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The Photochemistry of Large-ring Cycloalkanones[1]

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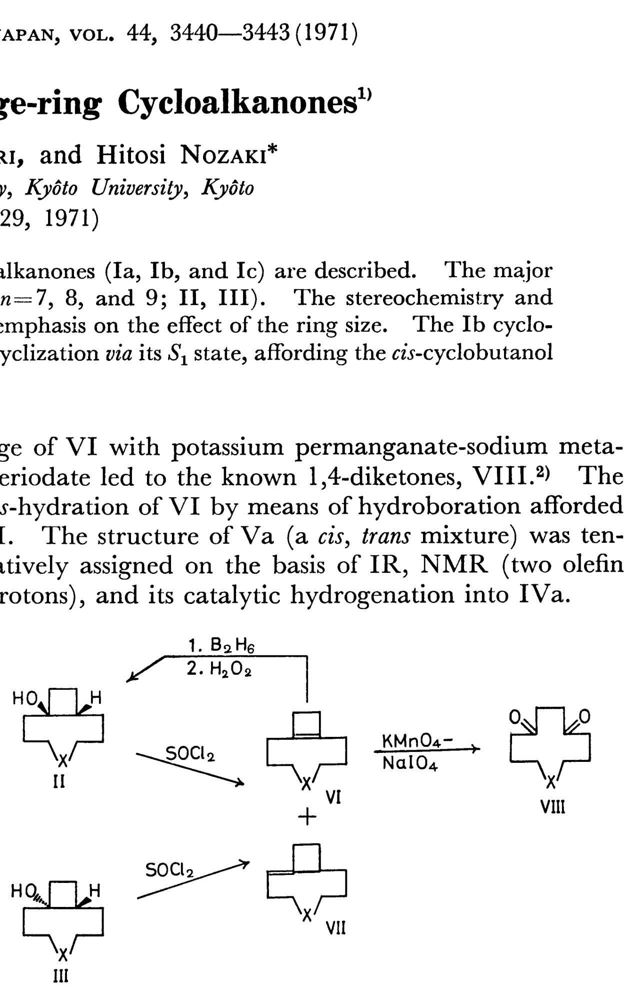
The photoreactions of 11-, 12-, and 13-membered cycloalkanones (Ia, Ib, and Ic) are described. The major products are *cis*, *trans* isomers of bicyclo[*n*.2.0]alkan-1-ol ($n=7$, 8, and 9; II, III). The stereochemistry and multiplicity of the reactive species have been discussed with emphasis on the effect of the ring size. The Ib cyclododecanone is most readily susceptible to the photochemical cyclization *via* its S_1 state, affording the *cis*-cyclobutanol IIb stereoselectively.

The interest in the effect of the ring size upon transannular reactivity as well as in the syntheses of 1,4-cycloalkanedione[2] prompted the present authors to investigate the photoreactions of 11-, 12-, and 13-membered cycloalkanones; we have found a remarkable influence of the ring size upon the behavior of the reactive photoexcited species. As is known already, the irradiation of cyclodecanone gives 9-hydroxydecalin or bicyclo-[4.4.0]decan-1-ol,[3] whereas that of cyclododecanone affords bicyclo[8.2.0]dodecan-1-ol.[4] We first wanted to learn further details on the photoreaction of cyclododecanone (Ib), including its stereochemistry,[5] and then we proceeded to examine a borderline case, the reaction of cycloundecanone (Ia) and cyclotridecanone (Ic). We obtained the results summarized in Table 1.

The structures of the II and III cyclobutanols were determined to be as shown in Scheme 1. The dehydration of both II and III with thionyl chloride gave a mixture of olefins, VI and VII. The oxidative cleavage of VI with potassium permanganate-sodium metaperiodate led to the known 1,4-diketones, VIII.[2] The *cis*-hydration of VI by means of hydroboration afforded II. The structure of Va (a *cis*, *trans* mixture) was tentatively assigned on the basis of IR, NMR (two olefin protons), and its catalytic hydrogenation into IVa.



