[17] D. A. Jaeger, to be submitted for publication.

[18] R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry," Academic Press, New York, N.Y., 1970, pp 114–119.

[19] Photochemically the process should proceed with retention of configuration at the benzyl carbon.[18] However, from photolysis of (−)-3,5-dimethoxybenzyl-*1-d* acetate in 50% (v/v) aqueous methanol, recovered starting material was ~85% racemized.[17] Therefore, a concerted [1,3] shift for photoexcited **1a** is unlikely.

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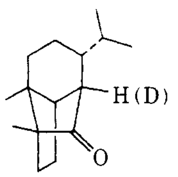
An Unusually Facile Bridgehead Enolization. Locked Boat Forms in Anti-Bredt Olefins[1]

Sir:

Exchange of hydrogens *via* bridgehead enolates ordinarily requires vigorous alkaline treatment when the ketonic rings are not large. For example, in copacamphor (**1**) and in *ent*-17-norkauran-16-one (**2**), the indicated bridgeheads underwent exchange in the presence of very strong base (KO-*t*-Bu) at high temperatures (185° for **1**[2] and 172° for **2**[3]).



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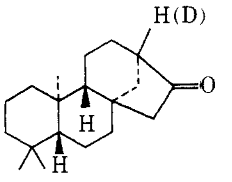

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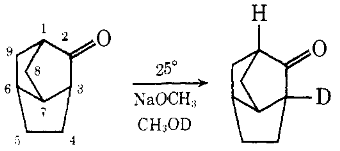
The bridgehead enolates in each of these ketones involves a transoid double bond in a seven-membered ring. We wish to report a remarkably easy bridgehead exchange at C-3 in brendan-2-one (**3**), in which the corresponding anti-Bredt enolate also contains a transoid olefin in a seven-membered ring.

Brendan-2-one (**3**)[4] in CH_3OD containing $NaOCH_3$ incorporates deuterium at 25°. Table I, which summarizes three separate exchanges that differed only in the base/ketone ratio, reveals uptake of one deuterium and no multiple deuteration under this mild treatment. That the deuterium is virtually entirely at C-3 (see **4**) was established with the europium-shifted nmr of the ketone-*d* from run 3 (92% d_1).[5] Integration indicated 7% H at C-3 (therefore 93% D), thus accounting for all the deuterium.

Table I. Deuterium Incorporation by Brendan-2-one in CH_3OD-$NaOCH_3$ at 25°

		Molar concn		Mass spectral *d* Assay (rel % ±1)		
Run	Time (hr)	NaOCH₃	Ketone	d_0	d_1	d_2
1	69	0.82	0.44	88	12	0
2	69	1.70	0.42	67	33	0
3	69	4.84	0.50	8	92	0



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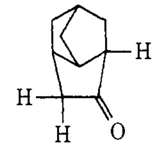

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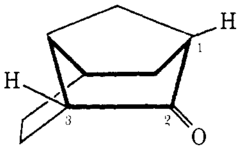
The reason why bridgehead replacement occurs so readily in **3** is of considerable interest especially as the mild conditions are more typical of those used for ordinary enolizations. The "s" character[6] of the carbon in the bridgehead C–H together with inductive stabilization of the carbanion by the carbonyl[7] cannot entirely account for the enhanced acidity because no deuteration occurred at the C-1 bridgehead and because the C-3 hydrogen does not undergo ready exchange when the carbonyl is located at C-4. Thus we found that brendan-4-one (**5**)[4] at room temperature in MeOD-NaOMe exchanged only its two enolizable protons at C-5 (1% d_0, 11% d_1, 88% d_2) under conditions close to those of run 3. The amount of double bond character in the bridgehead enolate from **3** is surely a dominant factor, and yet its extent is surprising for the ring sizes involved in this anti-Bredt situation.[8]

Wiseman has noted that a bridgehead double bond is endocyclic to two rings and necessarily transoid in one of them, and that bridgehead strain should be related to the strain in the transoid cycloalkene.[9] Brendan-2-one and its isomer noradamantan-2-one (**7**)[10] provide a direct way to test this view because a 2,3-olefin is transoid in the *seven-membered* ring if the cyclohexanone is a locked boat, as in brendan-2-one (see perspective **6**), whereas it is transoid in the *six-membered* ring if the cyclohexanone is rigidly chair locked as in noradamantan-2-one (**7**).[11,12] Indeed we found that **7** requires much more vigorous treatment to replace any of its hydrogens. Table II shows that even with KO-*t*-Bu a temperature around 80–87° was needed to abstract the first hydrogen. Interestingly, even after 69 hr at 140° (run 5), the ketone remains largely monodeuterated with only 5% polydeuteration, although at still higher temperatures extensive multideuteration sets in due to homoenolization[13] at various sites.[14]



