To test the proposed mechanism the pyrolysis of 1-phenyl-*2',4',6'*-d_3-1,3-butadiene[28] was carried out at 490°. 1,2-Dihydronaphthalene-*2',5,7*-d_3, the predicted product, was obtained in 78% yield as well as naphthalene-*1,3,6*-d_3 (5%). The formation of naphthalene as a minor product under our reaction conditions and as the major product under more vigorous conditions can be explained by the observation that 1,2-dihydronaphthalene undergoes dehydrogenation under slightly more vigorous pyrolysis conditions (550°) to yield naphthalene.

This reaction is also useful for the synthesis of substituted 1,2-dihydronaphthalenes. Thus pyrolysis of 1-phenyl-1,3-pentadiene[30] at 450° in the gas phase yields 1-methyl-1,2-dihydronaphthalene (60%)[7] and 1-methylnaphthalene (6%). On the other hand, pyrolysis at 475° of a mixture of *cis*- and *trans*-1-methyl-1-phenyl-1,3-butadiene[31] yields the thermodynamically more stable isomer 1-methyl-3,4-dihydronaphthalene[32] in 86% yield. Pyrolysis of *trans,trans*-1,4-diphenyl-1,3-butadiene under similar conditions yields 1-phenyl-1,2-dihydronaphthalene[33] (45%) and 1-phenylnaphthalene.[7] *trans*-1-Mesityl-1,3-butadiene[34] was pyrolyzed at 470° to give the predicted product 2,5,7-trimethyl-1,2-dihydronaphthalene in 25% yield. The third step of the reaction may involve a suprafacial 1,5-sigmatropic rearrangement of a methyl group rather than a hydrogen. This might be expected to be less facile.[35] The scope of this reaction is under active investigation.[36]

Procedure for the pyrolysis of substituted 1-phenyl-1,3-butadienes is as follows. The pyrolysis was performed using a vertical tube oven. The pyrolysis tube consisted of a 30 cm long Pyrex glass tube (o.d. 12.5 mm, i.d. 9 mm) packed with 1 cm long pieces of 3-mm Pyrex tubing. The exit of the column was connected to one neck of a two-necked flask which was immersed in a Dry Ice-acetone bath. The second neck of the flask was connected to a gas flow meter. The nitrogen flow rate was adjusted to 30 cm³/min. The entire apparatus was flame dried while allowing the column to come to temperature. The substituted 1-phenyl-1,3-butadiene was added at the rate of one drop every 10–15 sec. The material from the trap was collected and subjected to analysis by GLPC on a 0.25 in. × 24 ft 20% polyphenyl ether on chromosorb P column maintained at 170°.

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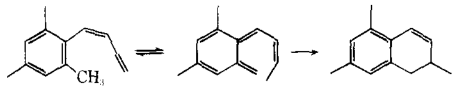
(35) An alternative mechanism suggested by a referee would involve a 1,7 sigmatropic hydrogen migration followed by an electrocyclic reaction of the triene thus generated.



(36) At least one limitation to the reaction has already been noted. Thus pyrolysis of *ortho*-butadienylphenol yields 2-methylbenzopyran rather than 1,2-dihydro-5-naphthol. E. S. Schweizer, D. M. Crouse, and D. L. Dalrymple, *Chem. Commun.*, 354 (1969).

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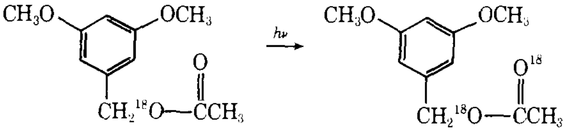
Photochemistry of Aromatic Compounds. Internal Return in the Photosolvolysis of 3,5-Dimethoxybenzyl Acetate

Sir:

Photochemical solvolyses of substituted and unsubstituted benzyl systems including acetates,[1] ethers,[2] halides,[1,3] and ammonium[4] and sulfonium[5] salts have been studied. In general, carbenium ion intermediates have been proposed but conclusively demonstrated only with 2-bromohomotriptycene[3a] and with α-phenylethyltrimethylammonium iodide.[4b] Equilibration of carboxyl oxygen atoms in esters undergoing ground state solvolysis without rearrangement has been employed[6] in detection of internal return of ion pairs, and the same principle can be applied to photosolvolysis. Mechanistic interest in photosolvolysis and in photochemistry of esters led us to investigate the possibility of carboxyl oxygen equilibration (eq 1) accompanying photosolvolysis of 3,5-dimethoxybenzyl acetate-*ether*-^{18}O (**1a**).[7,8]



1a **1b**

(1)

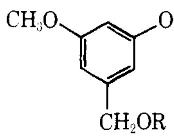
Table I. ^{18}O Equilibration and Product Distribution in Photolysis of **1a**[a]

