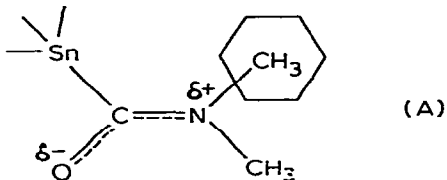
Fig. 1. The chemical shifts of the $NCH_3$ protons (a) *trans* and (b) *cis* to the carbonyl group in (dimethyl-carbamoyl)triphenyltin in solutions of dichloromethane containing varying amounts of benzene.

diamagnetic influence of the benzene ring should be assigned to the $NCH_3$ group *cis* to the triphenyltin group. Similar experimental results have also been obtained for compounds (II) and (III), and the signals are assigned as shown in Table 1.

The above assignments have been confirmed from a study of the paramagnetic shift induced in the presence of a shift reagent, tris(dipivaloylmethanato)europium. Figure 2 shows the signal movements of the $NCH_2CH_3$ protons of (III) upon addition of the shift reagent in chloroform-$d_1$. The magnitude of the paramagnetic shift is mainly determined by the distance of a given proton from the europium atom[9,10]. In *N,N*-dialkylamides, the *N*-alkyl signals *cis* to the carbonyl group have been reported as moving to a lower field in the presence of the shift reagent[10]. Assuming that (III) is coordinated to the europium atom through the carbonyl oxygen as occurs for the interactions between amides and the proton[11] or metal halides[12], the $NCH_2CH_3$ protons *trans* to the tin nucleus would be expected to undergo a larger shift. This is observed with (III), the result being consistent with the assignments made by the benzene-dilution method. Assignments for (dimethylcarbamoyl)tin and -lead compounds have also been confirmed in a similar manner (see Table 1).
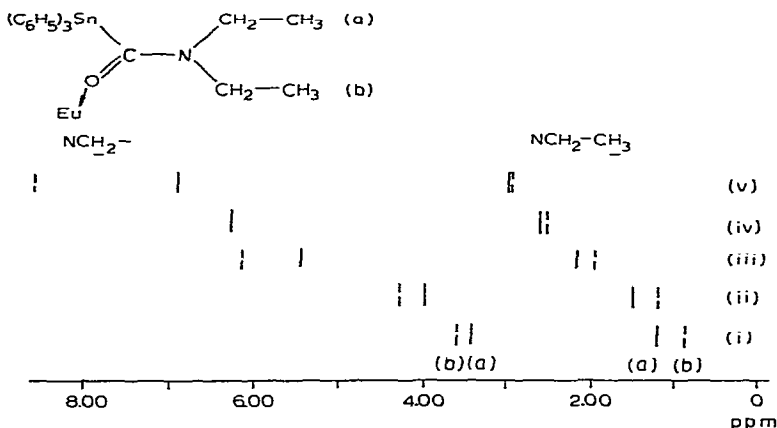


Fig. 2. The chemical shifts of the $NCH_2CH_3$ protons of (diethylcarbamoyl)triphenyltin in chloroform-$d_1$ solution containing (i) no $Eu(DPM)_3$, (ii) 0.32, (iii) 0.56, (iv) 0.82, and (v) 1.19 $M$ $Eu(DPM)_3$.

It is very noteworthy that the $N$-alkyl signals *cis* to the tin or lead atom have larger spin–spin couplings with respect to the tin or lead nucleus. With $N,N$-dimethyl-formamide, it has been deduced that *trans* coupling between the formyl proton and the $NCH_3$ protons is greater than *cis* coupling[11,13]. This deduction is, however, not in agreement with our results, if it is assumed that the four-bond couplings in the compounds studied in this work have the same sign. In an attempt to explain the larger *cis* couplings observed in this work, PMR experiments involving several dialkylcarbamoyl organometallic compounds are now in progress.

The $N$-alkyl proton signals are temperature-dependent, coalescing at a higher temperature to form a sharp singlet; the $NCH_3$ signals of (I) coalesce at 68° and the $NCH_2$ and $NCCH_3$ signals of (III) at 85° and 101° respectively, in chlorobenzene. The activation free energy for hindered rotation about the $C(O)–N$ bond of (I) has been estimated from Rogers' method[14] to be 18.3 kcal/mole at the coalescence temperature.

