Dehydrogenation of Secondary Formamides

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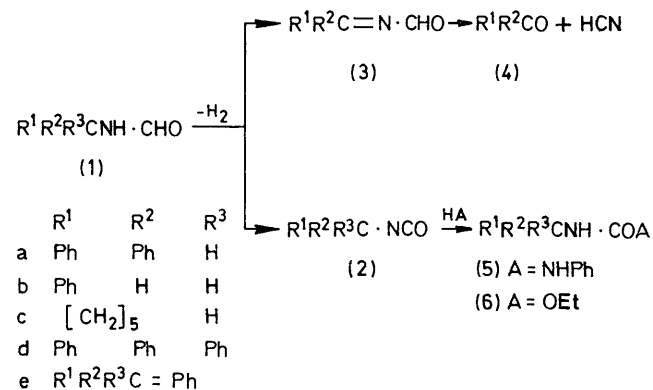
N-Diphenylmethyl- (1a), N-cyclohexyl- (1c), N-triphenylmethyl- (1d), and N-phenyl-formamide (1e) have been dehydrogenated to give the corresponding isocyanates (2) by treatment with diethyl azodicarboxylate (52—60% yields) or with palladium (8—37% yields). N-Benzylformamide (1b) gave only traces of benzyl isocyanate under both these conditions. N-Diphenylmethylformamide (1a) was also dehydrogenated to give N-formyl-diphenylmethanimine (3a), which dissociated to give benzophenone: N-benzylformimide similarly gave benz-aldehyde. The formamides were also decarbonylated by palladium to give amines, and these reacted *in situ* with the corresponding isocyanate: in this way the formamide (1a) gave NN'-bisdiphenylmethylurea (16), (1c) gave NN'-dicyclohexylurea (17), and (1e) gave NN'-diphenylurea (5e). Other products were obtained: (1c) gave NN'-dicyclohexylformamidine (18), (1d) gave triphenylmethane, isocyanic acid, benzophenone, and triphenyl-methanol, and (1e) gave oxanilide (19).

Thermolysis of the neat formamides (1a) and (1d) at >220° gave the same products as obtained in the catalysed reactions.

To account for the formation of an aldehyde or ketone (4) on heating a secondary formamide (1; $R^3 = H$) with Raney nickel at 190°, an intermediate N-hydroxy-methylimine, $R^1R^2C=NCH_2OH$, as its ring-closed tauto-mer (a 1,3-oxazetidine), was implicated,[1] but neither de-hydrogenation of the amide nor dissociation of the pro-posed intermediate into formaldehyde and an imine, $R^1R^2C=NH$, were considered. We now propose a reaction scheme involving initial dehydrogenation of the amide to give an isocyanate (2) and an N-formylimine (3), followed by dissociation of the latter to give a carbonyl compound (4) and hydrogen cyanide: thermolysis of other N-acylimines into carbonyl compounds has been recently reported.[2]

The dehydrogenation of the formamides (1a—e) was investigated. Each can give an isocyanate (2) but the N-t-alkylformamides (1d and e) cannot give an N-formylimine (3). Catalytic conversion of formamide into isocyanic acid is known,[3] but the only known example of dehydrogenation of a secondary formamide involves treatment of N-t-alkylformamides with t-butyl hypochlorite.[4] Thermal elimination of groups other than hydrogen from amides accounted for the formation of iso-

cyanic acid from acetamide,[5] and phenyl isocyanate from both trichloroacetanilide and acetoacetanilide.[6]

$$R^1R^2C=N\cdot CHO \rightarrow R^1R^2CO + HCN$$

$$\text{(3)} \qquad \text{(4)}$$

$$R^1R^2R^3CNH\cdot CHO \xrightarrow{-H_2}$$

$$\text{(1)}$$

	R^1	R^2	R^3
a	Ph	Ph	H
b	Ph	H	H
c	[CH$_2$]$_5$		H
d	Ph	Ph	Ph
e	$R^1R^2R^3C = Ph$		

$$R^1R^2R^3C\cdot NCO \xrightarrow{HA} R^1R^2R^3CNH\cdot COA$$

$$\text{(2)} \qquad \text{(5) A = NHPh}$$

$$\text{(6) A = OEt}$$

Only N-formylimines with αβ-unsaturation, $Y-\overset{|}{C}-\overset{|}{C}=$ NCHO, are known,[7] but the saturated forms (3) have been assumed as intermediates.[8] Isomerization between an N-formylimine and an isocyanate is presumably thermally allowed by a 1,5-sigmatropic shift for an αβ-unsaturated system, but thermally disallowed when a 1,3-sigmatropic shift is required. The established tauto-

[1] M. Metayer, *Compt. rend.*, 1948, **226**, 500.

