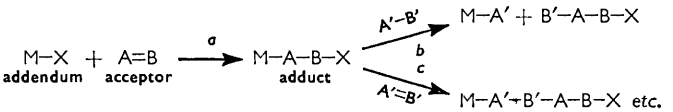
## 1267. *Organometallic Reactions. Part III.*[1,2] *Trimerisation of Isocyanates by Organotin Alkoxides and Oxides*

By A. J. Bloodworth and Alwyn G. Davies

Trialkyltin alkoxides and bistrialkyltin oxides react with isocyanates (⩾2 mol.) to give isocyanurates; different isocyanates can be interbred to give mixed isocyanurates. It is suggested that the reaction proceeds by successive insertion of isocyanate units between the tin atom and its attached group, giving successively intermediate (isolable) 1 : 1 (carbamate) adducts and (non-isolable) 1 : 2 (allophanate) and 1 : 3 adducts.

Some results obtained with similar reaction systems involving isocyanate dimers are correlated with this picture.

In Parts I [1] and II [2] the addition of organotin alkoxides and oxides (Scheme 1, *a*, M = Sn, X = O) to a variety of acceptor molecules (A=B) was described.

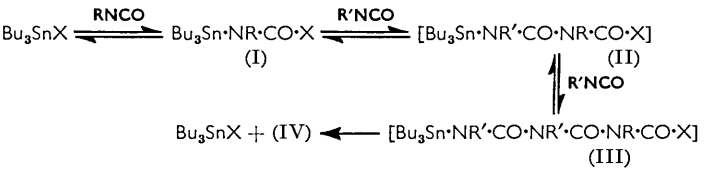



(1)

The new M–A bond in the adduct (often Sn–O or Sn–N) frequently shows a similar reactivity to the M–X bond in the initial addendum, and this was illustrated in some metathetical reactions (Scheme 1, *b*). It would also be expected that this 1 : 1 adduct should add further to a suitable acceptor molecule (A'=B') giving a 1 : 2 adduct, and thence, by insertion of further acceptor units, might build up an oligomer or polymer (1, *c*). This Paper reports the cyclic trimerisation of isocyanates to isocyanurates by, we believe, this repeated insertion mechanism, as illustrated in Scheme 2.

Tributyltin methoxide and bistributyltin oxide react rapidly and exothermically with isocyanates to give isolable 1 : 1 adducts (I; X = OMe and $OSnBu_3$, respectively).

If these adducts are treated with more of the same isocyanate (R = R'), or if the tin methoxide or oxide is treated with an excess of the isocyanate, the infrared and nuclear magnetic resonance spectra of the mixture show that at room temperature a further slow reaction occurs. The characteristic infrared absorption of the isocyanate at *ca.* 2275 $cm.^{-1}$ decays, and that of the isocyanurate at 1750—1613 $cm.^{-1}$ develops, and after 1—25 days the isocyanurate (IV; R = R') can be isolated in good yield. By reactions of this type, trimethyl isocyanurate, triethyl isocyanurate, triphenyl isocyanurate, and tri-1-naphthyl isocyanurate were obtained from the corresponding isocyanates.

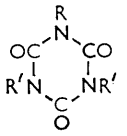


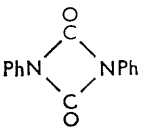

(2)

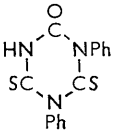
A corollary of this reaction scheme is that it should be possible to make two different isocyanates (R ≠ R') co-react by introducing the second at the stage of the carbamate (I). This proved possible. For example, when methyl *N*-phenyl-*N*-tributylstannylcarbamate

[1] Part I, A. J. Bloodworth and A. G. Davies, *J.*, 1965, 5238.
[2] Part II, A. J. Bloodworth and A. G. Davies, *J.*, 1965, 6245.

