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CONDENSATION REACTION OF 2-METHYLAZULENE DERIVATIVES WITH BENZALDEHYDE; FORMATION OF 2-STYRYLAZULENES

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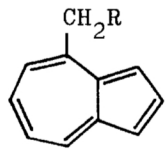
2-Methylazulene derivatives, possessing electron-withdrawing substituents, such as alkoxycarbonyl or cyano group, at the 1- and/or 3-positions, were reactive to undergo condensation reaction with benzaldehyde, in the presence of sodium alkoxide, yielding 2-styrylazulene derivatives, from which 2-styrylazulene itself could be derived by removal of the substituents.

It is known[1] that the proton at the α-carbon of 4(or 8)-alkylazulenes (1) is acidic enough to yield a carbanion (2), when treated with sufficiently strong bases, since the anion is stabilized because of the mesomeric effect owing to the contribution of a cyclopentadienide structure (2a), and the resulting anion undergoes condensation reaction with some electrophilic reagents, such as alkyl halides, aldehydes or ketones, yielding the products condensed with these reagents at the α-carbon. On the other hand, it is predicted that 2-methylazulene (3) is deprived of mesomeric stabilization owing to a cyclopentadienide structure in its anion, so that the methyl proton of 3 is not acidic sufficiently to yield a carbanion when



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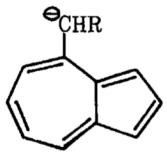

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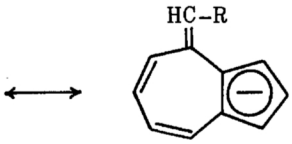
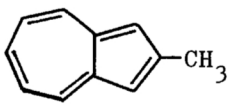


2a



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treated with bases. However, we have now found that 2-methylazulene derivatives (4a,b), possessing electron-withdrawing substituents, such as alkoxycarbonyl or cyano group, at the 1- and/or 3-positions, were reactive to undergo condensation reaction with benzaldehyde, in the presence of sodium alkoxide, yielding 2-styrylazulene derivatives. 2-trans-Styrylazulene, a parent hydrocarbon, could be derived

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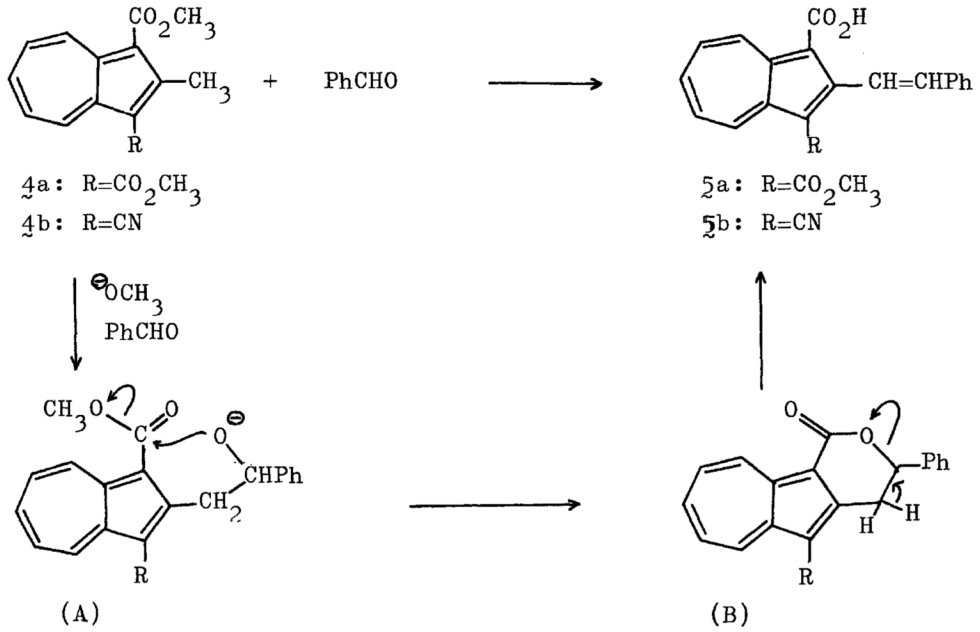
from the resulting styrylazulene derivatives by removal of the substituents. The results will be described in this communication.

2-Methylazulene (3) has been found to do not react with benzaldehyde in the presence of sodium methoxide. In contrast with this, when dimethyl 2-methylazulene-1,3-dicarboxylate (4a)[2] and methyl 3-cyano-2-methylazulene-1-carboxylate (4b)[3] were allowed to react with benzaldehyde in anhydrous methanol in the presence of sodium methoxide, the reaction proceeded easily at room temperature with formation of condensation products (5a): red prisms, mp 177~178°C, and (5b): reddish brown prisms, mp 238~239°C, in 90% and 98% yields, respectively. These compounds, 5a,b, are acidic to be soluble in sodium hydrogen carbonate solution and gave methyl esters (6a): red scales, mp 136~137°C, and (6b): red needles, mp 149~150°C, respectively, on methylation with diazomethane. On the basis of these facts and the spectral data shown in Tables 1 and 2, as well as the results of the elemental analysis,[4] 5a and 5b are assigned the structures of 3-methoxycarbonyl- and 3-cyano-2-trans-styrylazulene-1-carboxylic acids, respectively.

In a similar manner, 1-cyano-2-methylazulene (7a)[3] also reacted easily with benzaldehyde to give 1-cyano-2-trans-styrylazulene (8a): green needles, mp 119~120°C, in a 67% yield. 1-Carbamoyl-2-methylazulene (7b)[3] also reacted with benzaldehyde to give 1-carbamoyl-2-trans-styrylazulene (8b): green needles, mp 207~208°C, although the reaction proceeded under a refluxing condition and gave the product in a low yield of 14%. The structures of 8a and 8b were determined on the basis of the spectral data shown in Table 1 and some chemical evidence. Thus, 8a was derived from 5b by decarboxylation on heating in 85% phosphoric acid. Further, 8a gave 8b on treatment with conc. sulfuric acid at about 100°C.

