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STUDIES ON HETEROCYCLIC ANALOGUES OF AZULENE. PART 5.[1]

REARRANGEMENT OF 7H-6a-AZACYCLOBUTA[j]CYCLOPENT[1,2,3-cd]AZULENE RING SYSTEM ON SILICA GEL

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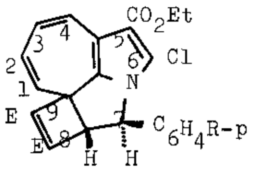
Abstract -- Rearrangement of 7H-6a-azacyclobuta[j]cyclopent[1,2,3-cd]-azulene ring system to 3H-2a-azacyclopenta[ef]heptalene ring system by contact with silica gel was reported.

It is known that contacts of some organic substances with adsorbents (i.e. alumina or silica gel) cause structural changes.[2] Sometimes silica gel displays as catalyst in the isomerization reactions of olefines[3] or bicyclic compounds.[4] We now report that 7H-6a-azacyclobuta[j]cyclopent[1,2,3-cd]azulene ring system rearranges to 3H-2a-azacyclopenta[ef]heptalene ring system on silica gel.

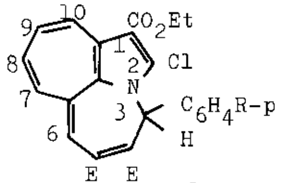
Contact of 5-ethyl 8,9-dimethyl 6-chloro-7-phenyl-7H-6a-azacyclobuta[j]cyclopent[1,2,3-cd]azulene-5,8,9-tricarboxylate (**1a**)[5] with silica gel[6] for 5 days at room temperature gave 1-ethyl 4,5-dimethyl 2-chloro-3-phenyl-3H-2a-azacyclopenta-[ef]heptalene-1,4,5-tricarboxylate (**2a**)[7,8] as brown needles; mp 148-149° (decomp.); 56 %; IR (nujol) 1725, 1705, and 1700 cm^{-1} (C=O). In ^{1}H nmr spectrum ($CDCl_3$), two 1H singlets to be assignable to H-3 and H-6 are seen at δ 5.31 and 6.11, respectively. Another signals are seen at δ 1.36 (3H, t, *J* 7 Hz, $CO_2CH_2C\underline{H}_3$), 3.59 (3H, s, $CO_2C\underline{H}_3$), 3.84 (3H, s, $CO_2C\underline{H}_3$), 4.23 (2H, q, *J* 7 Hz, $CO_2C\underline{H}_2CH_3$), 5.95-6.2 (1H, m, H-9), 6.3-6.5 (2H, m, H-7,8), 7.30 (5H, m, phenyl), and 7.38 (1H, d, *J* 11 Hz, H-10). ^{13}C nmr spectrum ($CDCl_3$) of **2a** exhibits signal assignable to sp^3 carbon atom at δ 68.59 (d, C-3). The uv spectrum [λ_{max}^{EtOH} 228 (log ε 4.54), 260 (4.28), 434 (4.38), 492sh (3.95), 530 (3,74), and 570 nm (3.43)] resembles that of 3H-2a-azacyclopenta[ef]heptalene ring system.[9] From these results, we assigned the structure.[10]

In a similar mannar, **1b** gave **2b** as brown needles, mp 116-118°, in 60 % yield.[10]

On more active adsorbent (alumina), **1a** underwent decomposition and gave no



1a: E=CO_2Me, R=H
1b: E=CO_2Me, R=Me



2a: E=CO_2Me, R=H
2b: E=CO_2Me, R=Me

obvious products.

Formation of the products (2) can be accomodated by a mechanism started by the scission of the bond between nitrogen and benzilic-carbon atoms of 1, followed by formation of 4 and intramolecular cyclyzation of 4 with association of silica gel.[11] It is considered that adsorption of 1 on silica gel plays important roles which activates the bond between nitrogen and benzilic-carbon atoms of 1 and arranges to the suitable orientation for rearrangement to 4.[11]

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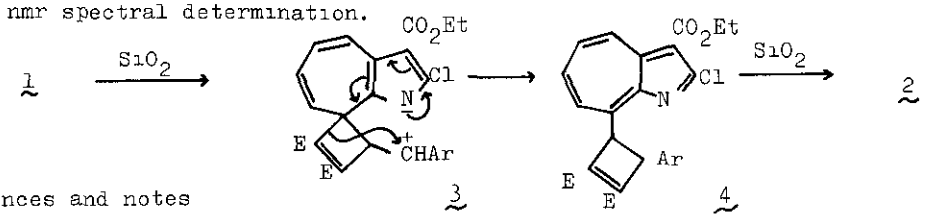

References and notes

1. Part 4, T. Nishiwaki, N. Abe, K. Ishida, and K. Miura, Bull. Chem. Soc. Japan, 1978, 51, 667.
2. L. Novotný and K. Kotva, Collection Czechoslov. Chem. Commun., 1974, 39, 2949; H. J. Seebald and W. Schunack, J. Chromatog., 1972, 74, 129; A. Szabó and E. Tömörkény, ibid., 1978, 151, 90.
3. B. B. West, G. L. Haller, and R. L. Burwell, Jr., J. Catal., 1973, 29, 486 and references cited therein.
4. I. I. Khochenko, E. M. Mil'vitskaya, A. F. Plate, and A. M. Pryanishnikova, Zh. Org. Khim., 1973, 9, 2307.
5. N. Abe and T. Nishiwaki, J. C. S. Chem. Commun., in press.
6. Merck Kieselgel 60 was used.
7. 1 was stable at room temperature but gave another rearranged products at reflux in benzene or xylene. These results were delineated in a separate paper.[5]
8. 2 was slightly unstable at room temperature in air or by prolonged contact with silica gel, and gave unidentified red substances.
9. N. Abe, Y. Tanaka, and T. Nishiwaki, J. C. S. Perkin I., 1978, 429.
10. Satisfactory elemental analyses and spectroscopical data other than partially given in this paper were obtained for all new compounds here described.
11. According to reference 3, catalytic activity of the commercial gels may result from traces of transition metals, most probably iron.

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