SYNTHESES AND REACTIONS OF CYCLOPENTADIENONES POSSESSING FIVE-MEMBERED HETEROCYCLES AS SUBSTITUENTS

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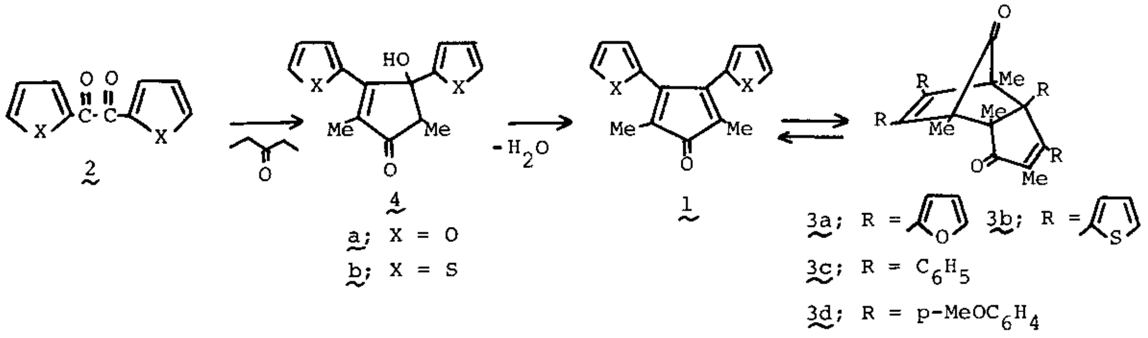
Abstract --- The syntheses and reactions of 3,4-di(2-furyl)-2,5-dimethylcyclopentadienone (1a) and 2,5-dimethyl-3,4-di(2-thienyl)-cyclopentadienone (1b) are described. They exist as dimers 3a,b at room temperature, while upon heating in solvents, the dimers become monomeric and undergo the Diels-Alder reaction with olefins.

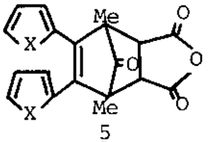
Cyclopentadienones are reactive and versatile diene components in the Diels-Alder reactions.[1] The cyclopentadienones possessing heterocyclic substituents have not yet been synthesized. These compounds are expected to be useful for synthesis of heterocyclic compounds and are also of interest from the viewpoint of the reactivity of the cyclopentadienones. This report describes the preparation and some reactions of cyclopentadienones 1 possessing furyl and thienyl substituents. Base-catalyzed condensation of furil (2a) with diethyl ketone in ethanol gave the cyclopentadienone dimer 3a (mp 196-198°C, 20%).[2] On the other hand, the reaction of 2b with diethyl ketone under the same conditions afforded 4b which, without purification, upon treating with conc. H_2SO_4 in acetic acid, gave the dimer 3b (mp 184-188°C, 35%).[2] The structures of dimers 3a,b were determined on the basis



of the spectral data along with chemical evidence. The IR spectra (KBr) exhibit peaks due to two carbonyl groups: **3a**; 1785, 1680 cm^{-1}, **3b**; 1780, 1675 cm^{-1}. The NMR spectra ($CDCl_3$) show four methyl signals: **3a**; δ0.74, 1.42, 1.67, 1.96, **3b**; 0.70, 1.36, 1.84, 2.19. In contrast to the above reactions, the base-catalyzed condensation of diketones **2a,b** with dibenzyl ketone gave no clear product, although the reaction of benzil with dibenzyl ketone affords tetraphenylcyclopentadienone. Certain cyclopentadienones such as 2,5-dimethyl-3,4-diphenylcyclopentadienone are known to exist as dimers at room temperature and become monomeric upon heating. Dissociation of the dimers **3a,b** was ascertained by the following addition reactions. Upon heating **3a,b** with maleic anhydride in boiling toluene, adducts **5a,b** were obtained. The thienyl and furyl substituents of **5** did not undergo further Diels-Alder reactions with maleic anhydride. Similarly, the addition reactions of the dimers **3a,b** with dimethyl acetylenedicarboxylate and cyclohexadiene gave adducts **6a,b** and **7a,b**, respectively.[2] The yields and melting points of these products are shown in Table 1. In particular, the formation of adduct **7**, which is formed by the Cope rearrangement of initially formed adduct **8**, is noteworthy because the reaction of **3c**, the dimer of 2,5-dimethyl-3,4-diphenylcyclopentadienone,[3] with cyclohexadiene under the same conditions gave only the **8** type adduct.[4] This

Table 1. Melting Points and Yields of the Adducts

Compd	M.P., °C	Yield, %	Compd	M.P., °C	Yield, %
5a	180-183	45	**5b**	184-185	55
6a	119-121	63	**6b**	174-176	71
7a	152-153	72	**7b**	129-130	72



