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INTRAMOLECULAR RING FORMATION OF PHENYL AZIDE AND FURAN

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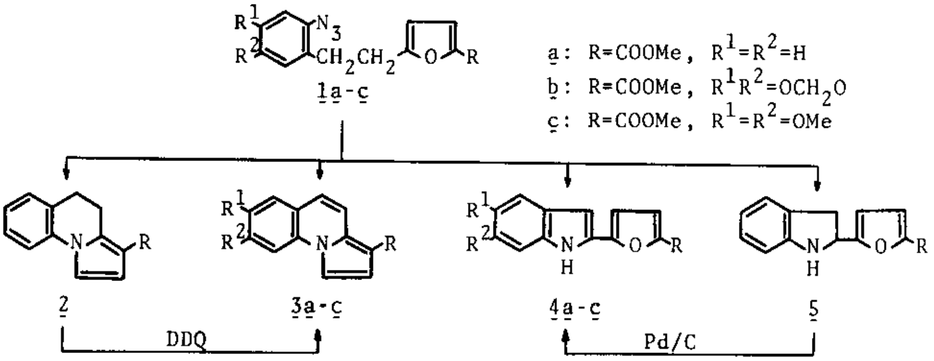
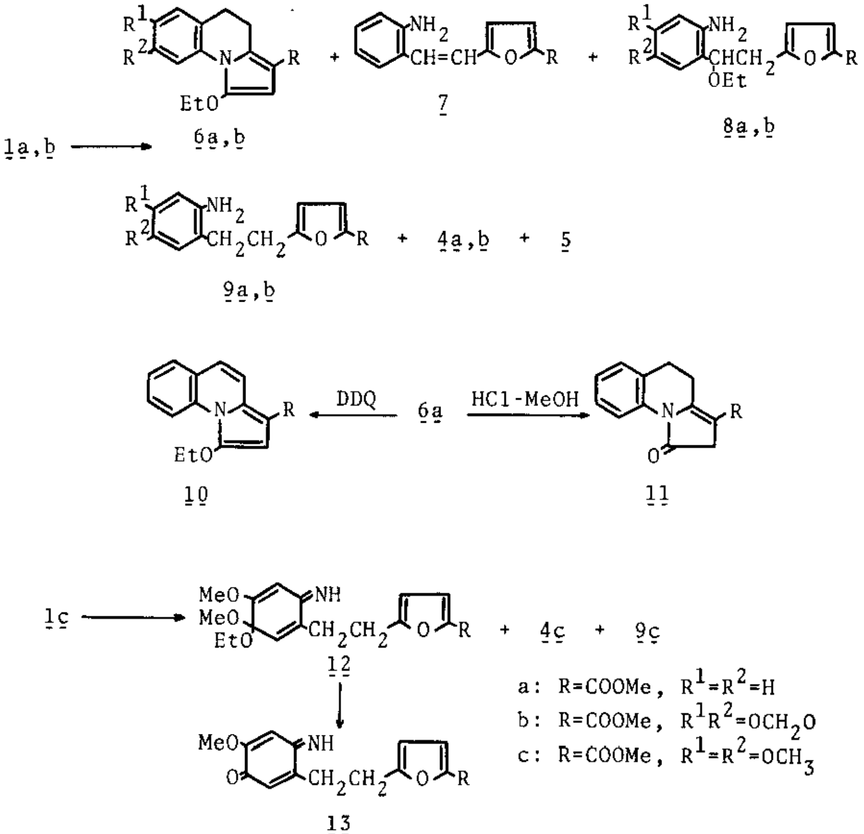
Abstract — Thermal and photochemical reaction of *o*-azidophenylethylfurans (1a-c) gave pyrrolo[1,2-a]quinolines (2, 3a-c and 6a,b) along with the usual nitrene products.