Scheme 1

The cyclobutanol formation was commonly observed in the irradiation of three ketones, Ia, Ib, and Ic, and no other bicyclic product was isolated. However, the reactivity of each ketone was strongly controlled by the ring size, as may be summarized as follows: (1) In a qualitative sense, the reaction of Ib proceeded most rapidly. (2) This ketone, Ib, afforded the best yield of the cyclobutanol derivatives, IIb and IIIb. (3) The highest *cis*/*trans* ratio (II/III) was observed with Ib; the next, with cycloundecanone (Ia), and the lowest,

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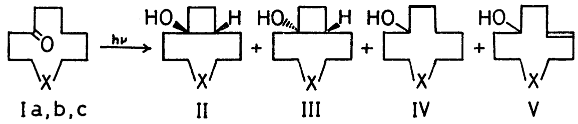
[1] A part of this work has been described in a preliminary communication: T. Mori, K. Matsui, and H. Nozaki, *Tetrahedron Letters*, **1970**, 1175.

[2] T. Mori, K. Matsui, and H. Nozaki, This Bulletin, **43**, 231 (1970).

[3] M. Barnard and N. C. Yang, *Proc. Chem. Soc.*, **1958**, 302.

[4] a) B. Camerino and B. Patelli, *Experientia*, **20**, 260 (1964). b) K. H. Schulte-Elte and G. Ohloff, *Chmia*, **18**, 183 (1964).

[5] The stereochemical aspect of the photochemical cyclization of $\mathrm{I_b}$ was briefly descrived by Schulte-Elts (Ref. 3b) in a footnote, with no experimental details. No further report has yet appeared.



a: $X=CH_2$, b: $X=CH_2CH_2$, c: $X=CH_2CH_2CH_2$

TABLE 1. THE PHOTOLYSIS OF CYCLOUNDECANONE (I_a), CYCLODODECANONE (I_b), AND CYCLOTRIDECANONE (I_c)

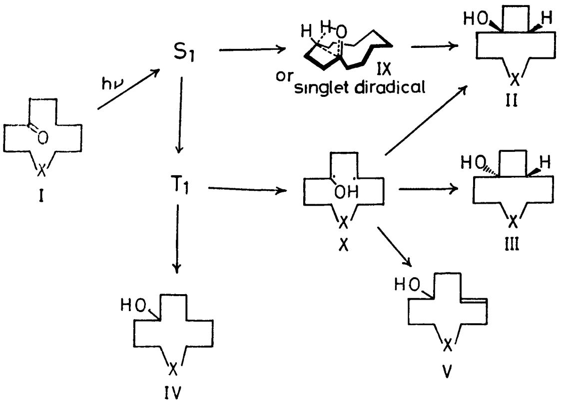
	Solvent	Irradiation time (hr)	Recovered I (%)	Product yields (%)				
				II	III	IV	V	unidentified
I_a	benzene	48	8	45	13	trace	8	4
	cyclohexane	48	5	34	9	7	5	3
	2-propanol	48	7	19	8	26	trace	3
	piperylene	144	69	0	0	0	0	trace
I_b	benzene	25	0	70	6	0	0	1
	cyclohexane	8	0	75	12	trace	0	1
	2-propanol	10	0	67	7	12	0	0
	piperylene	119	0	55	0	0	0	trace
I_c	benzene	48	8	36	19	trace[a]		3
	cyclohexane	48	8	37	20	trace[a]		3
	2-propanol	48	8	30	20	3[a]		2
	piperylene	130	21	38	0	0		trace

a) Identification could not be effected because of the small amounts obtained.

with cyclotridecanone (Ic). (4) Cycloundecanone (Ia) was most susceptible to photoreduction to IVa. (5) Only Ia gave unsaturated alcohol, Va.

The presence of piperylene as a triplet quencher drastically reduced the reaction rates. Remarkably, the single product from Ib was, stereoselectively, *cis*-cyclobutanol IIb when the starting material had completely disappeared. Under the same conditions, Ic gave IIc as a sole product; here the reaction proceeded rather sluggishly. In contrast, Ia afforded none of the products, IIa—Va, and decomposed slowly into a tarry product after prolonged irradiation in a piperylene solution.

