value in the water–acetone mixture, minus 10% for the ionic strength effect, or about 4×10^5. We actually found 3.4×10^5. With the combination pH meter and recorder it is difficult to ensure accuracy to 0.1 pH unit; thus the predicted and observed values agree within the limits of experimental accuracy.

Conclusions

The reaction product of formaldehyde and a simple xanthate in slightly acid solution is an S-hydroxymethyl alkylxanthate. In the absence of water, the reaction product is stable at room temperature and up to about 70°. In aqueous solution an equilibrium exists between the xanthate ions, formaldehyde, hydrogen ions, and the reaction product. In the case of the ethylxanthate, the equilibrium favors a larger fraction of the reaction product than in the case of the methylxanthate. The presence of acetone in the equilibrium solution favors a larger fraction of the reaction product than is present in a pure water solution.

Reaction of Benzoyl Isocyanate with a Phospholene Oxide Catalyst

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Benzoyl isocyanate with catalytic amounts of 1-ethyl-3-methyl-3-phospholene 1-oxide gives a product of empirical formula $C_{22}H_{15}N_3O_2$. Evidence indicates that the compound is 2,6-diphenyl-4-dehydrobenzamido-1,3,5-oxadiazine (I).

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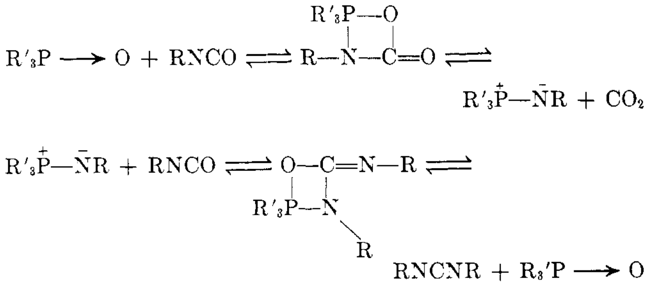
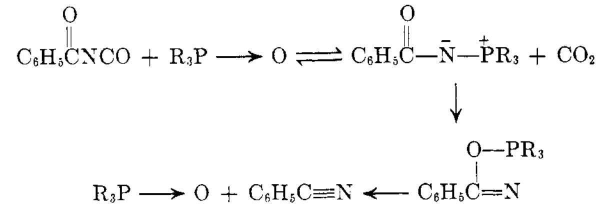
The conversion of aryl isocyanates to carbodiimides through the use of phospholene oxide catalysts has been described recently[1a–d] in the literature. The reaction proceeds cleanly and rapidly, with or without the use of a solvent, and the carbodiimide product can be isolated in nearly quantitative yield. The most active catalyst is 1-ethyl-3-methyl-3-phospholene 1-oxide. The kinetics of the reaction have been studied, and they support the formation of a phosphinimide intermediate, as described by the following mechanism.



$$R'_3P \rightarrow O + RNCO \rightleftharpoons \begin{matrix} R'_3P\text{—}O \\ | \quad\;\; | \\ R\text{—}N\text{—}C{=}O \end{matrix} \rightleftharpoons R'_3\overset{+}{P}\text{—}\overset{-}{N}R + CO_2$$

$$R'_3\overset{+}{P}\text{—}\overset{-}{N}R + RNCO \rightleftharpoons \begin{matrix} O\text{—}C{=}N\text{—}R \\ | \quad\;\; | \\ R'_3P\text{—}N \\ \quad\quad \diagdown \\ \quad\quad\quad R \end{matrix} \rightleftharpoons RNCNR + R_3'P \rightarrow O$$

On the basis of this mechanism, it was reasoned that a reaction of benzoyl isocyanate with the phospholene oxide catalyst should yield benzonitrile by the following route.