		Recovered **1**[b]		Product distribution, %[c,d]						
Run	Solvent	% ^{18}O[e,f]	% ^{18}O equilibration[g]	**1**	**3**[h]	**4**[h]	**5**	**6**	**7**	**8**
1	50% CH_3OH-H_2O	7.22 ± 0.08	68 ± 4	48.7	26.1	20.8	1.0	2.4	~1	
2	50% CH_3OH-H_2O	7.27 ± 0.08	63 ± 4	51.9	23.4	20.2	1.1	2.5	~1	
3	50% dioxane-H_2O	7.18 ± 0.08	68 ± 4	52.6	40.3		0.2	4.4	~0.5	1.6

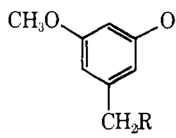
[a] Atom % excess ^{18}O at ether position, 7.36 ± 0.08%. [b] Analyses by mass spectrometry; footnote 9a. [c] By combined ^1H NMR and GLPC analyses. [d] For run 3, a trace of **9** and an unidentified compound (0.3%) were detected also. [e] Total atom excess at ether and carbonyl positions. [f] Average of three analyses. [g] Per cent of unsolvolyzed **1** with equal amounts of ^{18}O at ether and carbonyl positions; recovered **1** saponified with KOH in aqueous methanol or reduced with lithium aluminum hydride in ether and resultant **3** reconverted to **1** for analysis. [h] Contained no excess ^{18}O by mass spectral analysis.

Ester **1a** containing 7.36 ± 0.08% of one atom of excess ^{18}O at the ether position[9] was prepared with conventional procedures from 3,5-dimethoxybenzaldehyde-^{18}O, which was obtained by *p*-toluenesulfonic acid catalyzed exchange of unlabeled aldehyde[10] with $H_2{}^{18}O$ (10.3% ^{18}O, normalized) in dioxane. Under identical conditions[11] **1a** was irradiated in 50% (v/v) aqueous methanol and in 50% (v/v) aqueous dioxane. In both solvents carboxyl oxygens underwent equilibration (eq 1), and these results and product distributions are summarized in Table I.[12] Photolysis of an equimolar mixture of **1a** and 3,5-dimethoxybenzyl-*1,1*-d_2 acetate (**2**)[13] in 50% aqueous dioxane yielded starting material which contained[9a] no cross product corresponding to ^{18}O-labeled **2**, and that of a mixture (1:0.5 molar ratio) of unlabeled **1** and acetic acid-d_4 (99% D) in the same solvent yielded starting material which contained[9a] no excess deuterium. These two controls demonstrate that equilibration was intramolecular in aqueous dioxane, and it is assumed that the process was intramolecular in aqueous methanol also.

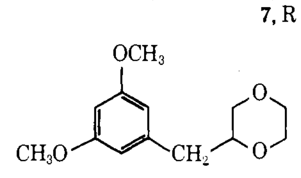
In both solvents **3**[10] and previously obtained[13] **5**, **6**, and **7** were products. Additionally, in 50% aqueous methanol, **4**[14] and, in 50% aqueous dioxane, **8**,[14] mp 53–54°, and **9**, mp 129–130°, lit.,[15] 131°, were obtained.[16]



3, R = H
4, R = CH_3



5, R = H
6, R = CH_3
7, R = 3,5-$(CH_3O)_2C_6H_3CH_2$



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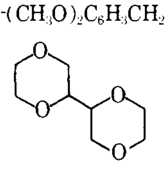

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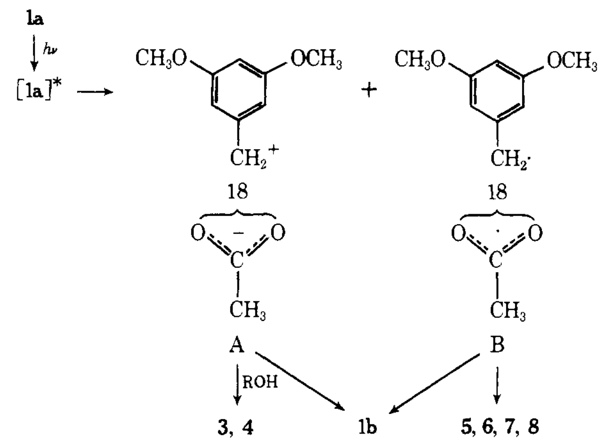
A unifying gross mechanism is outlined in Scheme I. Intramolecular carboxyl oxygen equilibration (eq 1) accompanying photosolvolysis is consistent with internal return[6] of intermediate ion pair A. Collapse to **1b** competes favorably with other processes of ion pair A which yield photosolvolysis products **3** and **4**. Formation of the minor amounts of **5**, **6**, **7**, **8**, and **9** is consistent with homolytic cleavage of the benzyl carbon oxygen bond to yield B and subsequent reactions[1,13] of 3,5-dimethoxybenzyl, acetoxy, and dioxanyl free radicals. A small amount of equilibration most likely proceeds through radical pair B. Under identical conditions[11] in nonpolar aprotic solvents (dioxane, hexane, cyclohexane), products from B were formed to a decidedly greater extent that in aqueous media, but the per cent equilibration increased only slightly.[17] An alternative mechanism for oxygen equilibration of **1a** involves concerted [1,3] *suprafacial* shift[18] of the 3,5-dimethoxybenzyl group.[19]

