

Na⁺ is also observed in reaction with less reactive complex (1b, entry 11). The dependence of reactivity on leaving group for 1a and 1b is similar to that observed in classical nucleophilic aromatic substitution⁹ (entries 1 and 8).

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- (7) Control experiment showed that 2' was oxidized by I₂ in ether within 20 minutes at room temperature, affording the ethoxybenzene quantitatively.
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Unusual Rearrangements of 3a, 7a-Dihydroindole Esters

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Tetramethyl 3a,7a-dihydro-1-methylindole-2,3,3a,4-tetra-carboxylate (2b), the 1:2 adduct from the reaction of 1-methylpyrrole (1b) with dimethyl acetylenedicarboxylate (DMAD), underwent quite unusual rearrangement upon reflux with sodium methoxide in methanol for 24 h to give indole-2,3,4,5-tetraester (4b).¹ The base-catalyzed rearrangement did not occur if there was no substituent on the nitrogen atom of the adduct (e.g. 2a). Instead, loss of the C_{3a}-ester group and eventual aromatization resulted to give 5a. When the compound 2b was heated to reflux in xylene, another type of rearrangement took place to give indoline derivative 3b. On the other hand, the unsubstituted analog 2a did not give any rearrangement under the same reaction conditions. The contrary results from the reactions of 2a and 2b led us to investigate the scope of the reactions and their mechanisms, and we report our preliminary results in the present paper.

At first, we attempted to prepare a series of N-substituted derivatives of 2 in order to examine the steric and electronic effect on the rearrangement. However, our persistent efforts to prepare the compounds of type 2 having bulky alkyl groups (e.g. *tert*-butyl, *sec*-butyl) or aryl groups (e.g. phenyl, *p*-methoxy-phenyl, *p*-nitrophenyl) have not been successful. Therefore, we decided to prepare a series of substituted benzyl derivatives (2c-g) which are sterically bulky and effectively electron-withdrawing or -donating through inductive effect.

Benzylpyrroles (1c-g) were prepared by a typical method using 2,5-diethoxytetrahydrofuran and substituted benzylamines.² By refluxing pyrroles (1c-g) with DMAD in

anhydrous ether were prepared the 1:2 adducts (2c-g). The yields and melting points of them are listed in the Table 1. Spectroscopic data are consistent with the structures.³ The yields of benzyl derivatives 2c-g were good but substantially lower than that of methyl compound 2b, indicating that the steric effect played a role. Approach of the dienophile seemed to be hindered by N-benzyl group. With pyrrole itself (1a) the observed lowest yield seems to be due to the predominant aromatic character which makes the conjugated double bonds poor diene system.¹

One of the spectroscopic characteristics of the 1:2 adducts (2c-g) was the appearance of an AB pattern in NMR spectra (CDCl₃) for benzylic CH₂ group at around δ 4.8 with J = 15-18 Hz.⁴ Free rotation of phenyl ring seems to be very much restricted and its spatial arrangement may be one of the critical factors in the reaction described below.

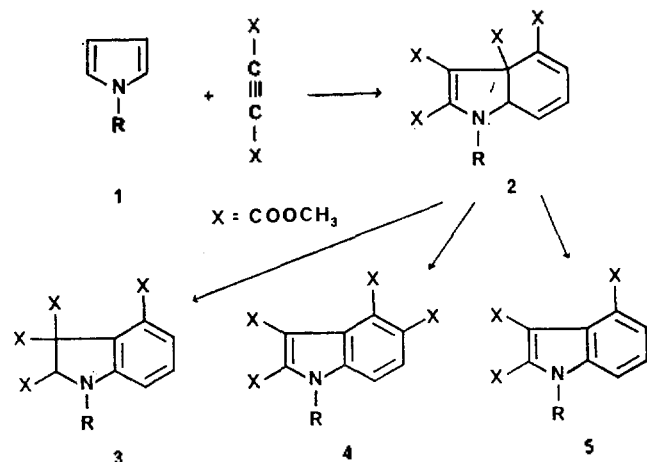
The rearrangements of 2b-g to indolines (3b-g) were found

