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THE BEHAVIOR OF 2,7-DIMETHYLOXEPIN TOWARD AZODICARBOXYLATE ESTERS: THE FORTUITOUS SYNTHESIS OF A CYCLOHEPTATRIENE FROM AN OXEPIN

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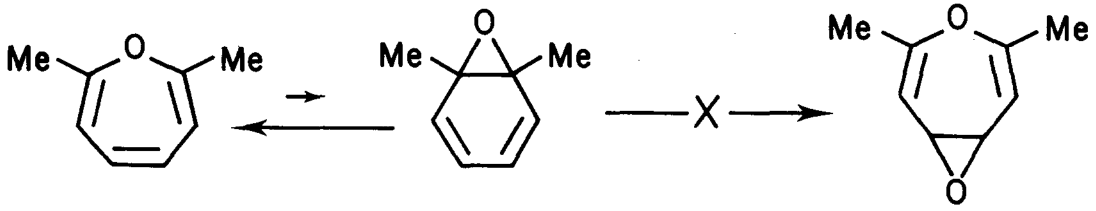
In our accompanying paper[1] we report the conversion of a dimethyloxepin/ benzene oxide to the corresponding *sym*-oxepin oxide. In principle, our route[2] could be applied to 2,7-dimethyloxepin (1) $\rightleftarrows$ 1,2-dimethylbenzene oxide (2)[3] for the synthesis of oxepin oxide 3.

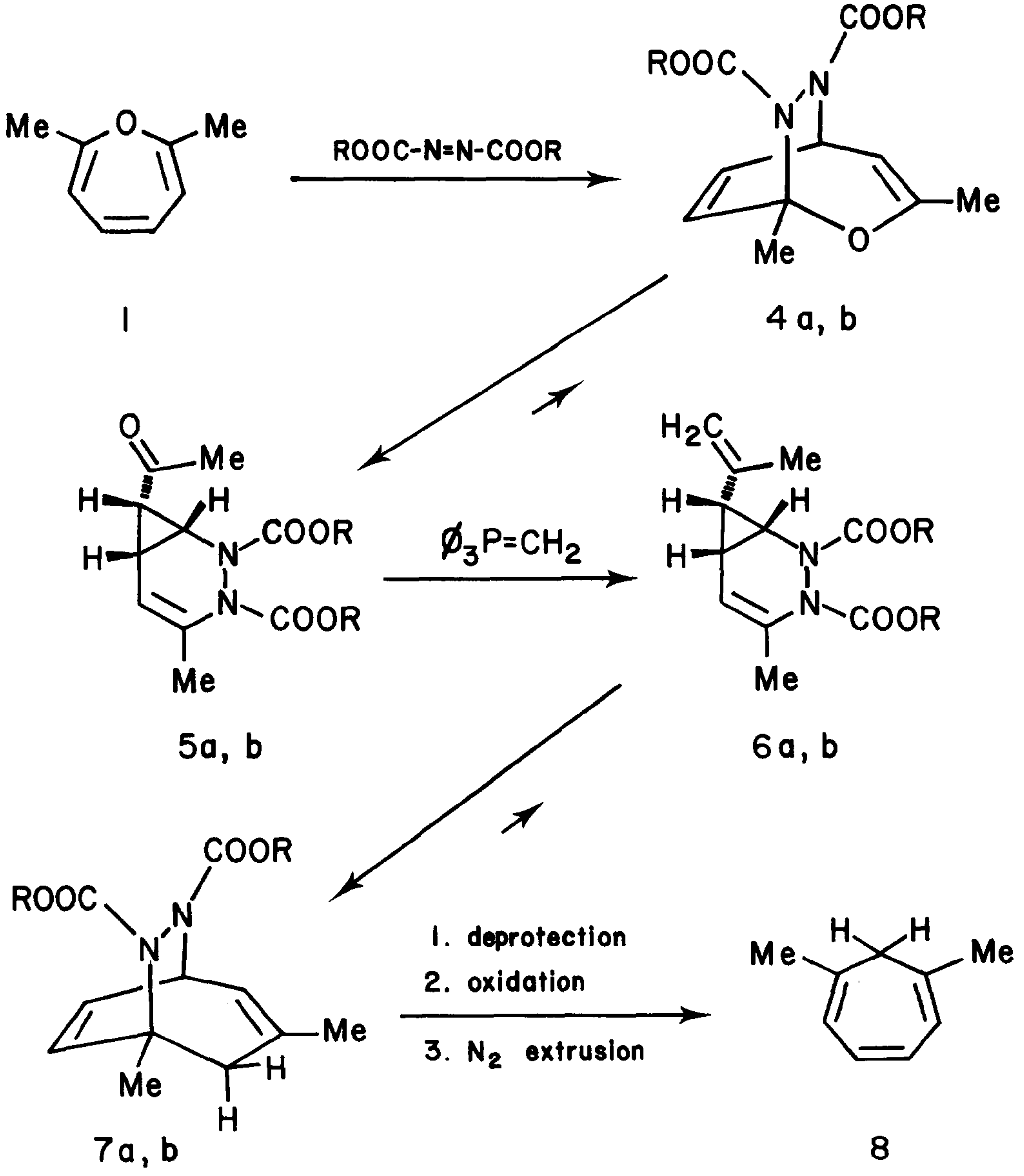


1 2 3

Herein we report the failure of this approach and examine the anomalous behavior of 1 $\rightleftarrows$ 2 toward the oxepin/benzene oxide $\longrightarrow$ *sym*-oxepin oxide conversion.[2]

