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The Migratory Aptitudes in the 1,3-Dipolar Cycloadducts of Substitiuted 1-Benzoyliminopyridinium Ylides with Dimethyl Acetylenedicarboxylate[1]

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The 1,3-dipolar cycloaddition of substituted 1-benzoyliminopyridinium ylides (**1**, **6**, and **9**) with dimethyl acetylenedicarboxylate (DAC) produced the corresponding rearrangement compounds (**3**, **4**, **7**, **8**, and **10**). On the other hand, the similar reaction of **11** with DAC in acetonitrile gave **12**, accompanied with a Sommelet-type rearrangement compound, **13**. The structural elucidation of these products was accomplished by spectral inspections.

In continuation of our previous work,[2] we wish to report here on a comparative study of the cycloaddition reactions of 1-benzoyliminopyridinium ylides[3] with DAC.

Results and Discussion

In the reaction of 2-methyl-1-benzoyliminopyridinium ylide (**1**) with DAC in benzene at room temperature, the products were characterized as 1-benzoyl-2,3-bis(methoxycarbonyl)-3a-methyl-1,3a-dihydropyrazolo[1,5-*a*]pyridine (**2**) (5%) and a mixture of two rearranged isomers, dimethyl α-(2-methyl-3-pyridyl)-α'-benzoylaminomaleate (**3**) and dimethyl α-(2-methyl-5-pyridyl)-α'-benzoylaminomaleate (**4**) (9%) in a ratio of 7: 2.[4] An unstable compound (**2**) was spontaneously transformed, after 3 days at room temperature, into a mixture of **3** and **4**, and the reaction of **2** with tetracyanoethylene in benzene afforded a crystalline Diels-Alder adduct, **5**.

Thus, the isomeric products, **3** and **4**, may be assumed to be formed through Path **a** *via* 1,2-migration (intermediates **A**→**B**) in competition with Path **b** *via* 1,4-migration (intermediates **C**→**D**) by the rearrangement of **2**.

The 2,4-dimethyl compound, **6**, did not react with DAC in benzene under the above conditions. The present reactions were carried out in refluxing benzene, they gave an isomeric mixture of the rearranged products, **7** and **8** (51%) in a ratio of 1: 1.2 (as determined by nmr analyses).

A similar reaction of **9** with DAC in benzene or acetonitrile at 60—65°C afforded the expected rearranged product, **10** (28%).

These results are summarized in Scheme 1.

The reaction of 2,6-dimethyl-1-benzoyliminopyridinium ylide (**11**) with DAC in benzene at room temperature afforded the rearranged product, **12**, in a 74% yield. The NMR spectrum showed signals at τ 7.65 (s, 3H, Me), 7.44 (s, 3H, Me), 6.01 (s, 3H, COOMe), 6.30 (s, 3H, COOMe), 2.92 (d, 1H, C_5-H), 2.3—2.8 (m, 6H, Ph and C_4-H), and 2.32 (br s, 1H, NH, exchanged by D_2O), suggesting the intermediacy of dihydropyrazolopyridine, which might then rapidly rearrange into a stable compound, **12**. However, in acetonitrile, two products, **12** and **13**, were produced in 44 and 10% yields respectively. The NMR spectrum of **13** showed signals of one methyl proton at τ 7.63 (s, 3H), of pyridine ring protons at τ 3.00 (dd, 2H, overlapped with each proton at C_3- and C_5-H), of methylene

