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## Organometallic Reactions. Part X.<sup>1</sup> The Preparation and Reactions of Some Alkynyl-lead Compounds

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Trialkylalkynyl-lead compounds have been prepared by treating trialkyl-lead methoxides with alkynes, and by thermal decarboxylation of trialkyl-lead alkynylcarboxylates.

The alkynyl-lead bond is more reactive than the alkyl-lead bond, and takes part in Grignard-like reactions. The alkynyl-lead compounds react with acetyl chloride to give the corresponding alkynyl methyl ketones. With aryl isocyanates, phenylethynyltriethyl-lead reacts to give a 1,3-diaryl-5-benzylidenehydantoin, which can also be prepared by ring-closure of an *NN'*-diaryl-*N*-phenylpropiolylurea, obtained by the addition of phenylpropiolic acid to a diarylcarbodi-imide. A similar ring closure, which would give 5-benzyl-1,3-diphenylhydantoin, could not be induced in *N*-cinnamoyl-*NN'*-diphenylurea.

THE high electronegativity of the alkynyl group differentiates the alkynyl-metallic compounds from the corresponding alkyl compounds. In Group IV, the alkynyl-metal bond can be formed more readily than the alkyl-metal bond. Very little is known about the

† Organometallic acetylides of the Main Groups III-V have been reviewed in ref. 2.

reactions of the products, but it is clear that in, for example, hydrolysis, the alkynyl-metal bond is also more readily broken.<sup>†</sup> This paper describes two new

<sup>1</sup> Part IX, A. G. Davies and R. J. Puddephatt, J. Chem. Soc. (C), 1967, 2663. <sup>2</sup> W. E. Davidsohn and M. C. Henry. Chem. Rev., 1967. 67.

<sup>2</sup> W. E. Davidsohn and M. C. Henry, *Chem. Rev.*, 1967, **67**, 73.

routes to alkynyl-lead compounds, and two reactions which these compounds undergo which exploit this high reactivity.

The alkynyl-lead compounds have usually been prepared by treating an organolead halide with a sodium acetylide in liquid ammonia or an organic solvent; two have also been obtained from triphenylplumbylsodium and a halogenoalkyne.<sup>2</sup>

In Part IX<sup>1</sup> it was shown that the Pb–O bond in organolead alkoxides was readily cleaved by weak acids such as cyclopentadiene or haloforms, to give the corresponding cyclopentadienyl- and trihalogenomethyl-lead compounds. A similar rapid and often exothermic reaction occurs with 1-alkynes at room temperature, to give alkynyl-lead compounds [equation (1)  $R^1 = Et$ ,  $R^2 = Ph$  or Bu;  $R^1 = R^2 = Ph$ ].

Bistrimethylplumbylacetylene was obtained by passing acetylene through a suspension of trimethyl-lead methoxide in boiling benzene.

$$R^{1}_{3}Pb^{*}OMe + HC \equiv CR^{2} \longrightarrow R^{1}_{3}Pb^{*}C \equiv CR^{2} + MeOH$$
 (1)

This emphasises again the high reactivity of the Pb-O bond compared with the Sn-O bond; Lutsenko, Ponomarev, and Petrii<sup>3</sup> prepared phenylethynyltriethyltin by heating triethyltin methoxide with phenylacetylene at  $150^{\circ}$  for 18 hr.

Alkynyl-lead compounds can also be prepared by the decarboxylation of triphenyl-lead alkynylcarboxylates.

Triphenyl-lead propiolate and phenylpropiolate, and bistriphenyl-lead acetylene dicarboxylate were prepared by treatment of triphenyl-lead hydroxide with the appropriate carboxylic acid. The phenylpropiolate decarboxylates in boiling toluene (112°) giving phenylethynyltriphenyl-lead in 65% yield [equation (2)].

Ph<sub>3</sub>Pb·O·CO·C≡CPh 
$$\longrightarrow$$
 Ph<sub>3</sub>Pb·C≡CPh  $+$  CO<sub>2</sub> (2)

The propiolate and acetylene dicarboxylate could not be induced to decompose in boiling toluene or xylene  $(140^{\circ})$ , although both compounds melted with decarboxylation at about 190°. In boiling mesitylene  $(164^{\circ})$  triphenyl-lead propiolate rapidly evolved carbon dioxide to give bistriphenylplumbylacetylene in 52% yield.

2 
$$Ph_3Pb O CO C = CH \longrightarrow Ph_3Pb C = C PbPh_3 + 2 CO_3 + CH = CH (3)$$

Similar decarboxylations of triphenyltin propiolate and of bistrialkyltin acetylenedicarboxylates between 170 and 200° have been reported;<sup>4</sup> there is apparently, therefore, no marked difference in the thermal stability of these triphenyltin and triphenyl-lead compounds.

