Redox-photosensitised Reactions. Part 6.[1] Stereospecific Ring Cleavage of 1-Phenoxy-1,2,2a,3,4,8b-hexahydrocyclobuta[*a*]naphthalene-8b-carbonitrile and its 2-Methyl Derivatives by Redox-photosensitisation

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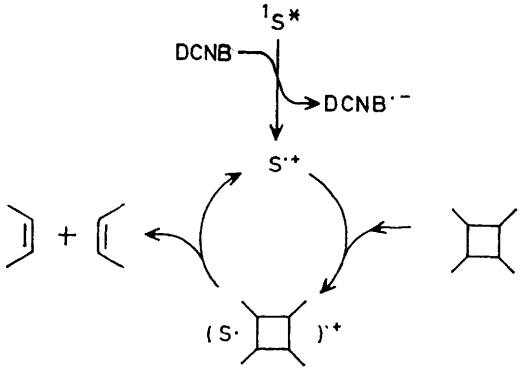
Ring cleavage of *endo*-1-phenoxy-1,2,2a,3,4,8b-hexahydrocyclobuta[*a*]naphthalene-8b-carbonitrile (1a) occurs to give phenyl vinyl ether and 3,4-dihydronaphthalene-1-carbonitrile in a 1 : 1 ratio upon the selective photoexcitation of phenanthrene, naphthalene, or triphenylene at 313 nm in the presence of *p*-dicyanobenzene in acetonitrile. With the *cis*- and *trans*-2-methyl derivatives of (1a), the photosensitised ring cleavage is stereospecific. The key mechanistic pathway is suggested to be the formation of a π-complex between the cyclobutanes and the cation radicals of the arenes, in which the phenoxy-group of the cyclobutanes plays important roles. It is speculated that the ring cleavage reaction proceeds by means of a concerted-like mechanism *via* the π-complex without complete hole transfer.

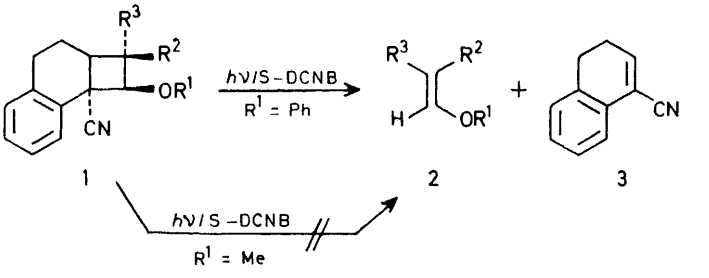
THE stereochemistry of olefin formation from cleavage of cyclobutane rings has received much interest from both theoretical and practical points of view. In the excited singlet state, splitting of the cyclobutane ring occurs stereospecifically.[2,3] On the other hand, losses of stereointegrity have been observed in both thermal [2-7] and triplet-photosensitised [2] reactions, although the former usually more or less favour stereoretention depending on the stereoelectronic structure of the cyclobutane.[2,3,8] In previous papers, we reported the redox-photosensitised chain cycloreversions of indene cyclobutane dimers [1,9] and of the *cis-cisoid*-dimer of *NN'*-dimethylthymine; [10] these have been demonstrated to be catalysed by the cation radical of aromatic hydrocarbons ($S^{+\cdot}$) which form π-complexes with the cyclobutanes (Scheme 1).



S: Aromatic hydrocarbon
DCNB: *p*-Dicyanobenzene

SCHEME 1

Ring cleavage reactions involving cation radicals of some cyclobutane compounds have previously been reported.[11-13] Redox-photosensitised cycloreversions on the other hand do not actually involve a discrete cation radical, and, as they thus provide a new route for cleavage of cyclobutane rings, it was of interest to study their stereochemical features. We found that redox-photosensitisation can be applied to ring cleavage of *endo*-1-phenoxy-1,2,2a,3,4,8b-hexahydrocyclobuta[*a*]-naphthalene-8b-carbonitrile (1a) and its *cis*- and *trans*-2-methyl derivatives (1b and 1c), which give stereospecifically the corresponding enol ethers and the dihydrocyanonaphthalene (3) (Scheme 2).