(I, R = Ph, X = OMe) or tributyltin *N*-phenyl-*N*-tributylstannylcarbamate (I, R = Ph, X = $OSnBu_3$) was treated with ethyl isocyanate (R′ = Et), diethyl phenyl isocyanurate (IV, R = Ph, R′ = Et) was obtained. Similarly methyl *N*-ethyl-*N*-tributylstannyl-


(IV)


(V)

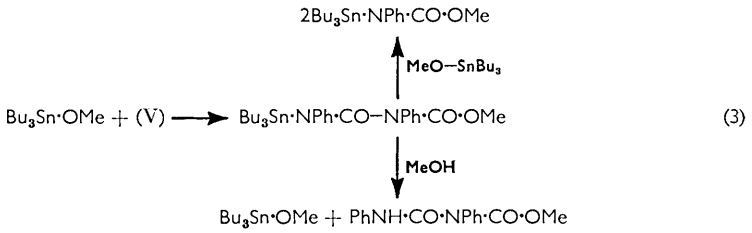

(VI)

carbamate * reacted with phenyl isocyanate giving ethyl diphenyl isocyanurate, and methyl *N*-ethyl-*N*-tributylstannylcarbamate with 1-naphthyl isocyanate gave (impure) ethyl di-1-naphthyl isocyanurate.

The only previous general route to mixed isocyanurates involves treatment of a mixture of the appropriate two isocyanates with a catalyst (*e.g.*, an amine or phosphine).[3] Because of the differing reactivity of the isocyanates, the statistical balance of groups is not necessarily obtained, and the subsequent separation of the mixed products may be difficult. The sequential incorporation of the isocyanate units as described here does not suffer from this disadvantage.

None of these reaction systems gave any direct evidence for the formation of 1 : 2 adducts (II) or 1 : 3 adducts (III). When the tin oxide or methoxide and the isocyanate were mixed in the molar ratio of 1 : 2, only the carbamate and isocyanurate (I and IV) were isolated, and no intermediate compound could be detected.† In an attempt to obtain evidence for the existence of the allophanate intermediates (II) we therefore investigated the reaction between tributyltin methoxide or bistributyltin oxide and diphenyldiazetidenedione (phenyl isocyanate dimer; V), where the allophanate would be expected to be the primary product.

With the methoxide, the product which was isolated was in fact the carbamate, even with equimolar proportions of reactants. It appears that the methoxide reacts metathetically and relatively rapidly with the allophanate at the CO–NPh·CO bond, as it does at the CO–O·CO bond in, say, acetic anhydride.



(3)

On the other hand, if the reaction was carried out in the presence of an excess of methanol, methyl *NN*′-diphenylallophanate was isolated; it seems that rapid methanolysis of the Sn–N bond now gives the parent allophanate which is stable to the methoxide.

* The reaction of tributyltin *N*-ethyl-*N*-tributylstannylcarbamate with phenyl isocyanate is more complex and involves decarboxylation. This will be reported later.

† However, reactions involving one mol. of tin alkoxide, one of isocyanate, and one of aldehyde do support the postulate of a repeating insertion reaction. Adducts such as $Bu_3Sn{\cdot}O{\cdot}CH(CCl_3){\cdot}NPh{\cdot}CO_2Me$, composed of one molecule of addendum and two of acceptor, can be isolated.

[3] E. C. Juenge and W. C. Francis, *J. Org. Chem.*, 1961, **26**, 3334; B.P. 856,732 (*Chem. Abs.*, 1961, **55**, P17,670); B.P. 927,173 (*Chem. Abs.*, 1963, **59**, P14,009); see also ref. 6.

