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COPE REARRANGEMENTS OF CYCLIC 1,5-DIENES POSSESSING A NORBORNENONE MOIETY[1]

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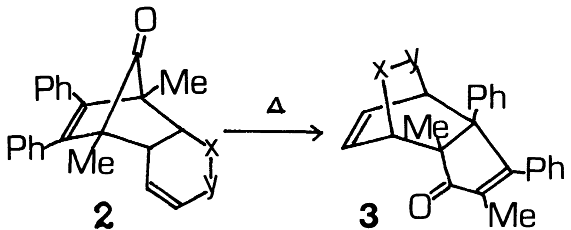
Cope rearrangements of tricyclo-dienones **2** and **4** containing a norbornenone moiety have been investigated to synthesize isomeric α, β-unsaturated ketones **3** and **5**. The facility of the Cope rearrangement depends on the structure of **2** and **4**. It was found that dienones **2b**, **2e**, and **4b** underwent the rearrangement, but not the similar compounds, **2c**, **2d**, and **4c**.

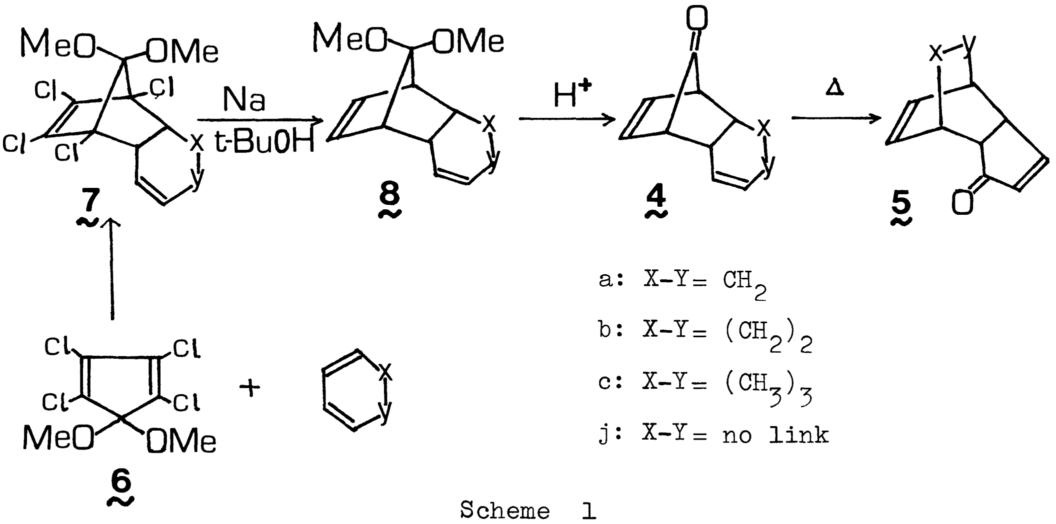
Cycloaddition reaction of 2,5-dimethyl-3,4-diphenylcyclopentadienone (**1**) to conjugated dienes or trienes is a useful method as a starting step for synthesis of cage ketones.[2] The [4+2] type adducts **2** obtained as the primary products, upon additional heating, usually undergo the secondary thermal reaction, i. e., the Cope rearrangement to give another type of [4+2] adducts **3**.[3] We have found that the facility of the Cope rearrangement of **2** is strongly dependent on the length of the bridge X-Y, which deforms the orientation of the double bonds. A similar finding which was recently found by Houk and Luskus[4] prompts us to report our experimental results on the relationship between the reactivity and the structure of dienones **2** and **4**.



2 **3**

a: X-Y= CH_2
b: X-Y= $(CH_2)_2$
c: X-Y= $(CH_2)_3$
d: X-Y= $(CH_2)_4$
e: X-Y= CH_2-CH=CH
f: X-Y= CH=CH-N(CO_2Et)
g: X-Y= CH=N-N(CO_2Et)
h: X-Y= CH=N-N(COPh)
i: X-Y= O-CPh=N
j: X-Y= no link

Although a rapid equilibrium consisting of 50 % of dienones 2a and 3a is reported to take place at 105°C,[3] we found that 2b and 2j,[2] upon heating in refluxing xylene, gradually underwent the Cope rearrangement to give the corresponding isomers, 3b and 3j. On the other hand, dienones 2c[3] and 2d[5] having a three or four methylene bridge were stable under the same conditions. Dienones 2e-i which possess a three-atom bridge containing an additional double bond, however, smoothly isomerized to 3e-i upon heating at 120°C in tetrachloroethylene. Because dienone 4a is known to undergo the Cope rearrangement even at room temperatures in ethanol,[6] we investigated the substituent-effect in more detail using other dienones 4b, 4c, and 4j. These compounds were synthesized by following the reaction paths shown in Scheme 1. As in the case of 1, tetrachlorocyclopentadienone acetal (6) was added to 1,3-dienes to give 1:1 adducts 7 in high yields, which upon dechlorination with sodium and *tert*-butyl alcohol, afforded acetals 8 in 50-60 % yields. Treating of 8 with a dilute acid easily produced dienones 4. When 4b and 4j were heated in refluxing toluene, the rearrangement smoothly occurred to give 5b and 5j. In contrast, 4c was stable at 120°C in refluxing xylene, implying that dienones possessing a three-methylene bridge are thermally stable regardless of the substituents. The isomerization rate constants of 2 and 4 were determined by monitoring the appearance of dienones 3 and 5 using UV spectroscopic methods. The results shown in Table 1, reveal that dienones 4b having no substituent undergo the Cope rearrangement more easily than the corresponding substituted derivatives 2b. On the other hand,