The values of the chemical shifts of the $N$-alkyl signals are considerably affected by solvents. In polar solvents this group is deshielded through the formation of a more stabilized dipolar structure:

$$\underset{\underset{O}{\delta^-}}{\overset{}{\diagdown}}C=\!\!=N\overset{\delta^+}{\diagup}\diagdown$$
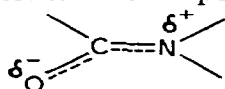
Further deshielding occurs in hydrogen-bonding solvents. Thus, in methanol-$d_4$, for example, the signals are shifted to a lower field by 0.20 ppm relative to the values observed in carbon tetrachloride solution. This may be attributed to the formation of the above stabilized dipolar structure resulting from the interaction between a hydrogen atom of the solvent and the oxygen of the carbonyl group. On the other hand, in acidic solutions, for example an addition of trifluoroacetic acid, (I) is readily decomposed and exhibits a triplet $NCH_3$, signal at 2.50 ppm, indicating the formation of the dimethylamino cation, as has been shown for the analogous silicon compound[6].

The infrared frequencies of the $C=O$ groups of the (dialkylcarbamoyl)tin compounds together with those of the analogous carbon, silicon and lead compounds are listed in Table 2. Larger low frequency shifts are observed for the tin compounds relative to the related carbon compound, suggesting a stronger inductive interaction between the tin atom and the carbonyl group to an extent similar to that in the silicon compound. In dichloromethane the $v(C=O)$ bands are shifted to a slightly higher

TABLE 2

IR FREQUENCIES CORRESPONDING TO $v(C=O)$ FOR (DIALKYLCARBAMOYL)METAL COMPOUNDS $(cm^{-1})$

| Compounds | Nujol mull | In $CH_2Cl_2$ | In $CHCl_3$ |
|---|---|---|---|
| $(C_6H_5)_3SnC(O)N(CH_3)_2$ | 1574 | 1585 | 1575 |
| $(p\text{-}CH_3C_6H_4)_3SnC(O)N(CH_3)_2$ | 1577 | 1585 | 1575 |
| $(C_6H_5)_3SnC(O)N(C_2H_5)_2$ | 1560 | 1578 | 1570 |
| $(C_6H_5)_3PbC(O)N(CH_3)_2$ | 1617 (1615)[a] | 1612 | 1605 |
| $(CH_3)_3SiC(O)N(C_2H_5)_2$ | 1560[b] | | |
| $(CH_3)_3CC(O)N(C_2H_5)_2$ | 1620[b] | | |

[a] Ref. 7. [b] Ref. 6; measured as a KBr disc.

frequency relative to those observed in the solid state. This suggests that in solution any intermolecular interaction which may exist in the solid state has disappeared. In the lead compound, the $v(C=O)$ band occurs at a higher frequency and the electronic effect arising from interaction between the lead atom and the carbonyl group seems to be of less importance. The shift to a slightly lower frequency observed in dichloromethane may be related to the weak acidity of the lead compound. The shift of the bands to a slightly lower frequency in chloroform may be attributed to hydrogen-bond formation between the solvent molecule and the carbonyl group as mentioned above in connection with the PMR results.

The UV spectrum of (I) in cyclohexane exhibits a $\pi-\pi^*$ transition for the carbonyl group at $\approx 233$ nm ($\varepsilon = \approx 8500$). The exact position of this band, however, has not been determined because of the occurrence of a very strong $\pi-\pi^*$ band at 205 nm for the triphenyltin group. This band exhibits a similar bathochromic shift to that for the corresponding band for the silicon compound[6]. It may be expected that an $n-\pi^*$ transition should be observed at ca. 260 nm, due to the appearance of a corresponding band in the spectrum of the silicon compound at 264 nm ($\varepsilon = 270$). However, the presence of a $\pi-\pi^*$ band for the phenyl group at 257 nm completely obscures such a band if it exists.

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