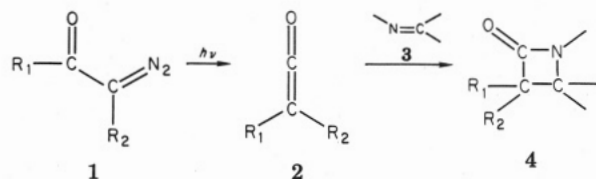


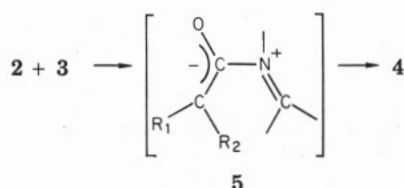
Observation of Zwitterions in the Thermal Reaction of Ketenes with Carbon-Nitrogen Double Bonds

Summary: Zwitterions have been detected in thermal reactions of ketenes with imidazoles. The direct observation of the zwitterions firmly establishes that the thermal cycloaddition of ketenes with carbon-nitrogen double bonds is a two-step process.

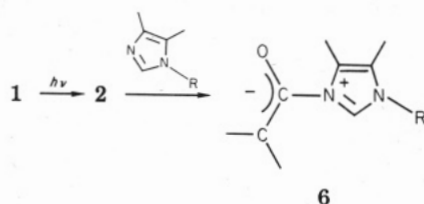
Sir: Diazo ketones **1** are radiation-sensitive materials that give ketenes **2** after photolysis.¹ It is known that ketenes **2** not only react with nucleophiles like water, alcohols, and amines² but also with carbon-carbon, carbon-nitrogen, and nitrogen-nitrogen double bonds.³ An interesting class of compounds are azomethines **3** that give β -lactams **4** with ketenes, as was shown by Staudinger⁴ for the first time.



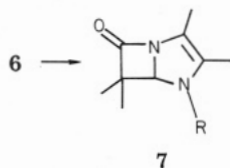
In these reactions, zwitterions **5** are discussed as intermediates.⁵ Although **5** could be trapped to give 2:1 or 1:1 adducts,⁶ they have never been detected by spectroscopic methods before. In the experiments reported here on



imidazoles and ketenes generated by photolyzing diazo ketones at 10 K in a film, the existence of zwitterions **5** is shown by IR spectroscopy for the first time. The results indicate that even if R = H, zwitterions **6** have high thermostability. Furthermore, some of the aromatic im-



imidazoles seem to give the nonaromatic β -lactams **7**. These



observations are of great technological interest for the

- (1) H. Meier and K. P. Zeller, *Angew. Chem., Int. Ed. Engl.*, **14**, 32 (1975).
- (2) D. P. N. Satchell and R. S. Satchell, *Chem. Soc. Rev.*, **4**, 231 (1975).
- (3) H. Ulrich, "Cycloaddition Reactions of Heterocumulenes", Academic Press, New York, 1967.
- (4) H. Staudinger, *Justus Liebig's Ann. Chem.*, **356**, 51 (1907).
- (5) R. Huisgen, B. A. Davies, and M. Morikawa, *Angew. Chem., Int. Ed. Engl.*, **7**, 826 (1968).
- (6) M. J. Haddadin and A. Hassner, *J. Org. Chem.*, **38**, 2650 (1973).

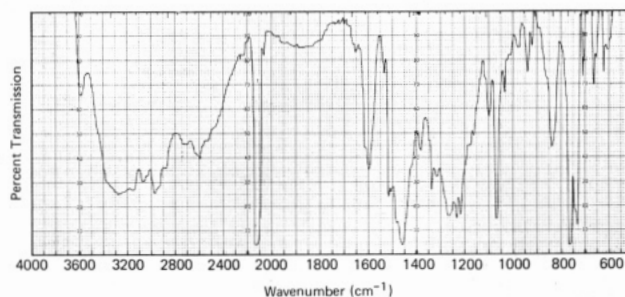


Figure 1. The infrared spectrum at $T = 10$ K of **8**, **9**, and **10**, after photolysis with UV light (3400–4400 Å). The irradiation converts diazo ketone **8** to ketene **11** which is characterized by the intense absorption centered at 2110 cm⁻¹. The imidazole **10** has intense absorption at 755, 838, and 1068 cm⁻¹.