[2] R. Ahmed and W. Lwowski, *Tetrahedron Letters*, 1969, 3611.

[3] R. A. Back and J. C. Boden, *Trnas. Faraday Soc.*, 1971, **67**, 88; N. W. Luft, *Monatsh.*, 1955, **86**, 671; G.-M. Schwab, *Z. anorg., Chem.*, 1950, **262**, 41.

[4] M. D. Hurwitz and R. W. Auten, U.S.P. 2,728,787 (*Chem. Abs.*, 1956, **50**, 107,706).

[5] H. E. Baumgarten, F. A. Bower, R. A. Setterquist, and R. E. Allen, *J. Amer. Chem. Soc.*, 1958, **80**, 4588; C. D. Hurd, ' The Pyrolysis of Carbon Compounds,' The Chemical Publishing Company (Reinhold), New York, 1929, p. 582.

[6] T. Mukaiyama, M. Tokisaua, H. Nohira, and H. Takei, *J. Org. Chem.*, 1961, **26**, 4381.

[7] G.P. 1,907,113 (*Chem. Abs.*, 1970, **73**, 98,965y); N. Toshima, M. Saeki, and H. Hirai, *Chem. Comm.*, 1971, 1424.

[8] (*a*) M. L. Moore, ' The Leuckart Reaction,' in *Org. Reactions*, 1949, **5**, 301; (*b*) T. Olijmsma, J. B. F. N. Engberts, and J. Strating, *Rec. Trav. chim.*, 1972, **91**, 209; (*c*) O. H. Oldenziel and A. M. Vanleusen, *Tetrahedron Letters*, 1973, 1357; (*d*) Y. L. Chow and A. C. H. Lee, *Canad. J. Chem.*, 1967, **45**, 311; (*e*) H. W. van Meeteren and H. C. van der Plas, *Rec. Trav. chim.*, 1969, **88**, 204.

merization between an α-chloroisocyanate and an N-(chlorocarbonyl)imine [9] may be an ionic rather than a concerted reaction.
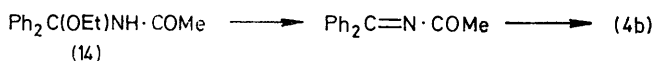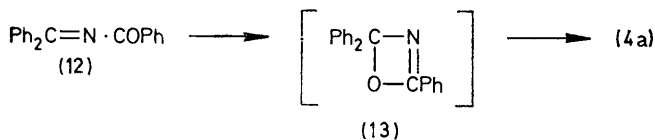
RESULTS AND DISCUSSION

The formamides (1b, c, and e) each resisted thermolysis when heated at 210—225° for 10—20 h * but neat N-diphenylmethylformamide (1a) at 210° for 30 h gave benzophenone (4a) (45% yield) and diphenylmethyl isocyanate (2a) (2% yield), indicating that initial formation of an N-formylimine (3) is preferred to formation of the isomeric isocyanate. Reduction of an N-formylimine or of its conjugate acid in the related reverse transformation (Leuckart reaction) of benzophenone, formic acid,

$$RCO \cdot NCO \longrightarrow \begin{bmatrix} O{=}C{-}N \\ | \quad || \\ O{-}CR \end{bmatrix} \longrightarrow RCN + CO_2$$
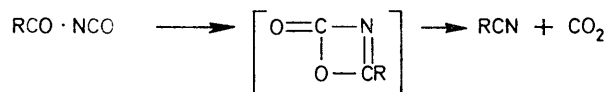
and ammonia to give (diphenylmethyl)amine has been postulated.[8a] Thermolyses of N-acylimines and acyl isocyanates may be mechanistically related; an intermediate 1,3-oxazetone has been proposed [10,11] in the transformation of the latter into a nitrile and carbon dioxide.