a: X-Y= CH_2
b: X-Y= $(CH_2)_2$
c: X-Y= $(CH_3)_3$
j: X-Y= no link

Scheme 1

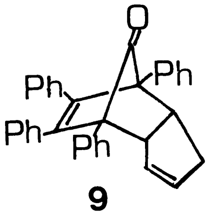
tetraphenyl derivative 9, upon heating in refluxing toluene, brought the retro-Diels-Alder reaction to give tetracyclone and cyclopentadiene instead of the Cope rearrangement.

Table 1 Rate Constant of the Cope Rearrangement

Compd	solvent	Temp, °C	10^4K, sec^{-1}
2a*	$Cl_2C=CCl_2$	90	4.0
2b	ethanol	120	0.72
2e	ethanol	120	18.1
4b	ethanol	80	6.49
4j	ethanol	80	2.46

* ref. 3

The effects of the bridge X-Y may be explained by the conformation of the dienones, i.e., the orientation of the two double bonds concerned. For example, the conformation of 2a and 4a is restricted to that of 10, which is the most favorable one for the Cope rearrangement. For other dienones, an equilibrium between two conformers A and B should be considered for the rearrangement, although the rearrangement occurs from conformer B but not from A. The typical example is shown in 11 for 2b and 4b, where two conformers A and B are in equilibrium.



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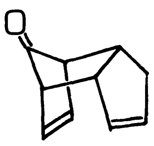

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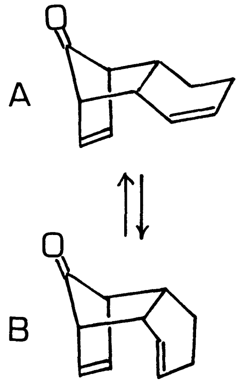

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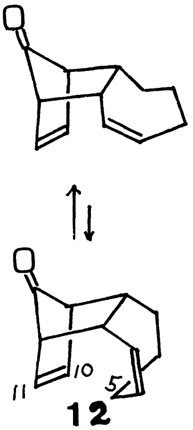

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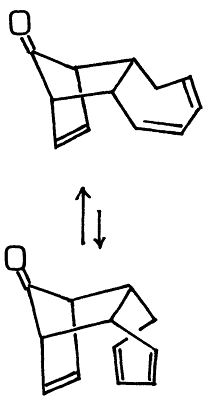

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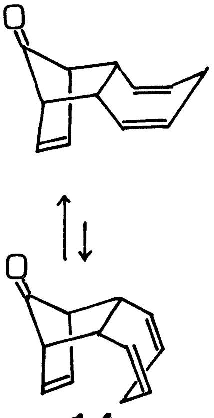

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Different from 11, however, in 12 for 2c and 4c the steric interference between the C_5-methylene protons and the π-orbital in the C_{10}-C_{11} double bond pushes its conformation to A. Thus, the orientation of the two double bonds in 12-A is unfavorable for the Cope rearrangement. The situation for 2d is considered to be similar to that for 2c. This is the reason for the low reactivity of 2c, 2d, and 4c which possess a three or four methylene bridge in the X-Y part. In contrast, the fact that the Cope rearrangement of 2e-i readily took place is rather surprising in light of the conformations of 13 for 2e and 2i and 14 for 2f, 2g, and 2h. The conformational analyses of such 5-7 fused ring systems have not been elucidated, but it is expected that the transition state for the Cope rearrangement is more conveniently attained in some ways by an additional double bond.

REFERENCE

1) Organic Thermal Reactions XLII. Part XLI, T. Toda, N. Shimazaki, and T. Mukai, submitted to J. Am. Chem. Soc.
2) T. Mukai, Y. Yamashita, H. Sukawa, and T. Tezuka, Chem. Lett., 423 (1975).
3) K.N. Houk and R.B. Woodward, J. Am. Chem. Soc., 92, 4143, and 4145 (1970).
4) K.N. Houk and L.J. Luskus, J. Org. Chem., 42, 4151 (1977).
5) Satisfactory elemental analyses were obtained for all new compounds.
6) R.C. Cookson, J. Hudec, and R.O. Williams, Tetrahedron Lett., 2621 (1970).

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