

Organic Reactions in Melts and Solids. Part 10.¹ Reactions of Carboxylic Acids and Anhydrides with Carbamates

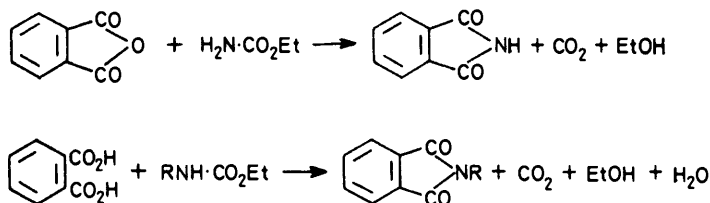
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Transacylation reactions have been carried out in melts between carboxylic acids and ethyl carbamate, mono-*N*-substituted carbamates, and di-*N*-substituted derivatives at 150–180 °C. Phthalic acid, pyromellitic acid, and phthalic anhydride reacted with ethyl carbamate and *N*-substituted ethyl carbamates to give the corresponding amides and imides, carbon dioxide, and ethanol in high yields. Benzoic acid, 4-methoxy- and 4-nitro-benzoic acid, and acetic acid gave with ethyl carbamate mono-*N*-substituted ethyl carbamates and phenyl *N*-phenylcarbamate gave amides in low yields. Ethyl *NN*-diethyl- and *NN*-diphenyl-carbamate did not react with either phthalic acid or the monocarboxylic acids mentioned. In the case of phthalic acid the rates of reactions and overall kinetic order are similar to those found for transacylations with amides. Two examples of the preparation of thermally stable polyimide oligomers are given.

TRANSACYLATION reactions in melts between acids and amides have been described in preceding publications of this series.¹ We now describe transacylation reactions involving carbamates instead of amides. Carbamates carry amide function which can be acylated by agents such as esters,^{2,3} carboxylic anhydrides,^{4,5} acyl halides,⁶⁻⁸ and ketens.^{9,10} Carboxylic acids are generally known to acylate the nitrogen atom of carbamates in the presence of additives such as phosphoryl chloride or acetic anhydride.¹¹⁻¹³

The reaction of carbamates is of interest since it is not

Reactions were carried out with 8:1 to 4:1 molar ratios of carbamate to acid or anhydride in order to obtain homogeneous melts, but yields were not decreased with lower ratios and heterogeneous environments. With phthalic acid and ethyl carbamate a 90% yield of phthalimide was obtained (150 °C; 12 h). Reactions were slower at 130 °C and hardly discernible at lower temperatures. With phthalic anhydride at 150 °C for 40 h, a 75% yield of phthalimide was obtained. This is in contrast with previously studied reactions with amides in which the anhydride did not react unless catalysts



SCHEME 1 R = H, Ph, 4-MeC₆H₄, 2-ClC₆H₄, 3-ClC₆H₄, 4-ClC₆H₄, 4-MeO·C₆H₄, or 4-O₂N·C₆H₄

possible to predict with certainty the behaviour of the ester moiety, which may decompose during the reaction to carbon dioxide and an alcohol or may be incorporated into the products in various ways, *e.g.* to yield heterocyclic compounds.¹⁴

RESULTS

We have studied the reactions of carboxylic acids and an anhydride with carbamates RNH·CO·OR', in which carbon dioxide and the alcohol R'OH are formed as volatile products, and the resulting amide or imide can be isolated easily. Reactions were carried out mostly with phthalic acid and phthalic anhydride so as to obtain results comparable with previous work¹⁵⁻¹⁷ (Scheme 1).

were added, but in agreement with an early report by Manske.⁵

Similar high yields were obtained in the reactions of phthalic acid with a series of *N*-aryl carbamates (Scheme 1). Monocarboxylic acids RCO₂H (R = 4-O₂N·C₆H₄, 4-MeO·C₆H₄, Ph, or Me) gave with ethyl carbamate the corresponding amides in low yields: 4-nitrobenzamide (25%; 160 °C; 24 h), 4-methoxybenzamide (*ca.* 5%; 160 °C; 24 h), benzamide (nil; 160 °C; 24 h). Benzoic acid yielded benzanilide (10%; 160 °C; 24 h) in its reaction with phenyl *N*-phenylcarbamate. Boiling acetic acid gave acetanilide with phenyl *N*-phenylcarbamate (5%; 42 h) despite the low temperature. Attempted reactions of ethyl carbamate with succinic, adipic, and pyridine-2,3-dicarboxylic acids failed. Ethyl *NN*-di-

¹ Part 9, M. Michman and D. Meidar, *J.C.S. Perkin II*, 1972, 300.

² O. Diels and H. Heintzel, *Ber.*, 1905, **38**, 297.

³ A. Hantzsch, *Ber.*, 1894, **27**, 1248.

⁴ D. M'Creath, *Ber.*, 1875, **8**, 1181.

