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INTERACTION OF DICHLOROCARBENE WITH IMINES

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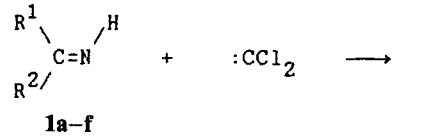
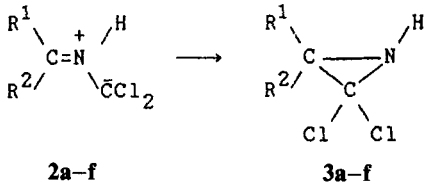
The interaction of dichlorocarbene with imines and ketene imines was studied by means of the MNDO method. The results indicate that the lack of ylide cyclization products in the reactions of dichlorocarbene with ketene imines is due to a high reactivity of ketene imine ylides in intermolecular reactions, rather than stereoelectronic factors preventing cyclization. It was shown that the dichlorocarbene reaction with *N*-benzylideneaniline resulting in *gem*-dichloraziridine proceeds through transient formation of ylide.

Dichlorocarbene reacts with aryl azomethines to form *gem*-dichloroaziridines.[1] However, the reaction of dichlorocarbene with ketene imines affords no products of cyclization of intermediate ketene imine (alkylideneazomethine) ylides.[2–7]

In connection with this problem, in this work the interaction of dichlorocarbene with methyleneamine (**1a**), (*Z*)- and (*E*)-1-azabutadiene (**1b, c**), ketene imine (**1d**), 1-azapenta-1,2,4-triene (**1e**) and benzylideneamine (**1f**) was investigated by the MNDO method. Calculations have shown that dichlorocarbene, with a small activation barrier, adds to the lone pair of the nitrogen atom of imine with the formation of ylides.



1a–f



2a–f **3a–f**

a, $R^1 = R^2 = H$; **b**, $R^1 = H_2C{=}CH{-}$, $R^2 = H$; **c**, $R^1 = H$, $R^2 = H_2C{=}CH{-}$; **d**, $R^1 + R^2 = H_2C{=}$; **e**, $R^1 + R^2 = H_2C{=}CH{-}CH{=}$; **f**, $R^1 = H$, $R^2 = Ph$.

The computed enthalpies of formation of ylides **2**, of aziridines **3**, of transition states for the reaction **2** → **3** and activation barriers for cyclization of ylides are listed in Table 1. The following observation can be made: (a) the ylides **2a–f** are thermodynamically less stable than the aziridines **3a–f**; (b) the activation barriers to cyclization of the ylides **2a–f** are close to 20 kcal/mol^{-1}, (1 kcal = 4·184 kJ); (c) the ylide **2c**, in contrast to the stereoisomer **2b**, has an optimum bent conformation, and in the optimum conformation of the ylide **2f** the phenyl ring plane is perpendicular to the C—N—CCl_2 plane of the ylide. This suggests that the lack of ylide cyclization products in the reactions of dichlorocarbene with ketene imines results from a high reactivity of ketene imine ylides towards dipolarophiles and nucleophiles[2–7] rather than from stereoelectronic factors which prevent cyclization of the ylides **2d** and **e** to aziridines. On the other hand, the 1,3-dipolar cycloaddition reactions of phenyl-substituted ylides are hindered as a consequence of a bent conformation of these ylides and the major path of ylide stabilization becomes cyclization to aziridine.

According to these conclusions, we now have shown that the reaction of dichlorocarbene with the *N*-benzylideneaniline **1g** leading to the aziridine **3g** also proceeds through the transient formation of an ylide (**2g**), which could be trapped by dimethyl acetylenedicarboxylate (**4**).