R^1 = Ph { a; R^2 = R^3 = H; b; R^2 = Me, R^3 = H; c; R^2 = H, R^3 = Me } R^1 = Me { d; R^2 = Me, R^3 = H; e; R^2 = H, R^3 = Me }

SCHEME 2

Irradiation of dry acetonitrile solution containing (1a), phenanthrene (P), and *p*-dicyanobenzene (DCNB) at 313 nm gave phenyl vinyl ether (2a) and compound (3) in a 1 : 1 ratio. At low conversion (<10%) no other products were detected. However, over-irradiation led to the formation of head-to-head cyclobutane dimers of (2a) [14] which appear to arise from redox-photosensitised dimerisation of the initially formed (2a).† The epimer of (1a) was not detected even at relatively high conversion either by g.l.c. of the photolysate or by the n.m.r. spectrum of the recovered (1a). The amounts of recovered P and DCNB did not significantly change even at high conversion. It was confirmed that irradiation in the absence of either P or DCNB results in no reaction.

Similarly, ring cleavage of (1b) and (1c) occurred to give 1-phenoxypropenes (2b) and (2c) and compound (3) in 1 : 1 ratios. The degree of stereoretention in the olefin

† It was confirmed that irradiation of an acetonitrile solution containing (2a), P, and DCNB at 313 nm afforded *cis*- and *trans*-1,2-diphenoxycyclobutanes in a 1 : 1 ratio in 26% isolated yields.

formation is very high at low conversion and decreases with irradiation time (Figure 1). Extrapolation to zero irradiation time reveals that stereoretention reaches 100% in both cases, thus confirming the stereospecific

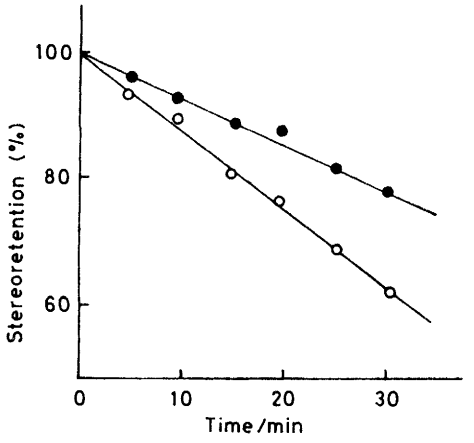


FIGURE 1 Dependence of stereoretention on irradiation time in the olefin formation from redox-photosensitised ring cleavage of (1b) (○) and (1c) (●); degassed acetonitrile solutions; [(1a, b)] 0.1M, [P] 0.01M, [DCNB] 0.1M; irradiation at 313 nm

nature of the reaction. The loss of stereointegrity during the irradiation must be caused by the redox-photosensitised stereomutation of the initially formed (2b) or (2c), as reported.[15] It was again confirmed that the epimers of (1b) and (1c) are not formed.

Triphenylene (TR) and naphthalene (N) can be effectively used in place of P for the photosensitised reactions of (1a—c), whereas chrysene (CR) effects only the reaction of (1b). Quantum yields for the formation of (2a—c) ($\phi_{(2)}$) for each effective S were determined at less than 1% conversion where the dimers of (2a—c) are not formed, and stereoretention in the formation of (2b,c) is over 95%. Figure 2 shows a typical plot of $\phi_{(2)}^{-1}$ *vs.*

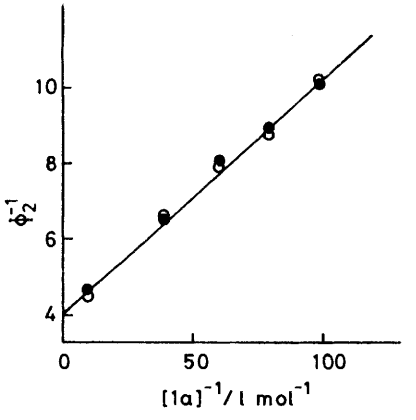


FIGURE 2 Plots of $\phi_{(2)}^{-1}$ *vs.* $[(1a)]^{-1}$: degassed acetonitrile solutions; irradiation at 313 nm with light intensities of 4.1×10^{-8} (○) and 8.9×10^{-7} (●) einstein min^{-1}; [P] 0.01M, [DCNB] 0.1M

reciprocals of concentration of (1a) which is linear and independent on the intensity of the incident light. In the other cases, similar linear plots were again obtained. The Table lists the intercepts and slopes of the linear plots and the limiting quantum yields ($\phi_{(2)}^{\infty}$) together with the oxidation potentials of (1a—c) and S.

