

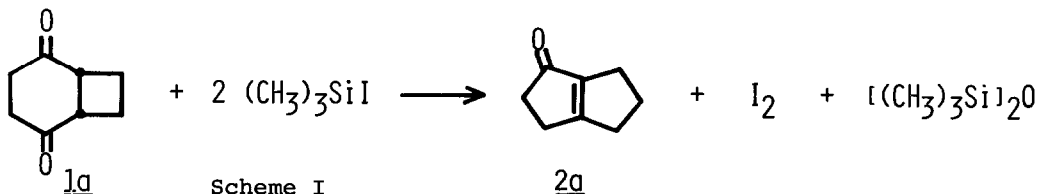
REARRANGEMENTS INITIATED BY TRIMETHYLSILYL IODIDE : READY DEOXYGENATIVE
REARRANGEMENT OF BICYCLO[4.2.0]OCTANE-2,5-DIONES TO
BICYCLO[3.3.0]OCT-1(5)-EN-2-ONES

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Summary: Reaction of bicyclo[4.2.0]octane-2,5-diones with trimethylsilyl iodide gave bicyclo[3.3.0]oct-1(5)-en-2-ones by a clean reductive rearrangement in good yields, providing a simple and efficient synthetic method for the enones.

The acid-catalyzed rearrangement of α -cyclobutyl ketones, particularly that of bicyclo[n.2.0]alkanones and [m.n.2]propellanones ($m, n > 2$), has proved to be useful in organic syntheses.¹ For these rearrangements have been usually used protic acids such as *p*-toluenesulfonic acid and hydrogen halides. Recently trimethylsilyl iodide (TMSI) has been recognized to be a versatile reagent in organic syntheses owing to its high reactivity.² In view of its strong electrophilicity and the marked affinity of the trimethylsilyl group towards oxygen, it would be expected that TMSI could induce the rearrangement of the ketones.³ We wish here to report that bicyclo[4.2.0]octane-2,5-diones, which are readily obtainable by photochemical [2+2]cycloadditions of 2-cyclohexene-1,4-dione and olefins,⁴ undergo a deoxygenative rearrangement to give bicyclo[3.3.0]oct-1(5)-en-2-ones when treated with TMSI.

Treatment of bicyclo[4.2.0]octane-2,5-dione 1a⁴ with TMSI (2.4 equiv.) in dichloromethane at room temperature for 3 h cleanly gave bicyclo[3.3.0]oct-1(5)-en-2-one 2a⁵ in 96% yield (Method A). In contrast, 1a was rather inert to *p*-toluenesulfonic acid and only decomposed on prolonged heating in benzene. For the completion of the reaction it was necessary to use at least two molar equivalent of TMSI; use of 1.06 equivalent of TMSI resulted in a 59:41 mixture (GLC) of the product 2a and the unchanged diketone 1a. The reaction was accompanied by the quantitative formation of iodine⁶ and hexamethyldisiloxane.⁷



The transformation was also brought about by *in situ* generated TMSI instead of expensive pure reagent as follows. Method B: stirring a mixture of 1a, 3,6-bis(trimethylsilyl)-1,4-cyclohexadiene (BTCHD) (1.5 equiv.) and iodine (0.2 equiv.) in dichloromethane (room temp., 12 h) gave 2a in 95% yield. Method C: stirring a mixture of 1a, trimethylsilyl chloride (3.5 equiv.) and dried sodium iodide (3.5 equiv.) in acetonitrile (room temp., 5 h) gave 2a in 91% yield.

Method B takes advantages of the ready formation of TMSI from BTCHD by action of iodine⁸ and the regeneration of iodine in the transformation 1a→2a. The latter fact should allow in principle the use of only a catalytic amount of iodine. Method C is the least expensive and hence may be the most practical for synthetic purposes, though usually takes longer reaction time than Method A.

These methods are applicable to the derivatives of 1a bearing substituent(s) on the four-membered ring (C-7,8).⁹ The results are summarized in Table 1.¹⁰

The symmetric tricyclic diketone 1b-1d gave the rearranged tricyclic enones 2b-2d, respectively, in high yields. Therefore, the present transformation would provide a simple, general and efficient synthetic way for the polycyclic compounds having bicyclo[3.3.0]octane moiety, which might be hardly prepared by the known methods for 1a⁵ and its derivatives.¹¹

On the otherhand, the unsymmetric diketone 1e-1j yielded the mixtures of two positional isomers (see Table 1). The ratio of the isomers was, however, markedly dependent on the configuration of the alkyl substituents; for example, while the *exo*-methyl diketone 1e gave the 7- and 8-methyl enones in a ratio of 85:15, the *endo*-methyl diketone 1h did in an almost reversed ratio of 10:90 at 25°C. The selectivity was slightly improved when the reactions were performed at 0°C or by warming up from -78° to room temperature; e.g. 7:93 for 1h at 0°C. The results, especially those of the geminal dimethyl diketone 1j, indicate that an *endo* substituent exerts stronger effect than an *exo* one on the selectivity.

