CHEMISTRY LETTERS, PP.3-4, 1973. Published by the Chemical Society of Japan

A CONVENIENT ROUTE TO 4,5-HOMOTROPONES[1)]

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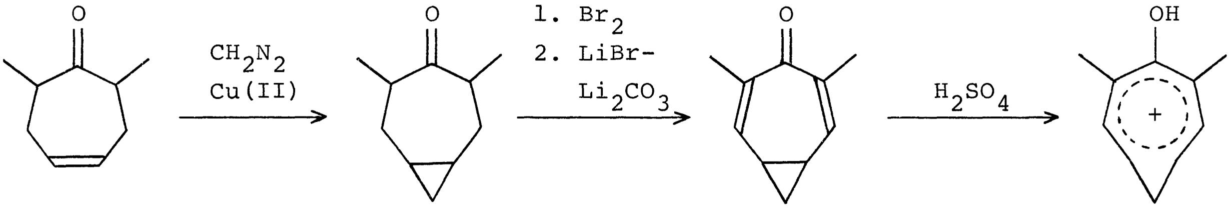
A new route to 4,5-homotropones starting with 4-cycloheptenone derivatives is described.

4,5-Homotropone is a molecule which has a cis-divinylcyclopropane structure but does not undergo Cope rearrangement, as was demonstrated by its first synthesis by Chapman and Fugiel.[2)] We wish to describe a new, convenient route to the alkylated derivatives starting with 4-cycloheptenones, which are now readily available via iron carbonyl-promoted cyclocoupling of α,α'-dibromo ketones and 1,3-dienes.[3)]

When diazomethane generated from N-methyl-N-nitrosourea (25 equiv) and KOH in decalin was diluted with nitrogen and introduced into a benzene—n-hexane (1:1) solution containing 2,7-dimethyl-4-cycloheptenone (I)[3)] and a catalytic amount of bis(N-α-phenylethylsalicylaldiminato)copper(II) (0.05 equiv) at 0°C,[4)] the bicyclic ketone II was obtained after usual work-up in 90% yield.[5,6)] Bromination of II using Br_2 (3.4 equiv) and sodium acetate (4 equiv) in chloroform (25°C, 8 hr) followed by treatment with a mixture of LiBr (10 equiv) and Li_2CO_3 (10 equiv) in dimethylformamide (150°C, 5 hr) afforded the desired homotropone III in 33% yield after silica gel chromatography, mp 34—35°C (from petroleum ether). Ir (CCl_4) 1645 (C=O) and 1615 cm^{-1} (C=C); uv (C_2H_5OH) 216 (log ε 3.77) and 281 nm (3.74); mass (70 eV) m/e 148 (M^+). As expected, the homotropone III in conc H_2SO_4 proved



I II III IV

to exist as the hydroxyhomotropylium ion IV: uv (96% H_2SO_4) 207 (log ε 4.08), 250 (4.25), and 328 nm (3.67). Nmr data of III and IV are shown in Figs. 1 and 2. The presence of an aromatic ring current in IV resulted in the large chemical shift difference between the methylene protons (5.0 ppm) compared with that of the parent dienone III (1.5 ppm).

The present method can be employed for the preparation of various 4,5-homotropones. Chemical behavior of the homotropones and their protonated species will be presented in a forthcoming paper.

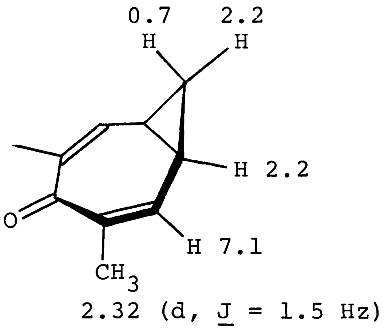


Fig. 1. Nmr of III in CCl_4, δ from TMS as the external standard.

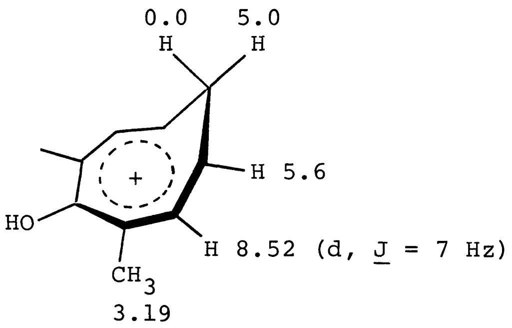


Fig. 2. Nmr of IV in 96% H_2SO_4, δ from TMS as the external standard.

Notes and References

1) Carbon-Carbon Bond Formations Promoted by Transition Metal Carbonyls. IV. Part III: R. Noyori, Y. Hayakawa, M. Funakura, H. Takaya, S. Murai, R. Kobayashi, and S. Tsutsumi, J. Amer. Chem. Soc., 94, 7202 (1972).

2) O. L. Chapman and R. A. Fugiel, ibid., 91, 215 (1969).

3) R. Noyori, S. Makino, and H. Takaya, ibid., 93, 1272 (1971).

4) For the detailed procedure for generating copper carbenoid, see H. Nozaki, H. Takaya, S. Moriuti, and R. Noyori, Tetrahedron, 24, 3655 (1968); R. Noyori, H. Takaya, Y. Nakanisi, and H. Nozaki, Can. J. Chem., 47, 1242 (1969).

5) A mixture of diastereomers.

6) All new compounds gave correct elemental analyses and/or molecular peak in mass spectra.

Acknowledgment. Financial support from the Matsunaga Science Foundation is gratefully acknowledged.

(Received October 27, 1972)