The reactivity of the alkynyl-lead bond in polar reactions is higher than that of the alkyl-lead bond but generally lower than that of the alkynyl-magnesium bond of a Grignard reagent. If a trialkylalkynyl-lead compound is treated with acetyl chloride, a mildly <sup>3</sup> I. F. Lutsenko, S. V. Ponomarev, and O. P. Petrii, *Zhur. obshchei Khim.*, 1962, **32**, 896.

<sup>4</sup> J. G. A. Luijten and G. J. M. van der Kerk, *Rec. Trav. chim.*, 1964, **83**, 295.

exothermic reaction occurs, giving the corresponding trialkyl-lead chloride and alkynyl methyl ketone (e.g., equation 4)

 $Et_3Pb\cdot C \equiv CPh + MeCOCI \longrightarrow Et_3PbCl + MeCO\cdot C \equiv CPh$  (4)

By this process, 1-phenylbut-1-yn-3-one and oct-3-yn-2-one were prepared in good yield. Only one of the two plumbyl groups in bistrimethylplumbylacetylene reacted with acetyl chloride at room temperature; in boiling carbon tetrachloride, both groups could be caused to react, but, under either set of conditions, only a black tar, and no ethynyl ketone, could be isolated.

These reactions can be compared with those which have been reported to take place between acetyl chloride and other ethynylmetallic compounds. The ethynylsilanes have been shown to react with acetyl chloride only in the presence of aluminium trichloride; only one silyl group in bistrimethylsilylacetylene reacted, to give 1-trimethylsilylbut-1-yn-3-one.<sup>5</sup> Phenylethynyl- and hexynyl-cadmium compounds react with acetyl chloride to give the appropriate methyl ketone in yields of 70 and 50% respectively,<sup>6</sup> but phenylethynylmagnesium chloride under similar conditions gives a low yield of ketone (8—15%), much of it reacting further to form 1,1-bis(phenylethynyl)ethanol.<sup>7</sup>

An exothermic reaction also occurs between alkynyllead compounds and phenyl or 1-naphthyl isocyanate, but the initial 1:1- adducts cannot be isolated, and the products have the composition  $R_3Pb\cdotC\equiv CPh,2ArNCO$ (R = Ph or  $C_{10}H_7$ ). We thought initially that these were derivatives of uracils (V),<sup>8</sup> but subsequent evidence has shown them in fact to be benzylidene-hydantoins (III).



The initial addition presumably occurs across the N=C bond of the isocyanate to give the plumbyl derivative of propiolylanilide (I); the Pb-N bond of this is a more powerful addendum group than the initial Pb-C bond, and adds to a second molecule of isocyanate to give an N-plumbyl-N'-propiolylurea (II). Ring closure

<sup>&</sup>lt;sup>5</sup> L. Birkofer, A. Ritter, and H. Uhlenbrauck, *Chem. Ber.*, 1963, **96**, 3280.

 <sup>&</sup>lt;sup>6</sup> O. G. Yashina, T. V. Zarva, and L. I. Vereschagin, *Zhur.* org. *Khim.*, 1967, 3, 219 (*Chem. Abs.*, 1967, 66, 94,664).
<sup>7</sup> J. W. Kroeger and J. A. Niewland, *J. Amer. Chem. Soc.*,

<sup>1936, 58, 1861.</sup> <sup>8</sup> A. G. Davies and R. J. Puddephatt, *Tetrahedron Letters*, 1967, 2265.

then occurs by intramolecular addition of the Pb-N bond across the ethynyl group.

This sequence of reactions is supported by the fact that the propiolylureas can be prepared by treating diarylcarbodi-imides with phenylpropiolic acid. Triethyl-lead methoxide or sodium methoxide then exothermically catalyse ring closure to give the hydantoin (equation 6).



4-Benzylidene-1,3-diphenylhydantoin (IV) (probably trans), has been prepared previously by desulphuration of the corresponding 2-thiohydantoin, and by condensing 1,3-diphenylhydantoin with benzaldehyde.<sup>9</sup> Its structure was confirmed by reducing it to the benzylhydantoin with phosphorus and hydriodic acid. Bird showed <sup>10</sup> that one of the products which Tyabji had obtained <sup>11</sup> from the reaction between phenyl isocyanate and sodium phenylacetylide was this same benzylidenehydantoin; we are very grateful to Dr. Bird for bringing his work to our attention, and for supplying us with a sample of his product.