We have reported the synthesis of the various fused furans by the applying the reaction of azide groups[1]. The intramolecular 1,3-dipolar cycloaddition of the dipolarophiles bearing phenyl azide in the molecule has been recently described by Fusco et al.[2]. We assumed that *o*-azidophenylethylfurans (1a-c) were possible causing above the reaction. Therefore, we expect the intramolecular cyclization between phenyl azide and furan, and the thermal and photochemical reaction of 1a-c were carried out. In this paper we report the thermal and photochemical decomposition reactions of 1a-c which lead to the formation of pyrrolo[1,2-a]quinolines (2, 3a-c and 6a,b) along with the usual nitrene products.
Methyl 5-[2-(2-azidophenyl)ethyl]-2-furoates (1a-c) were prepared from the condensation of *o*-nitrobenzaldehydes with 5-carbomethoxy-2-furfuryl triphenylphosphonium chloride[3], followed by the catalytic hydrogenation, diazotization



Scheme 1

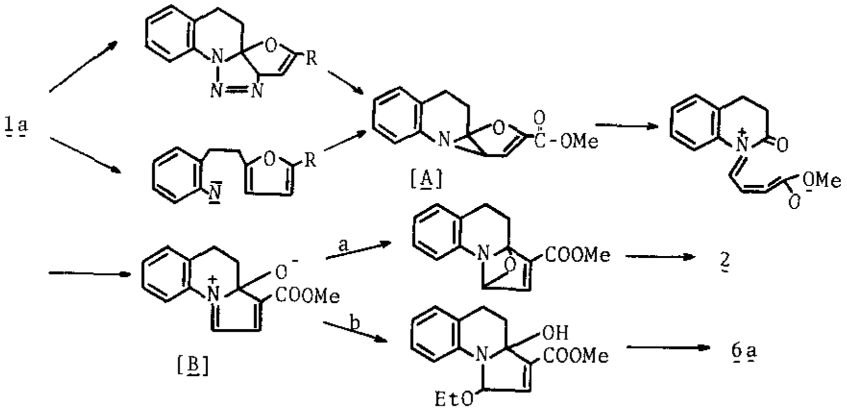
and the treatment of sodium azide. Thermolysis of 1a in refluxing *o*-dichlorobenzene for 2 hr gave methyl 4,5-dihydropyrrolo[1,2-a]quinoline-3-carboxylate (2) (colorless needles, mp 65-66°, 8%) and its dehydro compound (3a) (colorless needles, mp 129-130°, 8%), and 2-(2-furyl)indole (4a) (colorless needles, mp 165-166°, 11%) and 2-(2-furyl)indoline (5) (colorless prisms, mp 126-127°, 18%) by the purification with silica gel chromatography (C_6H_6, $CHCl_3$)[4]. 3a was established by the direct comparisons (mixed mp and IR) with the compound prepared from the method of Acheson et al.[5]. Treatments of 2 with DDQ in benzene and 5 with Pd/C in xylene afforded 3a and 4a in excellent yields, respectively. Similar thermolysis of 1b and 1c gave the corresponding 3b (colorless needles, mp 173-174°, 3%) and 3c (pale yellow needles, mp 184-185°, 3.5%) and 4b (colorless needles, mp 223-224°, 32%) and 4c (colorless needles, mp 176-177°, 41%). In the case of 1b,c, the reason why dihydro derivatives were not obtained, is



