

INTRAMOLECULAR PHOTOCHEMICAL REACTIONS OF RIGID DIENONES. PREPARATION AND PHOTOLYSIS OF
 10-SUBSTITUTED TRICYCLO [5. 3. 1. 0^{2,6}] UNDECA-3,9-DIEN-8-ONES AND -4,9-DIEN-8-ONES

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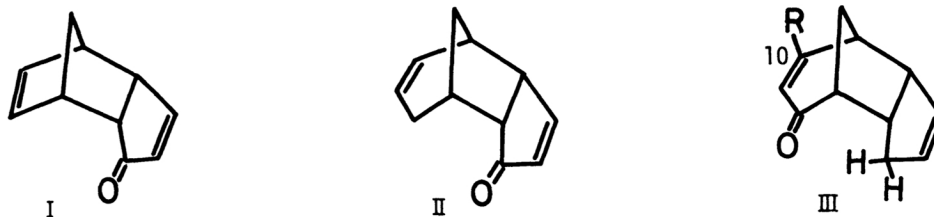
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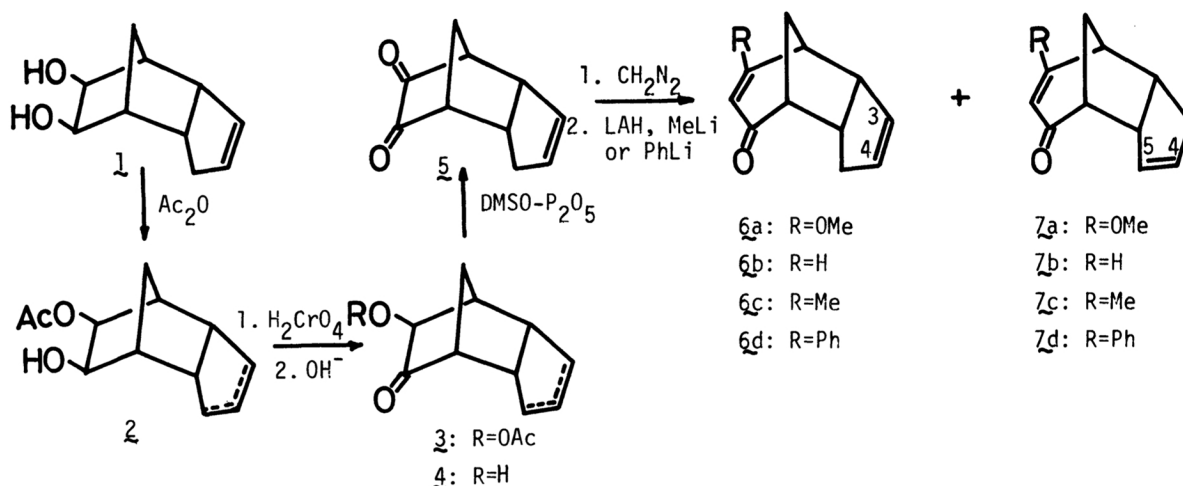
A series of the title compounds (R=OMe, H, Me, Ph) were prepared and photochemical behaviors of these compounds were examined. Although most of the substrates underwent intramolecular [2+2] cycloaddition to give novel trishomocubanes upon irradiation, the phenyl derivative of Δ^4 isomer gave a product via competing allylic hydrogen abstraction, as well as the cyclization product.

In view of the efficient construction of strained cage molecule and the solar energy storage, considerable interests have been focused on the photochemical [2+2] reaction of tricyclic bridged dienones such as the compound I.^{1,2} However there have been no photochemical studies on the homologous dienones II or III which have the novel structure carrying an allylic system facing to the conjugated enone moiety. These compounds are expected to undergo not only [2+2] cycloaddition to give novel trishomocubane frameworks but also competitive intramolecular hydrogen abstraction.

The present communication describes synthesis and photolysis of III variously substituted at β -carbon of the α,β -unsaturated enone (6a-d) and their isomers (7a-d).