⁵ R. H. F. Manske, *J. Amer. Chem. Soc.*, 1929, **51**, 1202.

⁶ W. Traub, Ger. Pat., 179,946, *Chem. Zentr.*, 1907, I, 433.

⁷ G. H. L. Nefkens, *Nature*, 1960, **185**, 309.

⁸ D. Ben Ishai and E. Katchalski, *J. Org. Chem.*, 1951, **16**, 1025.

⁹ N. V. Smirnova, A. P. Skoldinov, and K. A. Koscheshkov, *Doklady Akad. Nauk, S.S.S.R.*, 1952, **84**, 737 (*Chem. Abs.*, 1953, **47**, 3233b).

¹⁰ L. I. Smith and O. H. Emerson, *Org. Synth.*, Coll. Vol. III, 1955, p. 151.

¹¹ P. Adams and F. A. Baron, *Chem. Rev.*, 1965, **65**, 576.

¹² M. Conrad and K. Hock, 1903, **36**, 2206.

¹³ M. Conrad and A. Schultze, *Ber.*, 1909, **42**, 734.

¹⁴ Y. Wiesel, S. Patai, M. Michman, Proc. XLII Meeting, Israel Chem. Soc., 1972, p. 5.

¹⁵ M. Michman, S. Patai, and I. Shenfield, *J. Chem. Soc. (C)*, 1967, 1337.

¹⁶ M. Krasnoselsky and S. Patai, *J. Chem. Soc. (B)*, 1969, 24.

¹⁷ M. Michman and M. Frenkel, *J. Chem. Soc. (C)*, 1971, 3856.

phenyl- and *NN*-diethyl-carbamate did not react with phthalic acid or with benzoic, 4-nitrobenzoic, or 4-methoxybenzoic acid. However di-*N*-alkyl amides do react with phthalic acid.¹⁵ For the syntheses of phthalimides, the present method is more simple and convenient than traditional methods such as reactions of amines with phthalic anhydride or phthaloyl chloride, or the Gabriel method.

Similarly, pyromellitic di-imides were prepared from pyromellitic acid and carbamates. With ethyl carbamate the yield is nearly quantitative (160 °C; 24 h); hence this method is straightforward and simpler than others.¹⁸ Pyromellitimide is the building block of several types of specialty polyimide polymers.¹⁹ *NN'*-Diaryl-pyromellitimides, some of which have not been previously reported, are high-melting powders of low solubility in most organic solvents.

Two attempts were made to prepare polyimide polymers with the use of bifunctional reagents. From the reactions of pyromellitic acid with diethyl *m*- and *p*-phenylenebiscarbamate at 200–220 °C in melts, a polymeric product precipitated after 15 min. The powder obtained was slightly soluble in concentrated sulphuric acid but almost insoluble in many common

TABLE 1

Reactions of carbamates with phthalic acid and anhydride at 150 ± 1 °C; values of rate constant *k* according to second-order equation

Carbamate	Conc. (mol l ⁻¹)	Conc. (mol l ⁻¹)	10 ⁶ <i>k</i> /l mol ⁻¹ s ⁻¹	
Ethyl	8.12	Phthalic acid	2.03	4.2
Ethyl	9.4	Phthalic acid	1.17	4.3
Ethyl	9.94	Phthalic acid	0.62	5.4
Ethyl	8.24	Phthalic anhydride	2.06	2.7
Ethyl <i>N</i> -phenyl	5.4	Phthalic acid	0.68	13.0
Ethyl <i>N-p</i> -tolyl	5.2	Phthalic acid	0.65	12.0
Ethyl <i>N-p</i> -methoxyphenyl	4.9	Phthalic acid	0.61	11.6

organic solvents. Differential thermal analysis showed thermal stability up to 300 °C (in air or nitrogen) and decomposition (*ca.* 22% in 1 h) at a higher temperature (320 °C). *p*-Ethoxycarbonylaminobenzoic acid was heated above its m.p. and gave an immediate precipitate of an impure and intractable product. However 72 h in boiling *m*-cresol yielded polybenzamide, soluble in concentrated sulphuric acid. Solutions (5%) in this solvent showed relative viscosity ($\eta_{rel.}$) 0.1, indicating a polymer with molecular weight *ca.* 210. Thermogravimetric analysis showed the material to be stable up to 320 °C in air and 360 °C in nitrogen.

Rates of the reaction of phthalic acid and anhydride with several carbamates have been measured by measuring the volume of carbon dioxide evolved (Table 1).

¹⁸ S. S. Gitis, V. M. Ivanova, S. A. Nemleva, Z. N. Seina, and A. V. Ivanov, U.S.S.R. P. 187006 (Cl.C.07c) 1966 (*Chem. Abs.*, 1967, **67**, 64074t, 116726d).