Scheme 2

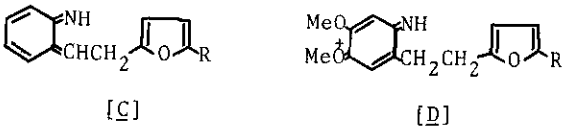
probably due to the effect of the electron-donating group in benzene ring[6]. Photolysis of 1a in EtOH[7] for 10 hr gave 4a (2.7%), 5 (16.7%), 6a (colorless needles, mp 126-127°, 24.6%) and three primary amines 7 (yellow needles, mp 123-124°, 1.6%), 8a (brownish oil, 10.1%) and 9a (colorless needles, mp 58-59°, 3.1%)[8]. Treatments of methyl 1-ethoxy-4,5-dihydropyrrolo[1,2-a]quinoline-3-carboxylate (6a) with DDQ in benzene and with 5% HCl-MeOH afforded methyl 1-ethoxypyrrolo[1,2-a]quinoline-3-carboxylate (10) (colorless needles, mp 114-116°, 97%) and methyl 1-oxo-1,2,4,5-tetrahydropyrrolo[1,2-a]quinoline-3-carboxylate (11) (colorless needles, mp 117-118°, 94%), respectively. *Trans*-methyl 5-[2-(2-aminophenyl)vinyl]-2-furoate (7) was identified with the compound prepared from the corresponding nitro vinyl derivative by the reduction with Zn and NH_4Cl in acetone[9] (mixed mp and IR). The structure of methyl 5-[2-(2-aminophenyl)-2-ethoxyethyl]-2-furoate (8a) was assigned confirmly on the basis of NMR, IR and mass spectra as followed: NMR δ ($CDCl_3$) 7.13 and 6.33 (2H, d x 2, J=3.6Hz, furan-H), 6.85 (4H, m, benzene-H), 4.60 (1H, m, CH), 4.00 (2H, b, NH_2), 3.90 (3H, s, CH_3), 3.45 and 1.13 (5H, C_2H_5), 3.02 (2H, m, CH_2); IR cm^{-1} ($CHCl_3$) 3430, 3350, 1720; UV nm (EtOH) 212, 259; MS *m/e* 289 (M^+). Similar photolysis of 1b afforded 4b (3%), 6b (colorless needles, mp 194-195°, 3%), 8b (brownish oil, 18%) and 9b (colorless needles, mp 119-120°, 12%). However, methyl 5-[2-(3-ethoxy-6-imino-3,4-dimethoxy-1,4-cyclohexadien-1-yl)ethyl]-2-furoate (12) (brownish oil, 13.7%) [IR cm^{-1} ($CHCl_3$) 1713; UV nm (EtOH) 206, 240 (sh), 263; NMR δ ($CDCl_3$) 7.03 and 6.10 (2H, d x 2, J=3.6Hz, furan-H), 6.24 (1H, s, $C_{2'}$-H), 5.58 (1H, s, $C_{5'}$-H), 3.84, 3.77 and 3.19 (9H, s x 3, CH_3 x 3), 3.36 and 1.16 (5H, C_2H_5), 2.84 (4H, m, CH_2 x 2)] was obtained from 1c along with 4c (5.7%) and 9c (colorless needles, mp 67-68°, 2.6%). Hydrolysis of 12 in H_2O at 90-95° for 24 hr gave methyl 5-[2-(6-imino-4-methoxy-3-oxo-1,4-cyclohexadien-1-yl)ethyl]-2-furoate (13) (colorless needles, mp 162-163°, 90%) [IR cm^{-1} ($CHCl_3$) 1718, 1675, 1648, 1602; UV nm (EtOH) 208, 262; NMR δ ($CDCl_3$) 6.98 and 6.06 (2H, d x 2, J=3.6Hz, furan-H), 6.38 (1H, s, $C_{2'}$-H), 5.85 (1H, s, $C_{5'}$-H), 3.82 and 3.77 (6H, s x 2, CH_3 x 2), 2.84 (4H, m, CH_2 x 2)]. The NMR spectral data of pyrrolo[1,2-a]quinolines is shown in Table I.

We propose the following mechanism for the formation of pyrrolo[1,2-a]quinolines (2) and (6a) by the decomposition of 1a (Scheme 3). Loss of the nitrogen after the addition of azide group to double bond or *the addition of nitrene to double*



Scheme 3

bond gives aziridine [A]. Recyclization after the cleavage of C-O bond forms pyrrolo[1,2-a]quinoline ring system [B] which led to 2 through the loss of oxygen atom (path a) or 6a by dehydration of EtOH adduct (path b), respectively. On the other hand, we assumed that the intermediate [C] or [D] gives amines 7 and 8a or 12 (*Scheme* 4).