Ph₃CR PhNH·CO·NH₂ EtO₂C·N=N·CO₂Et

(7) R = H   (8)   (10)
(9) R = OH   EtO₂C·NHNH·CO₂Et
   (11)
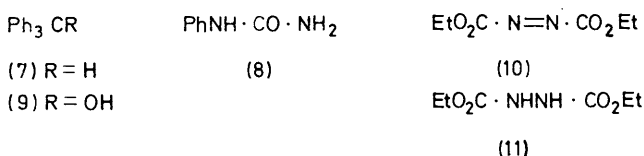
After slight fragmentation at 200°, neat N-triphenylmethylformamide (1d) at 245° for 3 h gave triphenylmethyl isocyanate (2d), triphenylmethane (7), benzophenone (4a), and isocyanic acid [isolated as phenylurea (8)]. Presumably the hydrocarbon (7) and isocyanic acid arose from one fragmentation reaction, and hydrogen and the isocyanate (2d) from another. In related reactions, triarylmethanes were produced from triarylmethanols and formamide above 180° (at lower temperatures the expected N-triarylmethylformamides were obtained).[12] By a similar reverse process, triphenylmethanol (9) was obtained by mild hydrolysis of triphenylmethyl isocyanate (2d).[13]

$$Ph_2C{=}N \cdot COPh \longrightarrow \begin{bmatrix} Ph_2C{-}N \\ | \quad || \\ O{-}CPh \end{bmatrix} \longrightarrow (4a)$$
(12)   (13)

$$Ph_2C(OEt)NH \cdot COMe \longrightarrow Ph_2C{=}N \cdot COMe \longrightarrow (4b)$$
(14)

* B. K. Barnett and T. D. Roberts (J.C.S. Chem. Comm., 1972, 758) have reported comparable thermal stability for formanilide (1e).
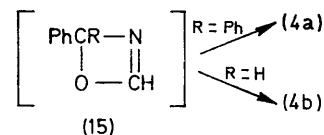
[9] V. A. Shokol, B. N. Kozhurshko, V. V. Doroshenko, and A. N. Kirsanov, Zhur. obshchei Khim., 1973, 43, 12; L. I. Samaraj, O. W. Wischnewskij, and G. I. Dekatsch, Angew. Chem. Internat. Edn., 1968, 7, 621.

[10] D. E. Douglas and A. M. Burdith, Canad. J. Chem., 1958, 36, 1256.

[11] J. A. Barltrop, A. C. Day, and B. D. Bigley, J. Chem. Soc., 1961, 3185.

The formamides (1) on heating in dichlorobenzene at >180° for 20—40 h were partially consumed in the presence of diethyl azodicarboxylate (10) [14] or palladium. To facilitate separation of products, either aniline or ethanol was added to the crude reaction mixture to convert the isocyanate (2a, c, d, or e) into the corresponding phenylurea (5) or carbamate (6). Reactions with (10) gave higher yields of isocyanates, but intractable mixtures were obtained from N-benzylformamide (1b) and either (10) or palladium. Yields of diethyl hydrazodicarboxylate (11) were not determined, since it may have been produced from (10) by reaction with ethanol or aniline as well as with a formamide. Substrate reactivity to both (10) [15] and palladium appears to be sensitive to α-substitution. This tends to support the generally predominant catalysed dehydrogenation to give isocyanates rather than N-formylimines and the exceptional behaviour of N-benzylformamide (1b). Apparently the greater reactivity of a benzylic hydrogen in the amide (1b) inhibited the formation of the isocyanate (2b) (detected in a trace amount in the crude mixture by its i.r. peak at $\nu_{max.}$ 2250 cm^{-1}).