Such measurements in melts have their limitations^{1,16} since comparison of *k* values for different materials must take into account that, in the absence of solvent, equimolecular quantities of different materials represent different concentrations and that effects due to polarity, dipole-dipole interaction, *etc.*, are not buffered by large amounts of solvent, as is usually the case. The results indicate a reaction of overall second order, first order

TABLE 2

Rate measurement of the reaction of phthalic acid and ethyl carbamate at 150 °C. Initial concentrations: phthalic acid (a) 2.030M; ethyl carbamate (b) 8.120M. Initial density of melt 1.060 g ml⁻¹. Sample weight 3.94 g. Temperature of gas burette 299.5 K; barometric pressure 0.908 atm.

Time (10 ³ t/s)	Vol. of CO ₂ evolved (ml corr. to S.T.P.)	$\frac{x}{\text{mmol l}^{-1}}$	$\frac{1}{b-a} \ln \left[\frac{a(b-x)}{b(a-x)} \right]$	$\frac{10^6 K}{\text{mol}^{-1} \text{s}^{-1}}$
3	4.9	0.06	0.003 694	12.3
6	7.95	0.095	0.006 259	10.4
15	13.1	0.16	0.010 056	6.7
21	15.7	0.19	0.012 719	6.0
24	17.5	0.21	0.013 621	5.6
30	20.85	0.25	0.017 095	5.6
42	26.5	0.32	0.021 038	5.0
48	29.5	0.35	0.024 309	5.0
57	33.6	0.40	0.028 166	4.9
63	36.1	0.43	0.029 938	4.7
72	39.4	0.47	0.032 716	4.5
79	42.2	0.50	0.036 217	4.5
84	44.0	0.53	0.038 355	4.5
96	47.7	0.57	0.042 443	4.4

$$k = 4.17 \times 10^6 \text{ l mol}^{-1} \text{ s}^{-1}$$

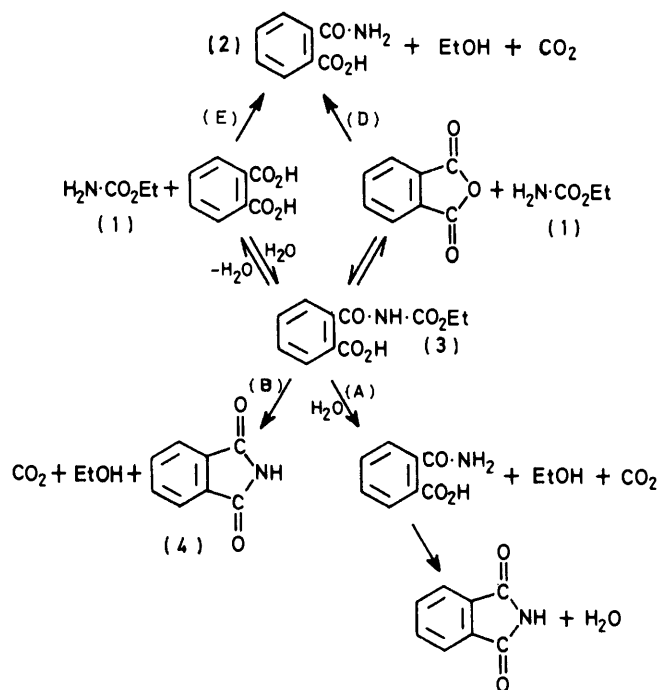
in each phthalic acid (or anhydride) and carbamate. The kinetic behaviour is similar to that of previously studied transacylation reactions.^{1,16} The effect of *para*-substituents on the phenyl group in the three *N*-arylcaramates studied is small, but all three react three times as fast as ethyl carbamate (Table 1). A typical sample run is given (Table 2). At 160 °C phthalic acid reacts 1.6 times faster than the anhydride.

DISCUSSION

Scheme 2 represents some possible sequences for the reaction. These may involve three main types of process: (1) acyl group transfer; (2) acyl group transfer accompanied by cyclisation and formation of water; (3) hydrolysis by water formed in the melt. The reaction of phthalic acid with ethyl carbamate (1) may yield either phthalamic acid (2) or *N*-ethoxycarbonylphthalamic acid (3). Only the second possibility is reasonable in the case of phthalic anhydride since for the first case the presence of water would be needed. For the formation of products from *N*-ethoxycarbonylphthalamic acid, again two routes are possible. Route (A) is hydrolysis leading to phthalamic acid and route (B) is an intramolecular cyclisation. Amide hydrolysis is not easily achieved. Experience accumulated in the studies of transacylations in melts does not support the possibility

¹⁹ R. M. Campbell, jun., 'Modern Plastics Encyclopedia,' McGraw-Hill, New York, 1970–1971, vol. 41, p. 207; N. C. W. Judd and W. W. Wright, *Reports Progr. Appl. Chem.*, 1974, **59**, 87.