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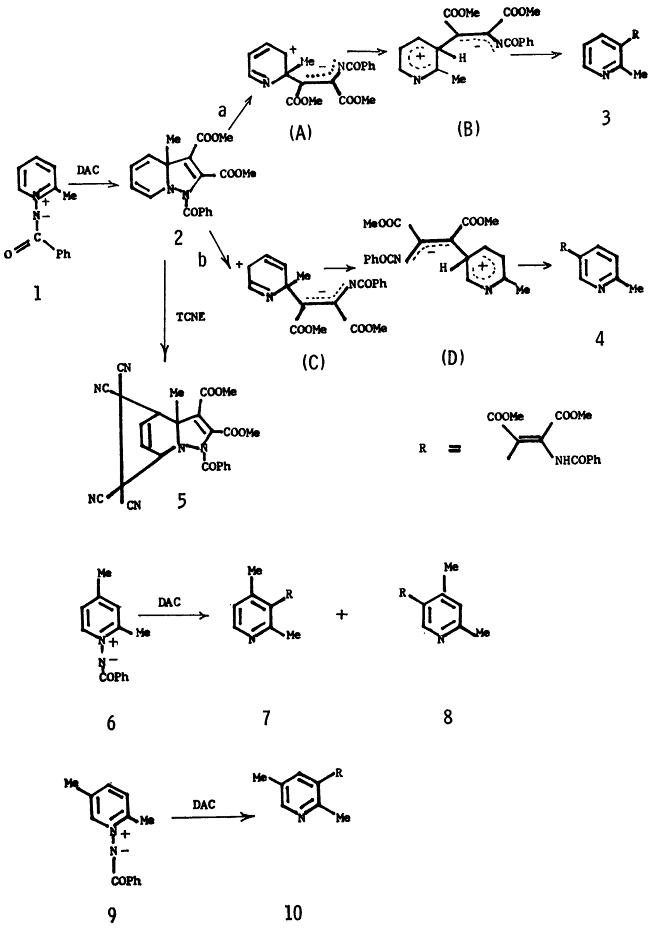
[1] Studies of Heteroaromaticity. Part LVI. Part LV of this series: T. Sasaki, K. Kanematsu, and M. Murata, *Tetrahedron*, **27**, 5359 (1971).

[2] T. Sasaki, K. Kanematsu, and A. Kakehi, *J. Org. Chem.*, **36**, 2978 (1971).

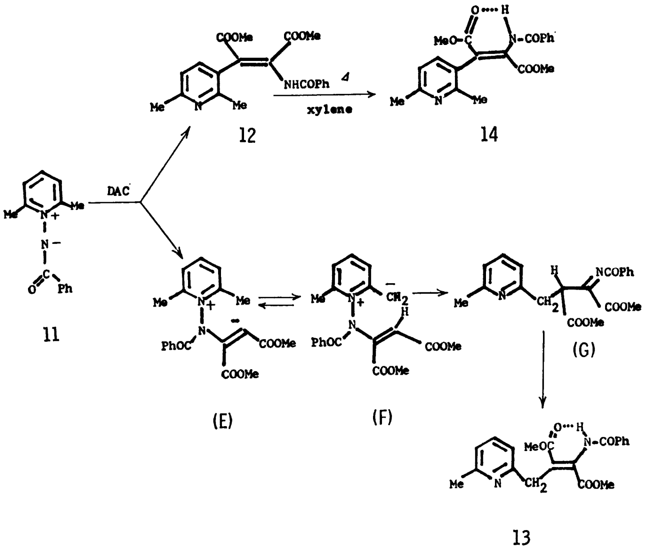
[3] Several ring-substituted 1-benzoyliminopyridinium ylides have been prepared by a modification of the Gösl method; see T. Okamoto, M. Hirobe, C. Mizushima, and A. Osawa, *Yakugaku Zasshi*, **83**, 308 (1963).

[4] These products were assigned on the basis of the foregoing data; see Ref. 2.



Scheme 1.

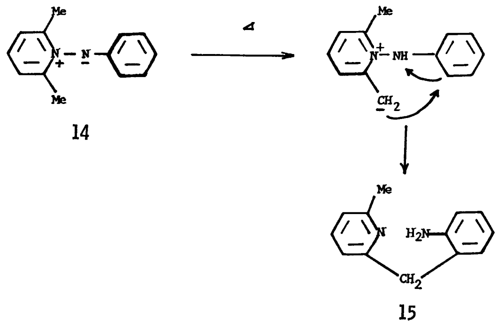
protons at τ 6.08 (s, 2H), of phenyl protons and C_4-H at τ 1.75—2.80 (m, 6H), of two methoxycarbonyl protons at τ 6.12 (s, 3H) and 6.20 (s, 3H), and of NH proton at τ −2.02 (br s, 1H, exchanged by D_2O). In particular, the singlet signal at τ 6.08 clearly arises from the methylene group at the 2-position in the pyridine moiety, suggesting that a Sommelet-type rearrangement has occurred. Moreover, a signal at τ −2.02 indicates the presence of a hydrogen-bonding amido group, showing that *cis-trans* isomerization has occurred. The heating of **12** in xylene at reflux for 5 hr afforded **14**, suggesting the presence of a hydrogen-bonding amido group at τ −2.09 (br s, exchanged by D_2O) by NMR. These results are summarized in Scheme 2.



Scheme 2.

