midazole, and the higher melting material (II) was designated 1,1′-dimethyl-2,2′-bibenzimidazole. Formation of the bibenzimidazole derivatives occurred in 53.5% yield.

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Acetylation of Imides with Ketene

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Previous studies, in our laboratories, have involved an extension of the acetylation of alcohols, mercaptans, carboxylic acids, glycols, polyhydroxy compounds, amides, hydrocarbons, nitroparaffins, and carbohydrates, with ketene. All of the above classes of compounds are similar in that they contain activated or readily replaceable hydrogen. Ketene is characterized by its ability to form combinations with such organic substances. Although somewhat toxic and difficult to prepare, it ranks first in reactivity among the common acetylating reagents. The predominating advantage of ketene, as compared to acetic acid, acetyl halides, and acetic anhydride, is the fact that it theoretically produces no objectionable by-products.

Since amides have been found to be readily acetylated with ketene to form monoacetyl derivatives,[1] it seemed highly probable, by analogy, that imides could be similarly acetylated to the corresponding *N*-acetyl derivatives. In addition, several similar reactions have been observed during recent years. Rice and coworkers,[2] for instance, prepared *N*-phenyldiacetylimide by passing ketene into acetanilide at 140°. They suggested that *N*-acetylbenzamide was formed similarly from benzamide at 180°, but that it decomposed into benzonitrile as the reaction progressed. Later, Padgham and Polya[3] isolated *N*-acetylbenzamide and diacetylimide by passing ketene into molten benzamide and acetamide, respectively. The use of sulfuric acid in the production of *N*-phenyldiacetylimide from ketene and molten acetanilide was reported by Smirnova[4] and others, who also reported the preparation of *N*-formyldiacetylimide, and described it as a liquid. Our findings, however, indicate that this triacylated ammonia is a crystalline product.[1] For these reasons it seemed desirable to conduct an extended study of the reaction of ketene with any and all available imides.

The first difficulty encountered in this study was the selection of a suitable inert solvent. Among those employed were carbon tetrachloride, benzene, ether, ligroin, dioxane, and chloroform. Hot benzene seemed to be the most efficient solvent for the imides, but it also induced excessive polymerization. Dioxane appeared to be a better solvent but could not be readily removed without causing the acetylated imide to decompose. This was probably due to the formation of peroxides while the dioxane was exposed to air. Also, acetylation was extremely slow when this solvent was employed. A suspension of the imide in carbon tetrachloride yielded maximum acetylation with little or no polymerization.

It was found that the imides could not be acetylated when treated with ketene alone. A catalyst was therefore necessary. Concentrated sulfuric acid has been found, by other investigators, to be a very satisfactory catalyst in similar reactions. When concentrated sulfuric acid was used with the imides, however, no acetylation took place. There was no change in the melting point from that of the parent compound, either before or after the attempted acetylation. Fused sodium acetate produced positive results. The compounds which were unaffected by the ketene in previous attempts, acetylated readily with no noticeable by-products when sodium acetate was used. This catalyst was found to be satisfactory with every imide treated.

This work could be valuable from the standpoint of the organic analytical student, because derivatives of imides are as yet little known. The literature is very sketchy concerning imide derivatives, and they are difficult to prepare. The acetyl derivatives of imides have previously been prepared by reaction with acetic anhydride followed by long hours of refluxing to affect a reaction. The yields are low. Attempts to acetylate imides using acetic acid or acetyl halides have been unsuccessful. Ketene will react readily with the imides producing satisfactory yields in a matter of minutes. The gas can be produced satisfactorily on a laboratory scale. Seven imides, namely naphthalimides, 4-nitrophthalimide, pyromellitic diimide, tetrahydrophthalimide, phthalimide, saccharin, and succinimide; and one anilide, namely acetanilide, have been successfully acetylated with ketene for the first time. Of these, the first four were acetylated for the first time by any means. The other four compounds involved in the study have been previously acetylated by using acetic anhydride. The results are summarized in Table I.

EXPERIMENTAL

The ketene for this study was prepared by the use of a Hurd type "lamp."[5] It was prepared by the pyrolysis of purified acetone. The acetone was vaporized by boiling, and the vapors were passed over an electrically heated wire. It

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[1] R. E. Dunbar and Gerald C. White, *J. Org. Chem.*, **23**, 915 (1958).

[2] F. O. Rice, J. Greenberg, C. E. Waters, and R. E. Vollrath, *J. Am. Chem. Soc.*, **56**, 1760 (1934).

[3] D. N. Padgham and J. B. Polya, *Australian J. Sci.*, **13**, 113 (1951).

[4] N. V. Smirnova, A. P. Skoldinov, and K. A. Kocheshkov, *Doklady Akad. Nauk S.S.S.R.*, **84**, 737 (1952).