that water obtained *in situ* by anhydride formation or other cyclisations will be an effective hydrolytic agent. Thus, phthalic acid did not hydrolyse amides with which it was mixed in melts at 180 °C.¹⁵ The alternative route (B) (transacylation followed by cyclization) does not involve hydrolysis and is a more direct and simple one. Examples of such processes are known, *e.g.* 1,4-benzdiazapine (the first to be described) was obtained by a similar (not identical) cyclic dehydration.²⁰ Davidson and his co-workers have reached similar conclusions²¹⁻²³ in regard to reactions between acids and amides. Finally, the likelihood that *N*-ethoxycarbonylphthalamic acid is an intermediate is demonstrated by its decomposition at 150 °C to phthalic anhydride (76%), ethyl carbamate, and phthalimide (23%), when melted alone but its decomposition to phthalimide in 87% yield when melted in the presence of an excess of ethyl carbamate at the same temperature. Therefore, the route from (1) to (4) through (3) *via* (B) fits well with experimental data.



Hydrolysis of *N*-ethoxycarbonylphthalamic acid yields phthalic acid.

The case of phthalic acid must be further considered. The reaction does not seem to involve phthalic anhydride as an intermediate since, as the rate measurements show, it reacts 1.6 times faster than the latter. Formation of phthalamic acid would be analogous to the formation of amides from monocarboxylic acids and to previously studied transacylations.¹⁵ As it is not known

²⁰ S. Gärtner, *Annalen*, 1904, **332**, 226.

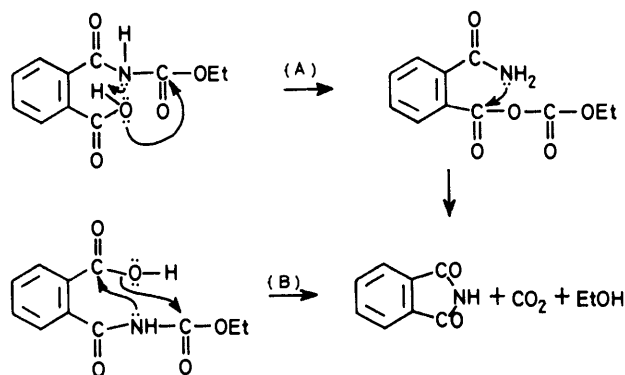
²¹ D. Davidson and H. Skovronek, *J. Amer. Chem. Soc.*, 1958, **80**, 376.

²² R. N. Ring, J. G. Sharefkin, and D. Davidson, *J. Org. Chem.*, 1962, **27**, 2428.

²³ D. Davidson and M. Karten, *J. Amer. Chem. Soc.*, 1956, **78**, 1066.

at what stage during the transacylation of phthalic acid the losses of carbon dioxide, water, and ethanol occur, both phthalamic and ethoxycarbonylphthalamic acids can equally be the intermediates. It is interesting that phthalic anhydride is only a slightly slower transacylating agent than phthalic acid, whereas in the case of amides the anhydride did not react at all in the absence of catalysts. As carbamates are not expected to differ much in nucleophilicity from the amides studied, this difference is striking.

The rate measurements (Table 1) indicate almost no substituent effect with different aryl groups attached to the nitrogen atom, and the rate differences between unsubstituted and aryl-substituted carbamates are small.



We believe that since the reaction involves both a strongly developed electrophilic centre¹ (*i.e.* the carbonyl carbon atom of either a carboxy or a carbamoyl group) and an inherently strong nucleophilic centre (*i.e.* the amide nitrogen atom), the small sensitivity to aryl substitution on the *para*-carbon atom of the aryl group, can be reasonably accepted, even if one could not have predicted it (Scheme 3). These conclusions as summarized in pathway (B) in Scheme 3 are related to our previously suggested mechanisms for the transacylation of amides in which acylium ions or their precursors were assumed to have a significant role.^{1,15-17} However there are still widely differing ideas as to the detailed mechanisms of transacylations, some of which have recently been reviewed.²⁴

The possibility that decomposition of ethyl carbamate to alcohol and isocyanate plays an important role in such reactions as assumed by Mukaiyama *et al.*²⁵ seems unsupported by our control experiments, which showed the carbamates to be thermally stable at 150–160° and up to 180 °C. Since the kinetics are first order in acid and in carbamates, it can at least be stated that such decomposition of the carbamate, if it takes place at all, is not a rate-controlling step.

Transacylations with amides have been shown to be reversible reactions^{15,24} reaching completion in the case of

²⁴ R. Puffr and J. Šebenda, *Coll. Czech. Chem. Comm.*, 1975, **40**, 3339.

