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PREFERENTIAL PHOTOCHEMICAL CYCLOBUTANE-RING FORMATIONS OF 2-CYCLOHEXENE-1,4-DIONE WITH OLEFINS AND ACETYLENES. A SIMPLE AND GENERAL SYNTHESIS OF BICYCLO[4.2.0]OCTANE-2,5-DIONES

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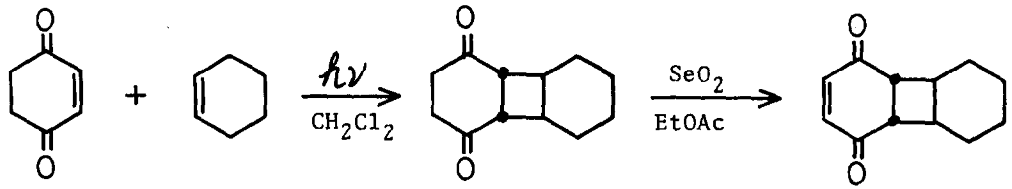
Although photochemical [2+2] cycloadditions of α,β-unsaturated ketones with carbon-carbon multiple bonds have been extensively studied and applied to organic syntheses,1) much fewer [2+2] cycloadditions of 2-ene-1,4-diones have been described.2-6) Differing from α,β-unsaturated ketones, 2-ene-1,4-diones tend to form oxetanes (or oxetene-derived products with acetylenes) depending on their structures, which has limited their application to organic syntheses. In search of a new and practical synthetic way of bicyclo[4.2.0]octane-2,5-diones as a part of our study on eight-membered ring compounds, we examined photoreactions of 2-cyclohexene-1,4-dione 1 7) and found that 1 underwent [2+2] cycloadditions exclusively or predominantly with varieties of olefins and acetylenes, fulfilling our need. The compound 1 can be readily prepared from p-quinone in three steps according to the procedure of Chapman et al.8) (60-65% improved total yield at 1.5 mol scale in our hand). Although 1, which is the keto-form of hydroquinone, is extremely sensitive to acids and bases, it is susceptible of intramolecular photoreactions in neutral aprotic solvents.

Irradiations of a solution of 1 (10 mmol) and cyclohexene (20 mmol) in dichloromethane (100 ml) through a water-cooled pyrex probe using a 100 W high pressure Hg lamp for 2 hr gave a [2+2] adduct in 72% yield along with a small amount of hydroquinone. No oxetane formation was observed. A similar result (73% yield) was obtained in acetonitrile. In ether, however, the yield of 2 was only 20%, though again no oxetane was formed. The stereochemistry of the adduct 2 was assigned to be cis-anti-cis from the following observation and remark: (i) selenium dioxide oxidation of 2 in refluxing ethyl acetate gave the corresponding ene-dione 3 9) (95%) in which more informative PMR spectrum C-2 and C-7 protons appear as a doublet of J=4.5 Hz, indicating a cis-cis configuration; (ii) though the coupling constant between the cyclobutane-ring protons does not tell about the syn-anti problem, photo-dimerizations and -cycloadditions of cyclopentenone and cyclohexenone have been revealed to yield anti adducts exclusively or most predominantly in accordance with stereochemical point of view.1)



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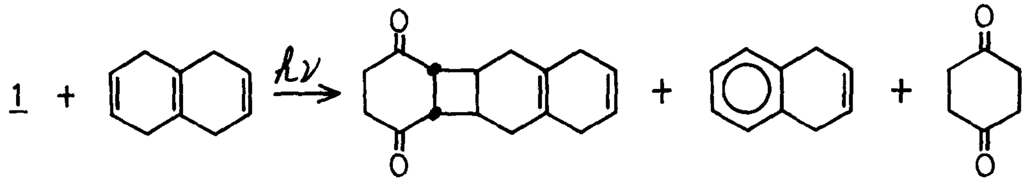
The results obtained with varieties of olefins and acetylenes are listed in Table I in which the yields of oxetanes are not included on account of lack of space. While 2-butenes and tetramethylethylene yielded a small and an appreciable amount of oxetanes (3% and 30%, respectively)$^{10)}$, the others did no trace or only a trace of oxetanes or oxetene-derived compounds. Both Z- and E-2-butene gave a mixture of exo-cis and trans [2+2] adducts in almost the same composition of 55:45 (GLC), indicating an intermediacy of an 1,4-diradical and hence triplet nature of the photo-excited reactive species. Cyclooctene, of which trans [2+2] adduct is much less strained than those of cyclopentene and cyclohexene, also gave a 5:4 mixture of cis-anti-cis and cis-trans adducts.$^{11)}$

When 1,4,6,8-tetrahydronaphthalene, which is composed of two disubstituted double bonds and a tetrasubstituted double bond, was used as an olefin, 1,4-dihydronaphthalene (42%), cyclohexane-1,4-dione (37%), and hydroquinone (9%) were obtained in addition to the [2+2] adduct at the disubstituted double bond, 4 (45%)$^{12)}$. The reaction, in this case, apparently involves an oxidation-reduction process as a side path.