A possible reaction pathway is shown in Scheme II. The first mole of TMSI should cause the rearrangement of 1a to give the trimethylsiloxy iodide B via the carbonium ion A. The second mole of TMSI may be required for the elimination reaction from B to the enone C, and this step must be rapid because the use of 1 equiv. of TMSI resulted in nearly 1:1 mixture of 1a and 2a. Ready elimination of vicinal trimethylsiloxy iodides to olefins by TMSI is precedented.¹² However, the observed configurational effect by the substituents on the isomeric ratio of the products has not yet been fully understood by the scheme.

Further experiments directed to full elucidation of the reaction pathway and examinations of TMSI-induced rearrangement in other systems are under way.

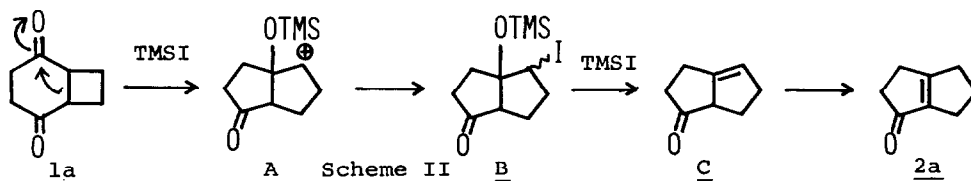
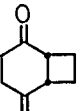

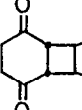

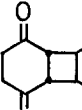

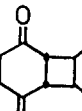

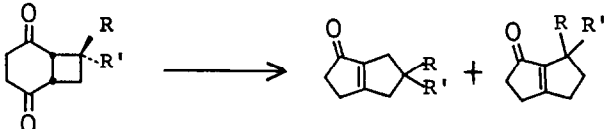
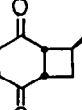
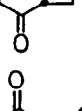
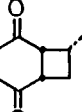
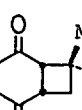
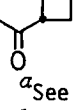
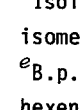


Table 1. Deoxygenative rearrangement of bicyclo[4.2.0]octane-2,5-diones induced by trimethylsilyl iodide

Diketone	Method ^a	Time h	Yield % ^b	Product(s) (ratio ^c)	B.p. °C/torr
 <u>1a</u>	A	3	96	 <u>2a</u>	74/2.0 (lit. 66/0.5 ^d)
	B	12	95		
	C	5	91		
 <u>1b</u>	A	3.5	90	 <u>2b</u>	97/2.0
	C	48	92		
 <u>1c</u>	A	3.5	89	 <u>2c</u>	104/0.8
	B	15	91		
 <u>1d</u>	A	5	84	 <u>2d</u>	105/0.3
					
 <u>1e</u> R=Me	A (25°)	3.5	(86)	(85 : 15)	62-64/2.0 ^e
	C	5	(84)	(80 : 20)	
	A	5	(96)	(83 : 17)	
 <u>1f</u> R=Et	A	5	(96)	(83 : 17)	(150/1.5) ^h
 <u>1g</u> R=vinyl	A	3	(61)	(>95 : <5)	(150/1.5) ^h
 <u>1h</u> R=Me	A (25°)	3.5	(93)	(10 : 90)	
	A (0°)	8		(7 : 93)	
	C	5	(96)	(11 : 89)	
 <u>1i</u> R=Et	A	5	(95)	(10 : 90)	
 <u>1j</u>	A	21	(40)	(36 : 64)	(140/1.0) ^h
	C	31	(65)	(20 : 80)	

^aSee the text. Reactions were performed at room temperature unless otherwise indicated.

^bIsolated yield after distillation. The yields in parentheses are those of mixture of the isomers. ^cThe ratios were determined by GLC (10% SE 30). See also ref. 10. ^dSee ref. 5a

^eB.p. of the mixture. ^fThese *exo* derivatives were obtained as the major photoadduct of 2-cyclohexene-1,4-dione and the corresponding olefins. ^gThese *endo* derivatives were stereoselectively obtained by catalytic hydrogenation (Pd-C) of the photoadduct of 2-cyclohexene-1,4-dione and the corresponding acetylenes. ^hBath temp./torr at Kugelrohr distillation.

References and Notes

†All correspondences should be sent to the Osaka address.

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- 6) Titration of the reaction mixture (1.0 mmol scale) with 0.2 M Na₂S₂O₃ after quenching with 0.2 M NaHCO₃ indicated 1.0 mmol of I₂.
- 7) Although the isolation of this compound was not attempted, ¹H-NMR spectrum of the reaction mixture indicated its clean formation by showing a sharp and strong singlet at δ 0.06.
- 8) M. E. Jung and T. A. Blumenkopf, *Tetrahedron Lett.*, 3657 (1978).
- 9) It is most likely that the derivatives bearing substituent(s) on the other carbon atoms undergo similar rearrangement by TMSI.
- 10) All the new compounds gave satisfactory spectral data and elemental analyses. The isomers were isolated by preparative GLC, and their structures were assigned with the aid of their Eu(fod)₃ shifted ¹H-NMR spectra. It turned out that all the 8-alkyl enones here examined had shorter retention time than the corresponding 7-alkyl ones upon GLC analysis (SE 30, Apiezon grease).
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