²⁵ T. Hoshino, T. Mukaiyama, and H. Hoshino, *Bull. Chem. Soc. Japan*, 1952, **25**, 392; T. Mukaiyama, S. Motogi, and Y. Hamada, *ibid.*, 1953, **26**, 49; T. Mukaiyama and Y. Hoshino, *J. Amer. Chem. Soc.*, 1956, **78**, 1946.

phthalic acid owing to the consecutive and irreversible cyclisation to phthalimide.^{15,17} It was therefore expected that with carbamates the irreversible evolution of carbon dioxide, water, and alcohol would offer an efficient transacylation procedure. In fact monobasic acids are recovered in high yields, indicating a low reactivity of the system, leaving as its main asset the fact that the transacylation product is obtained alone, the other products being evolved as gases. These advantages are demonstrated by the straightforward preparation of pyromellitic acid imides, and by the two types of polymerization described.

EXPERIMENTAL

*N-Arylcarbamates.*¹¹—(i) Alkyl chloroformate (0.22 mol) was added with stirring at room temperature to a solution of an amine (0.2 mol) in pyridine (250 ml) during 1 h. After an additional 15 min the liquid was concentrated to half its volume and poured on ice (500 g). The product was extracted with methylene chloride and the extract washed with 10% hydrochloric acid and water, dried (MgSO₄), and evaporated. The residue was crystallized from light petroleum or purified by distillation.

(ii) Alkyl chloroformate (0.11 mol) was added to the amine (0.1 mol) and *NN*-dimethylaniline (1.0 mol) in dry benzene (150 ml) and the mixture worked up as above.

The following carbamates were prepared and identified by elemental analysis, n.m.r. spectra, and m.p. or b.p.: 4-Me-C₆H₄·NH·CO₂Et, m.p. 46 °C (lit.,²⁶ 51 °C); 4-MeO·C₆H₄·NH·CO₂Et, m.p. 56 °C (lit.,²⁷ 56 °C); 4-ClC₆H₄·NH·CO₂Et, m.p. 67 °C (lit.,²⁷ 69 °C); 3-ClC₆H₄·NH·CO₂Et, b.p. 130 °C at 3 mmHg (lit.,²⁸ 95 °C at 0.5 mmHg); 2-ClC₆H₄·NH·CO₂Et, b.p. 92 °C at 2 mmHg (Found: C, 54.2; H, 5.1; N, 7.2. C₉H₁₀ClNO₂ requires C, 54.1; H, 5.05; N, 7.0%), δ (neat) 1.02 (3 H, t), 3.92 (4 H, q), 6.35–7.10 (4 H, m), 4-NO₂·C₆H₄·NH·CO₂Et, m.p. 125 °C (lit.,^{26,29} 129 °C); PhNMe·CO₂Et, b.p. 127 °C at 3 mmHg (lit.,³⁰ 127 °C); PhNEt·CO₂Et, b.p. 60 °C at 3 mmHg (lit.,³¹ 63 °C at 14 mmHg); PhNMe·CO₂Ph, m.p. 57 °C (lit.,³² 57 °C); PhNH·CO₂Et, m.p. 52 °C (lit.,³³ 52 °C).

Ethyl NN-diphenylcarbamate. Diphenylamine and ethyl chloroformate were heated without solvent according to the method of Hager,³⁴ to yield the *product*, m.p. 72 °C, which was dried in vacuum (P₂O₅) to eliminate traces of pentyl alcohol used for crystallization; δ (CDCl₃) 1.2 (3 H, t), 4.2 (2 H, q), and 7.0br (10 H, s) (Found: C, 74.7; H, 6.3; N, 5.8. C₁₅H₁₅NO₂ requires C, 74.7; H, 6.2; N, 5.8%).

Stability of Carbamates under Reaction Conditions.—Ethyl carbamate (5 g) was heated for 24 h at 150, 160, or 180 °C; it was unchanged in the first two cases. In the third case about 2% of high-melting material was formed—possibly by self condensation. Ethyl *N*-4-nitrophenylcarbamate (0.18 g) partially sublimed (0.16 g) when heated for 24 h at 150 °C. The sublimate as well as the residue were identical with the starting material. Other carbamates were similarly stable at 150 °C.

²⁶ G. M. Dyson and T. Harrington, *J. Chem. Soc.*, 1942, 150.

²⁷ C. W. Whitehead and J. J. Traverso, *J. Amer. Chem. Soc.*, 1955, **77**, 5872.

²⁸ S. L. Shapiro, V. Bandurco, and L. Freedman, *J. Org. Chem.*, 1961, **26**, 3710.

²⁹ R. L. Shriner and R. F. B. Cox, *J. Amer. Chem. Soc.*, 1931, **53**, 1601.

³⁰ W. Gebhardt, *Ber.*, 1884, **17**, 3042.

³¹ J. von Braun, *Ber.*, 1903, **36**, 2287.

³² E. Lellmann and E. Benz, *Ber.*, 1891, **24**, 2108.