Conversion of N-benzhydrylformamide (1a) into benzophenone (4a) in 17 and 20% yields by treatment with palladium and (10) respectively is comparable to the formation of acetophenone in 19% yield by treating N-α-phenylethylformamide with Raney nickel at 180—190°.[1] The intermediacy of an N-formylimine is supported by the fragmentation of both N-benzoyldiphenylmethanimine (12) at 115° and the ethanol adduct (14) of N-acetyldiphenylmethanimine at 220° into benzophenone (4a) in 40% yields.[2] Presumably the latter reaction proceeded by initial loss of ethanol. Formation of benzophenone (4a) was attributed to thermolysis of an intermediate 1,3-oxazete (13), the ring-closed isomer of an N-acylimine.[2] In a similar way, benzophenone (4a)

$$\begin{bmatrix} PhCR{-}N \\ | \quad || \\ O{-}CH \end{bmatrix} \begin{array}{l} R{=}Ph \nearrow (4a) \\ \\ \searrow R{=}H \\ \qquad (4b) \end{array}$$
(15)

and benzaldehyde (4b) are available from an intermediate 1,3-oxazete (15) which is isomeric with the appropriate N-formylimine obtained on dehydrogenation of amides (1a) and (1b).

Benzophenone (4a) could possibly have been generated by hydrolysis of diphenylmethanimine (Ph₂C=NH), which is in turn a formal product of either hydrolysis or hydrogenolysis of the N-formylimine (3a). This possibility was rejected when the diphenylmethanimine could

[12] H. Bredereck, R. Gomper, and D. Bitzer, Chem. Ber., 1959, 92, 1139.

[13] M. S. Kharasch and L. B. Howard, J. Amer. Chem. Soc., 1934, 56, 1370.

[14] F. Yoneda, K. Suzuji, and Y. Nitta, J. Amer. Chem. Soc., 1966, 88, 2328; E. C. Taylor and F. Yoneda, Chem. Comm., 1967, 199; J. H. Boyer and P. J. A. Frints, J. Org. Chem., 1968, 33, 4554.
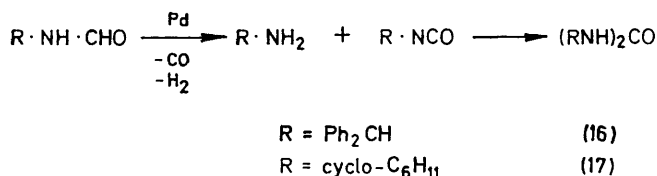
[15] G. E. Wilson, jun., and J. H. E. Martin, J. Org. Chem., 1972, 37, 2510.

not be isolated or detected as its hydrochloride on treating the anhydrous crude mixture from amide (1a) and palladium with hydrogen chloride in anhydrous acetone or chloroform. The hydrochloride was quantitatively prepared from the authentic imine by similar treatment.

Cyclohexanone was not detected in mixtures obtained from N-cyclohexylformamide (1c) and either (10) or palladium. When the amide (1c) was treated with Raney nickel an unspecified (presumably low) yield of the ketone was obtained.[1] These results are consistent with a decrease in α-hydrogen reactivity partially brought about by steric factors.

Decarbonylation, previously observed for N-t-alkyl-formamides when treated with nickel at 190°,[1] gave (tri-phenylmethyl)amine [isolated as triphenylmethanol (9)] from N-triphenylmethylformamide (1d), and aniline from formanilide (1e) (cf. ref. 16) when each amide was heated at >180° with palladium. Addition of aniline to the phenyl isocyanate (2e) produced by dehydrogenation gave NN'-diphenylurea (5e).

Decarbonylation of N-s-alkylformamides was previously unknown, but the formation of NN'-bisdiphenyl-methyl- (16) and NN'-dicyclohexyl-urea (17) can best be explained by reactions of the benzhydryl- and cyclo-hexyl-amines with the corresponding isocyanates. Thus palladium appears to cause both decarbonylation to give amines and dehydrogenation to give isocyanates.

$$R \cdot NH \cdot CHO \xrightarrow[\substack{-CO \\ -H_2}]{Pd} R \cdot NH_2 \quad + \quad R \cdot NCO \longrightarrow (RNH)_2CO$$

R = Ph$_2$CH	(16)
R = cyclo-C$_6$H$_{11}$	(17)

NN'-Dicyclohexylformamidine (18) and oxanilide (19) were produced from the formamides (1c) and (1e) respectively on treatment with palladium. Phenyl isocyanate, phenyl isocyanide, and water also gave oxanilide (19) by a reaction similar to that for formation of thio-oxanilide from phenyl isothiocyanate, phenyl iso-cyanide, and water.[17] Substitution of amide (1e) for phenyl isocyanide failed to produce oxanilide (19), indicating that the amide (1e) was not dehydrated to phenyl isocyanide during treatment with palladium.

