Formation and reactivity of 1,3-benzodioxol-2-yl, 1,3-benzodioxan-2-yl, and related radicals. A search for an aromatic analog of the radical acetoxy rearrangement (Surzur–Tanner reaction)

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Reaction of the 1,3-dioxole, **9**, the 1,3-dioxan, **18**, and the 1,3-dioxepin, **29**, with *tert*-butoxy radicals gave evidence in each case for formation of the corresponding 1,1-dioxyethyl radicals. No conclusive evidence for formation of any of these radicals by cyclization of acetoxyaryl radicals could be obtained. Several of the 1,1-dioxyethyl radicals reacted by rearrangement.

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Lors de la réaction du dioxole-1,3 (**9**), du dioxanne-1,3 (**18**) et de la dioxépine-1,3 (**29**) avec les radicaux *tert*-butoxy, on a observé dans chacun des cas la formation des radicaux dioxy-1,1 éthyles correspondants. On n'a pas pu prouver que ces radicaux peuvent être préparés par la cyclisation des radicaux acétoxyaryles. Plusieurs de ces radicaux réagissent en se transposant.

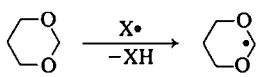
[Traduit par le journal]

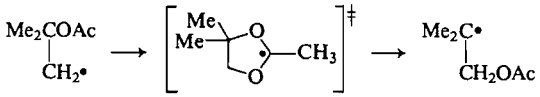
1,3-Dioxan-2-yl radicals (**1**) and 1,3-dioxol-2-yl radicals (**2**) have recently been the subject of intense investigation (1, 2). The most common

1

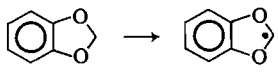
2

route for formation of these species has been hydrogen atom abstraction from the dioxane or dioxole (e.g. eq. [1]). Rearrangements of 2-acyloxyethyl radicals (the Surzur–Tanner reaction)[1] (3) evidently proceed through transition states resembling **2** as illustrated in eq. [2], but cyclized radical intermediates apparently are not formed in these processes (3).

[1] 

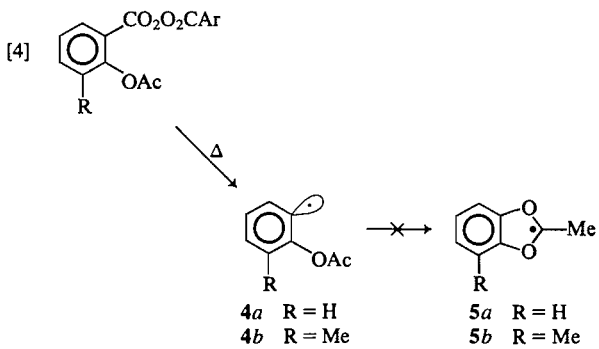
[2] 

Only recently have there been any studies of the benzo analogs of **1** or **2**. Radical **3** was generated by hydrogen atom abstraction (eq. [3]) and its esr spectrum was observed (1*a*). However, when α-acetoxyphenyl radicals (4) were generated by thermolysis of diacyl peroxides (eq. [4]), no rearrangement to dioxolyl radicals **5** could be detected (4). This rearrangement involves breaking a carbon–oxygen double bond and forming an aryl carbon–oxygen single bond and would be exothermic by about 13 kcal/mol.[2] It was suggested that geometrical constraints prevented favorable orbital overlap in the transition state for cyclization and precluded the rearrangement from occurring.

[3] 

3

Recently we have been interested in the formation of substituted furanyl radicals by cyclization reactions involving free radicals (5) and report

[4] 

4*a* R = H **5***a* R = H
4*b* R = Me **5***b* R = Me

herein studies of 1,3-benzodioxan-2-yl and 1,3-benzodioxol-2-yl radicals and attempts to form these species by free radical cyclizations.

Results and discussion

tert-Butyl acetylperoxysalicylate (**6**) (6) appeared to be an attractive source of radical **4***a* in order to test for the possible occurrence of the cyclization to

[1]So named following a suggestion of Barclay *et al.* (17). This reaction was evidently discovered independently by Tanner and Law (3*a*) and Surzur and Teissier (3*f*).

[2]See the Appendix for the basis of this estimate.