The photochemical cyclization of open-chain ketones has been the subject of previous investigation,[6] and mechanisms have been discussed by Jeger,[7] Yang,[8] and their co-workers. Some possible explanations of the present case are shown in Scheme 2.



Scheme 2

The stereoselective formation of the *cis*-cyclobutanols, IIb and IIc, on the quenching of Ib (T_1) and Ic (T_1) might be explained by assuming the concerted cyclization of Ib (S_1) and Ic (S_1) through a transition state such as IX or, alternatively, through a singlet diradical intermediate of a similar geometry. The direct cyclization from Ia (S_1) must be conformationally much less favored, as is evident on an inspection of the model. In this case, therefore, Ia (T_1) is the sole active species undergoing transannular cyclization. The cyclotridecanone, Ic, appears to be least porne to cyclization, possibly for conformational reasons.

The selective formation of the IIc *cis*-cyclobutanol under the condition of triplet-quenching may be explained in terms much like those used to explain the IIb formation. The lowest ratio of IIc/IIIc in other solvents indicates that Ic (T_1) is the more important species of the photocyclization in such solvents.

We may conclude that the product distributions are strongly controlled by the transannular proximity of the excited carbonyl group and the reacting methylene proton, which depends on the conformation of the respective ring and, therefore, on the presence or absence of an additional methylene in the long undecamethylene group of Ib. The cyclization of Ib is characterized by the fact that the greatest contribution to the ring closure is made by the excited singlet (S_1). This is in sharp contrast with the open-chain case of ketones and also with 11- and 13-membered cycloalkanones (Ia, Ic).

Experimental

All the temperatures are uncorrected. The NMR spectra were obtained on a JOEL C-60-H spectrometer in CCl_4 solutions, with tetramethylsilane as the internal reference. Chemical shifts are given in ppm from this reference, with a multiplicity of signals in an abbreviated form. The glc

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6) D. R. Coulson and N. C. Yang, *J. Amer. Chem. Soc.*, **88**, 4511 (1966), and the references cited there.

7) I. Orban, K. Schaffner, and O. Jeger, *ibid.*, **85**, 3033(1963).

8) N. C. Yang, S. P. Elliot, and B. Kim, *ibid.*, **91**, 7551 (1969).

was performed on HVSG on Chromosorb W, with nitrogen as the carrier gas. The tlc was conducted on Silica-gel G, with *n*-hexane or benzene as the developing solvent. The product yields were calculated on the basis of the peak areas of glc.

Photoreaction of Cycloalkanones (Ia—c). General Procedure: A solution of I (1.00 mmol) in a purified and degassed solvent (20 m*l*) was placed in a Pyrex tube (25 mm in diameter) and covered with nitrogen. Irradiation was effected externally with a high-pressure mercury lamp (200 W). The solution was then evaporated, and the residual oil was distilled. The products were effectively separated from each other by preparative tlc, using benzene or a mixed solvent of *n*-hexane and ether (10: 1) as the eluant. *cis*-Cyclobutanols (II) were more polar than *trans*-isomers (III) on tlc. Monocyclic alcohols (IV, V) were more polar than II and III. Each product was purified by recrystallization or by distillation.

cis-*Bicyclo*[*7.2.0*]*undecan-1-ol (IIa).* Separation and distillation gave IIa as a colorless solid; mp 42—43°C. IR (Nujol): 3350 cm^{-1} (OH). NMR δ: 1.05—2.60 (m, 19H), 2.75 (s, 1H). Found: C, 78.8; H, 11.8%. Calcd for $C_{11}H_{20}O$: C, 78.5; H, 12.0%.

trans-*Bicyclo*[*7.2.0*]*undecan-1-ol (IIIa).* The IIIa *trans*-isomer formed a colorless oil. IR (neat): 3470 cm^{-1} (OH). NMR δ: 1.05—2.30 (m, 19H), 2.30—2.80 (m, 1H). Found: C, 78.8; H, 11.7%. Calcd for $C_{11}H_{20}O$: C, 78.5; H, 12.0%.

