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INTRAMOLECULAR CARBENE-TYPE 1,1-CYCLOADDITION BY NITRILE IMINES

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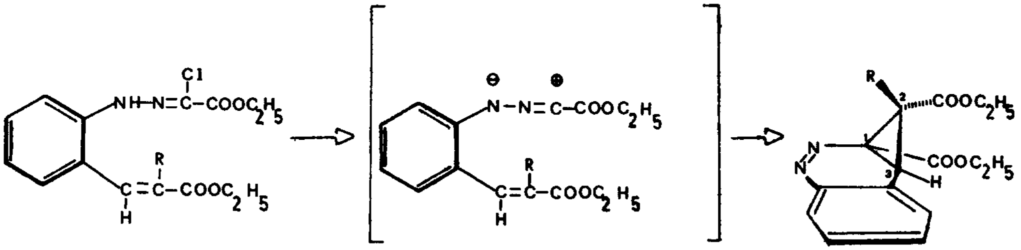
The presence of a carbene-type structure, among the resonance forms of the nitrile imines, suggests these compounds may undergo a 1,1-cycloaddition to the ethylenic function leading to cyclopropyl derivatives.(1) The present communication reports the first example of such a reaction.

Within the framework of research on the behaviour of 1,3-dipoles bearing an alkenyl substituent,(2) 1-chloro-hydrazones 1a,b were considered as precursors of the functionalized nitrile imines 2a,b.



1 2 3

a, R = CH_3; b, R = C_6H_5

Compounds 1a,b were synthesized from the proper ortho-substituted anilines by diazotization and coupling with ethyl 2-chloro-acetoacetate. Physical, analytical, and spectral data will be reported elsewhere.

The treatment of 1a and 1b with triethylamine (4 moles) in boiling benzene at 0.1 M concentration resulted, after 2 and 1 hours respectively, in pale yellow crystalline compounds of formula $C_{16}H_{18}N_2O_4$ (78%, m.p. 51°) and $C_{21}H_{20}N_2O_4$ (80%, m.p. 89°), as shown by elemental analyses and molecular weights measured by mass spectrometry.

Structures 3a and 3b were assigned to these"products on the basis of PMR(3) and CMR(4) data. In fact, in the low field region of the CMR spectra, only the signals of the aromatic and carbonyl carbons are present, thus discarding isomeric structures with a $>C{=}N-$ group. On the other hand, the cyclopropyl carbons absorb in the appropriate region.(5)

The *endo* position for the R substituent in compound **3a** is unequivocal, since the observed proton chemical shift is consistent only with the methyl group located in the shielding region of the π-electron system. Since some of the aryl protons of **3b** appear to be somewhat shielded, the *endo* configuration may reasonably be assumed also in the case of **3b**.

The above results can be rationalized in terms of a cheletropic addition of the electron-deficient carbon atom of **2a,b** to the neighbouring ethylenic function.(6) Likely, the mutual disposition of the reactive groups, while imposing restrictions to the 1,3-cycloaddition, provides favourable constraints for such an unprecedented reaction path.(7)

Somewhat similar 1,1-cycloadditions by nitrile oxides(8) and ylides(9) have been reported.

References and Notes

(1) R.Huisgen, R.Sustmann, K.Bunge, Chem.Ber., *105*, 1324 (1972).

(2) R.Fusco, L.Garanti, G.Zecchi, J.Org.Chem., *40*, 1906 (1975); L.Garanti, A.Sala, G.Zecchi, J.Org.Chem., *40*, 2403 (1975); L.Garanti, A.Scandroglio, G.Zecchi, Tetrahedron Letters, 3349 (1975).

(3) PMR (ppm from TMS at 60 MHz, in $CDCl_3$): **3a**, 0.62(3H,s,CH_3) 1.34,1.37(6H,two t, $CH_2C\underline{H}_3$) 3.68(1H,s,CH) 4.39,4.47(4H,two q,$CH_2C\underline{H}_3$) 7.3-7.7 and 8.1-8.4(3H and 1H,m,ar); **3b**, 1.21,1.43(6H,two t,$CH_2C\underline{H}_3$) 4.04(1H,s,CH) 4.17,4.44(4H,two q, $CH_2C\underline{H}_3$) 6.7-7.9(9H,m,ar).

(4) CMR (at 20 MHz): **3a** (ppm from HMDS in DMSO-d_6) 12.1(R) 30.0(C_2) 34.9(C_3) 70.5 (C_1) 120.2,132.8,133.3,135.2,137.8,143.7(ar) 169.9,173.9(C=O); **3b** (ppm from TMS in acetone-d_6) 33.6(C_3) 40.1(C_2) 66.7(C_1) 117.9,128.4,128.9,129.4,128.5, 129.8,131.8,132.9,134.0,141.0(ar) 167.4,169.6(C=O).

(5) L.F.Johnson, W.C.Jankowski, "Carbon-13 NMR Spectra", Wiley-Interscience, New York, 1972; J.B.Stothers, "Carbon-13 NMR Spectroscopy", Academic Press, New York, 1972.

(6) The formation of *endo* isomers would be consistent with the retention of stereochemistry in the addition of singlet carbenes to olefins.

(7) Dreiding models suggest that, on assuming a bent geometry for the nitrile imine group, bonding contact in the linear mode might occur without torsional strain.

(8) G.LoVecchio, G.Grassi, F.Risitano, F.Foti, Tetrahedron Letters, 3777 (1973).

(9) A.Padwa, P.H.J.Carlsen, J.Am,Chem.Soc., *97*, 3862 (1975).