In contrast, the related 1-methoxy-compounds (1d) and (1e) were entirely unreactive to redox-photosensitisation using any S, starting materials being almost quantitatively recovered even after long irradiation times.

It was confirmed that the cyclobutanes (1a—c) neither quench the fluorescence of S nor can be cleaved by triplet photosensitisation using benzophenone, whose triplet energy is higher than that of any S used.[16] We previously reported that the fluorescence of S is quenched by DCNB at a diffusion-controlled rate in acetonitrile and that the calculated free energy changes associated with electron transfer from the excited singlet state of S

Slopes and intercepts of Stern–Volmer plots for redox-photosensitised ring cleavage of (1a—c) [a]

Cyclobutanes ($E_{1/2}^{ox.}$/V) [c]	S [b] ($E_{1/2}^{ox.}$/V) [c]	10^2 Slope/mol l^{-1}	Intercept	$\phi_{(2)}^{\infty}$
(1a) (1.50)	TR (1.29)	4.74	3.25	0.31
	N (1.22)	5.37	3.54	0.28
	P (1.17)	6.03	3.97	0.25
(1b) (1.48)	TR	2.16	1.58	0.63
	N	2.44	1.72	0.58
	P	2.89	2.02	0.50
	CR (1.05)	15.8	6.08	0.16
(1c) (1.48)	TR	3.09	2.10	0.48
	N	3.66	2.32	0.43
	P	4.00	2.47	0.41

[a] Valucs at 313 nm; [S] = 0.01M, and [DCNB] = 0.1M in degassed acetonitrile. [b] TR = Triphenylene, N = naphthalene, P = phenanthrene, and CR = chrysene. [c] Half-peak potentials *vs.* Ag/Ag$^+$ in acetonitrile measured by cyclic voltammetry.

(^{1}S*) to DCNB are substantially negative.[17] Therefore, electron transfer from ^{1}S* to DCNB is responsible for the initiation process of redox-photosensitisation; the cation radical of S ($S^{+\cdot}$) and the anion radical of DCNB ($DCNB^{-\cdot}$) are thus formed.

The values of $\phi_{(2)}^{\infty}$ and the slopes depend slightly, but significantly, on the oxidation potentials of S, strongly suggesting that an interaction of $S^{+\cdot}$ with (1a—c) should be involved as a key mechanistic pathway. The phenoxy-group of (1a—c) appears to be important in the interaction with $S^{+\cdot}$, since both (1d) and (1e) have a higher oxidation potential (1.60 V) compared with those of (1a—c) and are unreactive to redox-photosensitisation.

With regard to mechanistic elucidation, it should be noted that the oxidation potentials of (1a—c) are considerably higher than those of S. For example, the difference between the oxidation potentials of (1b) [or (1c)] and P is 0.31 V (30 kJ mol^{-1}). Therefore, complete hole transfer from $S^{+\cdot}$ to (1a—c) appears to be considerably endothermic, and is perhaps unlikely to occur. Moreover, the stereospecific nature of the redox-photosensitised ring cleavage of (1b,c) is not compatible with a mechanism involving the intermediacy of the discrete cation radicals of (1b,c). If $(1b,c)^{+\cdot}$ were the reaction intermediate, it should form the cation radical of (2b,c) by ring cleavage, *i.e.* $(1b,c)^{+\cdot} \longrightarrow (2b,c)^{+\cdot} + (3)$. Since the cation radical of *cis*-but-2-ene is known to undergo rapid isomerisation to the *trans*-isomer,[18] $(2b)^{+\cdot}$ would

lose stereointegrity before receiving electrons from S, $DCNB^{-\cdot}$, and others. Therefore, this mechanism can not be accepted.