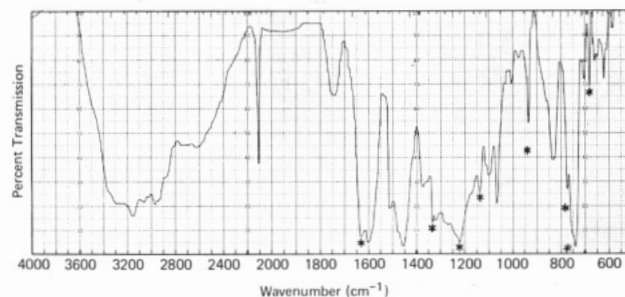


Figure 2. The infrared spectrum of **8**, **9**, and **10** after photolysis at $T = 10$ K and raising the temperature to 200 K. Note that the absorption for the ketene **11** and imidazole **10** have almost completely vanished. The bands centered at 682, 775, 937, 1008, 1138, 1224, 1335, and 1630 cm⁻¹ are assigned to the zwitterion **12**. The band at ~ 1750 cm⁻¹ is due to the carbonyl stretching frequency of the ester **13**.

applicability of diazo ketones as photoresists,⁷ and for the thorough understanding of the reactions of ketenes.

Due to the high reactivity of ketenes with nucleophiles, it is very difficult to follow the reaction spectroscopically. As a consequence, we use a very simple "matrix isolation technique" whereby the photochemical precursor **1** is mixed with an imidazole in a polymeric matrix.⁸ After a film consisting of the three components is cast onto a CsI substrate, the sample is enclosed in a vacuum system, cooled to $T = 10$ K, and irradiated with UV light (3400–4400 Å) to convert **1** to ketene. At the very low temperatures, no thermal reactions of the ketene are observed; however, thermal chemistry is induced and may easily be controlled by raising the temperature of the film. The progress of the reaction is followed by using infrared spectroscopy.

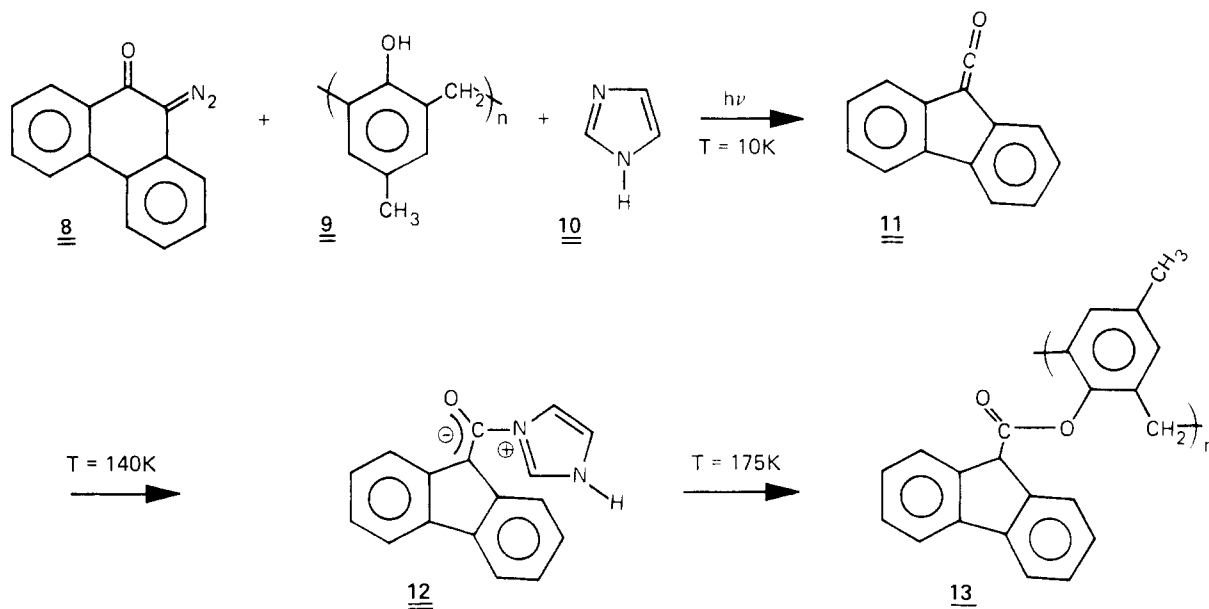
Equimolar quantities of the diazo ketone **8**, imidazole **10**, and the phenolic resin **9** (see Scheme I) were dissolved in *p*-dioxane and cast into a thin film on a CsI substrate. The infrared spectrum of the film after photolysis with a band of light between 3400 and 4400 Å is shown in Figure 1. This latter spectrum is due only to **9**, **10**, and the ketene **11**.⁹ Changes in the infrared spectrum only occur when the temperature reaches 140 K, at which a rather broad absorption appears at 1635 cm⁻¹. This synchronously increases in intensity with a decrease intensity of the ketene absorption at 2110 cm⁻¹ and the absorptions for imidazole.