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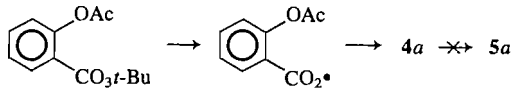
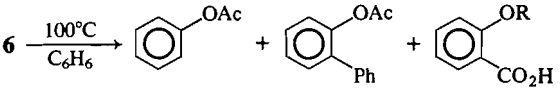
[5] 

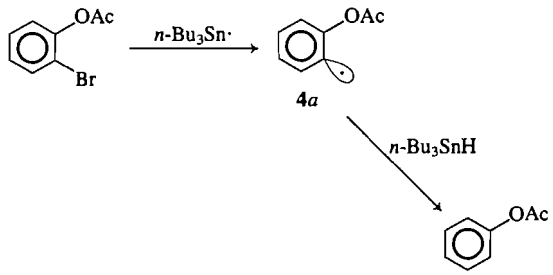
6 7

5 (eq. [5]). Thermal decomposition of **6** in benzene at 100°C gave the products shown in eq. [6] (the carboxylic acids were isolated by first esterifying with CH_2N_2 or $PhCHN_2$). Acetylsalicyclic acid (**8***a*) was found to be converted to salicyclic acid (**8***b*) under the reaction conditions so **8***a* is apparently a precursor to the **8***b* found in the reaction product.

[6] 

10% 36% **8***a* (R = Ac) 12%
8*b* (R = H) 42%

Similarly reaction of *o*-bromophenyl acetate with *n*-Bu_3SnH gave phenyl acetate but no cyclized product (eq. [7]). These results confirm the conclu-

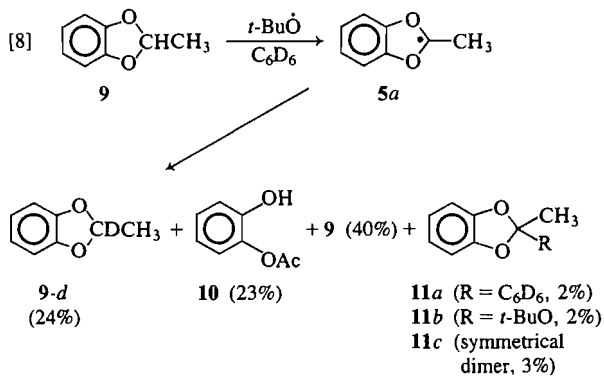
[7] 

sion of Evanochko and Shevlin (4) that the cyclization of eq. [4] is slow. These authors also concluded (4) that radical **7** has less of a tendency to decarboxylate than $PhC\dot{O}_2$, and the high yields of the nondecarboxylated products **8***a* and **8***b* observed in our work are consistent with this finding.

In order to confirm the postulated stability of **5***a* this radical was generated independently by hydrogen abstraction by *tert*-butoxy radicals from the dioxole **9** (7*a*, *c*). When this reaction was carried out in benzene-d_6 the products shown in eq. [8] were identified by gc/ms (gas chromatography/mass spectroscopy) and nmr. The nmr of recovered **9** revealed the presence of deuterium at the methine position (Fig. 1). These products indicate that radical **5***a* was formed; this conclusion was confirmed by observation of the esr spectrum of **5***a* when **9** was photolyzed with *t*-BuOO–*t*-Bu at −110°C: $a^H_{CH_3}$ = 12.41 G, *a* (4 aryl H) = 0.26 G, *g* = 2.00329.[3]

[3]This experiment was carried out by Dr. D. Griller and Dr. K. U. Ingold at the National Research Council, Ottawa.

The source of the deuterium in **9**-*d* is evidently a cyclohexadienyl radical or cyclohexadiene derived from addition of *tert*-butoxy, methyl, or another reactive radical to benzene-d_6.

[8] 

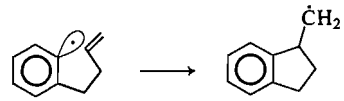
9 **5***a*

9-*d* (24%) **10** (23%) **11***a* (R = C_6D_6, 2%)
11*b* (R = *t*-BuO, 2%)
11*c* (symmetrical dimer, 3%)

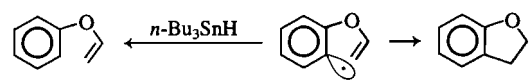
Product **10** apparently arises from decomposition of **11***b* which was observed to occur during gas chromatography. Products **11***a* and **11***b* could arise from combination of **5***a* with C_6D_6 or *t*-$Bu\dot{O}$, and **11***c* from dimerization of **5***a*. The fact that these products form indicates a reasonable lifetime for **5***a*.

Our results, and those of Evanochko and Shevlin (4), are all consistent with a greater thermodynamic stability of **5***a* relative to **4***a*. The failure of the rearrangement to occur can be accounted for by the proposal (4) that the geometry of **4***a* does not permit facile bond formation between the singly occupied σ orbital of **4***a* and the bonding π orbital at the carbonyl oxygen. Such geometrical and stereoelectronic constraints on free radical reactions are becoming increasingly well identified (3*d*, 5, 8). Acetoxyalkyl radicals (eq. [2]) are apparently sufficiently less rigid than acetoxyaryl radicals so that rearrangement is feasible.