Reactions of Ethyl Carbamate and Ethyl N-Phenylcarbamate with Phthalic Acid and Phthalic Anhydride.—(i) A mixture of phthalic acid (0.02 mol) and ethyl carbamate (5.34 g, 0.06 mol) in a flask equipped with a distillation head and condenser was flushed with dry nitrogen and heated in an oil-bath at 150 °C for 12 h. Volatile products such as water and ethanol were collected in a cold trap, dissolved in deuterium oxide (1–2 ml) (Merck Uvasol 99.75%), and analysed by n.m.r. to show the presence of equivalent amounts of water and ethanol. Carbon dioxide was trapped in a clear barium hydroxide solution and yielded barium carbonate.

The residue was washed with saturated aqueous sodium hydrogen carbonate and recrystallized from ethanol. Phthalimide (2.65 g, 90%) formed was identical with authentic samples (m.p. and mixed m.p. 235 °C; i.r. spectrum). Alternatively the residual mixture was triturated with cold diethyl ether and filtered. The insoluble phthalimide was crystallized from ethanol. The filtrate contained ethyl carbamate.

(ii) The reactions with phthalic anhydride were run for longer periods (40 h). The volatile products consisted solely of ethanol and carbon dioxide. The residue was treated with sodium hydrogen carbonate for 24 h to ensure complete extraction of residual anhydride. The single product was phthalimide (2.24 g, 75%).

(iii) The reaction of phthalic acid (0.50, 0.003 mol) and ethyl *N*-phenylcarbamate (1.5 g, 0.01 mol) (150 °C; 24 h) yielded carbon dioxide and equimolar amounts of water and ethanol. Phthalanil was obtained as above, identical (m.p. 217 °C and i.r.) with an authentic sample.

(iv) *Kinetic runs.* Mixtures of phthalic acid or anhydride with the carbamate were prepared by grinding the constituents together, and kept in a desiccator (CaCl₂). Samples of 4 g were used in a 50 ml flask equipped with a reflux condenser (air-cooled), which was in turn connected to a gas burette containing 10% hydrochloric acid previously saturated with carbon dioxide. To start a reaction, the flask was dipped into an oil bath at 150 °C, and measurements were started exactly 5 min later, by which time a homogeneous melt had been obtained. The volume of carbon dioxide formed was measured at 5 min intervals for 30 min, and 15 or 30 min intervals thereafter. Volume fluctuations due to temperature fluctuations in the oil-bath and reaction apparatus were ± 1 ml. The initial densities of the mixtures were determined as described previously,¹ and concentrations of reactants were calculated accordingly.

Reactions of Phthalic Acid with N-Arylcarbamates.—*N*-Arylphthalimides were prepared by melting a mixture of phthalic acid (3.32 g, 0.02 mol) and the corresponding carbamate (0.04 mol) at 180 °C for 24 h. After cooling, unchanged carbamate and acid were removed by grinding the residue in cold ethanol and recrystallizing the solids from ethanol. *N*-Arylphthalimides [C₆H₄(CO)₂NAr] were identified by elemental analysis, i.r., and n.m.r. spectra, and m.p. Yields were as follows: Ar = Ph, m.p. 217 °C (lit.,^{35a} 211 °C),

³³ T. Wilm and G. Whischin, *Annalen*, 1868, **147**, 157.

³⁴ H. Hager, *Ber.*, 1885, **18**, 2573.

³⁵ (a) M. L. Sherrill, F. L. Schaeffer, and E. P. Shoyer, *J. Amer. Chem. Soc.*, 1928, **50**, 474; (b) O. L. Brady, W. G. E. Quick, and W. F. Welling, *J. Chem. Soc.*, 1925, **127**, 2264; (c) S. Gabriel, *Ber.*, 1878, **11**, 2260; (d) 'Dictionary of Organic Chemistry,' eds. J. R. A. Pollock and R. Stevens, 4th edn., Oxford University Press, New York, vol. 5, p. 2742; (e) A. Piutti and G. Abbatti, *Ber.*, 1903, **36**, 1000; (f) C. L. Butler, jun., and R. Adams, *J. Amer. Chem. Soc.*, 1925, **47**, 2610.

66%; 4-MeC₆H₄, m.p. 209 °C (lit.,^{35b} 204 °C), 66%; 4-ClC₆H₄, m.p. 196 °C (lit.,^{35c} 194—195 °C), 77%; 3-ClC₆H₄, m.p. 163 °C (lit.,^{35a} 163—164 °C), 84%; 2-ClC₆H₄, m.p. 143 °C (lit.,^{35a} 132—140 °C; lit.,^{35d} 143 °C), 61%; 4-MeO·C₆H₄, m.p. 159 °C (lit.,^{35c} 161—162 °C), 60%; 4-NO₂·C₆H₄, m.p. 274 °C (lit.,^{35f} 271—272 °C), 80%.