As was discussed for the redox-photosensitised cycloreversion of indene cyclobutane dimers,[1,9] the π-complex of $S^{+\cdot}$ with (1a—c), $[S\cdot(1a—c)]^{+\cdot}$, is again suggested to be the key intermediate, by way of which the cyclobutanes (1a—c) undergo ring cleavage without complete hole transfer. The independency of $\phi_{(2)}$ on the light intensity (Figure 2) demonstrates that charge neutralisation between cation radicals and $DCNB^{-\cdot}$ is not important in the olefin formation. In a previous paper, we reported that the limiting quantum yield for the formation of $P^{+\cdot}$ from $^1P^*$ and DCNB is 0.2.[1] Therefore, the $\phi_{(2)}^{\infty}$ values for the P·(1a—c) pairs indicate the occurrence of short chain reactions, thus demonstrating the validity of Scheme 1 in the present reactions. However, deactivation of the π-complex appears to compete with the ring cleavage reactions at similar rates, as is shown in Scheme 3.

$$[S\cdot(1a—c)]^{+\cdot} \longrightarrow S^{+\cdot} + (2a—c) + (3)$$
$$[S\cdot(1a—c)]^{+\cdot} \longrightarrow S \text{ and/or others}$$
$$[S\cdot(1a—c)]^{+\cdot} + S \longrightarrow S_2^{+\cdot} + (1a—c)$$
$$[S\cdot(1a—c)]^{+\cdot} + X \longrightarrow S + (1a—c) \text{ and/or others}$$
(X = impurities involving water)

SCHEME 3

In the π-complex, the positive charge probably develops partially on the phenoxy-group of (1a—c), depending on ΔE^{ox} {[$E_{1/2}^{ox}$ of (1a—c)] — ($E_{1/2}^{ox}$ of S)}. This would lead to weakening of the C-1–C-8b bond and, perhaps also to a lesser extent of the C-2–C-2b bond, thus causing the stereospecific cleavage of the cyclobutane ring; the smaller the values of ΔE^{ox}, the faster the ring cleavage reactions from the π-complex. Thus, development of the positive charge on the side of (1a—c) might lower activation barriers for concerted-like cleavage of the cyclobutane ring. The stereospecific nature of the redox-photosensitised ring cleavage disfavours the intervention of such long-lived intermediates as 1,4-biradicals.

It should, however, be noted that while ΔE^{ox} is important, it is not the only factor in the ring cleavage reactions. For example, *cis*- and *trans*-1,2-diphenoxycyclobutanes, which possess a lower oxidation potential (1.40 V), were not cleaved at all by redox-photosensitisation using any S. The bicyclic structure might be another factor. Moreover, steric repulsion between the substituents should also be taken into consideration. For example, chrysene is effective in the ring cleavage of (1b), but not in that of (1c), although both (1b) and (1c) possess identical oxidation potentials; (1b) is the most strained because of its all-*cis* configuration.

EXPERIMENTAL

Spectrograde acetonitrile was distilled three times from P_2O_5 and then from CaH_2 before use. The aromatic hydrocarbons and *p*-dicyanobenzene were recrystallised from methanol and benzene, respectively, and sublimed *in vacuo*. Phenyl vinyl ether,[19] 1-phenoxypropene,[20] and 3,4-dihydronaphthalene-1-carbonitrile (3) [21] were prepared by known methods. *cis*- and *trans*-1-Phenoxypropenes were separated by preparative g.l.c.

M.p.s were taken on a Kofler hot-stage apparatus. Analytical g.l.c. was carried out on a Shimadzu GC-3BF machine with flame ionisation detectors using a 75 cm × 8 mm (i.d.) stainless steel column packed with 25% Ucon Oil LB-550X on Neopak-1A at 120 °C for quantitative analyses of (2a—c) and (3); n-tridecane was used as internal standard. G.l.c. analyses of the cyclobutanes, the aromatic hydrocarbons, and *p*-dicyanobenzene were carried out with 75 cm × 8 mm columns of 5% SE-30 on Shimalite W and 10% PEG-20M on Shimalite W.

Oxidation potentials were measured for N_2-saturated acetonitrile solutions (10^{-3} M) *vs.* an Ag/Ag^+ reference electrode by cyclic voltammetry. Tetraethylammonium tetrafluoroborate (0.1M) was used as supporting electrolyte. The scan speed was 0.2 V s^{-1} and the temperature was kept at 23 ± 0.1 °C. No cyclic voltammograms showed reversible cathodic peaks corresponding to reduction of cation radicals. Therefore, the half-peak values (< ±0.015 V) were employed as oxidation potentials. Details of measurements were identical to those described previously.[1]

N.m.r. spectra were taken for solutions in deuteriochloroform on a JEOL JNM-60 spectrometer at 60 MHz and on a JEOL JNM-PS-100 spectrometor at 100 MHz using tetramethylsilane as internal standard. I.r. spectra were obtained with a Shimadzu IR-400 spectrometer and mass spectra with a Hitachi RMU-6E instrument.