The 4-benzylidene-1,3-diphenylhydantoin from each of the three above routes is yellow, and from our two routes white, but otherwise (m. p., mixed m. p., i.r., u.v., and n.m.r. spectra) they are identical; furthermore our compound was reduced with phosphorus and hydriodic acid to the corresponding benzyl compound. The colour could not be removed from the yellow material by chromatography, but treatment with alkali gave the white compound to which the colour could not be restored by acid. Hahn and Endicott have shown that 4-benzylidenehydantoin can be obtained in yellow and white forms which are interconvertible by this technique.12

The identity of our products as hydantoins rather than uracils is therefore beyond doubt, and we have to accept the surprising fact that the ring-closure reaction  $(II) \longrightarrow$ (III) proceeds by nucleophilic attack of nitrogen at the carbon atom  $\alpha$  to the carbonyl group, rather than at the  $\beta$ -position which would be expected to be more highly activated.<sup>13</sup> For example, the polar addition of tri-

\* Note added 3 October, 1967. Professor Neumann has informed us that the reaction is complete after 18 hr. at 120°, and that the product has been independently identified as the 5-benzylidene-1,3-diphenylhydantoin.17

12 D. A. Hahn and M. M. Endicott, J. Amer. Chem. Soc., 1937, 59, 2741.

methyl-lead hydride to propiolonitrile or methyl propiolate involves nucleophilic attack of hydride at the β-carbon atom.<sup>14</sup>

It appears that activation of the  $\beta$ -position by mesomeric electron attraction by the carbonyl group, is accompanied by a weaker activation of the  $\alpha$ -position by inductive relay similar to the differential activation of the ortho, para, and meta position of an aromatic ring by a substituent. Steric strain in the linear ethynyl group may preclude the transition state which would lead to the formation of the uracil (V), thereby permitting the unusual direction of addition to be observed.

Such a steric restriction might not apply to the ring closure of the corresponding olefinic compound, Ncinnamoyl-NN'-diphenylurea (VI) to give 1,3,6-triphenyl-5,6-dihydrouracil.



The cinnamoylurea was readily prepared from diphenylcarbodi-imide and cinnamic acid, but it could not be induced to undergo ring closure, and only cleavage of the molecule could be observed. Sodium methoxide in boiling methanol reacted to give diphenylurea and, presumably, methyl cinnamate, and treatment with boiling pyridine or with triphenyl-lead methoxide gave cinnamoylanilide.

The differences that exist between the behaviour of the ethynyl-lead compounds reported here, and the ethynyl derivatives of other metals, are often subtle, and may give the lead compounds some specific applications in synthesis. Thus, whereas the phenylethynyl-lead compounds and phenyl isocyanate give 5-benzylidene-1,3-diphenylhydantoin in good yield, phenylethynylmagnesium bromide under similar conditions gives phenylpropiolylanilide, PhNH•CO•C=CPh, in 90% yield,<sup>15</sup> presumably because of the different differential reactivity of the C-Mg and N-Mg bonds as addenda. The reaction of phenylethynylsodium with phenyl isocyanate is more complicated and some benzodiazepinedione is apparently formed together with the hydantoin.<sup>10,11</sup> Triethylphenylethynyltin has been reported to undergo a series of consecutive reactions with phenyl isocyanate, perhaps of the type discussed here, but the reaction conditions and products have not yet been described.<sup>16</sup> \*

<sup>13</sup> E. Winterfeld, Angew. Chem. Internat. Edn., 1967, 6, 423.

15 J. R. Johnson and W. L. McEwen, J. Amer. Chem. Soc., 1926, 48, 469.

<sup>16</sup> W. P. Neumann and F. C. Kleiner, unpublished work, referred to by K. König and W. P. Neumann, *Tetrahedron Letters*, 1967, 495. <sup>17</sup> W. P. Neumann and F. Kleiner, personal communication;

F. Kleiner, Ph.D. Thesis, University of Giessen, May 1967.

<sup>&</sup>lt;sup>9</sup> S. E. Hadley and T. B. Johnson, J. Amer. Chem. Soc., 1915, 37, 171.

<sup>&</sup>lt;sup>10</sup> C. W. Bird, J. Chem. Soc., 1965, 5762.

<sup>&</sup>lt;sup>11</sup> A. Tyabji, J. Univ. Bombay, 1942, 10, 110.

<sup>14</sup> A. J. Leusink and G. J. M. van der Kerk, Rec. Trav. chim., 1965, 84, 1617.

## EXPERIMENTAL

General methods have been described in Part IX.<sup>1</sup>

Alkynyl-lead compounds were handled in a dry gloved box. Mass spectra were recorded on an A.E.I. M.S.9 spectrometer.