Reaction of Ethyl Carbamate with 4-Nitrobenzoic Acid.—A mixture (4 g) of ethyl carbamate and 4-nitrobenzoic acid in 8 : 1 molar ratio was heated in an evacuated sealed ampoule (20 ml) at 160 °C for 24 h. The ampoule was opened and the residue treated with sodium hydrogen carbonate solution and recrystallized from water to yield 4-nitrobenzamide, m.p. 201 °C (25%) (Found: C, 50.35; H, 4.15; N, 16.9. C₇H₆N₂O₃ requires C, 50.6; H, 3.65; N, 16.9%).

Reaction of Ethyl Carbamate with 4-Methoxybenzoic Acid.—The procedure was as above except for crystallizing the residue from diethyl ether after the hydrogen carbonate treatment. The 4-methoxybenzamide obtained was recrystallized from water (yield 5%), m.p. 163 °C (lit.,²⁶ 163 °C).

Reaction between Ethyl N-Phenylcarbamate and Acetic Acid.—Ethyl N-phenylcarbamate (0.05 mol) was dissolved in acetic acid (30 g, 0.6 mol) and the solution refluxed for 42 h. After cooling and neutralization with 10% sodium carbonate solution the mixture was extracted with chloroform; the extract was dried (MgSO₄) and evaporated. The residue was boiled several times in light petroleum to remove unchanged carbamate and the acetanilide was recrystallized from benzene (yield 0.286 g, 4.2%), m.p. 116 °C, mixed m.p. 115 °C.

Attempted Reactions with Other Acids and with NN-Dialkylcarbamates.—An attempted reaction of ethyl carbamate with pyridine-2,3-dicarboxylic acid yielded unchanged ethyl carbamate, carbon dioxide, and nicotinic acid, m.p. 236 °C. Attempted reactions of NN-diphenylcarbamates, ethyl NN-diethylcarbamate (170 °C, 24 h), and ethyl N-methyl-N-phenylcarbonate (150 °C; 24 h) with phthalic acid, and attempted reactions of ethyl NN-diethylcarbamate with benzoic, 4-methoxybenzoic, and 4-nitrobenzoic acids (170 °C; 24 h) left the starting materials essentially unchanged. Phthalic acid was recovered (90%) as the anhydride.

N-Ethoxycarbonylphthalamic Acid.—A suspension of N-ethoxycarbonylphthalimide (Fluka) (20 g) in distilled water was warmed to 70 °C until most of the material had dissolved, quickly filtered, and cooled. The precipitate was recrystallized from chloroform or light petroleum (b.p. 40—60 °C); yield 12 g, m.p. 55—70 °C (lit.,³⁷ 40—50 °C), δ(CDCl₃) 1.23 (3 H, t, CH₃·CH₂·O), 4.20 (2 H, q, CH₃·CH₂·O), 7.41—7.82 (3 H, m, arom.), 8.10—8.25 (1 H, m, arom.), 8.65 (1 H, s, CO₂H), and 9.3 (1 H, s, CO·NH·CO). Prolonged treatment with hot water yields phthalic acid.

Pyrolysis of N-Ethoxycarbonylphthalamic Acid at 150 °C.—N-Ethoxycarbonylphthalamic acid (2.3 g, 0.01 mol) was heated (150 °C; 12 h) under a slow stream of dry nitrogen in a distillation system. Small amounts of carbon dioxide formed were trapped in barium hydroxide solution. Some solid material sublimed into the condenser and after separation with dry ether was identified as a mixture of phthalic anhydride (1.1 g, 74%) and ethyl carbamate. The residue in the distillation flask was recrystallized from ether to yield phthalimide (0.34 g, 23%). The same procedure was repeated with a mixture of N-ethoxycarbonylphthalamic

acid (2.3 g, 0.01 mol) and ethyl carbamate (0.04 mol). After heating (150 °C; 10 h) the residue in the distillation flask yielded phthalimide (washed with aq. NaHCO₃) (1.27 g, 86.5%).