[16] A. Mailhe, *Matieres Grasses*, 1923, **15**, 6488, 6538 (*Chem. Abs.*, 1923, **17**, 3859).
[17] J. H. Boyer and V. T. Ramakirshnam, *J. Org. Chem.*, 1972, **37**, 1360.
[18] G. W. H. Cheeseman, *J. Chem. Soc.*, 1957, 115.
[19] H. Bredereck, R. Gomper, H. Rempfer, K. Klem, and H. Keck, *Chem. Ber.*, 1957, **92**, 329.
[20] T. J. Kealy and R. E. Benson, *J. Org. Chem.*, 1961, **26**, 3126.
[21] H. Bredereck, R. Gomper, and G. Theilig, *Chem. Ber.*, 1954, **87**, 537.
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[23] B. Franzus and J. Surridge, *J. Org. Chem.*, 1962, **27**, 1951.
[24] M. J. T. Bornwater, *Rec. Trav. chim.*, 1912, **31**, 108.
[25] J. J. Donleavy and J. English, jun., *J. Amer. Chem. Soc.*, 1940, **62**, 218.
[26] A. L. Wilds, J. V. D. Berghe, C. H. Winsetock, R. L. V. Trebra, and N. F. Woolsey, *J. Amer. Chem. Soc.*, 1962, **84**, 1503.
[27] T. N. Ghosh, *J. Indian Chem. Soc.*, 1948, **25**, 515.
[28] L. Horner and A. Christman, *Chem. Ber.*, 1963, **96**, 388.
[29] H. C. White and F. W. Bergstrom, *J. Org. Chem.*, 1942, **7**, 497.

The formation of benzophenone (4a) from the amide (1d), the formamidine (18) from the amide (1c), and oxanilide (19) from (1e) are being investigated further.

(18)	(19)
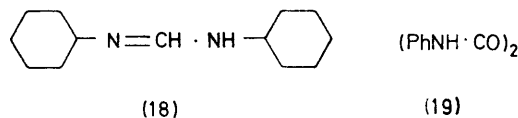
EXPERIMENTAL

Spectral data were obtained on a Perkin-Elmer model 237B grating i.r. spectrophotometer, a Varian A-60 n.m.r. spectrometer, and a Perkin-Elmer model 270 mass spectrometer. M.p.s were determined on a Thomas–Hoover capillary apparatus. Elemental analyses were obtained from Microtech Laboratories, Skokie, Illinois. Except where noted, yields are based on recovered starting material and known products were identified by comparison with authentic samples (i.r., n.m.r., and mass spectra, t.l.c., g.l.c., and mixed m.p.).

The following compounds were either commercial samples or obtained by published procedures: amides (1a),[18] (1b),[19] (1c),[20] (1d),[21] (1e),[22] (11),[23] and (19);[24] isocyanates (2a)[25] and (2d);[26] ureas (5a),[27] (5e),[28] (8),[29] (16),[18,30] and (17);[31] carbamates (6a),[32] (6c),[33] (6d),[34] and (6e);[35] the azodicarb-oxylate (10),[36] triphenylmethane (7);[37] triphenylmethanol (9);[38] cyclohexylamine hydrochloride;[32] NN'-dicyclo-hexylformamidine (18) hydrochloride;[39] diphenylmethan-imine hydrochloride.[40]

Hydrolysis of Triphenylmethyl Isocyanate (2d).—Tri-phenylmethyl isocyanate (2d) (394 mg, 13·8 mmol), water (5 ml), and benzene (10 ml) were stirred at room temperature for 3 days and then dried in a stream of air. The residue was placed on a silica gel column (3 × 20 cm). Hexane-benzene (3 : 2) eluted the isocyanate (2d) (32 mg, 8% recovery). Benzene eluted triphenylmethanol (9) (95 mg, 29%), m.p. 161—163°.[38] Further elution with benzene and benzene-chloroform (1 : 1) gave an unidentified yellow solid. Chloroform and ethyl acetate eluted NN'-bistriphenyl-methylurea (203 mg, 59%), m.p. 251—252°.[41]