Preparation of Triphenyl-lead Propiolates.—(i) Triphenyllead phenylpropiolate. Triphenyl-lead hydroxide (3.70 g., 8.11 mmole) was dissolved in a solution of phenylpropiolic acid (1.40 g., 9.60 mmoles) in benzene (15 c.c.). The mixture was filtered then cooled in ice, to yield crystals of triphenyl-lead phenylpropiolate (3.84 g., 81%), m. p. 159— 160° (decomp.),  $v_{max}$  2220 (C=C) cm.<sup>-1</sup> (Found: C, 55.6; H, 3.1. C<sub>27</sub>H<sub>20</sub>O<sub>2</sub>Pb requires C, 55.2; H, 3.4%). It could not be redissolved in benzene or acetone, and was too insoluble for the molecular weight or n.m.r. spectrum to be determined.

(ii) Bistriphenyl-lead acetylenedicarboxylate. Solutions of triphenyl-lead hydroxide (3.36 g., 7.38 mmoles) in acetone (10 c.c.) and acetylene dicarboxylic acid (0.45 g., 3.95 mmole) in acetone (10 c.c.) were mixed. A solid rapidly separated. The mixture was shaken for 15 min., then filtered; the precipitate was washed with acetone, to yield bistriphenyl-lead acetylenedicarboxylate (2.25 g., 62%), m. p. 186—187° (decomp.) (Found: C, 48.6; H, 3.0.  $C_{40}H_{30}O_4Pb_2$  requires C, 48.6; H, 3.0%).

(iii) Triphenyl-lead propiolate. Propiolic acid (0.86 g., 5.88 mmoles) was added to a suspension of triphenyl-lead hydroxide (2.68 g., 5.88 mmoles) in benzene (15 c.c.). The mixture was shaken for 15 min., then filtered. The solid was recrystallised from acetone to yield triphenyl-lead propiolate (1.82 g., 61%), m. p. 189–190° (decomp.),  $v_{max}$ . 2100w (C=C), 3300w (CH) cm.<sup>-1</sup> (Found: C, 50.9; H, 3.2. Calc. for C<sub>21</sub>H<sub>16</sub>O<sub>2</sub>Pb: C, 49.7; H, 3.2%).

Preparation of Ethynyl-lead Compounds.—Phenylethynyl triethyl-lead. Phenylacetylene (1·20 g., 11·78 mmoles) was added to triethyl-lead methoxide (2·85 g., 8·78 mmoles) in benzene. The mixture became warm and darkened in colour. Distillation gave phenylethynyltriethyl-lead (2·98 g., 86%) as a colourless liquid, b. p. 94—97°/0·05 mm.,  $v_{max}$ . 2125 (C=C) cm.<sup>-1</sup>. It decomposed within a few hours to yield a black precipitate and hence was analysed by titration with hydrochloric acid in aqueous acetone with Methyl Red indicator (Found: Equiv. wt., 407. Calc. for C<sub>14</sub>H<sub>20</sub>Pb: 395). The integrated n.m.r. spectrum showed that the ratio of phenyl to ethyl protons was 1:3.

Masson and Cadiot <sup>18</sup> prepared the same compound in 41% yield by treating triethyl-lead chloride with phenylethynyl-sodium in pentane, but report b. p. 66°/1 mm.,  $\nu_{max}$  2220 (C=C) cm.<sup>-1</sup>; the product was not analysed.

*Hexynyltriethyl-lead.* Hex-1-yne (1.05 g., 12 mmoles) was added to triethyl-lead methoxide (2.37 g., 6.31 mmoles) in benzene (5 c.c.). to yield *hexynyltriethyl-lead* (2.05 g., 75%) as a colourless liquid, b. p. 61—63°/0.05 mm.,  $v_{max}$ . 2135 (C=C) cm.<sup>-1</sup> (Found: C, 39.2; H, 6.8%; Equiv. 380. C<sub>12</sub>H<sub>24</sub>Pb requires C, 38.4; H, 6.4%; Equiv. 375).

Phenylethynyltriphenyl-lead. (i) Triphenyl-lead chloride  $(5\cdot 0 \text{ g.}, 10\cdot 6 \text{ mmoles})$  in benzene (50 c.c.) was added to a solution of sodium methoxide [from sodium  $(0\cdot 29 \text{ g.}, 12\cdot 6 \text{ mmoles})$ ] in methanol (10 c.c.). Phenylacetylene (2.0 g., 19.6 mmoles) was then added, and the mixture was stirred

<sup>18</sup> J. C. Masson and P. Cadiot, Bull. Soc. chim. France, 1965, 3518.