Pyromellitimides.—Well ground mixtures of pyromellitic acid (5.08 g, 0.02 mol) and the appropriate carbamate (0.04—0.08 mol) were heated for 24 h, at 160 °C (with ethyl carbamate) or 180 °C (with N-phenylcarbamates). Evolution of carbon dioxide and precipitation in the initially homogenous melt were observed. After cooling, the solid mass was ground, the residual acid removed with aqueous 10% sodium carbonate, and the carbamate extracted with ether or with boiling ethanol. Usually, no solvent for recrystallization was found; some products were purified by boiling in pyridine or dimethylformamide (DMF). None of the products melted below 300 °C. The following NN-diarylpyromellitimides were prepared: Ar = Ph, yield 70% (Found: C, 71.8; H, 3.35. C₂₂H₁₂N₂O₄ requires C, 71.75; H, 3.25%), λ_{max.} 257 nm (log ε 4.4); Ar = 4-Me-C₆H₄, 42% (Found: C, 72.05; H, 3.95; N, 7.05. C₂₄H₁₆N₂O₄ requires C, 72.7; H, 4.05; N, 7.05%), crystallized from DMF, λ_{max.} 267 nm (log ε 4.7); Ar = 4-ClC₆H₄, 65% (Found: C, 59.75; H, 2.4; Cl, 15.5; N, 5.9. C₂₂H₁₀Cl₂N₂O₄ requires C, 60.4; H, 2.3; Cl, 16.25; N, 6.4%), λ_{max.} 267 nm (log ε 4.7); Ar = 2-ClC₆H₄, 76% (Found: C, 60.35; H, 2.6; Cl, 15.6; N, 6.4%), washed with pyridine, λ_{max.} 312 nm (log ε 3.42); Ar = 3-ClC₆H₄, 65% (Found: C, 60.55; H, 2.7; Cl, 15.7; N, 6.35%), washed with boiling pyridine, λ_{max.} 257 nm (log ε 4.57); Ar = 4-MeO·C₆H₄, 82% (Found: C, 67.05; H, 3.75; N, 6.35. C₂₄H₁₆N₂O₆ requires C, 67.3; H, 3.75; N, 6.55%), washed with pyridine, λ_{max.} 282 nm (log ε 4.23); Ar = 4-NO₂·C₆H₄, 41% (Found: C, 57.4; H, 2.05; N, 12.0. C₂₂H₁₀N₄O₈ requires C, 57.65; H, 2.2; N, 12.2%), washed in pyridine, λ_{max.} 288 nm (log ε 4.75). Typical i.r. absorptions (1 715 and 1 735 cm⁻¹) were observed in all cases.

Diethyl m- and p-Phenylenebiscarbamates.³⁸—These were prepared by the dropwise addition with stirring, of ethyl chloroformate (Fluka purum; 25 g, 0.25 mol) to a solution of the appropriate phenylenediamine (10.8 g, 0.1 mol) in pyridine (100 ml). The mixture was left to cool and poured on crushed ice. The precipitate was filtered off, dried, and recrystallized from ethanol-water or from ether. The *para*-isomer, m.p. 195 °C (lit.,³⁸ 195 °C), was recrystallized from ethanol. The *meta*-isomer had m.p. 143 °C (lit.,³⁸ 143—145 °C).

Reactions of Phenylenebiscarbamates with Pyromellitic Acid.—A mixture (10 g) of the biscarbamate and acid in 3 : 1 molar ratio was heated in a distillation apparatus at 160—180 °C. Carbon dioxide was evolved along with ethanol and water, detected as above. After several hours the mixture was cooled, crushed, and treated with an excess of sodium hydrogen carbonate (until no more carbon dioxide was evolved). Repeated washings with boiling ethanol left a yellowish amorphous solid, m.p. >300 °C, insoluble in all solvents tried. The i.r. spectrum displayed aromatic absorptions at ca. 800 cm⁻¹ and carbonyl bands similar to those of pyromellitimide [Found (impure powder): C, 63.1; H, 3.4; N, 9.95. Calc. for C₁₆H₆N₂O_{4n}: C, 66.2; H, 2.05; N, 9.65%].

Polymerization of p-Ethoxycarbonylaminobenzoic Acid.—The acid³⁹ [m.p. 208 °C (lit.,³⁹ 208—209 °C)] (4.13 g, 0.02 mol) in *m*-cresol (150 ml) was refluxed for 72 h. While still hot,

³⁶ L. Gattermann, *Annalen*, 1888, **244**, 62.

³⁷ G. Heller and P. Jacobsohn, *Ber.*, 1921, **54**, 1112.

³⁸ E. Davidis, *J. prakt. Chem.*, 1896, **54**, 66.

³⁹ H. King and W. O. Murch, *J. Chem. Soc.*, 1924, **125**, 2595.

the solvent was removed by filtration and the solid was then boiled in ethanol (200 ml), filtered off, and washed with acetone [Found (impure powder): C, 70.9; H, 4.75; N, 12.0. Calc. for $(C_7H_5NO)_n$: C, 70.6; H, 4.2; N, 11.75%]. The i.r. spectrum showed carbonyl absorptions.

Viscosity was determined in concentrated sulphuric acid (AnalaR) at 25 ± 0.1 °C with an Ubbelohde Viscometer at 0.5% concentration; ⁴⁰ the value of $n_{rel.}$ was 0.1, corresponding to *ca.* 10 units per chain (*M* 210).

This research was sponsored by a grant in aid from the European Research Office of the United States Army, London.

[6/1973 Received, 25th October, 1976]

⁴⁰ F. W. Billmeyer, jun., 'Textbook of Polymer Science,' Wiley, New York, 1971, 2nd edn., p. 84.