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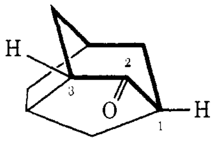

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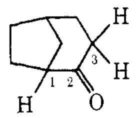

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From Eu(fod)₃-shifted nmr,[5] it was qualitatively clear that the first replacement in noradamantan-2-one occurs at C-3, but a quantitative assay was best done on the shifted nmr of epinoradamantanol[10] obtained by $LiAlH_4$ reduction of the exchanged ketone. For example, in the alcohol derived from run 5, nmr integration indicated 10% H at C-3

Table II. Deuterium Incorporation by Noradamantan-2-one with KO-*t*-Bu in *t*-BuOD

			Molar concn		Mass spectral *d* assay (rel % ±1)					
Run	Temp (±3 °C)	Time (hr)	KO-*t*-Bu	Ketone	d_0	d_1	d_2	d_3	d_4	d_5
1	80	48	0.20	0.10	100					
2	87	69	0.84	0.24	97	3				
3	120	69	0.84	0.23	69	30	1			
4	118	185	0.84	0.24	33	64	3			
5	140	69	0.84	0.23	9	86	4	1		
6	160	69	0.84	0.24	5	59	21	14	1	
7	195	50	0.64	0.32	5	39	29	24	2	1

(therefore 90% D). If we assume, reasonably, that the d_2 and d_3 species contain one of their deuteriums at C-3, the total at C-3 should be 91% D (i.e., 86 + 4 + 1), which agrees closely with the nmr integration.[15]

The ready bridgehead exchange in brendan-2-one is not paralleled in its bicyclic analog, bicyclo[3.2.1]octan-2-one (**8**), in which the ketonic ring is conformationally more flexible. Thus ketone **8** exchanged virtually only its two enolizable protons (3% d_0, 24% d_1, 72% d_2, 1% d_3), when treated with $NaOCH_3$ under the conditions of run 3, Table I. Use of KO-*t*-Bu-*t*-BuOD at 40° gave closely similar incorporation, and, even at 170° with KOD in 1:1 D_2O-dioxane, the recovered ketone showed very little uptake beyond d_2 (0% d_0, 10% d_1, 87% d_2, 2% d_3, 1% d_4).[16]

The unusual ease of bridgehead replacement in **3** and its relative difficulty in **7** and **8** demonstrate that the bridged boat form markedly enhances enolate stability at the side of the boat (but not at the bow) and that this stabilization is diminished considerably in a locked chair form. Our results imply that boat-locked substrates might be used to advantage in pursuit of certain anti-Bredt olefins.[17] The findings also raise the interesting possibility that prior to enolization of *equatorial* hydrogens, ordinary cyclohexanones may prefer to change to boat-like shapes to improve initial stereoelectronic alignment. We are pursuing some of these suggested lines.

References and Notes

(1) Supported by the National Institutes of Health (Grant GM06304) and by the National Science Foundation.

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(4) A. Nickon, H. Kwasnik, T. Swartz, R. O. Williams, and J. B. DiGiorgio, *J. Am. Chem. Soc.*, **87**, 1615 (1965).

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(7) A. Nickon and J. L. Lambert, *J. Am. Chem. Soc.*, **88**, 1905 (1966).

(8) For recent reviews on Bredt's rule, see G. Köbrich, *Angew. Chem., Int. Ed. Engl.*, **12**, 464 (1973); G. L. Buchanan, *Chem. Soc. Rev.*, **3**, 41 (1974).

(9) (a) J. R. Wiseman, *J. Am. Chem. Soc.*, **89**, 5966 (1967); (b) J. R. Wiseman and W. A. Pletcher, *ibid.*, **92**, 956 (1970).

(10) A. Nickon, G. D. Pandit, and R. O. Williams, *Tetrahedron Lett.*, 2851 (1967).

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(12) In sulfones containing a bicyclo[3.3.1]nonane skeleton strong evidence exists for transient formation of isomeric *cis-* and *trans*-cyclohexenes. C. B. Quinn, J. R. Wiseman, and J. C. Calabrese, *J. Am. Chem. Soc.*, **95**, 6121 (1973).

(13) A. Nickon and J. L. Lambert, *J. Am. Chem. Soc.*, **84**, 4604 (1962); A. Nickon, J. L. Lambert, R. O. Williams, and N. H. Werstiuk, *ibid.*, **88**, 3354 (1966), and references cited.

(14) The higher homolog adamantan-2-one, which also has a chair-locked cyclohexanone, is reported to be very resistant to exchange. J. E. Nordlander, S. P. Jindal, and D. J. Kitko, *Chem. Commun.*, 1136 (1969). In our own studies with adamantanone, we found only 8% d_1 after 192 hr in *t*-BuOD-KO-*t*-Bu at 195°, and at higher temperature (205°) the exchange produced d_1, d_2, and d_3 species due to bridgehead and homoenolate abstraction. J. B. Stothers and C. T. Tan (private communication) independently observed exchange in adamantan-2-one and also established that the relative ease of replacement is $4\text{-H}_{exo} > 1\text{-H} > 4\text{-H}_{endo}$.