<sup>19</sup> C. Beermann and H. Hartman, Z. anorg. Chem., 1954, 276, 20.

for 15 min. The methanol was distilled off, the solution was centrifuged to remove sodium chloride, and the benzene was then removed to yield phenylethynyltriphenyl-lead (from carbon tetrachloride–light petroleum) as a white solid (3.71 g., 65%), m. p. 55—56°,  $\nu_{\rm max}$  2130 (C=C) cm.<sup>-1</sup> (lit.,<sup>18</sup> m. p. 56°,  $\nu_{\rm max}$  2130 cm.<sup>-1</sup>). (ii) A suspension of triphenyl-lead phenylpropiolate

(ii) A suspension of triphenyl-lead phenylpropiolate (1.59 g., 2.72 mmoles) slowly dissolved in boiling toluene (10 c.c.) with the evolution of a gas. After 15 min., the mixture was cooled and filtered, and the solvent was removed to yield phenylethynyltriphenyl-lead (0.95 g., 65%) (from carbon tetrachloride-light petroleum at *ca*.  $-10^{\circ}$ ), m. p. 58–59° (Found: C, 57.9; H, 3.6. Calc. for C<sub>26</sub>H<sub>20</sub>Pb: C, 58.0; H, 3.7%).

Bis(trimethylplumbyl)acetylene. Dry acetylene was bubbled through a suspension of trimethyl-lead methoxide (6.45 g., 22.8 mmoles) in distilling benzene, so that the methanol which was liberated was continually removed. The methoxide slowly dissolved to give a clear solution. The solvent was removed to leave bis(trimethylplumbyl)acetylene as a white solid which was sublimed at 80—  $100^{\circ}/0.1$  mm. (5.90 g., 99%), m. p. 99— $101^{\circ} \tau$  (in CCl<sub>4</sub>) 8.96 (CH<sub>3</sub>),  $J_{\rm Pb-H} = 76$  c./sec. (Found: C, 17.9; H, 3.9. C<sub>8</sub>H<sub>18</sub>Pb<sub>2</sub> requires C, 18.2; H, 3.4%).

Bis(triphenylplumbyl)acetylene. Bistriphenyl-lead acetylenedicarboxylate and triphenyl-lead propiolate did not undergo decarboxylation when they were suspended in boiling toluene or xylene. However, triphenyl-lead propiolate (0.86 g., 1.70 mmoles) rapidly dissolved in boiling mesitylene, as a gas was evolved. After 15 min. the mixture was filtered and the filtrate yielded bis(triphenylplumbyl)acetylene (0.40 g., 52%) (from carbon tetrachloride-light petroleum at low temp.), m. p. 134—136° (lit.,<sup>19</sup> 138.5°) (Found: C, 51.3; H, 3.3. Calc. for  $C_{38}H_{30}Pb_2$ : C, 50.8; H, 3.3%).

Reactions of Alkynyl-lead Compounds with Acetyl Chloride. —(i) Phenylethynyltriethyl-lead (2.51 g., 6.36 mmoles) and acetyl chloride (0.47 c.c., 6.55 mmoles) were mixed; after ca. 2 min. some crystals separated, and the mixture became warm and then solidified. It was extracted with pentane (10 c.c.) to yield triethyl-lead chloride (2.00 g., 96%) and 1-phenylbut-1-yn-3-one (0.87 g.), b. p. 114—116°/14 mm. (lit.,<sup>20</sup> b. p. 120—125°/14 mm.),  $\tau$  (in CCl<sub>4</sub>) 7.60 (CH<sub>3</sub>);  $\nu_{max}$ . 1670 (C=O), and 2170s (C=C) cm.<sup>-1</sup>.

The ketone was contaminated with a little tetraethyllead, and was therefore isolated as its 2,4-dinitrophenylhydrazone (62%), m. p. 199–200°,  $\nu_{max}$  2160w (C=C) cm.<sup>-1</sup> (Found: C, 58.9; H, 3.6; N, 17.3. C<sub>16</sub>H<sub>12</sub>N<sub>4</sub>O<sub>4</sub> requires C, 59.1; H, 3.7; N, 17.3%).

(ii) Hexynyltriethyl-lead (1·59 g., 4·23 mmoles) and acetyl chloride (0·34 c.c., 9·74 mmoles) similarly gave oct-3-yn-2-one (0·51 g., 84%), b. p. 74—76°/14 mm. (lit.,<sup>21</sup> 74°/12 mm.),  $\tau$  7·70 (CH<sub>3</sub>),  $\nu_{max}$ . 1680 (C=O), 2210s (C=C) cm.<sup>-1</sup>; 2,4-dinitrophenylhydrazone, m. p. 87—88° (lit.,<sup>21</sup> 87—88°)  $\nu_{max}$ . 2200w (C=C) cm.<sup>-1</sup> (Found: C, 54·8; H, 5·3. Calc. for C<sub>14</sub>H<sub>16</sub>N<sub>4</sub>O<sub>4</sub>: C, 55·2; H, 5·3%).