Bistributyltin oxide reacts with di(phenylisocyanate) to give a mixture of bistributylstannyl-*NN'*-diphenylurea and bistributyltin carbonate. This might be an example of the unimolecular decarboxylation of an allophanate (to be discussed in Part IV), the tin oxide trapping the carbon dioxide giving carbonate; or might involve a bimolecular reaction between the oxide and the distannyl allophanate, now at the CO·NPh–CO bond.

$$Bu_3Sn{\cdot}O{\cdot}SnBu_3 + (V) \longrightarrow [Bu_3Sn{\cdot}NPh{\cdot}CO{\cdot}NPh{-}CO{\cdot}O{\cdot}SnBu_3] \quad (4)$$

$$[Bu_3Sn{\cdot}NPh{\cdot}CO{\cdot}NPh{\cdot}CO{\cdot}O{\cdot}SnBu_3] \xrightarrow{Bu_3Sn{\cdot}O{\cdot}SnBu_3} Bu_3Sn{\cdot}NPh{\cdot}CO{\cdot}NPh{\cdot}SnBu_3 + Bu_3Sn{\cdot}O{\cdot}CO{\cdot}O{\cdot}SnBu_3$$

There are some interesting similarities and differences between the reactions discussed here involving tin, and those between carbamates and isocyanates under other conditions. Ghosh and Guha [4] found that the reaction between ethyl *N*-sodiocarbamate and phenyl isocyanate stopped at the stage of the 1 : 2 adduct, and would not react further to give the trimer.* On the other hand, the reaction with phenyl isothiocyanate could not be stopped at the stage of a 1 : 2 adduct, and gave the dithioisocyanurate (VI) whatever the ratio of reagents.

$$PhNNa{\cdot}CO{\cdot}NH{\cdot}CO{\cdot}OEt \xleftarrow{PhNCO} NaNH{\cdot}CO{\cdot}OEt \xrightarrow{PhNCS} (VI) \quad (5)$$

The trimerisation of phenyl isocyanate in the presence of ethanol and a base (*N*-methylmorpholine) has been investigated by Kogon.[6] He suggests that the reaction involves the allophanate and the phenyl isocyanate dimer, which, under his conditions, is in equilibrium with the monomer. The carbamate and isocyanate react to give the allophanate (equation 6); this then transfers the same isocyanate unit to phenyl isocyanate dimer to give the trimer, regenerating the carbamate (equation 7). The isocyanate unit in the carbamate is therefore not incorporated into the trimer, in direct contrast to what we observe in the formation of co-trimers in our reactions.

$$ArNH{\cdot}CO{\cdot}OEt + PhNCO \longrightarrow PhNH{\cdot}CO{\cdot}NAr{\cdot}CO{\cdot}OEt \quad (6)$$

$$PhNH{\cdot}CO{\cdot}NAr{\cdot}CO{\cdot}OEt + (PhNCO)_2 \longrightarrow (PhNCO)_3 + ArNH{\cdot}CO{\cdot}OEt \quad (7)$$

It is not clear why it should be necessary to assume that whereas the carbamate is more reactive towards the monomer, the allophanate is more reactive towards the dimer. The incorporation of two isocyanate units, before elimination occurs, may reflect the demands of the elimination rather than the addition process, the presence or absence of tin governing the stage at which cyclic elimination occurs.

$Bu_3Sn(NPh{\cdot}CO)_3OMe$ (VII)

$H(NPh{\cdot}CO)_3NPh{\cdot}CO{\cdot}OEt$ (VIII)

If tin is present, cyclisation occurs on the structure (VII), eliminating tributyltin methoxide. If tin is absent, the equivalent elimination of alcohol cannot occur at this stage, and cyclisation, by elimination now of carbamate, has to await the formation of the 1 : 4 adduct (VIII).

* Yet triphenyl isocyanurate can be prepared by treating phenyl isocyanate with sodium methoxide;[5] methyl *N*-phenylcarbamate is a byproduct.

[4] T. N. Ghosh and P. C. Guha, *J. Indian Chem. Soc.*, 1930, **7**, 263.
[5] A. Michael, *Ber.*, 1905, **38**, 22.
[6] I. C. Kogon, *J. Amer. Chem. Soc.*, 1956, **78**, 4911.