The key compounds 6a and 7a were prepared by the following route.³ The diol 1 prepared from *endo*-dicyclopentadiene *via* the oxidation with KMnO_4 in non-aqueous dichloromethane solution⁴ was partially acetylated with Ac_2O at room temperature to give the monoacetate 2. Chromic acid oxidation of compound 2 followed by alkaline hydrolysis of the resulting ketoacetate 3 afforded the α -ketol 4 in 60 % overall yield from 1. Compound 4 was transformed into the α -diketone 5 by the reaction with DMSO at 80-90 °C in the presence of P_2O_5 in 56 % yield. Ring expansion and methylation of the resulting β -diketone occurred in one pot upon treatment of 5 with diazomethane in ether in the presence of a small amount of methanol to produce an isomeric mixture of 6a and 7a

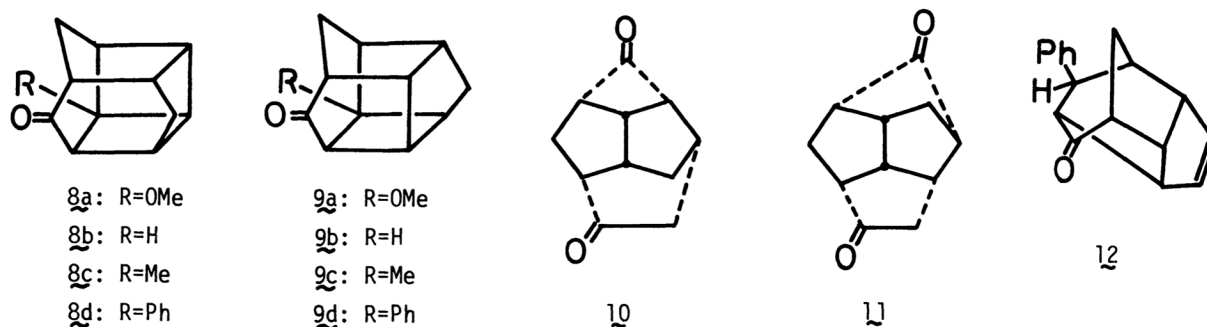


in a 6:4 ratio and these were chromatographically separated.⁵

Compound **6a** (R=OMe) was converted to **7b** (R=H), **7c** (R=Me), and **7d** (R=Ph) by reactions with LiAlH_4 , MeLi, and PhLi respectively, and in the same manner, compound **7a** (R=OMe) was converted to **6b** (R=H), **6c** (R=Me), and **6d** (R=Ph).³

Irradiation of compound **6a** in benzene in a Pyrex tube using a 500-W high pressure mercury lamp afforded the cage compound **8a** quantitatively, which was converted to **10**, a diketone of novel tetracyclic structure, *via* de Mayo reaction⁶ (treatment with hydrochloric acid in methanol at 50 °C). In the same manner, compound **7a** gave the unstable cage compound **9a**, which decomposed to the tetracyclic diketone **11** on standing in a refrigerator overnight. The structures of these compounds (**8a**, **9a**, **10**, **11**) were clearly differentiated from other isomers by their spectral data³ and consistent with the position of double bond of starting compounds (**6a**, **7a**) determined by NMR with a shift reagent.⁵

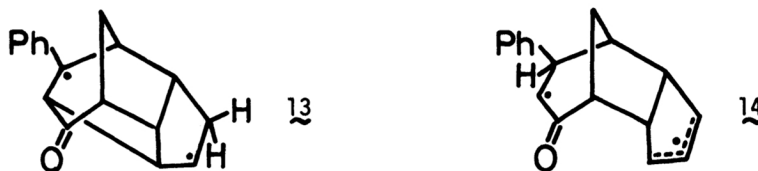
Irradiation of **6b-d** and **7b-c** all resulted in the quantitative formation of the corresponding stable cage compounds; **6b** → **8b**, **6c** → **8c**, **6d** → **8d**, **7b** → **9b**, **7c** → **9c**.³ The cage structures of **8b-d** and **9b-c** were supported especially by their mass spectra which are almost superimposable on those of the respective starting dienones.



More intriguing results were obtained with the irradiation of **7d**. Thus, the half cage compound **12** was produced *via* allylic hydrogen abstraction by β -carbon of α,β -unsaturated enone along with the trishomocubane **9d** *via* [2+2] cycloaddition (**9d**:**12**=4:1).

Several examples of the enone photoreactions which involve intramolecular allylic or benzylic hydrogen abstraction by β -carbon are now documented.⁷ However, a few examples of the reaction in which hydrogen abstraction occurred at β -carbon in competition with intramolecular photocycloaddition to the isolated double bond are known with citral⁸ and related compounds.⁹ We are not aware of any other example of this type of reaction with rigid system.¹⁰

Of the two possible biradical intermediates **13** and **14**, **13** (probably in common with the formation of **9d**) seems to be more attractive for the formation of **12**, since stabilization by the phenyl group accounts for the fact that only **7d** gave the hydrogen transfer product. This is compatible with the proposed mechanism for the photoreaction of citral.⁸ Further studies are in progress directed toward clarification of the mechanistic aspect of this reaction.