(iii) Acetyl chloride (0.90 c.c., 12.4 mmoles) was added to bis(trimethylplumbyl)acetylene (3.24 g., 6.12 mmoles) in carbon tetrachloride (5 c.c.). Trimethyl-lead chloride (1.76 g., 6.11 mmoles) slowly separated, and was sublimed at 185—195°/0.1 mm. (Found: Cl, 12.4. Calc. 12.1%).

<sup>20</sup> D. V. Nightingale and F. Wadsworth, J. Amer. Chem. Soc., 1945, **67**, 416.

<sup>21</sup> K. Bowden, I. M. Heilbron, E. R. H. Jones, and B. C. L. Weedon, *J. Chem. Soc.*, 1946, 39.

The solvent was removed under reduced pressure from the dark brown filtrate, to leave an intractable black tar.

A solution of bis(trimethylplumbyl)acetylene (2.89 g., 5.48 mmoles) in carbon tetrachloride (5 c.c.) was added dropwise to a refluxing solution of an excess of acetyl chloride (4.0 c.c.) in carbon tetrachloride (10 c.c.). The solution quickly became deep brown, and was boiled for 2 hr. Trimethyl-lead chloride was isolated in 84% yield, but again the other product was a tar.

Reaction of Phenylethynyltriethyl-lead with Phenyl Isocyanate.--Phenyl isocyanate (0.50 c.c., 4.57 mmoles) was added to phenylethynyltriethyl-lead (1.80 g., 4.56 mmoles). After 5 min., heat was evolved, and after 10 min. the band of the isocyanate group disappeared from the infrared spectrum; a very viscous, yellow-brown oil was left,  $\nu_{max}$ 1620m, 1710s, and 1760s cm.<sup>-1</sup>. This reacted exothermically with acetic acid (0.5 c.c.) to give a white product which was dissolved in benzene (15 c.c.) and extracted with 2N-sodium hydroxide solution (3  $\times$  20 c.c.) to remove triethyl-lead hydroxide. Evaporation of the benzene gave 5-benzylidene-1,3-diphenylhydantoin (0.62 g.) which crystallised from benzene-light petroleum as white crystals m. p. 197-198° [Found: C, 77.3; H, 4.4; N, 8.6%; M (in  $C_6H_6$ ), 321.  $C_{21}H_{16}N_2O_2$  requires C, 77.5; H, 4.7; N, 8.2%; M, 340].

Reaction of Phenylpropiolic Acid with Diphenylcarbodiimide.—During 2 days, a mixture of diphenylcarbodi-imide (1·18 g., 6·08 mmoles) and phenylpropiolic acid (0·89 g., 6·09 mmoles) in benzene (15 c.c.) deposited white crystals of NN'-diphenyl-N-phenylpropiolylurea (0·99 g., 46%), m. p. 139—140° (benzene),  $\tau$  (in Me<sub>2</sub>CO) – 1·58 (NH) \*  $v_{max}$  3300 (NH), 2225 (C=C), 1645 (C=O), and 1715 (C=O) cm.<sup>-1</sup> (Found: C, 77·4; H, 5·05; N, 8·2. C<sub>22</sub>H<sub>16</sub>N<sub>2</sub>O<sub>2</sub> requires C, 77·5; H, 4·7; N, 8·2%). Mass spectrum: 340·1207 (Calc. for M, 340·1212), 211 (PhNH·CO·C=CPh), 129 (OC·C=CPh), 119 (PhNCO), 93 (PhNH<sub>2</sub>), and 91 (PhN).

The propiolylurea (0.46 g., 1.36 mmoles) in benzene (20 c.c.) was treated with triethyl-lead methoxide (0.42 g., 1.29 mmoles) in benzene (5 c.c.), when an exothermic reaction took place. After 10 min., the solution was washed with 2N-sodium hydroxide ( $3 \times 20$  c.c.) and the benzene was removed to yield 5-benzylidene-1,3-diphenylhydantoin (0.42 g., 91%), m. p. 193-194°, identical (mixed m. p., i.r. and n.m.r. spectra) with the specimen prepared above.

Identification of 5-Benzylidene-1,3-diphenylhydantoin.— (a) Mass spectrum. The mass spectrum showed the presence of a molecular ion at  $340 \cdot 1220$  (Calc. for  $C_{22}H_{16}N_2O_2$ :  $340 \cdot 1212$ ), with the major fragment at  $193 \cdot 0904$  (Calc. for  $C_{14}H_{11}N$ :  $193 \cdot 0891$ ), corresponding to loss of CO·NPh·CO. This mode of fragmentation can readily be accepted for the hydantoin structure (IV), where the fragment would be the stable ketenimine, PhCH=C=NPh, but would be less easy to understand for the uracil structure (V). 5-Benzylidene-1,3-di-1-naphthylhydantoin behaved similarly (see below).