Shashoua *et al.* have shown that some anionic catalysts (*e.g.*, sodium cyanide or naphthalene sodium but not triethylamine or triethylphosphine) will convert isocyanates into cyclic trimers or linear polymers (1-Nylons), depending on the reaction conditions.[7] These compounds were regarded as the products of competing reactions of now the growing anion, $X(CO{\cdot}NR)_2{\cdot}CO{\cdot}\bar{N}R$, polymerisation being favoured by low temperature, high monomer concentration, and low catalyst concentration.

We attempted to convert phenyl isocyanate into a linear polymer at −35° under Shashoua's conditions, but no polymerisation was observed. When the mixture warmed to room temperature, the cyclic trimer was formed.

## Experimental

Compounds containing Sn–N and Sn–O bonds were stored and manipulated under dry nitrogen.

Molecular weights were determined at 25° by using a Mechrolab vapour pressure osmometer model 301A. Concentrations are expressed as percentages, w/v.

Proton magnetic resonance spectra were recorded at 60 Mc./sec. on a Perkin-Elmer spectrometer. Solutions were prepared in carbon tetrachloride unless otherwise stated.

*Trimethyl Isocyanurate.*—Bistributyltin oxide (2·28 g.) was added to methyl isocyanate (7·0 g.; 32 mol.), cooled in ice to moderate the initial exothermic reaction. Crystals of the trimer began to separate after 19 hr.; after 62 hr. the mixture had solidified and the odour of the isocyanate was no longer apparent. The product was washed with cyclohexane (yield, 53%), and crystallised from acetone giving trimethyl isocyanurate, m. p. 180°, $\nu_{max.}$ 1440 (C=O) cm.$^{-1}$, $\tau$ 6·56 ($CH_3$) [Found: *M* (in $CH_2Cl_2$), 165, 169; mean 167. Calc. for $C_6H_9N_3O_3$: *M* 171].

The same product was obtained (m. p. i.r., and n.m.r. spectra) when the isocyanate (5·7 g.) was treated with 4-dimethylaminopyridine (0·36 g.; 1/32 mol.); solidification occurred during 4 weeks.

Slotta and Tschesche [8] polymerised methyl isocyanate, using triethylphosphine as catalyst, and reported m. p. 175° for the symmetrical trimer $(NMe{\cdot}CO)_3$, and 114° for an unsymmetrical isomer of the structure $\overline{NMe{\cdot}CO{\cdot}C(=NMe)O{\cdot}NMe{\cdot}CO}$. We obtained no indication of the formation of this isomer.

*Triethyl Isocyanurate.*—(*a*) Bistributyltin oxide (0·19 g.) was added to ethyl isocyanate [2 c.c., 87 mol.; $\tau$, quartet centred at 6·63 ($CH_2$), triplet centred at 8·70 ($CH_3$), $J$ = 7 c./sec.]. After 25 days, the i.r. spectrum showed a considerable number of new bands, particularly a broad intense one at 1750—1610 cm.$^{-1}$. Volatile compounds were removed at the rotary pump leaving triethyl isocyanurate as a white wax which, crystallised from benzene, had m. p. 92—93·5° (lit., 95°); $\nu_{max.}$ 1680vs, broad (C=O), 770vs; $\tau$, quartet centred at 6·05 ($CH_2$), triplet centred at 8·76 ($CH_3$), $J$ = 7 c./sec. [Found: *M* (in $CHCl_3$), 210 (1%), 208 (5%), 204 (7%); mean, 207. Calc. for $C_9H_{15}N_3O_3$: *M*, 213].

(*b*) Ethyl isocyanate (0·685 g.; 1·98 mol.) was added to bistributyltin oxide (2·906 g., 1 mol.). The characteristic peak of the isocyanurate at 1695 cm.$^{-1}$ was visible atfer 2 hr. After 6 days a considerable quantity of colourless plates had separated, and after 10 days the i.r. spectrum showed that all the isocyanate had reacted, and was compatible with a mixture of tributyltin *N*-ethyltributylstannylcarbamate and triethyl isocyanurate. The crystals were separated, rapidly washed with pentane, and identified as the isocyanurate, m. p. 94—95° (Found: C, 51·2; H, 7·45; N, 19·9. Calc. for $C_9H_{15}N_3O_3$: C, 50·7; H, 7·1; N, 19·7%).