This work was supported, in part, by grant-in-aid from the Ministry of Education, Science and Culture (No. 56540295).

References

1. R. C. Cookson, J. Hudec and R. O. Williams, *Tetrahedron Lett.*, 29 (1960); *J. Chem. Soc. (C)*, 1382 (1967).
2. G. Jones, II and B. R. Ramachandran, *J. Org. Chem.*, 41, 798 (1976).
3. Physical properties for isolated new compounds.
 - 5**: IR (CHCl₃) 1770, 1750 cm⁻¹; ¹H NMR (CCl₄) δ 5.53 (2H, br s); UV (EtOH) λ^{\max} 263 (ϵ =141), 475 (ϵ =24) nm; M⁺ m/e 162; mp 58-60 °C.
 - 6a**: IR (CHCl₃) 1640, 1600 cm⁻¹; ¹H NMR (CDCl₃) δ 3.53 (3H, s), 4.93 (1H, s), 5.50 (1H, m); UV (EtOH) λ^{\max} 254 (ϵ =9300) nm; M⁺ m/e 190.0983 (Calcd for C₁₂H₁₄O₂: 190.0993); mp 62-65 °C.
 - 7a**: IR (CHCl₃) 1640, 1600 cm⁻¹; ¹H NMR (CDCl₃) δ 3.64 (3H, s), 4.91 (1H, s), 5.48 (2H, s); UV (EtOH) λ^{\max} 254 (ϵ =12900) nm; M⁺ m/e 190.0997 (Calcd for C₁₂H₁₄O₂: 190.0993).
 - 6b**: IR (CHCl₃) 1665 cm⁻¹; ¹H NMR (CDCl₃) δ 5.56 (2H, br s), 5.90 (1H, d, J=10 Hz), 6.93 (1H, dd, J=10, 7 Hz); UV (EtOH) λ^{\max} 230 (ϵ =4860) nm; M⁺ m/e 160.
 - 7b**: IR (CHCl₃) 1665 cm⁻¹; ¹H NMR (CDCl₃) δ 5.55 (2H, br s), 5.83 (1H, dd, J=10, 2 Hz), 7.10 (1H, br t, J=8 Hz); UV (EtOH) λ^{\max} 236 (ϵ =5800) nm; M⁺ m/e 160; mp 40-45 °C.
 - 6c**: IR (CHCl₃) 1655, 1620 cm⁻¹; ¹H NMR (CDCl₃) δ 1.83 (3H, s), 5.53 (2H, br s), 5.68 (1H, br s); UV (EtOH) λ^{\max} 238 (ϵ =7950) nm; M⁺ m/e 174; mp 42-45 °C.
 - 7c**: IR (CHCl₃) 1655, 1620 cm⁻¹; ¹H NMR (CDCl₃) δ 2.02 (3H, s), 5.55 (2H, br s), 5.65 (1H, br s); UV (EtOH) λ^{\max} 237 (ϵ =7300) nm; M⁺ m/e 174.

6d: IR (CHCl₃) 1655, 1600 cm⁻¹; ¹H NMR (CDCl₃) δ 5.43 (2H, m), 6.22 (1H, s), 7.42 (5H, br s); UV (EtOH) λ^{max} 222 (ε=7530), 290 (ε=13800) nm; M⁺ m/e 236; mp 98-100 °C.

7d: IR (CHCl₃) 1655, 1600 cm⁻¹; ¹H NMR (CDCl₃) δ 5.57 (2H, br s), 6.20 (1H, s), 7.43 (5H, br s); UV (EtOH) λ^{max} 222 (ε=9540), 290 (ε=15800) nm; M⁺ m/e 236.1243 (Calcd for C₁₇H₁₆O: 236.1201); mp 68-71 °C.

8a: IR (CHCl₃) 1700 cm⁻¹; ¹H NMR (CDCl₃) δ 3.20 (3H, s).

9a: IR (CHCl₃) 1730-1700 cm⁻¹ (br); ¹H NMR (CDCl₃) δ 3.50 (3H, s).

8b: IR (CHCl₃) 1695 cm⁻¹; M⁺ m/e 160.