The planned conversion of 1 $\rightleftarrows$ 2 to oxepin oxide 3 was thwarted in the first step of the synthetic sequence, the attempted trapping of valence tautomer 2 by the dienophile, bis(trichloroethyl)azodicarboxylate. Rather than the Diels-Alder adduct of diene 2 we isolated the crystalline cyclopropyl methyl ketone 5a[4,5] (*Scheme*) in 92% yield. Ketone 5a is thought to arise *via* Claisen rearrangement of vinyl allyl ether 4a, the Diels-Alder adduct of oxepin 1 with the dienophile. Despite the formation of a cyclopropane, the equilibrium 4 $\rightleftarrows$ 5 is driven toward 5 by the formation of the strong ketone carbonyl.

Scheme



a series, $R = CH_2CCl_3$

b series, $R = Me$

The unexpected trapping of valence tautomer **1** is attributed to the position of the equilibrium $\mathbf{1} \rightleftharpoons \mathbf{2}$[3,6] which, unlike the parent system, heavily favors the oxepin (**1**). A similar adduct (**5b**)[4,7] is formed by reaction of **1** with dimethylazodicarboxylate (yield, 60%).

To confirm the structures of **5a,b**, these compounds have been converted *via* the reactions of the *Scheme* to 1,6-dimethyl-1,3,5-cycloheptatriene (**8**). Thus, **5b** was converted to the *cis*-divinylcyclopropane **6b**[8] by reaction with triphenylphosphonium methylide in THF (-78°/2 hrs, then ambient temperature/11 hrs; yield 59%). Upon heating in CCl_4 at reflux the *cis*-divinylcyclopropane **6** is converted quantitatively (^1H nmr) to the less strained diene **7b**[9]. Deprotection, oxidation and nitrogen extrusion (*Scheme*) proceeded smoothly upon sequential treatment of **7b** with trimethylsilyliodide[10] and aqueous cupric chloride, producing **8** in quantitative yield.[11] Cyclopropyl methyl ketone **5a** also can be converted *via* a similar sequence[12] to **8**, albeit in much lower yield.

Acknowledgment

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References and Footnotes

1. W.H. Rastetter and T.J. Richard, preceding paper, this journal.
2. W.H. Rastetter, J. Amer. Chem. Soc., 98, 6350 (1976).
3. E. Vogel and H. Günther, Angew. Chem., Int. Ed. Eng., 6, 385 (1967).
4. Satisfactory combustion analysis was obtained for this compound.
5. Data for 5a: m.p. 125-126°; ^1H nmr ($CDCl_3$) δ (Me_4Si) 2.30(m, 8H); 3.83 (m, 1H); 4.40-5.40(br m, 5H); ir (KBr) 1758, 1728, 1690 cm^{-1}.
6. Despite the position of the equilibrium $1 \rightleftarrows 2$, valence tautomer 2 is trapped by Diels-Alder reaction with maleic anydride (see reference 3).
7. Data for 5b: m.p. 124-125°; ^1H nmr ($CDCl_3$) δ (Me_4Si) 2.15(m, 2H); 2.19 (s, 3H); 2.23(s, 3H); 3.63(s, 3H); 3.74(s, 3H); 3.61-3.74(m, 1H); ir (KBr) 1733, 1708, 1693, 1663 cm^{-1}.
8. Data for 6b: oil purified by silica gel column chromatography (1:1 Et_2O/pet. ether); ^1H nmr ($CDCl_3$) δ (Me_4Si) 1.88(br s, 5H); 2.10(br m, 3H); 3.45 (t, 1H); 3.69(s, 3H); 3.78(s, 3H); 4.67(m, 1H); 4.76(m, 1H); 5.43(m, 1H); ir (film) 1710-1750 (br strong), 1656 cm^{-1}.
9. Data for 7b: m.p. 107.5-108.5° (yield 87% after recrystallization); ^1H nmr ($CDCl_3$) δ (Me_4Si) 1.65(br s, 3H); 1.71(s, 3H); 2.02(d, J = 18 Hz, 1H); 3.18 (d, J = 18 Hz, 1H); 3.62(s, 3H); 3.66(s, 3H); 4.85(m, 1H); 5.49(m, 1H); 5.69 (m, 1H); 6.50(m, 1H); ir (KBr) 1690-1720 (br strong) cm^{-1}; exact mass, calculated, 266.126; found, 266.124.
10. M.E. Jung and M.A. Lyster, J. Amer. Chem. Soc., 99, 968 (1977).
11. Yield determined by ^1H nmr and by gc vs an internal standard; 8 produced via the reactions of the Scheme was indistinguishable by ^1H nmr, ir and gc co-injection from an authentic sample (E. Vogel, W. Wiedemann, H.D. Roth, J. Eimer, and H. Günther, Justus Liebigs Ann. Chem., 759, 1 (1972).
12. The deprotection step in the case of 7a → 8 utilized Zn°/HOAc rather than Me_3SiI.

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