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THE REACTION OF 2-CHLOROAZULENE DERIVATIVES WITH ALKALI METAL ACETYLIDES IN LIQ. AMMONIA

Taira Fujita, Tadayoshi Morita, and Kahei Takase*
Depatment of Chemistry, Faculty of Science, Tohoku University
Aramaki-aza-Aoba, Sendai 980, Japan

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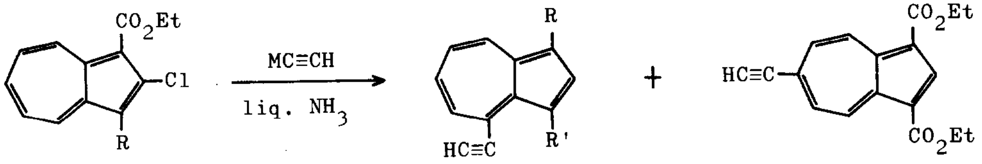
It is known[1,2,3) that the halogeno substituents of haloazulenes are directly replaced by some nucleophilic reagents, such as alkoxides, amines or mercaptides, giving the corresponding "normal substitution products". On the other hand, it has been found[4) that the reaction of diethyl 2-chloroazulene-1,3-dicarboxylate (1) with phenylmagnesium bromide gave dihydroazulene-type addition products, which, on dehydrogenation, yielded 4- and 6-phenylazulene derivatives in which the chloro substituent remained at the 2-position as it was. This communication will describe the third type of the reaction of haloazulenes with nucleophilic reagents, that is, the reaction of 2-chloroazulene derivatives (1 and 2) with alkali metal acetylides (MC≡CH; M=Li or Na) in liq. NH_3, which yielded "abnormal substitution products".

Diethyl 2-chloroazulene-1,3-dicarboxylate (1)[1) was allowed to react with acetylides as follows: A solution of 1 in THF was added to a solution of 3 equimolar amounts of acetylides in liq. NH_3, after which the mixture was allowed to stand at -40°C for 1 hr and then the excess of acetylides was decomposed by addition of methanol and liq. NH_3 was removed. The residue was extracted with benzene, washed with 6N HCl and chromatographed over a silica gel column. Thus, diethyl 4-ethynyl- (3): blue violet needles, mp 81-82°C, and diethyl 6-ethynylazulene-1,3-dicarboxylates (4): reddish violet needles, mp 164-165°C, were obtained in 41% and 39% yields respectively. In the same manner as with 1, ethyl 2-chloroazulene-1-carboxylate (2)[1) was allowed to react with lithium acetylide



1: R=CO_2Et
2: R=H

3: R=R'=CO_2Et
5: R=CO_2Et, R'=H
6: R=H, R'=CO_2Et

4

to give ethyl 4-ethynyl- (5): blue violet needles, mp 61-62°C, and ethyl 8-ethynylazulene-1-carboxylates (6): blue oil, in 73% and 4% yields respectively. In this case no 6-ethynyl derivative could be obtained. The structures of the ethynyl derivatives, 3, 4, 5 and 6, were determined on the basis of their spectral data (ir, uv and nmr)[5] as well as the results of the elemental analyses.[6] In contrast with 1 and 2, 2-chloroazulene itself did not react with acetylides under the same reaction condition.

As described above, it was found that the reaction of 2-chloroazulene derivatives with acetylides in liq. NH_3 yielded "abnormal substitution products", 3, 4, 5 and 6, which were formed in such a way that the reagent entered at the position different from that at which the leaving chloro substituent was attached. A probable mechanism for this "abnormal substitution reaction" is presumed to be that involving an addition-elimination process via cyclopentadienide-type and dihydroazulene-type intermediates.

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REFERENCES AND FOOTNOTES

* Address correspondence to this author.

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5) The satisfactory spectral data have been obtained for all new compounds reported and are available upon request.

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