cis-*Bicyclo*[*8.2.0*]*dodecan-1-ol (IIb).* A work-up gave IIb as a colorless solid; mp 47—49°C (lit,[4b] mp 48—49°C). IR (Nujol): 3380 cm^{-1} (OH). NMR δ: 1.05—1.70 (m, 16H), 1.70—2.10 (m, 4H), 2.10—2.70 (m, 1H), 2.27 (s, 1H, OH).

trans-*Bicyclo*[*8.2.0*]*dodecan-1-ol (IIIb).* The IIIb *trans*-isomer was isolated as a colorless oil. IR (neat): 3470 cm^{-1} (OH). NMR δ: 1.05—1.70 (m, 16H), 1.69 (s, 1H, OH), 1.70—2.20 (m, 4H), 2.20—2.75 (m, 1H).

cis-*Bicyclo*[*9.2.0*]*tridecan-1-ol (IIc).* The IIc *cis*-alcohol formed a colorless solid; mp 45—47°C. IR (Nujol): 3400 cm^{-1} (OH). NMR δ: 0.75—2.30 (m, 23H), 2.74 (s, 1H, OH). Found: C, 79.5; H, 12.5%. Calcd for $C_{13}H_{24}O$: C, 79.5; H, 12.3%.

trans-*Bicyclo*[*9.2.0*]*tridecan-1-ol (IIIc).* The IIIc *trans*-alcohol was a colorless oil. IR (neat): 3460 cm^{-1} (OH). NMR δ: 1.05—2.15 (m, 23H), 2.10—2.65 (m, 1H). Found: C, 79.7; H, 12.3%. Calcd for $C_{13}H_{24}O$: C, 79.5; H, 12.3%.

Dehydration of II and III. General Procedure:[9] A solution of II or III (2.75 mmol) in dry ether (2.00 m*l*) was stirred, drop by drop, into a solution of thionyl chloride (0.40 m*l*) and pyridine (1.00 m*l*) in dry ether (2.00 m*l*) at 3—5°C. After the reaction had subsided (*ca.* 2 hr), the mixture was poured into ice water and extracted with *n*-hexane. The combined extracts were washed once with water, once with aqueous sodium bicarbonate, and twice more with water. Distillation afforded a mixture of *cis* and *trans* olefins, which were separated by preparative glc (HVSG 2 m, helium).

$\Delta^{1(9)}$-*Bicyclo*[*7.2.0*]*undecene (VIa).* Separation and distillation gave VIa as a colorless oil in a 31% yield. IR (neat): 1450, 877 cm^{-1}. NMR δ: 0.65—2.65 (m, 14H), 2.68 (s, 4H). Found: C, 87.4; H, 12.2%. Calcd for $C_{11}H_{18}$: C, 87.9; H, 12.1%.

Bicyclo[*7.2.0*]*undec-1-ene (VIIa).* A work-up gave VIIa as a colorless oil in a 25% yield. IR (neat): 1475, 1450, 869, 792 cm^{-1}. NMR δ: 0.70—2.95 (m, 17H), 4.80—6.15 (m, 1H). Found: C, 87.5; H, 12.2%. Calcd for $C_{11}H_{18}$: C, 87.9; H, 12.1%.

$\Delta^{1(10)}$-*Bicyclo*[*8.2.0*]*dodecene (VIb).* The VIb olefin was a colorless oil (35% yield). IR (neat): 1465, 1442, 882 cm^{-1}. NMR δ: 1.25—1.85 (m, 12H), 1.95—2.20 (m, 4H), 2.26 (s, 4H). Found: C, 88.0; H, 11.8%. Calcd for $C_{12}H_{20}$,: C, 87.8; H, 12.2%.

Bicyclo[*8.2.0*]*dodec-1-ene (VIIb).* The VIIb isomer was a colorless oil (28% yield). IR (neat): 1470, 1440, 887, 858, 750, 700 cm^{-1}. NMR δ: 1.15—2.70 (m, 18H), 3.10—3.45 (m, 1H), 4.75—5.15 (m, 1H). Found: C, 87.8; H, 11.9%. Calcd for $C_{12}H_{20}$: C, 87.8; H, 12.2%.

