

THE ACTION OF CARBENES ON N-HETEROCYCLES (I)

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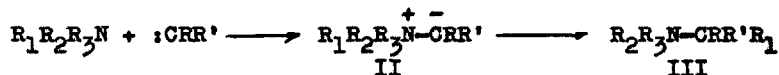
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Ylids of $\text{>N}^+\text{-C}^-$ (I) type can be obtained by two methods known so far : by the addition of dienophiles to a suitable nitrogen compound¹ or by eliminating hydrogen halides from ammonium salts². By these two methods many stable ylids have been obtained.

A third method for the synthesis of the zwitterionic products of type (I) relies on the addition of a carbene to a tertiary amine.

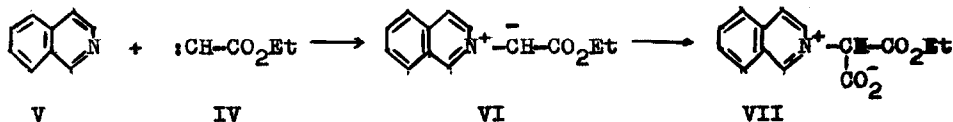


In such a case the amine (III) is obtained as a result of a rearrangement process.

The reaction³ between fluorenyliden-carbene and dimethylbenzylamine leads to 9-benzyl-9-dimethylamino-fluoren and it is thought to proceed via an ylidic intermediate similar to (II).

The isolation of the ylid from the carbene is possible if the two reactants are chosen in such way that no rearrangement of the ylid can take place and the two charges are sufficiently stabilized. Thus, the addition of carbethoxymethylen-carbene to isoquinoline was studied.

Isoquinolinium-carbethoxymethylid (VI) has been obtained by the thermal decomposition of ethyldiazoacetate in CHCl_3 in the presence of isoquinoline.

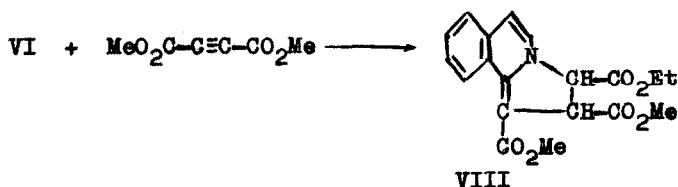


In the addition reaction a singlet electronic state can be presumed for the carbene (IV). The red isoquinolinium-carbethoxymethylid (VI) is stable in the

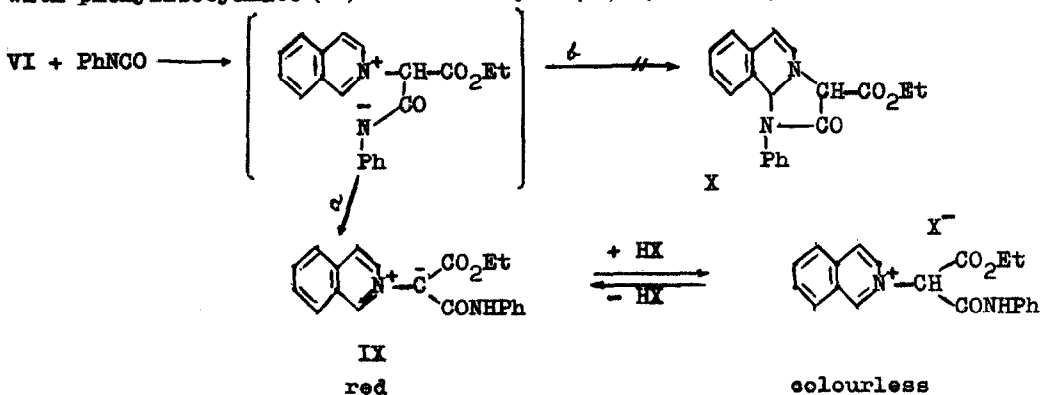
absence of humidity and with CO_2 it gives (VII).

The same ylid (VI) has been obtained from N-carbethoxymethylen-isoquinolinium bromide by the elimination of HBr.

Evidence for the dipolar character of the product (VI) is provided by its cycloaddition reaction with dimethylacetylenedicarboxylate which leads to (VIII).



With phenylisocyanate (VI) forms a new ylid (IX). (cf. ref. 4)



Reaction (a) competes with the normal cycloaddition (b) which does not take place. Ylide (IX) is stable in alcohol-water and is a good pH indicator.

The structures of the VI, VII, VIII and IX have been determined by chemical analyses, IR and NMR spectra.

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