halogenation, dehalogenation

O 0230 16 - 121 Anomalous Iodination and Iodochlorination of 3,4-Dimethyl-cisbicyclo(4.3.0)nona-3,7-diene. — Whereas addition of I2 to the title compound (I) in CCl4 gives unexpected tricyclic monoiodides as a mixture of epimers (cf. (II), (III)), iodination of (I) in pyridine results in a regiospecific addition of iodine and pyridine to the cyclopentene double bond (cf. (VI)). Iodochlorination of (I) in CHCl3 yields tricyclic monoiodides as well as addition products of chlorine and iodine to the cyclopentene double bond (cf. (IV)). Mechanistic suggestions for these unusual halogenation reactions are given. — (ANDREEV, V. A.; PEKHK, T. I.; ANFILOGOVA, S. N.; BELIKOVA, N. A.; BOBYLEVA, A. A.; Zh. Org. Khim. 27 (1991) 7, 1450-1458; Mosk. gos. univ. im. Lomonosova, USSR; RU)

Me H
$$I_2$$
 I_2 I_3 I_4 I_5 I_6 I_7 I_8 I_8

ds.: diastereoselectivity ~10% (87% ds.)

$$I \xrightarrow{N} (V) \qquad \text{Me} \xrightarrow{H} \stackrel{I}{\longrightarrow} H$$

$$VI \qquad 35\% \ (75\% \ ds.)$$