(b) Comparison with Bird's product. Bird's product (A) was distinctly yellow, whereas ours (B) was white, but otherwise the two compounds were identical:  $\nu_{max}$ . 314 m $\mu$ ,  $\epsilon$  15,100;  $\nu_{max}$ . 1645, 1720, and 1760 cm.<sup>-1</sup>:  $\tau$  (in CDCl<sub>3</sub>) 2.37

(CH) surrounded by a complex pattern for the aromatic rings. M. p.s: (A)  $189-190^{\circ}$ , (B)  $191-192^{\circ}$ , (A) + (B)  $189-190^{\circ}$ .

The yellow material (A) in acetone was chromatographed over a column of silica gel, but remained yellow. The yellow colour was not removed when (A) was recrystallised from acetone, but recrystallisation from aqueous acetone containing a trace of sodium hydroxide gave a white product, identical in all respects with compound (B). The colour was not restored when this white product was heated in boiling acetic acid for 2 hr.

(c) Reduction to 5-benzyl-1,3-diphenylhydantoin. Hydrogen iodide solution (5 c.c., sp. gr. 1·7) was added to the benzylidenehydantoin (B) (1·7 g.) and red phosphorus (0·4 g.) in glacial acetic acid (20 c.c.). The mixture was heated under reflux for 2 hr., then the deep red-brown solution was filtered into water (50 c.c.), when a gummy solid separated. This was dissolved in ether, washed with sodium hydrogen sulphite, dried, and the ether removed to give crystalline 5-benzyl-1,3-diphenylhydantoin (0·65 g., 35%), which melted partly at 60—62°, then finally at 105— 110° (lit.,<sup>9</sup> m. p. 58—62°),  $v_{max}$ , 1720 and 1770 (C=O) cm.<sup>-1</sup>;  $\tau$ (in CDCl<sub>3</sub>) doublet 6·60 (CH<sub>2</sub>), triplet 4·81 (CH)  $J_{CH-CH_2}$  3·9 c./sec., rel. areas C<sub>6</sub>H<sub>5</sub>: CH<sub>2</sub>: CH = 15: 2: 1 (Found: N, 8·35. Calc. for C<sub>22</sub>H<sub>18</sub>N<sub>2</sub>O<sub>2</sub>: 8·2%). The compound rapidly became gummy when it was exposed to air.

Reaction of Phenylethynyltriethyl-lead with 1-Napthyl Isocyanate.—Heat was evolved when 1-naphthyl isocyanate (0.83 c.c., 5.78 mmoles) and phenylethynyltriethyl-lead (2.28 g., 5.78 mmoles) were mixed, to give a glassy resin. This was treated with acetic acid (2.0 c.c.) in benzene (5 c.c.) when a thick white precipitate separated. This solid, which consisted of a mixture of the hydantoin and triphenyl-lead acetate was washed twice with a warm solution of 2N-sodium hydroxide (20 c.c.) in acetone (10 c.c.) to remove triethyl-lead hydroxide, then recrystallised from hot acetone (50 c.c.) and water to give 5-benzylidene-1,3-di-1-naphthylhydantoin as white crystals (0.46 g., 38%), m. p. 252—255°, identical with the material described below.

Reaction of Phenylpropiolic Acid with Di-1-naphthylcarbodi-imide.—A mixture of di-1-naphthylcarbodi-imide (0.85 g., 2.90 mmoles) and phenylpropiolic acid (0.43 g., 2.90 mmoles) was heated under reflux in methanol for 2 hr., during which time a pale yellow solid separated. This was filtered off and washed with methanol to give NN'-di-1naphthyl-N-phenylpropiolylurea (1.02 g.), m. p. 154—155°,  $\tau$  (in C<sub>6</sub>H<sub>6</sub>) — 2.46 (NH),  $v_{max}$ . 3250 (NH), 2200 (C=C), 1625 (C=O), 1620 (C=O) and 1720 (C=O) cm.<sup>-1</sup> [Found: C, 81.9; H, 4.9; N, 6.2%; *M* (in acetone), 433. C<sub>30</sub>H<sub>20</sub>N<sub>2</sub>O<sub>2</sub> requires C, 81.8; H, 4.5; N, 6.4%; *M*, 440]. Mass spectrum: 440 (Calc. for *M*, 440) 312 (C<sub>10</sub>H<sub>7</sub>NH·CO·NHC<sub>10</sub>H<sub>7</sub>), 271 (C<sub>10</sub>H<sub>7</sub>NH·CO·C=CPh), 169 (C<sub>10</sub>H<sub>7</sub>NCO), 143 (C<sub>10</sub>H<sub>7</sub>NH<sub>2</sub>), and 129 (C<sub>6</sub>H<sub>5</sub>·C=C·CO).