In selected cases it is possible for a phenyl radical to cyclize with formation of a 5-membered ring, as in the reported example shown in eq. [9] (8). Such

[9] 

cyclizations involving formation of exocyclic radicals are predicted (8*b*, 9) to be favored, as opposed to reactions such as that of eq. [4], which is not observed, and is predicted not to be favored. The observation (8*a*) that the radical in eq. [10] cyclized

[10] 

94% <1%

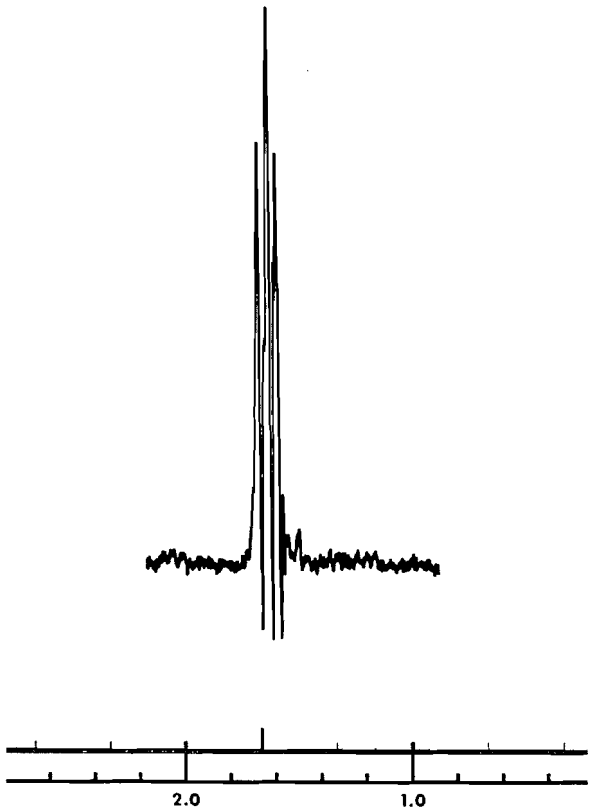
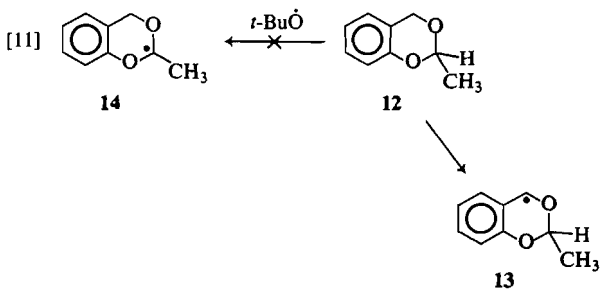


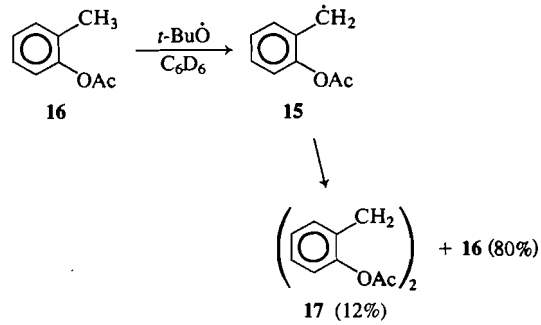
FIG. 1. The ^1H nmr absorption of CH_3 in a mixture of **9** and **9-*d***.

to the extent of less than 1% is another example of the barrier to formation of endocyclic radicals.

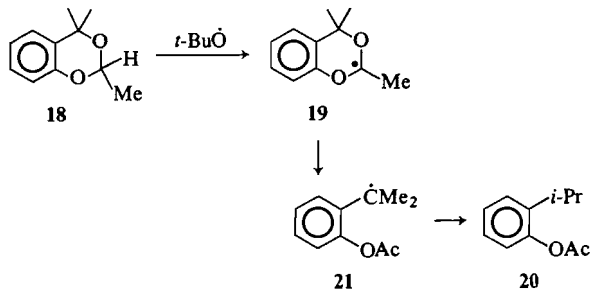
When the homologous acetal **12** was reacted with *tert*-butoxy radicals the only radical visible by esr was **13** (eq. [11]). Evidently formation of the

[11] 

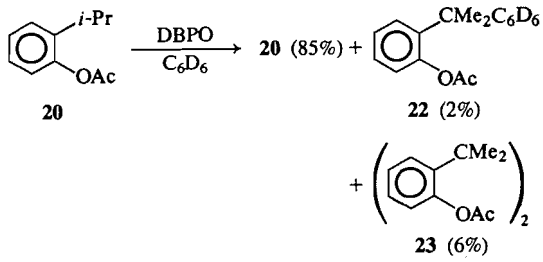
isomeric radical **14** was not competitive with abstraction to give the benzylic radical **13**. An attempt to generate **14** from cyclization of 2-acetoxybenzyl (**15**) also failed. Thus 2-acetoxytoluene (**16**) was reacted with *tert*-butoxy radicals in C_6D_6 as shown in eq. [12]. The formation of the dimer **17** indicates formation of **15**, but no evidence of cyclization to **14** was obtained.