(15) The bridgehead hydrogens at C-3 and C-1 are not geometrically identical because of some distortion in the chair. For computer calculation on noradamantane geometry see E. M. Engler, J. D. Androse, and P. v. R. Schleyer, *J. Am. Chem. Soc.*, **95**, 8005 (1973).

(16) Similar results were obtained at room temperature with NaOD in MeOD by R. T. Lalonde, J. Ding, and M. A. Tobias, *J. Am. Chem. Soc.*, **89**, 6651 (1967).

(17) J. A. Chong and J. R. Wiseman, *J. Am. Chem. Soc.*, **94**, 8627 (1972).

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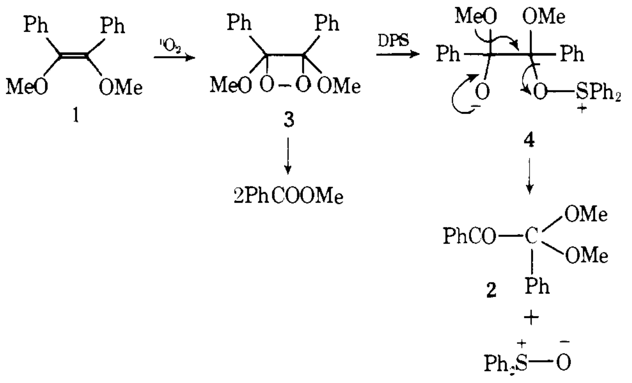
Trapping of Intermediates in Singlet Oxygen Reactions. Cleavage of Dioxetanes by Diphenyl Sulfide

Sir:

Recent investigations on the mechanisms of singlet oxygen reactions with acceptors have made use of various trapping agents to intercept peroxidic intermediates.[1-4] Among these, diphenyl sulfide (a species unreactive toward $^1O_2$) has been used effectively to bring about monodeoxygenation of persulfoxides formed in the sensitized photooxidation of alkyl sulfides.[1] We now report that diphenyl sulfide (DPS) may be used as a trapping agent to intercept dioxetanes formed in the reactions of singlet oxygen with certain electron-rich ethylenic and heterocyclic systems.

Methylene Blue-sensitized photooxidation of *cis*-dimethoxystilbene (**1**) (625-W Sylvania "Sun Gun") (0.005 *M*) in ether-methanol (85:15) in the presence of excess DPS (0.02 *M*) yielded methyl benzoate (32%) benzil dimethyl ketal (**2**)[5] (18%), and diphenyl sulfoxide (35%).[6] In the absence of DPS, we have found as has been reported earlier,[7,9] that reaction of **1** with singlet oxygen under the same conditions yields only the dioxetane (**3**) and its cleavage product, methyl benzoate.

We suggest that the formation of the rearrangement product (**2**), in the presence of DPS, takes place by a nucleophilic attack of the sulfide on the intermediate dioxetane (**3**) with cleavage of the oxygen-oxygen bond.[8] The zwitterion (**4**) thus formed then undergoes a benzylic acid-like rearrangement as shown.[10,11] This explanation receives strong support from a control experiment in which the dioxetane (**3**), isolated in pure form,[9] was treated with DPS at room temperature in ether-CD_3OD. The resulting mixture of products contained **2** (21%), diphenyl sulfoxide (32%), and methyl benzoate (43%). No incorporation of OCD_3 from the solvent was observed. In benzene, **3** reacted at a much slower rate with DPS to give the same products.



The effect of DPS on the photosensitized oxygenation of 2,3-diphenyl-*p*-dioxene (**5**) was next investigated. In the absence of trapping agent, this oxidation yields the 1,2-dioxetane (**6**) which cleaves to form the dibenzoate of ethylene glycol (**7**).[7,12] Photooxidation of **5** (0.02 *M*) in moist methanol (Methylene Blue) in the presence of DPS (0.16 *M*) yielded the *trans*-glycol **8**[13,14] (40%) and diphenyl sulfoxide (47%) along with the cleavage product **7** (18%). As the concentration of DPS was increased the ratio of **7** to **8** markedly decreased, as shown in Table I.[26] Using benzene as solvent, bisacenaphthalenethiophene as sensitizer, and DPS (0.05 *M*) as oxygen scavenger, the products formed were benzil ethylene ketal (**9**) (8%), epoxide (**10**) (19%), **7** (24%), and diphenyl sulfoxide (39%). Formation of products **8**, **9**, and **10** is shown in Scheme I.[14,27]

Diphenyl sulfide does not cause monodeoxygenation of