Quantum Yield Measurements.—All volumetric flasks and pipettes were dried before use in a desiccator *in vacuo*; irradiation tubes (Pyrex, 8 mm i.d.) were heated under high vacuum before use. Aliquots (3 cm^3) of solutions of samples and hexan-2-one actinometer [22] were introduced into the Pyrex tubes, degassed by freeze–pump–thaw method (five cycles) to a reduced pressure $< 5 \times 10^{-5}$ Torr, and then irradiated with an Eikosha PIH-300 high-pressure mercury lamp using a 'merry-go-round' apparatus immersed in water at 20 ± 1 °C. Potassium chromate solutions of different concentration in a Pyrex vessel were used to isolate the 313 nm light and change the intensity of the incident light.

Nitriles (1a—e).—The photocycloadducts of 1-cyanonaphthalene to phenyl vinyl ether,[23] *cis*- and *trans*-1-phenoxypropenes,[24] and *cis*- and *trans*-1-methoxypropenes [25] were hydrogenated in methanol over 5% palladium–carbon. The cyclobutanes (1a—e) were obtained in 95% yields and purified by recrystallization from methanol or by fractional distillation under high vacuum. endo-1-*Phenoxy*-1,2,2a,3,4,8b-*hexahydrocyclobut*[a]*naphthalene*-8b-*carbonitrile* (1a) had m.p. 73—74 °C; $\nu_{max.}$ (CCl_4) 2 220 and 1 220 cm^{-1}; δ 1.63—2.24 (m, 3 H), 2.30—2.68 (m, 2 H), 2.70—3.24 (m, 2 H), 5.09 (dd, *J* 9.6 and 8.3 Hz, 1 H), and 6.7—7.5 (m, 9 H); *m/e* 275 (M^+) (Found: C, 82.6; H, 6.1; N, 4.95. $C_{19}H_{17}NO$ requires C, 82.88; H, 6.22; N, 5.09%); endo-2-*methyl*-endo-1-*phenoxy*-1,2,2a,3,4,8b-*hexahydrocyclobuta*[a]-*naphthalene*-8b-*carbonitrile* (1b) had m.p. 46—48 °C; $\nu_{max.}$ (CCl_4) 2 220 and 1 220 cm^{-1}; δ 0.96 (d, *J* 6.9 Hz, CH_3), 1.67—2.18 (m, 2 H), 2.20—2.71 (m, 2 H), 2.66—3.65 (m, 2 H), 5.22 (dd, *J* 7.0 and 2.6 Hz, 1 H), and 6.5—7.5 (m, 9 H); *m/e* 289 (M^+) (Found: C, 82.6; H, 6.4; N, 4.65. $C_{20}H_{19}NO$ requires C, 83.01; H, 6.62; N, 4.84%); exo-2-*methyl*-endo-1-*phenoxy*-1,2,2a,3,4,8b-*hexahydrocyclobuta*[a]*naphthalene*-8b-*carbonitrile* (1c) had m.p. 67—67.5 °C; $\nu_{max.}$ (CCl_4) 2 220 and 1 225 cm^{-1}; δ 1.23 (d, *J* 6.1 Hz, CH_3), 1.68—2.17 (m, 2 H), 2.20—2.63 (m, 2 H), 2.65—3.08 (m, 2 H), 4.67 (d, *J* 8.0 Hz, 1 H), and 6.7—7.5 (m, 9 H); *m/e* 289 (M^+) (Found: C, 82.85; H, 6.5; N, 4.6. $C_{20}H_{19}NO$ requires C, 83.01; H, 6.62; N, 4.84%); endo-1-*methoxy*-endo-2-*methyl*-1,2,2a,3,4,8b-*hexahydrocyclobuta*[a]*naphthalene*-8b-*carbonitrile* (1d) was a colourless oil; $\nu_{max.}$ (CCl_4) 2 230 and 1 160 cm^{-1}; δ 0.87 (d, *J* 7.7 Hz, CH_3), 1.67—2.16 (m, 2 H), 2.10—2.58 (m, 2 H), 2.61—3.42 (m, 2 H), 3.20 (s, OCH_3), 4.26 (d, *J* 8.0 Hz, 1 H), and 6.9—7.5 (m, 4 H); *m/e* 227 (M^+) (Found: C,78.9; H, 7.35; N, 6.1. $C_{15}H_{17}NO$ requires C, 79.26; H, 7.54; N, 6.16%); endo-1-*methoxy*-exo-2-*methyl*-1,2,2a,3,4,-8b-*hexahydrocyclobuta*[a]*naphthalene*-8b-*carbonitrile* (1e) had m.p. 57—58 °C; $\nu_{max.}$ (CCl_4) 2 240 and 1 150 cm^{-1}; δ 1.20 (d, *J* 6.3 Hz, CH_3), 1.66—2.06 (m, 2 H), 2.16—2.33 (m, 2 H), 2.37—2.88 (m, 2 H), 3.46 (s, OCH_3), 3.86 (d, *J* 8.2 Hz, 1 H), and 6.9—7.5 (m, 4 H); *m/e* 227 (M^+) (Found: C, 79.0; H, 7.55; N, 6.15. $C_{15}H_{17}NO$ requires C, 79.26; H, 7.54; N, 6.16%).

