

SILVER ION-PROMOTED REARRANGEMENT OF DIELS-ALDER ADDUCTS FROM
2-CHLOROACRYLONITRILE AND 5-METHOXY-4,7-DIHYDROINDAN

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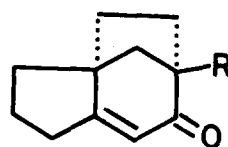
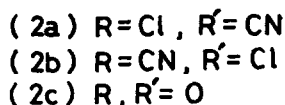
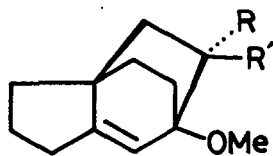
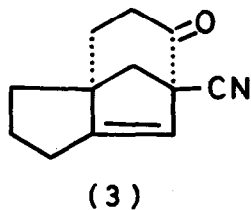
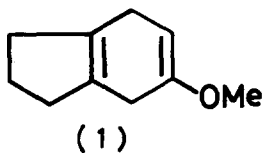
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Chloroacrylonitrile is frequently used as ketene equivalents with high regioselectivity in Diels-Alder synthesis¹⁾, and provides the chloro nitrile adducts which lead to key intermediates for several natural product syntheses²⁾.

Here we wish to describe the facile silver ion-promoted skeletal rearrangements of the chloro nitrile adducts (2a) and (2b), which are obtained by Diels-Alder synthesis of 2-chloroacrylonitrile and 5-methoxy-4,7-dihydroindan (1), resulting in formation of unique tricyclic derivatives (3) and (4), respectively. This furnishes a potentially easy access to the compounds involving bicyclo[3.2.1]octane skeleton such as (3) and (4) starting from the Diels-Alder adducts used 2-chloroacrylonitrile as a dienophile.

Reaction of 5-methoxy-4,7-dihydroindan (1) and 2-chloroacrylonitrile in benzene afforded the crystalline chloro nitrile adducts (2a) and (2b) in good yield (the ratio ; 1:2)³⁾.



The epimeric mixture (132 mg) of (2a) and (2b) was treated with silver tetrafluoroborate (1.0 equiv.) in dimethylformamide at 115° for 5 hr. Thus the chloro nitrile adducts disappeared completely to give two new rearranged products, which were separated on silica gel chromatography affording the tricyclo-[6.2.1.0^{1,5}]undecane derivative (4)⁴ [66 mg, m.p. 98-99°, IR(CHCl₃) 2250, 1670, 1635 cm⁻¹, NMR(CDCl₃) 5.80(1H,s) ppm] as a major product and the tricyclo-[5.3.1.0^{1,5}]undecane derivative (3)⁴ [34 mg, m.p. 117-118°, IR(CHCl₃) 2250, 1720, cm⁻¹, NMR(CDCl₃) 5.47(1H,s) ppm] as a minor one.

In this reaction, the rearrangement was obviously dependent on the configuration of the chlorine atom in the Diels-Alder adducts (2a) and (2b). The products (3) and (4) were derived almost quantitatively from (2a) and (2b), respectively, by the initial elimination of chlorine atom assisted by the silver ion followed by the trans-anti-parallel shift of the corresponding carbon-carbon bond. This was supported by the fact that (3) and (4) were formed in the same proportion as that of the epimeric chloro nitrile adducts (2a) and (2b) used.

Alternatively, on transforming both epimeric chlorides (2a) and (2b) into the ketone (2c) by a hydrolysis⁵, the ketol (5)⁴ [IR(CHCl₃) 3450, 1660, 1630 cm⁻¹, NMR(CDCl₃) 5.90(1H,s) ppm] was yielded by an acid-catalyzed rearrangement (HCl-AcOH, reflux).

REFERENCES

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The ratio of (2a) and (2b) (1:2) was determined from the intensities of the olefinic proton signals [(2a) 6.06 ppm, (2b) 5.90 ppm] in the NMR spectrum. These epimers were not separable on chromatography, although (2b) could be separated by repeated recrystallization.
- 4) New compounds gave satisfactory elemental analysis and appropriate spectroscopic data.
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