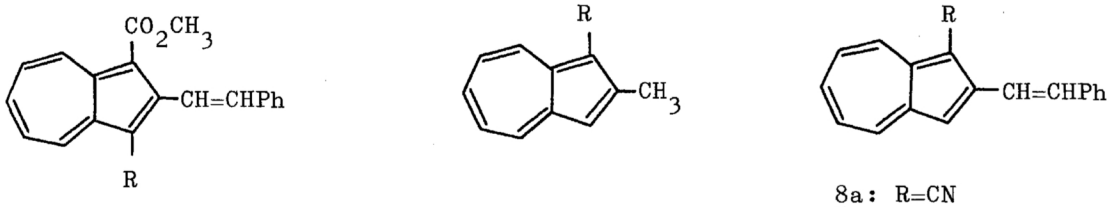
These findings indicate that, as predicted the methyl proton of 2-methylazulene, 3, is not acidic sufficiently to yield the carbanion when treated with sodium methoxide, whereas that of 2-methylazulene derivatives, 4a,b, and 7a,b is quite acidic to yield the carbanions which react with benzaldehyde. For this reason, it seems that the methyl group of the latter compounds is activated because of the electronic effect, that is, the mesomeric and inductive effects, of the alkoxycarbonyl or cyano substituents at the 1- and/or 3-positions of the azulene nucleus.

In spite of the fact that the reaction of 4a,b with benzaldehyde was carried out under an anhydrous condition, the carboxylic acid, 5a,b, being hydrolyzed products, were obtained instead of the esters, 6a,b. The alkoxycarbonyl groups at the



4a: R=CO_2CH_3
4b: R=CN

5a: R=CO_2CH_3
5b: R=CN



6a: R=CO_2CH_3
6b: R=CN

7a: R=CN
7b: R=$CONH_2$

8a: R=CN
8b: R=$CONH_2$
9: R=H

1(or 3)-position of the azulene nucleus are known to resist hydrolysis with alkali under a mild condition,[5] and in fact the esters, 6a,b, were not hydrolyzed entirely under the same reaction condition as in the reaction of 4a,b with benzaldehyde. Therefore, 5a,b are presumed to be formed through a reaction course which involves the formation of a lactone-type intermediate (B) via an intermediate (A), being produced by addition of the carbanions from 4a,b to benzaldehyde, and the elimination-type lactone ring opening of the intermediate (B), as shown in Scheme.

2-trans-Styrylazulene (9), a parent hydrocarbon, could be derived from 5a by hydrolysis with aq. ethanolic alkali under reflux and subsequent decarboxylation of the resulting dicarboxylic acid on heating with phosphoric acid[3] as green scales, mp 208°C, in an 88% yield. [uv and visible absorptions: λ_{max} (isooctane) 227 nm (log ε 3.99), 253 (4.04), 290 (4.34), 320 (4.71), 381 (4.11), 400 (4.44), 424 (4.36), 543 sh (2.48), 580 (2.63), 627 (2.61), 685 (2.14); ir (KBr): 3030, 1618, 1560, 1534, 1504, 1471, 1455, 1383, 960, 808, 723, 691 cm^{-1}; nmr (CF_3CO_2H): δ ppm 4.45 (2H, s),

7.41 (8H, m), 8.50 (5H, m)]. The same compound, 9, was also obtained from 8b, which was derived from 5b and 8a as described above, by decarbamoylation on heating in 85% phosphoric acid.

Table 1. The ir spectral data of 5a,b, 6a,b and 8a,b (in KBr).

compounds	absorptions cm^{-1}
5a	3200~2400, 1639, 920 (CO_2H), 1698 (C=O), 969 (trans -CH=CH-)
5b	3200~2400, 1642, 921 (CO_2H), 2212 (C≡N), 966 (trans -CH=CH-)
6a	1689 (C=O), 966 (trans -CH=CH-)
6b	2212 (C≡N), 1695 (C=O), 961 (trans -CH=CH-)
8a	2198 (C≡N), 955 (trans -CH=CH-)
8b	3360, 3190, 1625 ($CONH_2$), 952 (trans -CH=CH-)

Table 2. The nmr spectral data of 6a,b (in $CDCl_3$).

compounds	δ ppm (intensity, signal pattern, assignment)
6a	3.91 (6H, s, OCH_3), 6.85 (1H, d, J=17 Hz, trans -CH=CH-), 7.2~7.8 (8H, m, H-5,6,7, phenyl), 8.03 (1H, d, J=17 Hz, trans -CH=CH-), 9.3 (2H, dm, H-4,8)
6b	4.03 (3H, s, OCH_3), 7.3~7.8 (8H, m, H-5,6,7, phenyl), 7.88 (1H, d, J=17 Hz, trans -CH=CH-), 8.21 (1H, d, J=17 Hz, trans -CH=CH-), 8.6 (1H, dm, H-4), 9.4 (1H, dm, H-8)

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2) This compound, mp 112~112.5°C, was prepared by a method similar to that described in preparation of ethyl methyl 2-methylazulene-1,3-dicarboxylate.[3)]

3) T. Nozoe, K. Takase, T. Nakazawa, and S. Fukuda, Tetrahedron, 27, 3357 (1971).

4) All new compounds gave satisfactory analyses in accord with the assigned structures.

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