(7) W. S. DeForest, "Photoresist Materials and Processes", McGraw-Hill, New York, 1975.

(8) The imidazole appears to form a 1:1 complex with the diazo compound when cast into a film with the resin **9**; J. Pacansky and W. Schwarz, manuscript submitted for publication.

(9) J. Pacansky and D. Johnson, *J. Electrochem. Soc.*, **124**, 865 (1977); J. Pacansky and J. R. Lyster, *IBM J. Res. Dev.*, **23**, 43 (1979).

Scheme I



At $T = 175\text{K}$, a new absorption appears at 1750cm^{-1} . The spectrum of the system at $T = 200\text{K}$ is shown in Figure 2. Note that the rather large broad absorption between 1600 and 1650cm^{-1} is the most prominent feature in the spectrum and that the ketene absorption at 2110cm^{-1} is almost completely gone. Further increases in the temperature are characterized by the continual decrease in the broad absorption centered at 1635cm^{-1} with the synchronous increase in the 1750cm^{-1} absorption and the reappearance of the infrared spectrum of imidazole.

The species responsible for the 1750-cm^{-1} absorption is easily identified⁹ as the ester 13. The reaction of the ketene with the resin in the absence of imidazole begins at 250K ; this eliminates any problems associated with ester formation by a direct ketene plus resin route. The species responsible for the 1630-cm^{-1} band is identified as the zwitterion 12 on the following basis. The same analysis on a number of diazo ketones and imidazoles substituted in the 1-, 2-, or 3-position produced the same observation, i.e., the ketene thermally reacts with an imidazole to produce a species with an intense absorption at $\approx 1600\text{--}1700\text{cm}^{-1}$; furthermore, the thermal stability of the zwitterions may be dramatically and predictably changed by performing the proper substitutions on the imidazole ring. For example, when electron-donating substituents like CH_3 and benzyl are used to replace the hydrogen on the 1-position of the imidazole ring, zwitterions are pro-

duced whose IR spectra remain (under vacuum) for several days at room temperature. When electron-withdrawing groups like C_6H_5 , CH_3CO , and CN are used, the zwitterion spectra rapidly convert at very low temperatures to those of other species with absorptions at 1770cm^{-1} ; these, in turn, disappear in concert with the formation of an ester. These latter observations indicate that the new thermally labile species is a β -lactam, and are consistent with the formation of a zwitterion whose thermal stability toward ring closure may be controlled by substitution of suitable groups on the imidazole ring. Electron-withdrawing groups favor ring closure to 4, while electron-releasing groups impose a large barrier for formation of a β -lactam.

In summary, the results presented have demonstrated that the thermal reaction of ketenes with activated $\text{C}=\text{N}$ bonds proceeds via a zwitterionic species to a β -lactam and that some zwitterions exist at room temperature for days, even in the presence of a nucleophile like 9.

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