9b: IR (CHCl₃) 1720 cm⁻¹; M⁺ m/e 160; mp 116-118 °C.

8c: IR (CHCl₃) 1685 cm⁻¹; ¹H NMR (CDCl₃) δ 1.17 (3H, s); M⁺ m/e 174.

9c: IR (CHCl₃) 1710 cm⁻¹; ¹H NMR (CDCl₃) δ 1.10 (3H, s); M⁺ m/e 174.

8d: IR (CHCl₃) 1700 cm⁻¹; ¹H NMR (CDCl₃) δ 7.25 (5H, m); M⁺ m/e 236.

9d: IR (CHCl₃) 1725 cm⁻¹; ¹H NMR (CDCl₃) δ 7.25 (5H, m); M⁺ m/e 236.1221 (Calcd for C₁₇H₁₆O: 236.1201).

10: IR (CHCl₃) 1765, 1700 cm⁻¹; M⁺ m/e 176.0838 (Calcd for C₁₁H₁₂O₂: 176.0837); mp 64-67 °C.

11: IR (CHCl₃) 1730 cm⁻¹; M⁺ m/e 176.0868 (Calcd for C₁₁H₁₂O₂: 176.0837); mp 115-120 °C.

12: IR (CHCl₃) 1735 cm⁻¹; ¹H NMR (CDCl₃) δ 5.83 (1H, dd, J=6, 2.5 Hz), 6.33 (1H, dd, J=6, 2.5 Hz), 7.27 (5H, br s); M⁺ m/e 236.1201 (Calcd for C₁₇H₁₆O: 236.1201).

4. T. Ogino and K. Mochizuki, *Chem. Lett.*, **1979**, 443; T. Ogino, *Tetrahedron Lett.*, **21**, 177 (1980).

5. Position of the double bonds in the five membered ring of 6a and 7a was established by NMR using Eu(dpm)₃ as shift reagent (Table below). Unusual large shift observed with C₅-H in the

Table: Change in the chemical shift (ppm/mole).

	<u>6a</u>		<u>7a</u>	
	C ₃ -H	C ₄ -H	C ₄ -H	C ₅ -H
Δδ/Eu(ppm) ₃	0.014	0.014	0.020	0.051

compound 7a may be attributed to the proximity of this hydrogen to the carbonyl group.

6. P. de Mayo and H. Takeshita, *Can. J. Chem.*, **41**, 440 (1963); B. D. Challand, H. Hikino, G. Kornis, G. Lange, and P. de Mayo, *J. Org. Chem.*, **34**, 794 (1964).
7. See, for example, Y. Tamura, H. Ishibashi, and M. Ikeda, *J. Org. Chem.*, **41**, 1277 (1976); F. M. Schell and P. M. Cook, *J. Org. Chem.*, **43**, 4420 (1978); S. Wolff, W. L. Schreiber, A. B. Smith, III, and W. C. Agosta, *J. Am. Chem. Soc.*, **94**, 7797 (1972); A. B. Smith, III, and W. C. Agosta, *J. Am. Chem. Soc.*, **95**, 1961 (1973); M. Tada, H. Saiki, H. Mizutani, and K. Miura, *Bull. Chem. Soc. Jpn.*, **51**, 343 (1978); M. Tada, T. Maeda, and H. Saiki, *Bull. Chem. Soc. Jpn.*, **51**, 1516 (1978).
8. R. C. Cookson, J. Hudec, S. A. Knight, and B. R. D. Whitear, *Tetrahedron*, **19**, 1955 (1963); G. Büchi and H. Wüest, *J. Am. Chem. Soc.*, **87**, 1589 (1965); F. Barany, S. Wolff, and W. C. Agosta, *J. Am. Chem. Soc.*, **100**, 1946 (1978).
9. M. Yoshioka, K. Ishii, and H. R. Wolf, *Helv. Chim. Acta*, **63**, 571 (1980); S. Wolff, F. Barany, and W. C. Agosta, *J. Am. Chem. Soc.*, **102**, 2378 (1980).
10. An example of photochemical hydrogen abstraction by the β-carbon atom of enone in rigid system was reported by Herz and co-workers, see W. Herz and M. G. Nair, *J. Am. Chem. Soc.*, **89**, 5474 (1967). See also, W. Herz and V. S. Iyer, *J. Org. Chem.*, **42**, 1573 (1977), and references cited therein.

(Received March 31, 1982)