Scheme 4

Table I. NMR (δ, $CDCl_3$) spectral data of pyrrolo[1,2-a]quinolines

2	7.27 (4H, m, C_{6-9}-H), 7.08 (1H, d, J=3.2Hz, C_1-H), 6.67 (1H, d, J=3.2Hz, C_2-H), 3.82 (3H, s, CH_3), 3.30, 2.90 (4H, m x 2, $C_{4,5}$-H)
3a	8.13 (1H, d, J=9.4Hz, C_4-H), 7.58 (4H, m, C_{6-9}-H), 7.75 (1H, d, J=3.2Hz, C_1-H), 7.32 (1H, d, J=9.4Hz, C_5-H), 7.21 (1H, d, J=3.2Hz, C_2-H), 3.90 (3H, s, CH_3)
3b	8.00 (1H, d, J=9.4Hz, C_4-H), 7.51 (1H, d, J=3.2Hz, C_1-H), 7.27, 7.02 (2H, s x 2, $C_{6,9}$-H), 7.18 (1H, d, J=9.4Hz, C_5-H), 7.17 (1H, d, J=3.2Hz, C_2-H), 6.05 (2H, s, CH_2), 3.89 (3H, s, CH_3)
3c	8.04 (1H, d, J=9.5Hz, C_4-H), 7.59 (1H, d, J=3.2Hz, C_1-H), 7.23 (1H, d, J=9.5Hz, C_5-H), 7.22, 7.06 (2H, s x 2, $C_{6,9}$-H), 7.20 (1H, d, J=3.2Hz, C_2-H), 4.02, 3.96, 3.89 (9H, s x 3, CH_3 x 3)
6a	8.02 (1H, m, C_9-H), 7.21 (3H, m, C_{6-8}-H), 5.74 (1H, s, C_2-H), 4.14, 1.47 (5H, C_2H_5), 3.83 (3H, s, CH_3), 3.27, 2.84 (4H, m x 2, $C_{4,5}$-H)
6b	7.47 (1H, s, C_9-H), 6.60 (1H, s, C_6-H), 5.85 (2H, s, CH_2), 5.60 (1H, s, C_2-H), 4.05, 1.45 (5H, C_2H_5), 3.75 (3H, s, CH_3), 3.16, 2.70 (4H, m x 2, $C_{4,5}$-H)
10	8.90 (1H, bd, J=9Hz, C_9-H), 8.08 (1H, d, J=9.4Hz, C_4-H), 7.51 (3H, m, C_{6-8}-H), 7.15 (1H, d, J=9.4Hz, C_5-H), 6.35 (1H, s, C_2-H), 4.30, 1.60 (5H, C_2H_5), 3.91 (3H, s, CH_3)
11	8.34 (1H, bd, J=8Hz, C_9-H), 7.22 (3H, m, C_{6-8}-H), 3.80 (3H, s, CH_3), 3.48 (2H, m, C_2-H), 3.31, 2.86 (4H, m, $C_{4,5}$-H)

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2. R. Fusco, L. Garanti and G. Zecchi, J. Org. Chem., 1975, 40, 1906.
3. The diazotization of the compounds which had H and CH_3 instead of the carbomethoxy group of 1a failed.
4. Thermolysis of *o*-azidodiphenylethane in *o*-dichlorobenzene gave 2-phenylindoline (80-90%) and 2-phenylindole (trace).

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6. E. F. Platt and T. P. McGovern, *J. Org. Chem.*, 1964, **29**, 1540.

7. Photolysis of **1a** in benzene gave **2**, **3a**, **4a** and **9a** similar to thermolysis.

8. Irradiation was carried out by the use of 100 W high pressure mercury lamp, Taika HLV-B.

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