*Triphenyl Isocyanurate.*—(a) *From phenyl isocyanate and bistributyltin oxide.* Phenyl isocyanate (2 c.c.; 58 mol.) and bistributyltin oxide (0·19 g.) were mixed. After 7 days, crystals began to separate. These were filtered off after 12 days and washed with dry pentane, yielding triphenyl isocyanurate, m. p. 293·5—294°, mixed m. p. with authentic material,[5] 292·5—293·5°; $\nu_{max.}$ 1710vs (C=O) [Found: C, 70·6; H, 4·4; N, 12·1%; *M* (in $CHCl_3$), 345 (1%), 353 (1·8%), 356 (2·2%), mean 355. Calc. for $C_{21}H_{15}N_3O_3$, C, 70·6; H, 4·3; N, 11·75%; *M*, 357].

[7] V. E. Shashoua, *J. Amer. Chem. Soc.*, 1959, **81**, 3156; V. E. Shashoua, W. Sweeney, and R. F. Tietz, *ibid.*, 1960, **82**, 866.

[8] K. H. Slotta and R. Tschesche, *Ber.*, 1927, **60**, 295.

The m. p. quoted in the literature varies widely from 162° [9] to 285° [10] and 285—286°; [11] it has always been assumed that these products have the symmetrical structure $(PhN{\cdot}CO)_3$.

(b) *From phenyl isocyanate and tributyltin methoxide.* A mixture of phenyl isocyanate (2 c.c., 31 mol.) and tributyltin methoxide (0·19 g.) gave colourless crystals during 7 days. These were filtered off, washed with light petroleum, and shown by m. p. (293—295°) and i.r. spectrum to be identical with the isocyanurate obtained in experiment (*a*).

*Tri-1-naphthyl Isocyanurate.*—Bistributyltin oxide (0·28 g.) was added to a solution of 1-naphthyl isocyanate (4 c.c.; 58 mol.) in light petroleum (5 c.c.). After 12 weeks the crystals which had separated were filtered off, thoroughly washed with light petroleum, and identified as tri-1-naphthyl isocyanurate, m. p. 339—342° (decomp.), $\nu_{max.}$ 1710vs cm.$^{-1}$ (C=O) (lit.,[10] m. p. 335—342°; $\nu_{max.}$ 1713 cm.$^{-1}$) [Found: C, 77·9; H, 5·7; N, 7·8%; *M* (in $CHCl_3$), 532 (0·6%), 531 (1·3%). Calc. for $C_{33}H_{21}N_3O_3$: C, 78·1; H, 4·2; N, 8·2%; *M* 508).

*Diethyl Phenyl Isocyanurate.*—(a) *From ethyl isocyanate and tributyltin N-phenyl-N-tributylstannylcarbamate.* Bistributyltin oxide (2·936 g., 1 mol.) and phenyl isocyanate (0·595 g., 1·01 mol.) were mixed, whereupon the carbamate was formed exothermically. When the mixture had cooled, ethyl isocyanate was added (0·39 c.c.; 1 mol.). After 10 days, the i.r. spectrum showed that some isocyanate was still present, but new peaks at 1680 and 765 cm.$^{-1}$ had appeared.

After 28 days the solution was cooled in the refrigerator, whereupon crystals of *diethyl phenyl isocyanurate* separated. These were filtered off, washed with light petroleum, and crystallised from benzene; they had m. p. 95—97·4°, $\nu_{max.}$ 1680s broad (C=O); τ 2·4—2·8 (aromatic ring); quartet centred at 5·99 ($CH_2$); triplet centred at 8·70 ($CH_3$), $J = 7$ c./sec. (Found: C, 60·0; H, 5·6; N, 16·4. $C_{13}H_{15}N_3O_3$ requires C, 59·8; H, 5·8; N, 16·1%).