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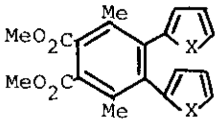

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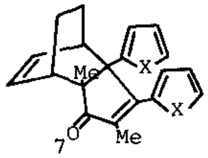

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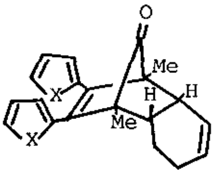
a; X = O

b; X= S



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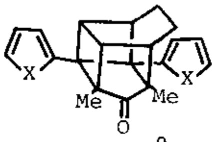

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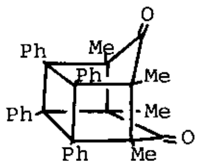
implies that the dienones 8 possessing furyl or thienyl substituents undergo the Cope rearrangement more readily than the corresponding phenyl substituted derivatives. Irradiation of dienones 7a,b in methanol with a high pressure mercury lamp gave the cage compounds 9a (mp 106-107°C, 7%) and 9b (mp 98-99°C, 30%), respectively, by the intramolecular [2+2] cycloaddition reaction.[5] The reactions of cyclopentadienones 1 with several olefins as shown here provide a useful method for syntheses of difuryl and dithienyl substituted compounds.

The relative reactivity of cyclopentadienone dimers in the reaction with maleic anhydride is in the following order; 3d>3c>3b>3a, which was determined by following appearance of the adducts using a nmr method. This order is coincident with the order of the substituent size; methoxyphenyl > phenyl > thienyl > furyl. The reactivity, therefore, seems to depend on the ease of dissociation of the dimers.

The photochemistry of cyclopentadienone dimers have attracted considerable attention.[6,7] Direct irradiation of the cyclopentadienone dimer 3c gives a cage compound 10.[7] For comparison, the photochemistry of the dimers 3a,b was studied. When the dimers 3a,b were irradiated with a high pressure mercury lamp in acetonitrile, the intramolecular [2+2] cycloaddition reaction occurred to give cage compounds 11a (mp 221-223°C, 23%), 11b (mp 240-242°C, 67%). No products derived from 1,3-shifts such as 10 were obtained.[8] The structures of cage ketones 11 were deduced from the spectroscopic data along with the result of the thermal reaction of 11. The IR spectra (KBr) of cage ketones 11a,b exhibit one carbonyl band (1760 cm^{-1}). The NMR spectra ($CDCl_3$) show two methyl signals: 11a; δ 0.74, 1.49, 11b; 0.59, 1.81. Upon heating at 250°C, cage compounds 11a,b were readily reverted to the dimers 3a,b in high yields, indicating that 11a,b were formed by the intramolecular [2+2] cycloaddition reaction. Further studies are in progress to investi-



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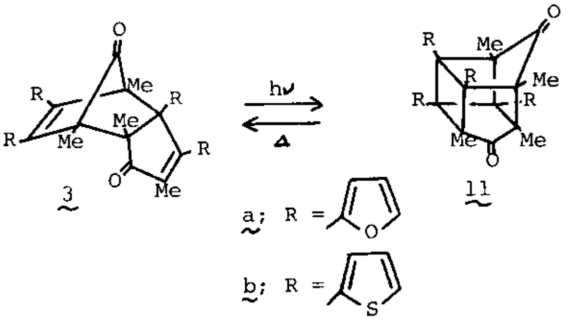

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gate the definite nature of the substituent effects on the photochemistry of cyclopentadienone dimers.

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2 All new compounds described herein provided the expected elemental analysis and spectral data.

3. C. F. H. Allen and J. A. VanAllan, *J. Amer. Chem. Soc.*, 1942, **64**, 1260.

4. Y. Yamashita and T. Mukai, *Chem. Lett.*, 1978, 919.

5. The methyl signals in the NMR spectra ($CDCl_3$) of adducts are as follows. **5a**; δ 1.68, **5b**; 1.64, **6a**; 2.19, 3.87, **6b**; 2.17, 3.87, **7a**; 0.98, 2.05, **7b**; 1.02, 1.95, **9a**; 0.98, 1.10, **9b**; 1.04, 1.13.

6. E. Baggiolini, E. G. Herzog, S. Iwasaki, R. Schorta, and K. Schaffner, *Helv. Chim. Acta.*, 1967, **50**, 297.

7. K. N. Houk and D. J. Northigton, *Tetrahedron Lett.*, 1972, 303; B. Fuchs, *J. Amer. Chem. Soc.*, 1971, **92**, 2544.

8. Irradiation of the dimer **3c** under the same conditions as that of **3a**,**b** gave only the cage ketone **10**.

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