When dipolarophile **4** was added to the reaction mixture containing imine **1g** and a source of $:CCl_2$ (sodium trichloroacetate and phase-transfer catalyst) along with aziridine **3g**, the derivative of pyrrole **5** (*ca* 2%) was obtained. On decreasing the ratio of imine to dipolarophile from 1:1·5 to 1:5, the ratio of the reaction products **3g** to **5** changed from 1:0·03 to

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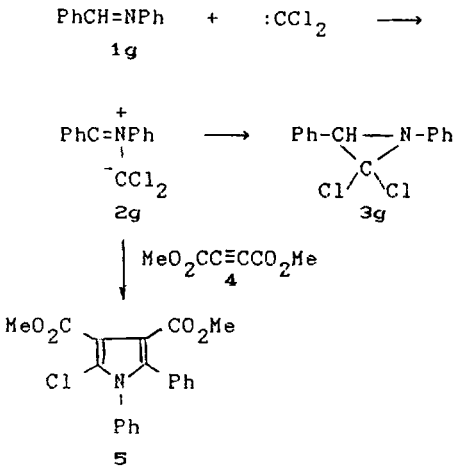
Table 1. Computed geometrical parameters for ylides, enthalpies of formation of ylides, of aziridines (ΔH_f^0) and of transition states for the reaction **2** → **3** (ΔH^*) and activation barriers for cyclization of ylides (E_a)

Ylide	Bond length (pm) C=N−	Bond length (pm) $=\overset{+}{N}-\overset{-}{C}Cl_2$	C−N−C angle (°)	ΔH_f^0 (ylide) (kcal mol^{-1})	ΔH^* (kcal mol^{-1})	E_a (kcal mol^{-1})	ΔH_f^0 (aziridine) (kcal mol^{-1})
2a	133·8	135·2	129·0	36·6	60·2	23·6	13·3
2b	135·0	135·1	128·3	47·4	70·6	23·2	31·5
2c[a]	134·6	135·0	132·6	50·7	73·3	22·6	31·1
2d	129·4	135·6	127·1	71·8	91·8	20·0	39·1
2e	129·3	135·6	127·2	86·0	105·3	19·3	53·0
2f[a]	–	–	–	61·0	81·4	20·4	39·8

[a] In ylides **2c** and **f** the R^2 groups are twisted relative to the $CNCCl_2$ plane of the ylide by 120° (**2c**) and 90° (**2f**).



1:0·06. By a control experiment, it was shown that under the above-mentioned reaction conditions pyrrole **5** was not formed in the presence of dimethyl acetylenedicarboxylate from aziridine **3g**, which could be a source of ylides **2g**, as follows from the work of De Kimpe *et al.*[8]

EXPERIMENTAL

Calculations were carried out by the MNDO method.[9]

Gas chromatography was performed on an LCM-80 gas chromatograph using an 1800 × 2 mm i.d. stainless-steel column with 3% SE-30 on Chromaton-N-Super and a flame ionization detector.

IR spectra were obtained on a UR-20 spectrometer.

Reaction of dichlorocarbene with N-*benzylideneaniline* **1g** *in the presence of dimethyl acetylenedicarboxylate.* A mixture of imine **1g** (0·18 g), dimethyl acetylenedicarboxylate (0·71 g), sodium trichloracetate (0·8 g) and triethylbenzylammonium chloride (0·07 g) in purified chloroform (14 ml) was vigorously stirred under argon at 65 °C (bath temperature) and monitored periodically by GC and TLC. After 5 h, the reaction mixture was cooled and filtered and the solvent was removed with a rotary evaporator. The residue was chromatographed on Silperl silica gel plates with 33% diethyl ether in hexane as eluent, giving 0·15 g (57%) of 2,2-dichloro-1,3-diphenylaziridine (**3g**) (m.p. 98–99 °C[10]), 0·031 g (12%) of 2-chloro-2-phenylacetanilide (m.p. 146 °C[10]) and 7 mg (1·9%) of dimethyl 2-chloro-1,5-diphenylpyrrole-3,4-dicarboxylate (**5**) [m.p. 125–127 °C (from hexane–diethyl ether) (lit.[8] m.p., 124 °C)]; IR spectrum (2% solution in $CHCl_3$): 1080, 1120, 1280, 1337, 1445, 1500, 1610, 1730, 2955 cm^{-1}. ^{1}H NMR and IR spectra of pyrrole **5** were identical with those of an authentic sample, which was prepared according to the reported method.[8]

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