(b) *From ethyl isocyanate and methyl N-phenyl-N-tributylstannylcarbamate.* Methyl *N*-phenyl-*N*-tributylstannylcarbamate (0·175 g.; 1 mol.) was prepared from tributyltin methoxide and phenyl isocyanate; ethyl isocyanate (0·097 g.; 1 mol.) was then added. The course of the reaction was followed by the decay of the isocyanate band at 2270 cm.$^{-1}$ and the growth of the isocyanurate band at 1680 cm.$^{-1}$. The reaction was complete after 22 days. Pentane (2 c.c.) was then added, and the flask transferred to the refrigerator whereupon a small amount of solid separated. This was filtered off, washed with pentane, and recrystallised from chloroform; m. p. 94·5—97°, mixed m. p. with the sample from experiment (a), 95—97° [*M* (in $CHCl_3$) 269 (1%), 266 (1·7%), mean 267. Cal. for $C_{13}H_{15}N_3O_3$: 261].

*Ethyl Diphenyl Isocyanurate.*—Methyl *N*-ethyl-*N*-tributylstannylcarbamate (2·098 g., 1 mol.) was prepared from ethyl isocyanate and tributyltin methoxide. Phenyl isocyanate (0·58 c.c., 1 mol.) was then added. Next day a small amount of crystalline solid had separated, and after 23 hr. the i.r. spectrum showed that all the isocyanate had reacted.

During the next 6 hr., a considerable amount of solid was formed. Pentane (5 c.c.) was added, the solid was filtered off, washed, and dried, giving *ethyl diphenyl isocyanurate*, m. p. 156·5—159° (67% yield); $\nu_{max.}$ 1695vs (C=O); τ 2·4—2·8 (aromatic ring), quartet centred at 5·96 ($CH_2$), triplet centred at 8·67 ($CH_3$), $J = 7$ c./sec. This material was identical (m. p., mixed m. p., i.r., and proton magnetic resonance spectra) with the product obtained by treating 3-ethyl-1,5-diphenyl-1,5-bistributylstannylbiuret with phenyl isocyanate [Found: C, 65·6; H, 5·05; N, 13·7%; *M* (in $C_6H_6$), 306 (0·5%), 317 (1·4%), 318 (1·9%), mean 314. $C_{17}H_{15}N_3O_3$ requires C, 66·0; H, 4·9; N, 13·6%; *M*, 309].

*Ethyl Di-1-naphthyl Isocyanurate.*—Methyl *N*-ethyl-*N*-tributylstannylcarbamate (1·84 g.) was treated with 1-naphthyl isocyanate (0·80 g., 1 mol.). After 6 days some white solid had separated, and the i.r. spectrum of the supernatant oil showed that very little isocyanate was left. Pentane (10 c.c.) was added; the insoluble solid was filtered off, thoroughly washed, and dried; the m. p. was 193—196° (0·42 g.). The n.m.r. spectrum indicated that this was the expected mixed isocyanurate contaminated with some 11% of bistributyltin carbonate.

No suitable solvent could be found for recrystallising the product. It was therefore shaken for 1 hr. with carbon tetrachloride; the insoluble material was impure ethyl di-1-naphthyl isocyanurate, m. p. 202—204°; $\nu_{max.}$ 1695s (C=O), τ (*a*) 1·85—2·60 (aromatic ring), (*b*) quartet centred at 5·80 ($CH_2$), (*c*) triplet centred at 8·59 ($CH_3$), $J = 7$ c./sec. Relative areas (*a*) : (*c*): Found, 13·8 : 3. Calc., 14 : 3. [Found: C, 67·4; H, 4·45; N, 11·65%; *M* (in $CHCl_3$), 425

[9] L. Horner and K. Klüpfel, *Annalen*, 1955, **591**, 69.
[10] J. Idris Jones and N. G. Savill, *J.*, 1957, 4392.
[11] S. L. Shapiro, V. Bandurco, and L. Freedman, *J. Org. Chem.*, 1961, **26**, 3710.