A similar reaction, on the same scale, in benzene gave the same propiolylurea (0.77 g.), m. p. 149–150°, and N-1naphthylpropiolylamide (0.31 g.), m. p. 166–167°,  $v_{max}$  3225 (NH), 2220 (C=C), and 1635 (C=O) cm.<sup>-1</sup> [Found: C, 83.7; H. 4.9; N, 5.3%; *M* (in acetone), 272. C<sub>19</sub>H<sub>13</sub>NO requires C, 84.0; H, 4.8; N, 5.2%; *M*, 271].

A suspension of NN'-di-1-naphthyl-N-phenylpropiolylurea (0.50 g., 1.14 mmoles) in methanol (10 c.c.) containing sodium methoxide [from sodium (0.014 g., 0.61 mmoles)] was heated under reflux, when the colour quickly changed from yellow to white. After 5 min., the mixture was cooled, and the precipitate was separated and recrystallised from

<sup>\*</sup> The very low values of the NH signal in the phenylpropiolyland cinnamyl-ureas reported here imply intramolecular hydrogen bonding between the NH and C=O groups, as in the corresponding allophanates.<sup>22</sup>

<sup>&</sup>lt;sup>22</sup> A. J. Bloodworth and A. G. Davies, J. Chem. Soc. (B), 1966, 125.

aqueous ethanol, to yield 5-benzylidene-1,3-di-1-naphthylhydantoin (0.36 g., 72%), m. p. 254–256°,  $\tau$  (in Me<sub>2</sub>CO) 2.75 (CH),  $\nu_{max}$  1650m, 1725s, and 1770m cm.<sup>-1</sup> identical with the sample described above (Found: C, 80.97; H, 4.75; N, 6.50. C<sub>30</sub>H<sub>20</sub>N<sub>2</sub>O<sub>2</sub> requires C, 81.8; H, 4.5; N, 6.4%), Mass spectrum: 440.1528 (Calc. for *M*, 440.1525); 243 (C<sub>10</sub>H<sub>7</sub>N:C:CHPh).

Reaction of Cinnamic Acid with Diphenylcarbodi-imide. Cinnamic acid (2.96 g.) and diphenylcarbodi-imide (3.88 g.) were mixed in methanol. After 16 hr. the solution was filtered and concentrated under reduced pressure, to yield NN'-diphenyl-N-cinnamoylurea (4.9 g., 72%), m. p. 112— 113°,  $v_{max}$ , 1705s, 1655m (C=O), 1615m (C=C), and 3170 (NH) cm.<sup>-1</sup>;  $\tau$  (in CCl<sub>4</sub>) doublet 2.03 (PhCH), doublet 3.69 (CH·CO),  $J_{CH=CH}$  16.2 c./sec., -1.94 (NH) (Found: C. 77.1; H, 5.6; N, 8.2. C<sub>22</sub>H<sub>18</sub>N<sub>2</sub>O<sub>2</sub> requires C, 77.2; H, 5.3; N, 8.2%).

Attempts to Cyclise NN'-Diphenyl-N-cinnamoylurea.—(a) The urea (1.0 g.) and sodium methoxide (0.05 g.) were heated under reflux in methanol (20 c.c.) for 1 hr. The solvent was removed at the pump to leave NN'-diphenyl-urea (0.3 g.).

(b) The cinnamoylurea (1.0 g.) was recovered after 2 days from its solution in a mixture of pyridine (2 c.c.) and tetra-

hydrofuran (10 c.c.). The urea  $(1 \cdot 0 \text{ g.})$  was therefore boiled in pyridine (10 c.c.) for 2 hr., to yield cinnamoylanilide  $(0 \cdot 46 \text{ g.})$ , identical with the material described below.

(c) The diphenylcinnamoylurea (0.8 g.) in benzene (10 c.c.) was added to triphenyl-lead methoxide (1.0 g.). The mixture became warm, the lead methoxide dissolved, and, after a few minutes, a solid began to separate. Water (0.5 c.c.) was added to precipitate triphenyl-lead hydroxide. The mixture was filtered and the solvent removed from the filtrate, to yield cinnamoylanilide (0.35 g.), m. p. 148–150° (lit.,<sup>23</sup> 150°)  $\nu_{max}$ . 1660 (C=O), 1625 (C=C), and 3280 (NH) cm.<sup>-1</sup>;  $\tau$  (in Me<sub>2</sub>CO) doublet 2.96 (CHCO),  $J_{CH=CH}$  16.2 c./sec.; the PhCH signal was obscured by that of the phenyl group; the NH signal was not observed.

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<sup>23</sup> W. Autenrieth, Ber., 1901, 34, 186.