$$C_6H_5\overset{O}{\overset{\|}{C}}NCO + R_3P \rightarrow O \rightleftharpoons C_6H_5\overset{O}{\overset{\|}{C}}\text{—}\overset{-}{N}\text{—}\overset{+}{P}R_3 + CO_2$$

$$\downarrow$$

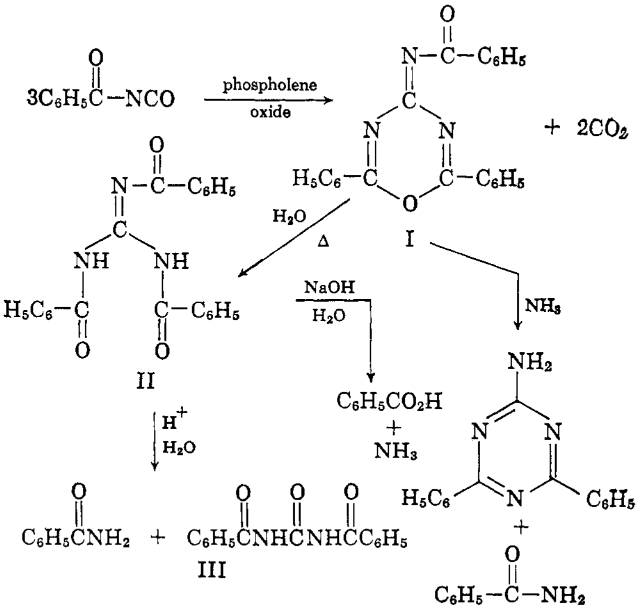
$$R_3P \rightarrow O + C_6H_5C{\equiv}N \longleftarrow C_6H_5\overset{O\text{—}PR_3}{\overset{|}{C}}{=}N$$

In ether solution[1b] or in xylene, however, benzoyl isocyanate reacted with 1-ethyl-3-methyl-3-phospholene 1-oxide to give a good yield of a solid product which could be decomposed subsequently into benzonitrile, carbon dioxide, and other products, but only at temperatures as high as 200°. Evidence is now presented to show that the compound, $C_{22}H_{15}N_3O_2$, is 2,6-diphenyl-4-benzoylimino-1,3,5-oxadiazine (I).

The reactions and structures discussed in this section are summarized in Chart I. Structure I is supported by elemental analysis, infrared spectrum (Fig. 1a), molecular weight measurements, and the degradative products subsequently described. Carbon dioxide was produced in the preparation, and the amount was quantitative for the stoichiometry of the reaction.

Chart I

Preparation and Structure Determination of 2,6-Diphenyl-4-benzoylimino-1,3,5-oxadiazine



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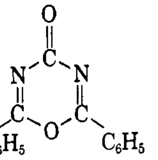
(1) (a) T. W. Campbell and J. J. Monagle, *J. Am. Chem. Soc.*, **84**, 1493 (1962); (b) T. W. Campbell, J. J. Monagle, and V. S. Foldi, *ibid.*, **84**, 3673 (1962); (c) T. W. Campbell, J. J. Monagle, and H. F. McShane, *ibid.*, **84**, 4288 (1962); (d) J. J. Monagle, *J. Org. Chem.*, **27**, 3851 (1962).

The oxadiazine (I) was hydrolyzed in two steps. In boiling water the heterocyclic ring was cleaved to yield a new product formulated as tribenzoylguanidine (II).

Structure II was assigned on the basis of elemental analyses and infrared spectrum which bears a great resemblance to that of dibenzoylurea (III). Further hydrolysis of II in dilute sodium hydroxide resulted in the formation of benzoic acid and ammonia.

Hydrolysis of oxadiazine (I) in dilute hydrochloric acid yielded dibenzoylurea (III) and benzamide.

A compound of the same general type of heterocyclic ring structure has been described in the literature by Terss and McEwen,[2] who prepared 2,6-diphenyl-4-keto-1,3,5-oxadiazine (IV) from the reaction of benzoyl isocyanate with benzoyl chloride, pyridine, and water.