Finally, an additional discussion may be made of these studies. The mechanisms of the formations of the several rearranged products were discussed in our previous report.[2] However, the rearrangement behaviour is different from that of the substituents between the alkoxycarbonyl and benzoyl groups attached to the iminopyridinium moiety. The former undergoes rearrangement in the 1,4-fashion, but the latter proceeds competitively in the 1,2- and 1,4-fashions.

In addition, a Sommelet-type rearrangement product, **13**, was obtained by the reaction of **11** with DAC; this reaction might be initiated by a prototropic shift *via* intermediates, **E**→**F**→**G**, followed by a rearrangement to **13**, as is illustrated in Scheme 2. A similar rearrangement has been observed in the case of 2,6-dimethyl-1-phenyliminopyridinium ylide (**14**) as is shown in Scheme 3.[5]



Scheme 3.

Experimental[6]

The 1,3-Dipolar Cycloaddition Reactions of the Ylides with DAC. General Method: Into a benzene or acetonitrile solution of DAC, an equimolar amount of the ylide was stirred at room temperature or at the reflux temperature. After the disappearance of the deep color of the solution, the solvent was removed *in vacuo* and the oily mixture was separated by column chromatography (silica gel), using benzene as the eluent.

Reaction of 1 with DAC. From 0.64 g of **1** and 0.43 g of DAC, we obtained **2** (0.055 g, 5%) as a pale yellow oil; ν_{max}^{neat} 1663, 1715, 1742 cm^{-1}, τ (CCl_4) 2.00—2.25 (m, 2H, 2,6-protons of C_6H_5), 2.40—2.80 (m, 3H, 3,4,5-protons of C_6H_5 and 1H, H_7), 4.30 (m, 2H, H_4 and H_5), 5.06 (m, 1H, H_6), 6.16 (s, 3H, OCH_3), 6.28 (s, 3H, OCH_3), 8.44 (s, 3H,

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[5] K. Dimroth, G. L. Buchanan, A. S. von Eichen, and G. Schiffler, *Ann. Chem.*, **604**, 221 (1947).

[6] The melting points were measured with a Yanagimoto micromelting point apparatus and are uncorrected. Microanalyses were performed on a Perkin-Elmer 240 Elemental Analyser. The UV spectra were determined with a JASCO Model ORD/UV-5 recorder. The NMR spectra were taken with a Japan Electric Optics Lab. Co., Ltd., Model C-60-XL NMR spectrometer and with a Varian A-60 recording spectrometer, with tetramethylsilane as the internal standard. The chemical shifts are expressed in τ values. The IR spectra were taken with a JASCO Model IR-S spectrophotometer.

CH_3), and a mixture of **3** and **4** (mp 163—169°C, 0.096 g, 9%), which was identified as a 7:2 mixture because the integrated areas for the ring-substituted methyl protons and the C_2–H of the pyridine ring appeared at τ 7.57 (s) and 1.46 (br d) in **3** and at 7.45 (s) and 1.71 (br s) in **4**. The isomers could not be separated either by column chromatography or by repeated recrystallization.

Found: C, 64.46; H, 5.13; N, 7.84%. Calcd for $C_{19}H_{18}O_5N_2$: C, 64.40; H, 5.12; N, 7.91%.

Preparation of the Adduct, 5. A solution of 0.05 g of **2** and 0.02 g of tetracyanoethylene in 20 m*l* of benzene was stirred at room temperature for 3 hr. The precipitated solid was collected by filtration and recrystallized from methanol to give **5** (0.02 g, 29%); mp 182—184°C; τ ($CDCl_3$) 8.43 (s, 3H, CH_3), 6.23 (s, 3H, $COOCH_3$), 6.26 (s, 3H, $COOCH_3$), 5.78 (dd, $J_{4,5}$ 7.5 Hz, $J_{4,6}$ 1.5 Hz, 1H, H_4), 5.54 (dd, $J_{7,6}$ 7.0 Hz, $J_{7,5}$ 1.5 Hz, 1H, H_7), 3.48 (br t, $J_{5,6}$ 7.5 Hz, $J_{6,7}$ 7.0 Hz, 1H, H_6), 3.18 (br t, $J_{5,4}$ 7.5 Hz, $J_{5,6}$ 7.5 Hz, 1H, H_5), 2.10—2.80 (m, 5H, C_6H_5).

Found: C, 62.24; H, 3.85; N, 17.52%. Calcd for $C_{25}H_{18}N_6O_5$: C, 62.24; H, 3.76; N, 17.42%.