Scheme I



Acknowledgment is made to Professor Sara Jane Rhoads for helpful discussions and to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

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(7) Zimmerman and Sandel first reported[1] photosolvolysis of unlabeled material in aqueous dioxane.
(8) Cristol and Schloemer detected[3a] a return process accompanying photosolvolysis of 2-bromohomotriptycene in 95% aqueous acetone, but its internal and/or external nature has not been established.
(9) (a) Analysis was made by a standardized mass spectrometry method based on the molecular ion group (12 eV; heated inlet; flat-top peaks). (b) Controls demonstrated that all of the excess ^{18}O was in the ether position.
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(11) For each run 250 ml of 0.006 *M* solution was degassed with purified nitrogen for 40 min prior to and during irradiation for 10.0 min with a 450-W Hanovia lamp through a Corex filter.
(12) Controls demonstrated the absence of thermal solvolysis and carboxyl oxygen equilibration of 1a during photolysis and isolation.
(13) D. A. Jaeger, *J. Am. Chem. Soc.*, **96**, 6216 (1974).
(14) The ^1H NMR, ir, and mass spectra were consistent with the structural assignment, and carbon and hydrogen analyses were within 0.3% of theory.
(15) K. Pfordte, *Justus Liebigs Ann. Chem.*, **625**, 30 (1959). Only a trace of this material, the lower melting of two diastereomers, was detected and isolated. Most likely the other diastereomer was also present.
(16) Acetic acid from photosolvolysis of 1a was lost in product isolation, but hexanoic acid was isolated from photosolvolysis of 3,5-dimethoxybenzyl hexanoate[14] in 50% (v/v) aqueous dioxane.

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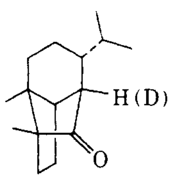
An Unusually Facile Bridgehead Enolization. Locked Boat Forms in Anti-Bredt Olefins[1]

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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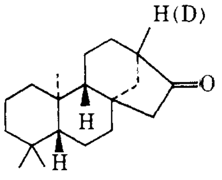

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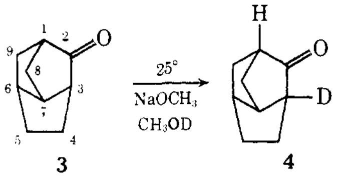
The bridgehead enolates in each of these ketones involves a transoid double bond in a seven-membered ring. We wish to report a remarkably easy bridgehead exchange at C-3 in brendan-2-one (**3**), in which the corresponding anti-Bredt enolate also contains a transoid olefin in a seven-membered ring.

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°

Run	Time (hr)	—Molar concn— NaO-CH_3	Ketone	Mass spectral *d* Assay (rel % ±1) 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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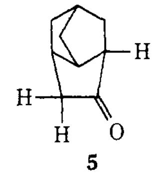

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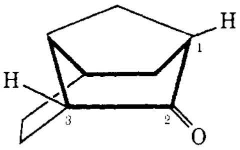
The reason why bridgehead replacement occurs so readily in **3** is of considerable interest especially as the mild conditions are more typical of those used for ordinary enolizations. The "s" character[6] of the carbon in the bridgehead C–H together with inductive stabilization of the carbanion by the 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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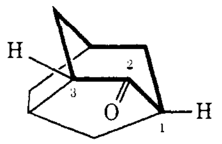

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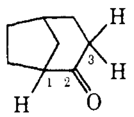

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From Eu(fod)$_3$-shifted nmr,[5] it was qualitatively clear that the first replacement in noradamantan-2-one occurs at C-3, but a quantitative assay was best done on the shifted nmr of epinoradamantanol[10] obtained by $LiAlH_4$ reduction of the exchanged 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

Run	Temp (±3°C)	Time (hr)	—Molar concn— KO-*t*-Bu	Ketone	—Mass spectral *d* assay (rel % ±1)— 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