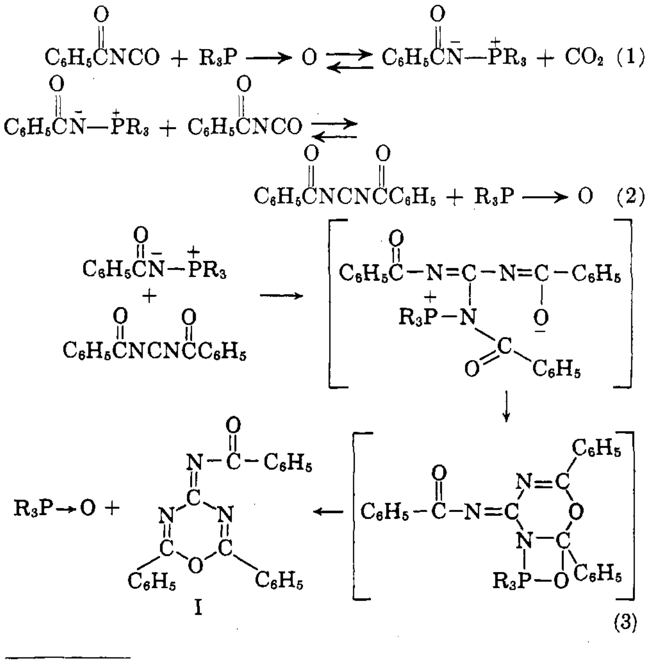
IV

Comparison of IV with I was made. Both show absorptions in the 1200–1400- and 1500–1800-cm.$^{-1}$ regions of the infrared and, in general, their spectra are quite similar (Fig. 1b). The oxadiazine (IV) also yielded dibenzoylurea on hydrolysis.

Additional proof for the proposed oxadiazine structure of the compound, $C_{22}H_{15}N_3O_2$, was provided by reaction with excess ammonia at 100°. Two products were isolated in good yield and these were identified as benzamide and 2-amino-4,6-diphenyltriazine (V).[3]

The empirical formula of oxadiazine (I), $C_{22}H_{15}N_3O_2$, at first suggested that one molecule of benzoyl isocyanate and two molecules of benzonitrile might be involved in the formation of the final product. Experiments showed, however, that the presence of benzonitrile in the reaction mixture did not enhance the yield of final product, and, therefore, it is not a necessary intermediate in the reaction. A tentative mechanism for the reaction has been formulated as shown in Chart II.

Chart II



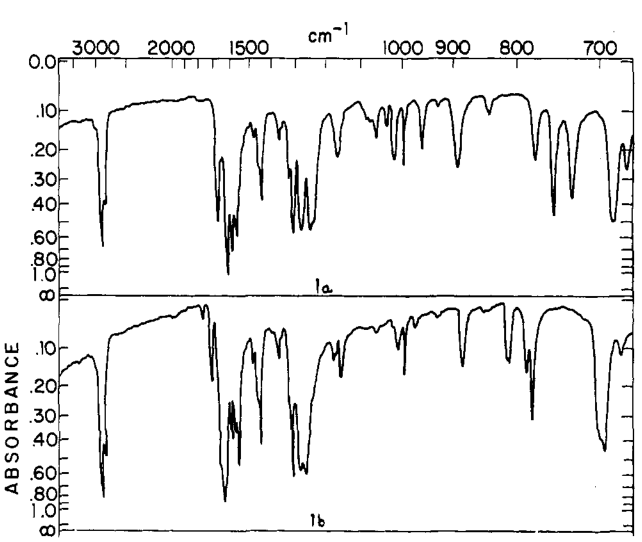


Fig. 1.—Infrared spectra of Nujol mull: a, 2,6-diphenyl-4-dehydrobenzamido-1,3,5-oxadiazine; and b, 2,6-diphenyl-4-keto-1,3,5-oxadiazine.

Steps 1 and 2 have already been well documented for the aryl isocyanates.[1] The dibenzoylcarbodiimide formed can be represented by a number of resonance forms, and it seems likely that its electron-poor carbon atom would be highly susceptible to nucleophilic attack by the ylide nitrogen as in step 3. Subsequent cyclization and splitting off of the tertiary phosphine oxide results in the formation of the oxadiazine product and regeneration of the catalyst.

The oxadiazine (I) has been found to undergo decomposition at 200° to form benzonitrile, carbon dioxide, and other unidentified products. The course of the decomposition is not known, but possibly a free-radical mechanism is involved. Benzonitrile and benzoyl isocyanate may be the initial products. (See Chart III.)

Experiments have shown that benzoyl isocyanate also decomposed at 200° to yield carbon dioxide, benzonitrile, and other products.