1-Phenyl-3-triphenylmethylurea (5d).—This was obtained (79% yield) from a mixture of triphenylmethyl isocyanate (2d), aniline, and benzene (25 ml) heated at >60° for 16 h; $\nu_{max.}$ (KBr) 3300 (NH) and 1648 cm^{-1} (CO), δ [(CD$_3$)$_2$SO] 7·25 (s, Ph), m.p. (after recrystallization twice from ethanol and twice from benzene) 266—268° (lit.,[41] 242°) (Found: C, 82·35; H, 5·95; N, 7·3%; M^+, 378. Calc. for C$_{26}$H$_{22}$N$_2$O: C, 82·5; H, 5·85; N, 7·4%; M, 378).

N-Triphenylmethylformamide was unaffected (180°;

[30] K. Hohenlohe-Oehringen, *Monatsh.*, 1958, **89**, 588.
[31] B. Milligan and J. M. Swan, *J. Chem. Soc.*, 1961, 1194.
[32] H. Heckel and R. Adams, *J. Amer. Chem. Soc.*, 1925, **47**, 1712.
[33] W. Lwowski and T. W. Mattingly, *Tetrahedron Letters*, 1962, 277.
[34] A. W. Johnson, A. Langemann, and M. Tisler, *J. Chem. Soc.*, 1955, 1622.
[35] G. Spiteller and H. Bretschneider, *Monatsh.*, 1961, **92**, 183.
[36] R. J. W. Le Fèvre, W. T. Oh, I. H. Reece, R. Roper, and R. L. Werner, *Austral. J. Chem.*, 1958, **11**, 92.
[37] G. W. H. Cheeseman and R. C. Poller, *Analyst*, 1962, **87**, 366; F. R. Jensen and R. L. Bedard, *J. Org. Chem.*, 1959, **24**, 874.
[38] S. O. Lawesson and N. C. Yang, *J. Amer. Chem. Soc.*, 1959, **81**, 4230.
[39] M. T. Leplawy, D. S. Jones, G. W. Kenner, and R. C. Sheppard, *Tetrahedron*, 1960, **11**, 39.
[40] R. Appel and A. Hauss, *Chem. Ber.*, 1960, **93**, 405.
[41] H. Bredereck and E. Reif, *Chem. Ber.*, 1948, **81**, 426.

several h—2 days) by nitrobenzene, dimethyl sulphoxide, *p*-benzoquinone, sulphur, and chloranil.

Reaction of N-*Triphenylmethylformamide* (1d) *and Diethyl Azodicarboxylate* (10).—The formamide (1d) (2·00 g, 7·0 mmol) and the azodicarboxylate (11) (1·24 g, 7·1 mmol) in *o*-dichlorobenzene (25 ml) were heated at 183°. I.r. monitoring revealed new absorptions at 3590 (NH), 2250 (NCO), and 1730 cm^{-1} (CO) after 10 min. The solution was heated at 183° for 18 h after which time the intensity of absorption at 2250 cm^{-1} became constant. Aniline (2·1 ml) was added at room temperature and the mixture was heated at 105° for 1·5 h, after which the absorption at 2250 cm^{-1} had disappeared. Evaporation of the solvent gave a yellow viscous oil which was placed on a silica gel column (3 × 30 cm). Hexane eluted an oil which solidified in light petroleum (b.p. 30—60°). Recrystallization from chloroform–light petroleum gave triphenylmethane (7) as a powder, m.p. 93—94° (31 mg, 2·3%). Hexane and hexane–benzene (2 : 1 and 1 : 1) eluted a light yellow solid. Recrystallization from chloroform–light petroleum gave triphenylmethanol (9) as prisms, m.p. 162—164° (313 mg, 21·9%). Hexane–benzene (1 : 3) eluted the starting formamide (1d) as a powder, m.p. 200—203° (decomp.) (428 mg, 21·4% recovery). Various combinations of hexane, benzene, and chloroform eluted mixtures of 1-phenyl-3-triphenylmethylurea (5d), NN'-diphenylurea (5e), and diethyl hydrazodicarboxylate (11). The ureas (5d) and (5e) precipitated from chloroform, and vacuum sublimation at 160° (0·4 mmHg) separated (5e) as a powder, m.p. 241·5—242·0° (188 mg, 10·3%).* The residue was recrystallized from ethanol–benzene to give (5d) as needles, m.p. 244—246° (616 mg, 29·6%). The earlier chloroform-soluble fraction was recrystallized from chloroform–light petroleum (b.p. 30—60°) to give the hydrazine (11) as needles, m.p. 130—132° (1·079 g). Ethyl acetate eluted phenylurea (8) as needles, m.p. 144—146° (77 gm, 10·3%). Ethyl acetate–methanol (1 : 1) eluted an unidentified purple tar (83 mg).