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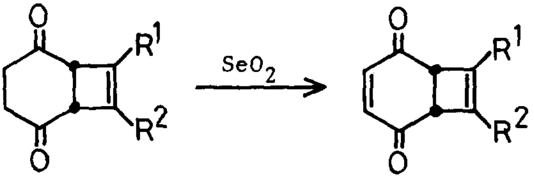
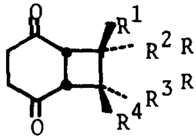
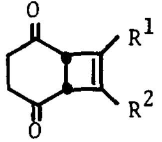
The exclusive [2+2] cycloadditions of 1 with acetylenes provide a simple and practical syntheses of bicyclo[4.2.0]octa-3,7-diene-2,5-diones 5$^{4,13)}$, since the adducts were readily dehydrogenated by selenium dioxide in refluxing ethyl acetate.



5a: $R^1=R^2=H$; 75%
5b: $R^1=Ph$, $R^2=H$; 83%
5c: $R^1=R^2=Ph$; 91%

Since the [2+2] adducts of 1 are convertible not only into the corresponding 2-ene-1,4-diones as described above but also into bicyclo[4.2.0]octa-2,4-dienes (or cyclooctatrienes as their valence isomers), benzocyclobutenes by dehydrogenation of the dienes, and cyclooctatetraenes, the present simple synthesis of the diones would provide a synthetic method for such classes of compounds.$^{14)}$

Table I. Photoadditions of 2-cyclohexene-1,4-dione with olefins and acetylenes[a)]

Olefins and acetylenes	[2+2] Adducts	Yield %	M.p.(b.p.) °C	PMR data, δ ppm (CCl_4)
ethylene[b)]	 $R^1=R^2=R^3=R^4=H$	80	(83/0.7 torr)	2.33(4H,m), 2.77(4H,s) 3.28(2H,m)
Z- or E-2-butene[c)]	$R^1=R^4=Me$, $R^2=R^3=H$	50	(oil)	15)
	$R^1=R^3=Me$, $R^2=R^4=H$	41	(oil)	
tetramethyl-ethylene	$R^1=R^2=R^3=R^4=Me$ d)	40	(oil)	16)
styrene	$R^1=Ph$, $R^2=R^3=R^4=H$ 17)	64	64-65	2.4-4.0(9H,m; s at 2.83), 7.2(5H,br s)
	$R^2=Ph$, $R^1=R^3=R^4=H$	8	77-78	2.0-4.2(9H,m), 7.2 (5H,m)
cyclopentene	$-R^1-R^4-=-(CH_2)_3-$ $R^2=R^3=H$	64	82-83	1.5-2.1(6H,m), 2.6-3.1(8H,m)
cyclohexene	$-R^1-R^4-=-(CH_2)_3-$ $R^2=R^3=H$	72	71-72	1.2-2.0(8H,m), 2.5-3.0(6H,m), 3.10(2H, br d, J=4 Hz)
1,4-cyclo-hexadiene	$-R^1-R^4-=-CH_2CH=CHCH_2-$ $R^2=R^3=H$	76	79-80	2.17(4H,br s), 2.85 (8H,d-like), 6.05 (2H,t,2 Hz)
cyclooctene	$-R^1-R^4-=-(CH_2)_6-$ $R^2=R^3=H$	30	57-59	1.0-2.1(12H,m) 2.1-3.2(8H,m)
	$-R^1-R^3-=-(CH_2)_6-$ $R^2=R^4=H$	24	82-83	0.8-2.1(12H,m) 2.1-3.3(8H,m)
acetylene[b)]	 $R^1=R^2=H$	40 ~ 55	(86/1.5 torr)	15)
methyl-acetylene[c)]	$R^1=Me$, $R^2=H$	64	(82/0.5 torr)	1.82(3H,d,1 Hz), 2.3-3.3(4H,m), 3.53(2H,s), 5.93(1H,br s)
phenyl-acetylene	$R^1=Ph$, $R^2=H$	50	97-98	2.2-3.3(4H,m), 3.71(1H, dd,4.0,1.5 Hz), 4.07 (1H,d,4.0), 6.53(1H,d, 1.5), 7.2-7.7(5H,m)
diphenyl-acetylene	$R^1=R^2=Ph$	61	133-134	2.4-3.3(4H,m), 4.05(2H, s), 7.2-7.7(10H,m)