Experimental

Preparation of Benzoyl Isocyanate.[4]—To a well-stirred solution of 61.0 g. (0.50 mole) of dry, recrystallized benzamide in 500 ml. of dry carbon tetrachloride was added in dropwise fashion a solution of 49 ml. (73.5 g., 0.58 mole) of freshly distilled oxalyl chloride in 125 ml. of dry carbon tetrachloride. The mixture was heated slightly during the addition and then was brought to a gentle reflux and held there for 17 hr. It was then filtered through a sintered-glass funnel to remove solid material, and the carbon tetrachloride was distilled at atmospheric pressure. Extreme care was taken to prevent the introduction of moisture into the sample during these manipulations. Distillation of the residue at reduced pressure yielded 57.7 g. (78%) of benzoyl isocyanate, b.p. 99–101° (20–22 mm.). An infrared spectrum of this material showed the characteristic strong isocyanate band at 2240 cm.$^{-1}$.

Reaction of Benzoyl Isocyanate with 1-Ethyl-3-methyl-2-phospholene 1-Oxide.—The apparatus used in the reaction and for the transference of benzoyl isocyanate was flamed out and stored in a drybox. The reaction vessel consisted of a 500-ml., round-

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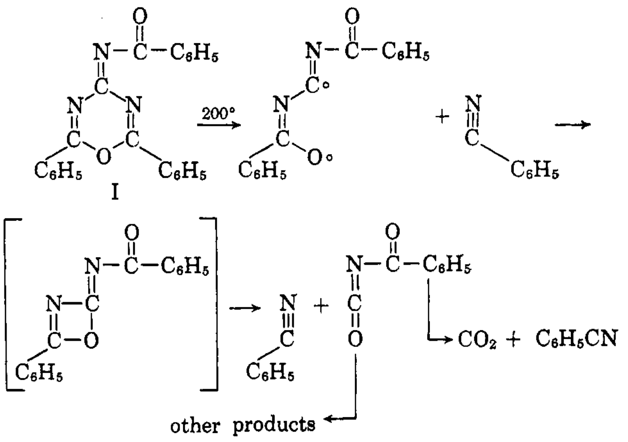
[2] R. H. Terss and W. E. McEwen, *J. Am. Chem. Soc.*, **76**, 580 (1954).

[3] P. B. Russell, *et al.*, *ibid.*, **74**, 5403 (1952).

[4] A. J. Speciale and L. R. Smith, *J. Org. Chem.*, **27**, 3742 (1962).

Chart III



bottom flask fitted with condenser and drying tube, Tru-Bore stirrer, and dropping funnel.

To a solution of 0.5 ml. of the freshly distilled phospholene oxide catalyst in 150 ml. of dry, refluxing xylene was added a solution of 20.0 ml. (24.8 g., 0.17 mole) of freshly prepared benzoyl isocyanate in 125 ml. of dry xylene. Addition was made dropwise with stirring over a period of 1 hr. The solution turned bright yellow immediately upon addition of the isocyanate. The mixture was refluxed with stirring for an additional 1.5 hr. On cooling the solution, a considerable amount of light yellow material separated and was collected, washed with cold ether, and air-dried. This afforded 13.5 g. (68%) of the product, 2,6-diphenyl-4-dehydrobenzamido-1,3,5-oxadiazine, m.p. 196–198°.

Anal. Calcd. for $C_{22}H_{15}N_3O_2$: C, 74.8; H, 4.27; N, 11.9; O, 9.1; mol. wt., 353. Found: C, 74.4; H, 4.23; N, 11.7; O, 9.5; mol. wt., 366 and 377.

In another experiment, 25.1 g. (0.18 mole) of benzoyl isocyanate was added to a solution of 0.5 ml. of the phospholene oxide catalyst in 200 ml. of refluxing xylene. Refluxing was continued for 2.5 hr., during which time 4.76 g. (64%) of carbon dioxide was evolved and trapped in weighing tubes filled with Indicarb®[5] carbon dioxide absorbent.

Hydrolysis of 2,6-Diphenyl-4-benzoylimino-1,3,5-oxadiazine.—The 1,3,5-oxadiazine product, 3.92 g., was refluxed in distilled water for 48 hr. At the end of this time, 3.25 g. of white solid was isolated from the mixture by filtration. Recrystallization from ethanol gave 0.72 g. of pure white tribenzoylguanidine, m.p. 196–197°. Infrared spectra of the initially isolated product showed it to be mostly tribenzoylguanidine, contaminated with some dibenzoylurea.

