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# A Cationic [3,4] Sigmatropic Rearrangement1)

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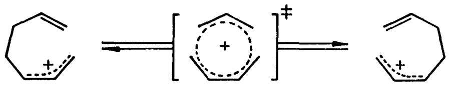
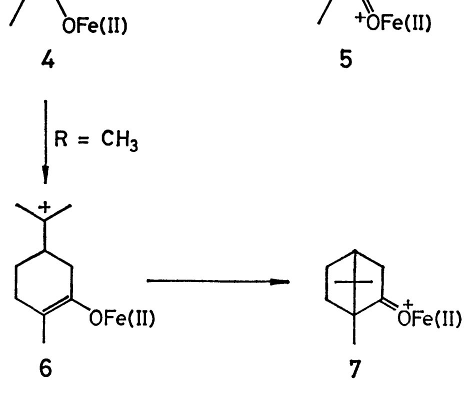
**Synopsis.** The first example of the cationic [3,4] sigmatropic reaction has been achieved by the reaction of 1,3-dibromo-3-methyl-6-hepten-2-one and diiron nonacarbonyl.

There is currently much interest in electrocyclic reactions which involve carbocations.2) In 1971, Dewar has predicted that the [3,4]sigmatropic rearrangement, **1a**$\rightleftarrows$**1b**, may take place *via* cyclic six-electron transition state.3) However, realization of such symmetry-allowed transformation has not yet been reported to date, at least to our knowledge. Here we report the first example of this type of cationic rearrangement.



1a 1b

When the dibromo ketone **2** was treated with diiron nonacarbonyl in refluxing benzene, the dienone **3** was obtained as the sole isolable product, identical with authentic sample prepared independently. The reductive skeletal change is interpreted in terms of the title pericyclic process *via* the oxyallyl-Fe(II) intermediate **4** (R=H).4) The high stability of the resulting carboxonium ion **5** would facilitate the forward reaction. It should be noted that reaction course of the oxyallyl **4** is highly dependent on the substitution pattern of the internal olefinic bond. When the double bond is substituted by carbocation-stabilizing methyl groups, the cationic species **4** (R=CH$_3$) undergoes the stepwise, double cyclization to give (±)-camphor, **4**→**6**→**7**.5,6)



## Experimental

*2-Methyl-1,6-heptadien-3-one (3).* A mixture of the dibromo ketone **2**7) (905 mg, 3.18 mmol) and diiron nonacarbonyl (2.13 g, 6.36 mmol) in dry benzene (12 ml) was heated at reflux for 2 h under argon atmosphere. The cooled mixture was filtered through a cotton-celite pad and the filtrate was concentrated under reduced pressure to give crude product (370 mg). The NMR and GLC analysis elucidated that this material contained **3** (80% GLC yield) and some unidentified minor products. An analytical sample (148 mg, 32%) was obtained by the preparative GLC (3% OV-1, 0.64×100 cm column, 100 °C). IR (neat) 3060 (=CH), 1680 (C=C), 1640 (C=C, enone), 1630 (C=C), 910 cm$^{-1}$ (=CH). $^1$H NMR (CCl$_4$) $\delta$ 1.85 (d, $J$=1.5 Hz, CH$_3$), 2.36 (t, $J$=7 Hz, =CHC$\underline{H}_2$), 2.70 (t, $J$=7 Hz, CH$_2$C=O), 4.94 (d, $J$=10 Hz, C$\underline{H}_2$=CHCH$_2$, a proton trans to CH$_2$), 4.98 (d, $J$=20 Hz, C$\underline{H}_2$=CHCH$_2$, a proton cis to CH$_2$), 5.70 (br s, C$\underline{H}_2$=CCH$_3$, a proton cis to CH$_3$), 5.80 (m, C$\underline{H}$=CH$_2$), 5.90 (s, C$\underline{H}_2$=CCH$_3$, a proton trans to CH$_3$). Found: *m/e* 124.08892. Calcd for C$_8$H$_{12}$O: (M$^+$), 124.08881.

*2-Methyl-1,6-heptadien-3-ol (8).* To a solution of 3-butenylmagnesium bromide prepared from 1-bromo-3-butene (1.5 g, 11.1 mmol) and magnesium (365 mg, 15 g-atom) in anhydrous ether (20 ml) was dropwise added a solution of methacrylaldehyde (770 mg, 11.1 mmol) in anhydrous ether (4 ml) over a period of 10 min at 0 °C. After stirring for 1 h at this temperature, aqueous saturated ammonium chloride (10 ml) was added, and the aqueous phase was extracted with ether. The combined organic materials was dried and concentrated. The resulting oil was subjected to column chromatography on silica gel using pentane–ether (8:1) as an eluent. The pure product was obtained as a colorless oil (1.21 g, 87%) after bulb-to-bulb distillation (110—118 °C, 15 mmHg). IR (neat) 3400 (OH), 3080 (=CH), 1640 (C=C), 910 cm$^{-1}$ (=CH). NMR (CCl$_4$) $\delta$ 1.23 (s, OH), 1.76 (s, CH$_3$), 4.02 (t, $\underline{H}$COH), 4.7—5.1 (m, 4H, =CH$_2$), 5.75 (m, C$\underline{H}$=CH$_2$). Found: C, 76.46; H, 11.27%. Calcd for C$_8$H$_{14}$O: C, 76.14; H, 11.18%.

*Oxidation of 8.* A suspension of the hydroxy compound **8** (150 mg, 1.19 mmol) and activated manganese dioxide (400 mg, 4.6 mmol) in pentane (3 ml) was stirred for 72 h at room temperature, and the resulting mixture was filtered through glass paper. The concentrated filtrate was subjected to column chromatography on silica gel using pentane–ether (50:1 and then 5:1) as an eluent to give 18 mg (12%, conversion yield 36%) of **3** and 101 mg (68%) of starting material **8**. The IR and NMR were identical with those of the product obtained from **2** and Fe$_2$(CO)$_9$.

## References

1) Carbon-Carbon Bond Formation Promoted by Transition Metal Carbonyls. 30. Part 29: Ref. 5; Part 28: Ref. 6.

2) Review: T. S. Sorensen and A. Rank, "Pericyclic Reactions," ed by A. P. Marchand and R. E. Lehr, Academic Press, New York (1977), Vol. II, Chap 1.

3) M. J. S. Dewar, *Angew. Chem., Int. Ed. Engl.*, **10**, 761 (1971).

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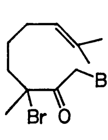
4) R. Noyori, *Acc. Chem. Res.*, **12**, 61 (1979).

5) R. Noyori, M. Nishizawa, F. Shimizu, Y. Hayakawa, K. Maruoka, S. Hashimoto, H. Yamamoto, and H. Nozaki, *J. Am. Chem. Soc.*, **101**, 220 (1979).

6) Attempted reaction of the dibromo ketones i—iii with $Fe_2(CO)_9$ gave neither cyclization nor rearrangement products.



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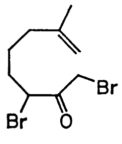

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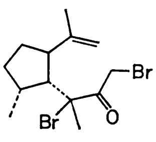

iii

7) The dibromo ketone **2** was prepared from 4-methyl-6-acetoxy-4-hexenal.[5,8]

8) G. Stork, M. Gregson, and P. A. Grieco, *Tetrahedron Lett.*, **1969**, 1391.