$\Delta^{1(11)}$-*Bicyclo*[*9.2.0*]*tridec-1-ene (VIc).* This olefin, VIc, was a colorless oil (33% yiled). IR (neat): 1470, 1447, 890, 862, 810, 788 cm^{-1}. NMR δ: 1.15—1.90 (m, 14H), 1.90—2.50 (m, 4H), 2.46 (s, 4H). Found: C, 88.1; H, 12.8%. Calcd for $C_{13}H_{22}$: C, 87.6; H, 12.4%.

Bicyclo[*9.2.0*]*tridec-1-ene (VIIc).* The VIIc isomer was a colorless oil (27% yield). IR (neat): 1462, 1448, 1010, 970, 887 cm^{-1}. NMR δ: 1.10—2.80 (m, 21H), 4.75—5.15 (m, 1H). Found: C, 88.1; H, 12.7%. Calcd for $C_{13}H_{22}$: C, 87.6; H, 12.4%.

Oxidative Ring Opening of Cyclobutene Derivatives (VIa—c). General Procedure:[10] To a solution of VI (1.00 mmol) in *tert*-butyl alcohol (70 m*l*) there was added a saturated aqueous solution of potassium carbonate (19 mg) and then a stock solution (40 m*l*) which had been freshly prepared from potassium permanganate (20 mg), sodium metaperiodate (1.04 g) and water (40 m*l*). The reaction mixture was stirred for 5 hr and extracted with *n*-hexane, and the extracts were evaporated *in vacuo*. The purification was effected by preparative tlc (Silica-gel G benzene) and distillation or by recrystallization. Each product was identified with an authentic sample.

Hydroboration of Cyclobutene Derivatives (VIa—c). To a solution of VIb (50 mg) in tetrahydrofuran (1.00 m*l*), a tetrahydrofuran solution of diborane (1M, 0.80 m*l*) was added drop by drop, after which the mixture was stirred for a half hour at 0—3°C. Water (1.00 m*l*) was then added carefully, and the mixture was treated with a 3N NaOH solution (1.00 m*l*). To this a 30% H_2O_2 solution was added, drop by drop, at room temperature, and then the whole was allowed to stand overnight. After the subsequent addition of an aqueous NaCl solution, the mixture was extracted with *n*-hexane and the combined extracts were evaporated *in vacuo*. Distillation afforded a colorless solid (43% yield), which was found to be identical with the IIb photoproduct (IR, glc, NMR, and mixed mp). Two other olefins VIa and VIc were treated similarly to afford IIa and IIc respectively.

Cycloundecenol (Va). A mixture containing IVa and Va was separated by preparative tlc (Silica-gel G, benzene). Perfect separation was effected by repeated preparative tlc. (The yield was calculated on the basis of the NMR peak areas of the olefinic protons. This product showed the following spectra in support of the assigned structure. IR (neat): 1645 cm^{-1} (C=C). NMR δ: 0.70—2.50 (m, 16H), 3.20—3.90 (m, 2H), 4.65—5.65 (m, 2H). Found: C, 78.3; H, 11.9%. Calcd for $C_{11}H_{20}O$: C, 78.5; H, 12.0%. The hydrogenation of Va on palladium charcoal afforded saturated monocyclic alcohol. The IR spectrum of its phenylurethane was superimposable on that of authentic cycloundecanol phenylurethane (mp 56—58°C) (literature[11] mp 58—59°C).

The IVa Photoreduction Product. This product was separated by preparative tlc (Silica-gel G, *n*-hexane: ether=

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[9] G. Darzens, *C. R. Acad. Sci.*, **152**, 1601 (1911).

[10] R. U. Lemieux and E. von Rudloff, *Can. J. Chem.*, **33**, 1701 (1955).

[11] M. Kobelt, P. Barman, V. Prelog, and L. Ruzicka, *Helv. Chim. Acta*, **35**, 256 (1949).

10: 1) and was found to be identical with authentic cycloundecanol (IR, glc and mp of phenylurethane). The presence of acetone in the photolysate was proven by the formation of 2,4-dinitrophenylhydrazone, mp 123—124°C (from EtOH-H_2O).

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