TABLE 1 Yields, Boiling Points or Melting Points of 1 and 2

| R | 1 | | 2 | |
|---|--------------|---------|----------------------|-----------------|
| | bp, °C (mm) | % yield | mp, °C | % yield |
| a H | * | | 162-165 ^b | 10 |
| b CH ₃ | * | | 146 ^c | 90 ^c |
| c CH ₂ -C ₆ H ₅ | 129 (10) | 65 | 135 ^c | 70 ^c |
| d CH ₂ -C ₆ H ₄ -CH ₃ - <i>p</i> | 99-105 (2.5) | 78 | 141-142.5 | 71 |
| e CH ₂ -C ₆ H ₄ -OCH ₃ - <i>p</i> | 109 (0.3) | 57 | 104-107 | 79 |
| f CH ₂ -C ₆ H ₄ -Cl- <i>p</i> | 104 (0.8) | 46 | 154-155 | 49 |
| g CH ₂ -C ₆ H ₄ -OCH ₃ - <i>m</i> | 85 (1.0) | 90 | 60.5-61 | 20 |

* Commercially available. ^b See reference 1. ^c See reference 5.

to be a general pathway which happened by reflux in xylene for 24–36 h. The products showed a characteristic singlet in their NMR spectra at around δ 5.5 due to C_2 -H. Benzylic CH_2 proton signal also splitted into an AB pattern at around δ 4.6 ($J=16$ –17 Hz). Appearance of new band at around 340 nm in UV spectra was another characteristic of the indolines 3.



When the adducts 2c–g were refluxed with sodium methoxide in methanol for 24 h, indole-2,3,4,5-tetraesters (4c–g) formed in low yields (20–40%). The positions of the ester groups in 4 were readily confirmed by the appearance of an AB pattern at around δ 7.8 due to C_6 - and C_7 -H ($J=8$ Hz). But the benzylic CH_2 signal appeared as a singlet at around δ 5.6, which is in contrast with the AB patterns observed in the spectra of 2 and 3. Since one of the C_3 -ester groups and N-benzyl group in 3 have to be *cis* each other, which may cause geminal coupling of CH_2 protons, we may say that the spatial arrangement of C_3 -ester and benzyl groups in 2 should be *cis*, too. Once aromatization takes place the benzylic CH_2 group is rather free from the influence of ester group and the observed singlet peak is not

surprising. We are currently investigating the mechanisms of both rearrangements.

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- (3) Complete spectroscopical data will be published elsewhere, but for comparison: **2d**: NMR ($CDCl_3$) δ 2.32 (s, 3 H, $C_6H_4CH_3$), 3.65, 3.69, 3.73, and 3.82 (all s, 3 H each, $COOCH_3$), an AB pattern centered at 4.21 (2 H, CH_2 , $J=15.6$ Hz), 4.78 (d, 1 H, 7a-H, $J_{7a,7}=3$ Hz), 5.80 (dd, 1 H, 7-H, $J_{7,7a}=3$ Hz, $J_{7,6}=9$ Hz), 6.19 (dd, 1 H, 6-H, $J_{6,7}=9$ Hz, $J_{6,5}=6$ Hz), 6.96 (d, 1 H, 5-H, $J_{5,6}=6$ Hz), 7.11 (s, 4 H, C_6H_4); UV (ethanol) 278 nm (ϵ 16300). **3d**: NMR ($CDCl_3$) δ 2.28 (s, 3 H, $C_6H_4CH_3$), 3.68, 3.70, 3.73 and 3.84 (all s, 3 H, each, $COOCH_3$), an AB pattern centered at 4.21 (2 H, CH_2 , $J=16$ Hz), 5.42 (s, 1 H, 2-H), 6.35 (d, 1 H, 7-H, $J_{7,6}=7$ Hz), 6.8–7.4 (m, 6 H, 5-H, 6-H, and C_6H_4); UV (ethanol) 340 nm (ϵ 22000).
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