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THE REACTION OF DIAZIRIDINE WITH DIPHENYLKETENE

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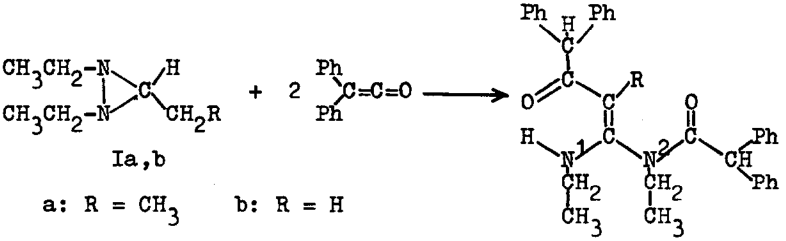
Compared with the reaction of oxaziridines with diphenylketene forming tetraphenylsuccinimide derivatives accompanied by elimination of carbonyl compounds,[1] the reaction of 1,2,3-trialkyldiaziridine with the ketene showed quite different participation of the C-alkyl group. The reaction gave a non-cyclic 1:2 adduct as a result of the migration of three hydrogen atoms, the one on the ring and two of the α-methylene of the C-alkyl group. Such a type of reaction has not been found for other three membered heterocycles and the mechanism is under investigation.



Ia,b

a: R = CH_3 b: R = H

		Yield
IIa:	153~4°	52 %
IIb:	175~6°	5 %

1,2,3-Triethyldiaziridine (Ia) (0.95 g) was allowed to react with diphenylketene (2.9 g) at 80° for 5 min in benzene (10 ml). The mixture was concentrated in vaccuo and the resultant precipitate was recrystallized from benzene-hexane to give 1.99 g of N-ethyl-N-(1-ethylamino-2-methyl-3-oxo-4,4-diphenylbut-1-enyl)diphenylacetamide (IIa) as colorless granules: mass spectrum (70 eV) m/e 516(M^+), 349(M^+- Ph_2CH), 321(M^+- Ph_2CHCO), 278(M^+- $Ph_2CHCONEt$), 221(Ph_2CCNEt^+), 194(Ph_2CCO^+), 155(349 - 194), 139(M^+- $2Ph_2CH$ - NEt), 128(M^+- 2X194), 110(155 - $EtNH_2$)

Anal. Found (Calcd): C, 81.59 (81.36); H, 7.11 (7.02); N, 5.49 (5.42).

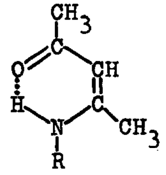
The reaction of the diaziridine Ib was carried out by the same procedure and mass spectrum and elemental analysis of the product also well agreed with IIb.

The structures were confirmed satisfactorily by ir and nmr data (Table). In

Table. Ir and nmr spectral data of the products.

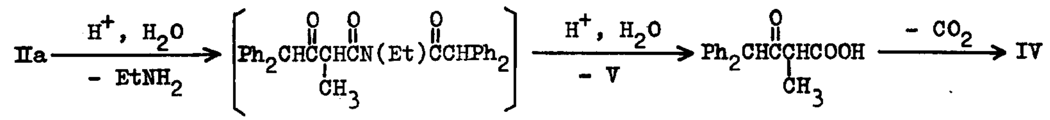
Compd.	IIa	IIb
Ir, cm^{-1} (Nujol)	3400(broad and weak, NH), 1668(amide CO), 1610(CO), 1580 and 1560(C=C)	3350(broad and weak, NH), 1665(amide CO), 1615(CO), 1582 and 1568(C=C)
Nmr ($CDCl_3$)	9.13(t, 3H, N^1-C-CH_3, 8.85(t, 3H, N^2-C-CH_3), 8.43(s, 3H, =C-CH_3), 6.9~7.6(m, 2H, N^1-CH_2), 6.2~6.9(m, 2H, N^2-CH_2), 5.11(s, 1H, CHCO), 4.58(s, 1H, CHCO), 2.5~3.1(m, 20H, 4Ph), -1.27(broad, 1H, NH)	9.07(t, 3H, N^1-C-CH_3), 8.90(t, 3H, N^2-C-CH_3), 6.7~7.5(m, 3H, N^1-CH_2, N^2-C$\underline{H}$H), 5.8~6.4(m, 1H, N^2-CH$\underline{H}$), 5.07(s, 1H, =CH), 5.01(s, 1H, CHCO), 4.83(s, 1H, CHCO), 2.6~3.1(m, 20H, 4Ph), -0.33(broad, 1H, NH)

the nmr spectrum of IIa, three signals of methyl protons are observed as one singlet and two triplets. The singlet can be assigned to the methyl protons of the substituent R, indicating the migration of the adjacent methylene protons, with the fact that the adduct IIb shows no corresponding singlet but a singlet assigned to the olefinic proton. The signal of N-methylene groups are assigned as shown in Table by decoupling method. The complex multiplets of the methylenes are due to nonequivalence of the geminal protons and nmr study on the multiplets are in progress. Appearance of the signal of the amino proton in very low field shows the existence of a strong hydrogen bonding. This signal disappears upon addition of D_2O. In the ir spectrum, the low frequencies of C=O and C=C stretching vibrations imply the conjugation between them and the hydrogen bonding mentioned above. These spectra show good agreement with those of the compound III.[2]



III

The structure was also confirmed by the following chemical evidence. Acidic hydrolysis of IIa gave 1,1-diphenylbutan-2-one (IV) (54 %) and N-ethyldiphenylacetamide (V) (71 %). The ketone IV is considered to be formed by decarboxylation of the initially produced β-ketocarboxylic acid.



$$\text{IIa} \xrightarrow[-\,EtNH_2]{H^+,\,H_2O} \left[Ph_2CH\overset{O}{\overset{\|}{C}}\underset{CH_3}{\underset{|}{C}}H\overset{O}{\overset{\|}{C}}N(Et)\overset{O}{\overset{\|}{C}}CHPh_2 \right] \xrightarrow[-\,V]{H^+,\,H_2O} Ph_2CH\overset{O}{\overset{\|}{C}}\underset{CH_3}{\underset{|}{C}}HCOOH \xrightarrow{-\,CO_2} \text{IV}$$

References

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2) H. Holtzclaw, Jr., J. Collman and R. Alire, J. Amer. Chem. Soc., 80, 1100 (1958); G. Dudek and R. Holm, ibid., 84, 2691 (1962).