*Reaction of **6** with DAC.* From 0.68 g of **6** and 0.43 g of DAC (in benzene at 80°C), we obtained a mixture of **7** and **8** (mp 169—171°C, 0.56 g, 51%), which was identified as a 1:1.2 mixture because the integrated areas for the methyl protons and the C_2 proton of the pyridine ring appeared at τ 7.63 (s, CH_3 at C_2) and 1.77 (d, $J_{5,6}$ 7.5 Hz, H_6) in **7**, and at τ 7.52 (s, CH_3 at C_2) and 1.83 (s, H_6) in **8**. The mixture could not be separated either by column chromatography or by repeated recrystallization, but it gave a satisfactory analytical value.

Found: C, 65.41; H, 5.46; N, 7.42%. Calcd for $C_{20}H_{20}O_5N_2$: C, 65.21; H, 5.47; N, 7.61%.

*Reaction of **9** with DAC.* From 1.2 g of **9** and 0.7 g of DAC (in benzene or acetonitrile at 65°C), we obtained **10** (mp 186—188°C, 0.51 g 28%); ν_{max}^{KBr} (C=O) 1671, 1719, 1739 cm^{-1}, τ ($CDCl_3$) 7.68 (s, 3H, CH_3), 7.58 (s, 3H, CH_3), 6.02 (s, 3H, $COOCH_3$), 6.30 (s, 3H, $COOCH_3$), 2.4—2.9 (m, 7H, 5H of C_6H_5, 1H of ring proton of C_4 and 1H of NH).

Found: C, 65.30; H, 5.50; N, 7.48%. Calcd for $C_{20}H_{20}C_5N_2$: C, 65.21; H, 5.47; N, 7.61%.

*Reaction of **11** with DAC.* 1) From 0.68 g of **11** and 0.43 g of DAC (in benzene at room temperature for 1.5 hr), we obtained **12** (mp 208—211°C, 0.83 g, 74%); ν_{max}^{KBr} (C=O) 1677, 1708, 1731 cm^{-1}, τ ($CDCl_3$) 7.65 (s, 3H, CH_3), 7.44 (s, 3H, CH_3), 6.01 (s, 3H, $COOCH_3$), 6.30 (s, 3H, $COOCH_3$), 2.92 (d, $J_{4,5}$ 8.0 Hz, 1H, H_5), 2.30—2.80 (m, 6H, 5H of C_6H_5 and 1H or H_4), 2.32 (br s, 1H, NH).

Found: C, 65.10; H, 5.52; N, 7.40%. Calcd for $C_{20}H_{20}O_5N_2$: C, 65.21; H, 5.47; N, 7.61%. 2) From 0.68 g of **11** and 0.43 g of DAC (in acetonitrile at room temperature for 1.6 hr), we obtained **12** (0.26 g, 44%) and **13** (mp 172—176°C, 0.06 g, 10%); ν_{max}^{KBr} (C=O) 1680, 1706, 1730 cm^{-1}, τ ($CDCl_3$) 7.63 (s, 3H, CH_3), 6.20 (s, 3H, $COOCH_3$), 6.12 (s, 3H, $COOCH_3$), 6.08 (s, 2H, CH_2), 3.00 (dd, $J_{3,4}=J_{4,5}$ 7.5 Hz, 2H, H_3 and H_5), 1.75—2.00 and 2.30—2.80 (br m, 6H, 5H of C_6H_5 and 1H of H_4), −2.02 (br s, 1H, NH).

*Thermal Isomerization of **12**.* A solution of 0.33 g of **12** in 20 m*l* of xylene was heated in an oil bath at 140—145°C for 5 hr. The solvent was then removed under reduced pressure, and the residue was purified by silica-gel chromatography, with benzene as the eluent, to give colorless crystals; **14** (0.20 g, 65%); mp 152—153°C; τ ($CDCl_3$) 7.56 (s, 3H, CH_3), 7.46 (s, 3H, CH_3), 6.45 (s, 3H, $COOCH_3$), 6.27 (s, 3H, $COOCH_3$), 3.07 (d, $J_{4,5}$ 8.0 Hz, 1H, H_5), 1.91—2.19 and 2.33—2.76 (br m, 6H, 5H of C_6H_5 and 1H of H_4), −2.09 (br s, 1H, NH, exchanged by D_2O).

Found: C, 65.41; H, 5.45; N, 7.57%. Calcd for $C_{20}H_{20}O_5N_2$: C, 65.21; H, 5.47; N, 7.61%.