[5] W. E. Hanford and J. C. Sauer, *Org. Reactions*, III, 108 (1946).

TABLE I

KETENE ACETYLATION PRODUCTS OF IMIDES

Imide Employed	Solvent	Catalyst	Appearance of Acetylated Product	M.P., °C.	Yield, %	Nitrogen, %	
						Theor.	Exptl.
Acetanilide[a]	CCl_4	H_2SO_4	White crystals	38[b]	76	7.91	7.65
Naphthalimide	$C_2H_5OC_2H_5$	AcONa	Pink crystals	275–277(dec.)	57	5.86	5.98
4-Nitrophthalimide	CCl_4	AcONa	Yellow crystals	105–107	22	11.96	11.67
Phthalimide	CCl_4	AcONa	Butter-scotch crystals	128–130[c]	18	7.41	7.30
Pyromelliticdiimide	C_6H_6	AcONa	Tan crystals	138–140(dec.)	50	9.34	9.31
Saccharin	C_6H_6	AcONa	White crystals	196–200(dec.)[d]	70	6.23	6.25
Succinimide	hot CCl_4	AcONa	Yellow crystals	38[e]	51	9.93	9.82
Tetrahydrophthalimide	CCl_4	AcONa	White crystals	123–124	27	7.26	7.23

[a] Not an imide but an *N*-phenyl amide. [b] J. J. Sudborough, *J. Chem. Soc.*, 533 (1901), reports a m.p. of 37°. [c] T. W. Evans and W. M. Dehn, *J. Am. Chem. Soc.*, 51, 3651 (1929), reports a m.p. of 135–136°. [d] A mixed melting point also. [e] C. Djerassi and C. T. Lenk, *J. Am. Chem. Soc.*, 75, 3493 (1953), reports a m.p. of 40–41°.

was then mixed with the compound to be acetylated in an absorption apparatus[6] that had been previously designed in our laboratories. The compound being acetylated was dissolved in a suitable solvent placed in the absorption apparatus.

The imides for this study were all suspended in carbon tetrachloride, benzene, or ethyl ether at room temperature, with the exception of succinimide, which was suspended in hot carbon tetrachloride. A common catalyst found to be effective with all the imides acetylated was sodium acetate. The imide was weighed out in a 0.03-mole quantity. This, together with 0.03 grams of catalyst, was added to an 80-ml. portion of the solvent in the absorption flask. Ketene was passed through the reaction mixture until an equivalent molar amount had been added. A slight excess was added to ensure complete reaction. After the addition was complete, the mixture was separated from any residue which failed to dissolve. This residue was found in each case to be traces of unreacted parent compound and was, therefore, discarded. The mixture was then cooled and the acetylated imide crystallized out in surprisingly pure form.

All acetylated imides were verified and identified by mixed melting points with samples of the same compounds prepared by other approved means, or by micro-Kjeldahl and micro-Dumas nitrogen determinations.

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[6] A. N. Bolstad and R. E. Dunbar, *Ind. Eng. Chem., Anal. Ed.*, 18, 337 (1946).

The Structure of Amidoximes[1]

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Amidoximes result primarily from the action of hydroxylamine on cyanides or the amination of hydroxamic acid chlorides with amines or ammonia. Neither the method of synthesis nor the reactions, however, permit a distinction between the isomeric structures Ia and Ib.

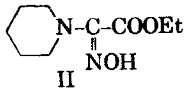
$$\underset{\displaystyle NH}{\overset{\displaystyle RCNHOH}{\|}}$$

Ia

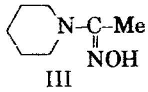
$$\underset{\displaystyle NOH}{\overset{\displaystyle RCNH_2}{\|}}$$

Ib

For this purpose the infrared absorption spectra of a few selected amidoximes have been compared with those of authentic oximino compounds of similar structure and with amidoximes derived from secondary amines (II and III) which can only possess structures corresponding to Ib.



II



III

A recent investigation of a series of amidoximes has described infrared absorption bands for these compounds which were assigned to NH stretching, OH stretching, NH deformation, C=N stretching, and N—O stretching.[2]

Similar bands have been observed in the present investigation (Table I). The broad bands in the region of 3.04–3.22 μ are probably due to associated NH and OH. They are much weaker in dilute solutions while the monomer bands at 2.80–2.93 μ are increased in intensity.

Strong bands at 5.95–6.24 μ are assigned to C=N stretching. Theoretical considerations permit the

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[1] This work was performed under the auspices of the U. S. Atomic Energy Commission.

[2] J. Barrans, R. Mathis-Noël, and F. Mathis, *Compt. rend.*, 245, 419 (1957).