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REFERENCES

[1] Part 5, T. Majima, C. Pac, and H. Sakurai, *J. Amer. Chem. Soc.*, in the press.
[2] C. Pac and H. Sakurai, *Bull. Chem. Soc. Japan*, 1978, **51**, 329.
[3] L. A. Paquette and G. L. Thompson, *J. Amer. Chem. Soc.*, 1972, **94**, 7172.
[4] H. R. Gerberich and W. D. Waters, *J. Amer. Chem. Soc.*, 1961, **83**, 4884.
[5] E. O'Neal and S. W. Benson, *J. Phys. Chem.*, 1968, **72**, 1866.
[6] G. Jones, II, and M. H. Williamson, jun., *J. Amer. Chem. Soc.*, 1974, **96**, 5617.
[7] L. M. Stephenson and T. A. Gibson, *J. Amer. Chem. Soc.*, 1974, **96**, 5624.
[8] G. Jones, II, *J. Chem. Educ.*, 1964, **51**, 175.
[9] T. Majima, C. Pac, A. Nakasone, and H. Sakurai, *J.C.S. Chem. Comm.*, 1978, 490.
[10] T. Majima, C. Pac, J. Kubo, and H. Sakurai, *Tetrahedron Letters*, 1980, 377.
[11] P. Beresford, M. C. Lambert, and A. Ledwith, *J. Chem. Soc.* (*C*), 1970, 2508.
[12] A. A. Lamola, *Mol. Photochem.*, 1972, 107.
[13] S. Takamuku and W. Schnabel, personal communication.
[14] S. Kuwata, Y. Shigemitsu, and Y. Odaira, *J. Org. Chem.*, 1973, **38**, 3803.
[15] T. Majima, C. Pac, and H. Sakurai, *Chem. Letters*, 1979, 1133.
[16] S. L. Murov, 'Handbook of Photochemistry,' Marcel Dekker, New York, 1973.
[17] C. Pac, A. Nakasone, and H. Sakurai, *J. Amer. Chem. Soc.*, 1977, **99**, 5806.
[18] Y. Harata, M. Matsui, and M. Imamura, *Chem. Letters*, 1977, 199.
[19] S. M. McElvain and B. Fajardo-Pinzon, *J. Amer. Chem. Soc.*, 1945, **67**, 650.
[20] P. W. Jolly, F. G. A. Stone, and K. Mackenzie, *J. Chem. Soc.*, 1965, 6416.
[21] W. Nagata, M. Yoshida, and M. Murakami, *Org. Synth.*, 1972, **52**, 90, 96.
[22] P. J. Wagner, *Tetrahedron Letters*, 1968, 5796.
[23] C. Pac, K. Mizuno, T. Sugioka, and H. Sakurai, *Chem. Letters*, 1973, 187.
[24] K. Mizuno, C. Pac, and H. Sakurai, *J.C.S. Chem. Comm.*, 1974, 648.
[25] K. Mizuno, C. Pac, and H. Sakurai, unpublished results.