Treatment of the formamides (1a, b, c, and e) with (10) was modified by replacing heating with aniline at 105° by heating with ethanol at 70—80° to permit the isolation of the isocyanates (2a, c, and e) as the corresponding ethyl carbamates (6a, c, and e). Recovery (%) of the formamides (1) was 17 for (1a), 57 for (1c), and 11 for (1e); yields (%) of the isocyanates (2) isolated as carbamates (6) were 60 for (2a), 53 for (2c), and 54 for (2e). Benzophenone (4a) (19·7% yield) was also obtained from the amide (1a).

Similar treatment of the amide (1b) (2·69 g, 19·9 mmol) gave several unidentified fractions, one of which was eluted by hexane–benzene (1 : 1) and distilled as a yellow viscous liquid, b.p. 91° at 0·15 mmHg (1·284 g), $n_D^{24·8}$ 1·5368, $\nu_{max.}$ (CHCl$_3$) 3430 and 1730 cm^{-1}, δ (CDCl$_3$) 1·23 (9H, t), 2·20br (1H,) 4·17 (6H, q), and 7·16 (20H, m), *m/e* (70 eV) M^+ >450 (Found: C, 65·0; H, 6·6; N, 8·6. Calc. for C$_{53}$H$_{64}$N$_6$O$_{12}$: C, 65·15; H, 6·6; N, 8·6%).

An unidentified product from reaction of (1e) and (11) was eluted from silica gel by combinations of benzene, chloroform, and ethyl acetate and distilled as a bright yellow, viscous liquid, b.p. 130° at 0·25 mmHg; $\nu_{max.}$ (CHCl$_3$) 3370 and 1725 cm^{-1}, δ (CDCl$_3$) 1·24 (6H, t), 4·20 (4H, m), and 7·37 (7H, d); *m/e* (70 eV) M^+ >450 (Found: C, 47·35; H, 6·5; N, 17·6. Calc. for C$_{31}$H$_{51}$N$_{10}$O$_4$: C, 47·25; H, 6·5; N, 17·8%).

Pyrolysis of N-*Triphenylmethylformamide* (1d).—The

* An amide interchange can produce the urea (5e) and (triphenylmethyl)amine from the urea (5d) and aniline.

formamide (1d) (0·287 g, 1·00 mmol) was heated at 245° for 3 h with stirring. I.r. monitoring indicated the formation of an isocyanate (2250 cm^{-1}) soon after heating commenced. After heating at 205° for *ca*. 10 min, triphenylmethane (7) was detected by t.l.c., and isocyanic acid by i.r. absorption at 2250 cm^{-1} of the condensed evolving gas. After cooling to room temperature, aniline (1·0 ml) in benzene (10·0 ml) was added and the mixture was heated at 40° for 8 h, as the isocyanate absorption disappeared. The solvent was replaced with chloroform (15 ml), and a solid, which separated on refrigeration overnight, was recrystallized from ethanol as needles of the urea (5d), m.p. 245—246° (26 mg, 12·0%). Removal of chloroform from the filtrate gave a yellow viscous liquid which was placed on a silica gel column (2 × 20 cm). Hexane eluted triphenylmethane (7) which was recrystallized from hexane as needles, m.p. 94—95·5° (102 mg, 72·7%). Hexane–benzene (4 : 1) eluted benzophenone (4a) (10 mg, 9·6%); 2,4-dinitrophenylhydrazone, m.p. 238—239°; benzene eluted the formamide (1d) (122 mg, 42·5%), m.p. 202—204°.

