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FORMATION OF INDOLO[1,2-a][3]BENZAZOCINE SYSTEM FROM 1-HALOGENOPHENETHYL-4,5-DIHYDRO-3H-2-BENZAZEPINE

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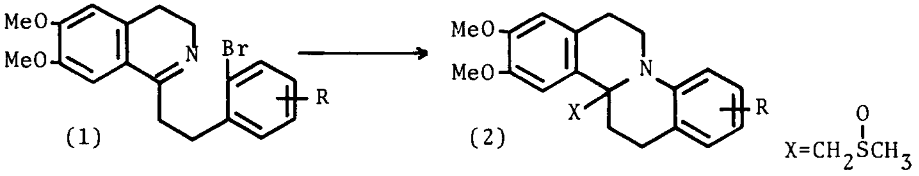
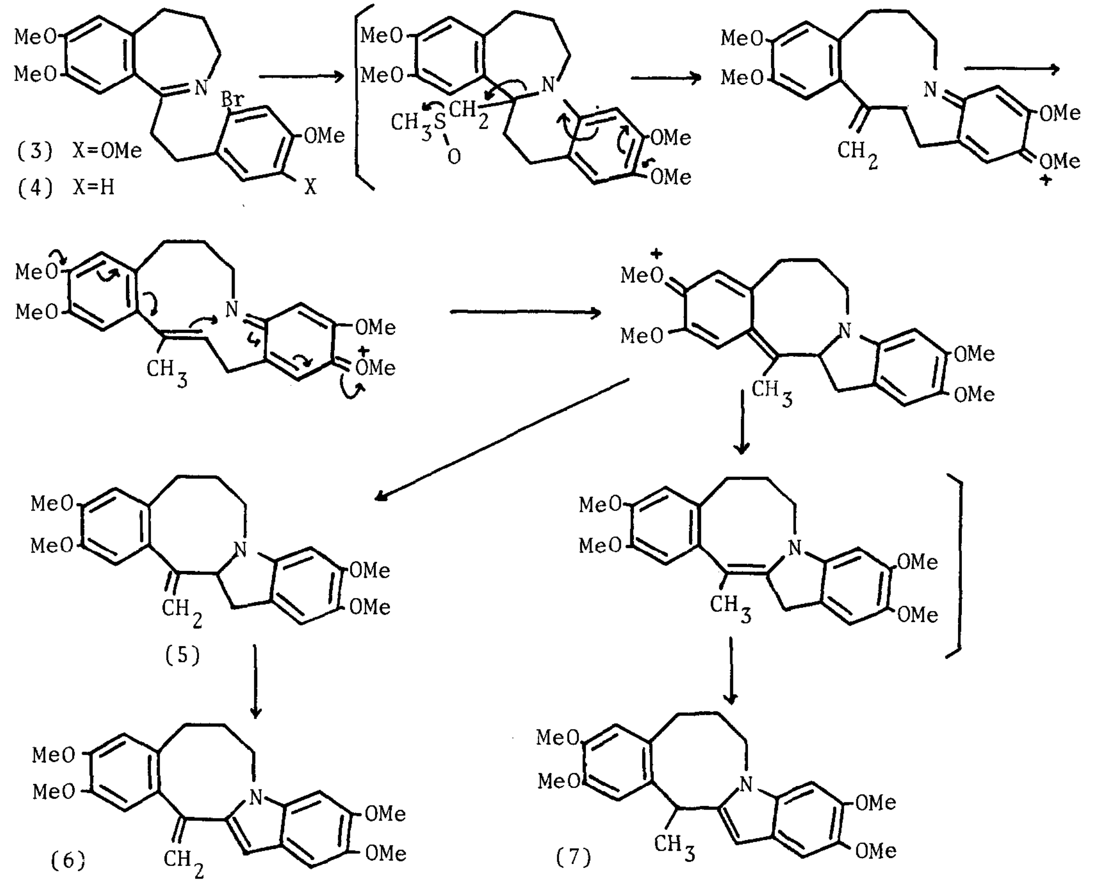
In the cource of the investigation of the reactions of 1-halogenophenethylisoquinolines with dimsylsodium[1], we found a formation of 13a-(methylsulfinyl)methyldibenzo[a,f]quinolizines (2) through the benzyne reaction of 1-(2-bromophenethyl)-3,4-dihydroisoquinolines (1) by the use of dimsylsodium as a base[2]. We had successively occasion to examine the reaction of 1-(2-bromo-4,5-dimethoxyphenethyl)-4,5-dihydro-7,8-dimethoxy-3H-2-benzazepine (3) with dimsylsodium and found a novel ring transformation yielding a new ring system, indolo[1,2-a][3]benzazocine derivatives from (3). We wish to report these results in this paper.



(1) (2)

$X=CH_2\overset{O}{\overset{\|}{S}}CH_3$

Treatment of (3) with dimsylsodium (6 eq. mol) in DMSO at room temperature for 14 hr to give two products (6) and (7), which were easily separated by column chramatography on silica gel using chloroform as an eluant, in 43 % and 8 % yield, respectively. The molecular formula of the first product (6), mp 170-171° (MeOH-ether), was established by mass spectral (M^+, m/e 379) and microanalysis[3] as $C_{23}H_{25}NO_4$ and that of the second one (7) was determined by high resolution mass spectral analysis[4] as $C_{23}H_{27}NO_4$, respectively. The NMR ($CDCl_3$)[5] of (6) showed a typical exo methylene signals at 5.26 (1H, d, J=1 Hz) and 5.85 (1H, d, J=1 Hz) ppm. Five aromatic proton siganls appeared at 6.56, 6.76, 6.79, 7.02 and 7.10 ppm as singlets, respectively. Catalytic hydrogenation of (6) over Raney Ni catalyst in ethanol afforded (7), which was identical with the second product in all respects. Five singlets attributable to aromatic protons appeared at 6.22, 6.48, 6.70, 6.85 and 6.95 ppm in its NMR ($CDCl_3$) spectrum. Methyl signals appeared at 1.79 ppm as doublet (J=7 Hz). Both (6) and (7) exhibited positive to the color test for indoles[6]. The results of the color test strongly indicated that (6) and (7) possessed indole moiety as a partial structure in their molecule. Based upon these facts, the structure of the first product obtained from (3) was assigned to (6) and the second one to (7), respectively. The plausible pathway leading to (6) and (7) was shown in the following scheme and (6) was formed by air oxidation of (5) as the isolated product. Furthermore, it would be certain that CH$_3$O group at the 5'-position played an important role in this reaction, since the same reaction using (4) did not give any desired product.



REFERNCES AND FOOTNOTES

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2 S. Kano, T. Yokomatsu, and S. Shibuya, *Chem. Pharm. Bull*. (Tokyo), **23**, 1098 (1975).
3 Calcd: C, 72.80; H, 6.64; N, 3.69. Found: C, 72.59; H, 6.75; N, 3.42.
4 Determined by Hitachi RMU-7L spectrometer; Calcd: 381.1933. Found: 381.1945.
5 NMR spectra were taken with JEOL PS-100 spectrometer.
6 F. Feigel, *Spot Test*, **2**, 198, Elsevier (1954).