Anal. Calcd. for $C_{22}H_{17}N_3O_3$: C, 71.1; H, 4.60; N, 11.3. Found: C, 70.8; H, 4.46; N, 11.4.

Hydrolysis of the tribenzoylguanidine (0.72 g.) in 0.5 *N* sodium hydroxide solution gave 0.60 g. of benzoic acid and an undetermined amount of ammonia.

In another experiment, 3.10 g. of the 1,3,5-oxadiazine product was refluxed for 10 min. in 75 ml. of 0.5 *N* hydrochloric acid in aqueous ethanol. After cooling, the white solid apparent in the reaction mixture was filtered off, washed with cold water, and dried over phosphorous pentoxide. The yield of 1.84 g., identified as dibenzoylurea, amounted to 84% of the theoretical. The product melted at 215–217°. An admixture with authentic dibenzoylurea melted at 216–218°. The infrared spectrum of the hydrolysis product was identical with that of an authentic sample of dibenzoylurea.

Concentration of the filtrate from the hydrolysis afforded an additional 0.11 g. of dibenzoylurea. Extraction of the filtrate with two 50-ml. portions of ether, followed by evaporation of the ether, left a residue of 0.50 g. (49%) of white solid which was shown to be a mixture of benzamide and benzoic acid by infrared analysis.

Pyrolysis of 2,6-Diphenyl-4-benzoylimino-1,3,5-oxadiazine.—A portion of the oxadiazine, 2.31 g., was heated in an oil bath at 198° for 6 hr. The outlet of the reaction vessel was connected to an absorption tube filled with Indicarb® carbon dioxide absorbent, and the system was swept with a slow stream of dry, carbon dioxide-free nitrogen. At the end of this heating period, gas evolution had ceased, and a total of 0.117 g. (41%) of carbon dioxide had been collected. The residue consisted of a yellow oil, mostly benzonitrile as determined by infrared analysis, and a high-melting, yellow solid.

In a separate experiment, the addition of a phospholene oxide catalyst to the system did not apparently increase the rate of decomposition nor the amount of carbon dioxide produced. In this experiment, 1.479 g. of the 1,3,5-oxadiazine was pyrolyzed to give 0.0799 g. (43%) of carbon dioxide.

Hydrolysis of 2,6-Diphenyl-4-keto-1,3,5-oxadiazine.—The hydrolysis of 2,6-diphenyl-4-keto-1,3,5-oxadiazine, 1.10 g., was effected by refluxing for 10 min. in 0.5 *N* hydrochloric acid in aqueous ethanol. The white solid product which separated on cooling was collected by filtration, washed with water, and dried over phosphorus pentoxide under vacuum. The yield of white crystalline product which melted at 216–218° was 93%. An infrared spectrum of the product was identical with that of dibenzoylurea.

Reaction of 2,6-Diphenyl-4-benzoylimino-1,3,5-oxadiazine with Liquid Ammonia.—2,6-Diphenyl-4-benzoylimino-1,3,5-oxadiazine, 2 g., was sealed in an autoclave with liquid ammonia, 30 g., and ammonium bromide, 0.1 g., and heated to 100° for 5 hr. Removal of the ammonia left a white residue which was fractionally crystallized from 90% ethanol to give a 60% yield of 2-amino-4,6-diphenyltriazine, m.p. 169–170° (lit.[3] m.p. 168–169°).

Anal. Calcd. for $C_{15}H_{12}N_4$: C, 72.6; H, 4.8; N, 22.6. Found: C, 72.7; H, 5.0; N, 22.2.

The ultraviolet spectrum in ethanol showed λ_{max} 254 mμ (lit.[3] λ_{max} 256 mμ). The infrared spectrum was consistent with that of a phenyl-substituted aminotriazine.

Evaporation of the mother liquor of the above crystallization and recrystallization of the residue from benzene gave benzamide, m.p. 120–124°.

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(5) Trade-mark of the Fisher Scientific Co.