After similar treatment of the formamides (1a—c and e), the recovery (%) of the amides was 69—81 for (1a), 90 for (1b), 73 for (1c), and 79 for (1e). Diphenylmethyl isocyanate (2a) [isolated as the corresponding phenylurea (5a)] and benzophenone (4a) were obtained from (1a) in corresponding yields of 2 and 45%. Minor products from amides (1b, c, and e) were detected but not identified.

Reaction of N-*Triphenylmethylformamide* (1d) *and Palladium.*—An anhydrous mixture of the formamide (1d) (2·42 g, 8·45 mmol), Pd–CaCO$_3$ (0·13 g), and *o*-dichlorobenzene (20 ml) was heated at 183° for 49 h, cooled, and filtered. Vacuum sublimation (160° at 7 mmHg) of the residue gave a mixture of (1d) and (2d) and left a residue of Pd–CaCO$_3$. Hexane separated the sublimate into (1d) (241 mg), m.p. 199—201° (decomp.), which was less soluble, and the isocyanate (2d) (32 mg, 4·2%), m.p. 96—98°. Evaporation of the original filtrate left a solid which was placed on a silica gel column (3 × 30 cm). Hexane–benzene (3 : 2) eluted a mixture of (2d) and triphenylmethane (7). Treatment of this with aniline (0·15 ml) in chloroform (15 ml) at 40° for 3 days gave (7) (160 mg, 24·8%), m.p. 91—93°, as a powder soluble in light petroleum (b.p. 30—60°) and recrystallized from hexane, and (5d) (38 mg, 3·8%), m.p. 255—258°, insoluble in light petroleum (b.p. 30—60°). Hexane–benzene (3 : 2) eluted an unidentified yellow viscous liquid, and hexane–benzene (3 : 7) eluted benzophenone (4a) as a light yellow liquid (126 mg, 25·8%). Benzene eluted a yellow solid (30 mg) containing triphenylmethanol (9), identified by i.r. (CHCl$_3$) and by t.l.c. Mixtures of benzene and chloroform eluted unidentified material. Benzene–chloroform (3 : 7) eluted the formamide (1d) (1·42 g; total recovery 68·7%).

From similar treatment of the formamides (1a—c and e) the recovery (%) of formamides (1) was 57 for (1a), 70 for (1b), 81 for (1c), and 73 for (1e). Yields (%) of isocyanates (2) isolated as ureas (5), (14), or (15) or as carbamates (6) were 36 for (2a), 37 for (2c), 8 for (2d), and 18 for (2e). Yields (%) of other products were 17 for benzophenone (4a) from (1a); 5 for benzaldehyde (4b) from (1b); 3 for cyclohexylamine and 30 for NN'-dicyclohexylformamidine (18) from (1c); and 3 for oxanilide (19) from (1e). Apparently hydrogenolysis of the solvent provided hydrogen chloride for the isolation of cyclohexylamine and the formamidine (18) as their hydrochloride salts.

A mixture of phenyl isocyanide (2·01 g, 19·6 mmol) (b.p.

29—30° at 0·45 mmHg) and phenyl isocyanate (2·48 g, 20·8 mmol) was placed on a silica gel column (3 × 30 cm) for 2 days. Hexane–benzene (4 : 1) eluted phenyl isocyanide. Elution with hexane–benzene (2 : 1) and 1 : 3) gave oxanilide (19) (97 mg), m.p. 245—247°.[42] Elution with benzene gave an unidentified yellow solid (115 mg). Elution with methanol gave NN'-diphenylurea (5e) (2·01 g). Oxanilide (19) was identical with authentic material prepared from oxalic acid and aniline by mixed m.p., $v_{max.}$ (KBr) 3300 (NH) and 1600 cm^{-1} (CO); and mass spectrum (70 e/V) m/e 240 (M^+).

[42] E. Beckmann and E. Gunther, Annalen, 1889, 252, 44.