a) CH_2Cl_2 was used as the solvent, and irradiations were performed at room temperature for 2-5 hr using 2 equiv. of the substrates unless noted. b) These gaseous compounds were constantly introduced into the solutions during the irradiations at ice-bath temperature. c) These low boiling point compounds were used in an excess at ice-bath temperature. d) 3:2 cis and trans mixture.

REFERENCES AND NOTES

1) P. E. Eaton, Accounts Chem. Res., 1, 50 (1968); P. G. Sammes, Quart. Rev., 24, 37 (1970); P. de Mayo, Accounts Chem. Res., 4, 41 (1971).

2) R. C. Cookson, E. Grundwell, R. R. Hill, and J. Hudic, J. Chem. Soc., 3062 (1964); D. Valentine and G. S. Hammond, J. Amer. Chem. Soc., 86, 5202 (1964); P. E. Eaton and S. A. Cerefice, Chem. Commun., 1494 (1970).

3) Z. Yoshida, M. Kimura, and S. Yoneda, Chemistry Lett., 519 (1975).

4) P. Yates and G. V. Nair, Synthetic Commun., 3, 337 (1973).

5) M. Oda, H. Oikawa, N. Fukazawa, and Y. Kitahara, Tetrahedron Lett., 4409, (1977).

6) Z. Yoshida, M. Kimura, and S. Yoneda, Tetrahedron Lett., 2519 (1974).

7) E. W. Garbish, Jr., J. Amer. Chem. Soc., 87, 4971 (1965).

8) D. D. Chapman, W. J. Musliner, and J. W. Gates, J. Chem. Soc. (C), 124 (1969)

9) ν 1675, 1605 cm^{-1}; δ (CCl_4) 1.48 (8H, m), 2.63 (2H, m), 3.15 (2H, d, J=4.5 Hz), 6.72 (2H, s).

10) The stereochemistry of these adducts were deduced from the PMR spectra of their ene-diones obtained by selenium dioxide oxidation.

Cis-anti-cis: m.p. 69-70°C; δ (CCl_4) 0.9-2.1 (12H, m), 2.5 (2H, m), 2.82 (2H, d, J=3 Hz), 6.65 (2H, s).

Cis-trans: m.p. 102-103°C; δ (CCl_4) 0.9-2.1 (12H, m), 2.15-3.1 (3H, m), 3.35 (1H, dd, 10, 7 Hz), 6.73 (2H, s).

11) ν 1680 cm^{-1}; δ (CCl_4) 1.1-1.6 (12H, methyls), 2.0-2.8 (4H, m), 5.92 (1H, d, J=10.0 Hz), 7.20 (1H, d, 10.0).

12) M.p.79-80°C; ν 1710 cm^{-1}; δ (CCl_4) 2.0 (4H, m), 2.4-3.0 (12H, m), 5.70 (2H,s)

13) M. Oda, Y. Kayama, and Y. Kitahara, Tetrahedron Lett., 2019 (1974).

14) These transformations will be described elsewhere.

15) G. A. Russell, J. R. Dodd, T. Ku. C. Tanger, and C. S. C. Chung, J. Amer. Chem. Soc., 96, 7255 (1974).

16) Cis: δ (CCl_4) 0.98 (6H, s), 1.15 (6H, s), 2.62 (4H, s), 2.87 (2H, s).

Trans: δ (CCl_4) 1.02 (6H, s), 1.15 (6H, s), 2.48 (4H, br. s), 2.74 (2H, s).

When treated with basic alumina, the trans isomer isomerized to the cis one.

17) The stereochemistry of these adducts were deduced from the PMR spectra of their ene-diones obtained by selenium dioxide oxidation.

Exo: oil; δ (CCl_4) 2.65 (2H, m), 2.8-4.1 (3H, m), 6.71 (2H, s), 7.23 (5H, br. s).

Endo: m.p. 105-106°C; δ ($CDCl_3$) 2.87 (2H, m), 3.1-4.3 (3H, m), 6.50 (1H, d, J=10.0 Hz), 6.75 (1H, d, 10.0), 7.2 (5H, m).

The greater non-equivalency of the olefin protons of the latter compound suggests their proximity to the phenyl group.

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