(0·9%), 415 (1·5%), 411 (2·3%), mean 417. Calc. for $C_{25}H_{19}N_3O_3$: C, 73·35; H, 4·7; N, 10·25%; *M*, 409].

*Attempted Polymerisation of Phenyl Isocyanate.*—Bistributyltin oxide (1·1 g.) was added to a solution of phenyl isocyanate (11 g.; 50 mol.) in ether under nitrogen at −35°. No reaction occurred during 5 days at −35° to 0°. The solvent was removed; after 13 days at room temperature the residue solidified, yielding triphenyl isocyanurate in 85% yield, m. p. (crude) 286—292°.

*Reactions involving Phenyl Isocyanate Dimer.*—Phenyl isocyanate was treated with pyridine yielding di(phenyl isocyanate),[12] m. p. 179—181°; $\nu_{max.}$ 1760vs, broad (C=O) cm.$^{-1}$ (Idris Jones and Savill [10] report two peaks at 1773 and 1756 cm.$^{-1}$; these were barely resolved on our spectrometer). The solution in tetrahydrofuran or in benzene showed a single sharp peak at 1780 cm.$^{-1}$ [Found: *M* (in benzene), 217 (0·5%), 241 (1·1%), mean 229. Calc. for $C_{14}H_{10}N_2O_2$: *M*, 238].

*Di(phenyl isocyanate) and tributyltin methoxide.* Tributyltin methoxide (1·166 g., 1 mol.) was added to a suspension of di(phenyl isocyanate) (0·86 g., 1 mol.) in benzene. After 4 days most of the isocyanate dimer had dissolved. The benzene was removed under reduced pressure, and pentane was added to the residue, whereupon the isocyanate dimer was recovered in 51% yield. The pentane was removed, giving an oil with an i.r. spectrum identical with that of methyl *N*-phenyl-*N*-tributylstannylcarbamate.

*Di(phenyl isocyanate), tributyltin methoxide, and methanol.* Tributyltin methoxide (0·932 g., 1 mol.) was added to a suspension of di(phenyl isocyanate) (0·692 g., 1 mol.) in benzene containing methanol (2% by volume). The solid dissolved after about 5 hr. After 3 days the solvent was removed under reduced pressure. The residue was washed with light petroleum and crystallised from carbon tetrachloride yielding *methyl NN'-diphenylallophanate*, m. p. 130—131·5°, $\nu_{max.}$ 1725s, 1690s (C=O); τ −0·98 (NH), *ca.* 2·58 (aromatic), 6·21 (OMe), identical with the product obtained by treating the isocyanate dimer with methanol in the presence of triethylamine (Found: C, 66·8; H, 5·2; N, 10·5. $C_{15}H_{14}N_2O_3$ requires C, 66·65; H, 5·2; N, 10·35%).

Apparently the only previous report of this compound was by Hoffmann in 1871, who claimed to have obtained it from di(phenyl isocyanate) and methanol, but recorded no analysis and an m. p. of 231°.[13] This compound was most probably *sym*-diphenylurea which has m. p. 238°.

*Di(phenyl isocyanate) and bistributyltin oxide.* Bistributyltin oxide (1·471 g., 2 mol.) was added to a suspension of di(phenyl isocyanate) (0·294 g., 1 mol.) in benzene (20 c.c.). After 3 hr. the solid had dissolved. Three days later the solvent was removed under reduced pressure leaving an oil; the i.r. spectrum showed that this was a mixture of diphenyl-*NN'*-bistributylstannylurea and bistributyltin carbonate, and that tributyltin *N*-phenyl-*N*-tributylstannylcarbamate was absent. At 100°, the carbonate underwent decarboxylation leaving a mixture of bistributyltin oxide and the urea derivative.

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[12] J. S. Blair and G. E. P. Smith, *J. Amer. Chem. Soc.*, 1934, **56**, 907.
[13] A. W. Hoffmann, *Ber.*, 1871, **4**, 248.