[12] 

Reaction of **18**, which has no reactive benzylic hydrogens, with *tert*-butoxy radicals led to esr observation of the radical **19** and isolation of the ring opened product **20**. Ring opening of **19** to give the benzylic radical **21** is likely to be exothermic so this path appears plausible.

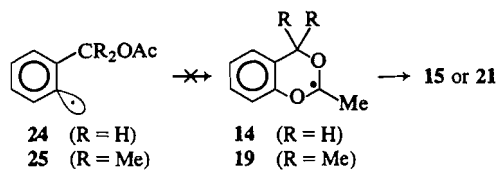


Reaction of **20** with *tert*-butoxy radicals gave the product distribution in eq. [13], as analyzed by

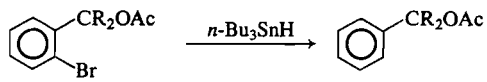
[13] 

gc/ms. These products indicate that radical **21** was formed, but there is no evidence for cyclization to **19**, in agreement with the observation that **19** rearranges to **21**.

These results suggest that evidence for the formation of the radicals **14** and **19**, or their rearrangement products **15** and **21**, could be obtained if these species were indeed formed from



aryl radicals **24** and **25**. Furthermore, conversion of **24** and **25** to **14** and **19**, respectively, ought to be exothermic. However, treatment of the appropriate aryl halide precursors **26** and **27** with *n*-Bu_3SnH

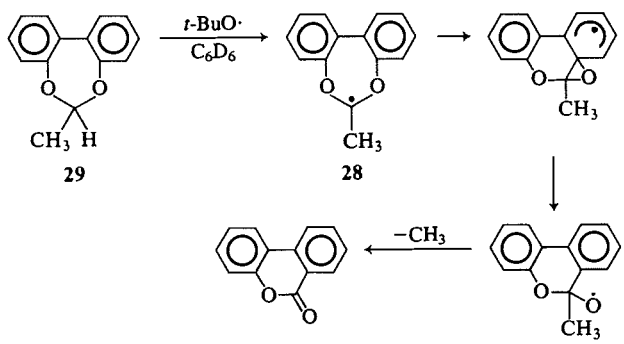


26 (R = H), **27** (R = Me)

gave only reduction to the unrearranged acetates. Evidently rearrangements to **14** and **19** suffer from sufficiently high kinetic barriers so as not to be able to compete with direct reduction. Rate constants for this latter process are high so the aryl radicals from **26** and **27** are short lived under these conditions.

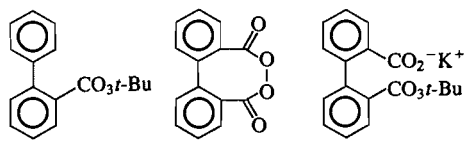
Generation of the 1,3-dioxepinyl radical **28** was also attempted by reaction of **29** with *tert*-butoxy radicals. No radical was detected by esr, but surprisingly an 85% yield of benzocoumarin (**30**) was identified in the reaction mixture by gc/ms, along with 10% recovered **29**. A reasonable mechanism for the formation of **30** is shown (eq. [14]).

[14]



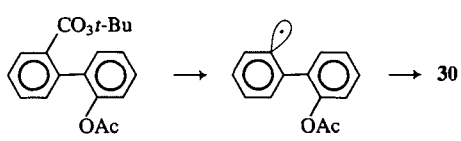
29 **28** **30**

There is a high propensity for formation of **30** from many precursors, including **31**–**33** (10, 11), but the extensive rearrangement from **28** is certainly one of the most unusual.



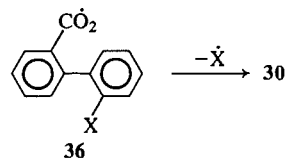
31 **32** **33**

Radical **34** appeared as a plausible precursor to give an aryl Surzur–Tanner cyclization, and photolysis or thermolysis of the perester **35** did give a high yield of **30** analogous to the reaction of **29**. However, this result does not confirm that acetoxy cyclization has occurred. Reaction of the biphenylpercarboxylate **31** also gave a high yield of **30** (10), but apparently by a route involving homolytic aromatic substitution by an intermediate carboxy radical. Similarly 2′-substituted biphenyl-2-carboxy radicals **36**, generated from peresters or by oxidation of carboxylic acids, also gave **30** by homolytic *ipso* substitution (12).



35 **34**

To test for the path followed by **35** the bromo analog **37** was prepared by the route shown from the lactone **38** and was found to reform this compound as the only lactonic product on decomposition. If a structure **39** analogous to **28** had been



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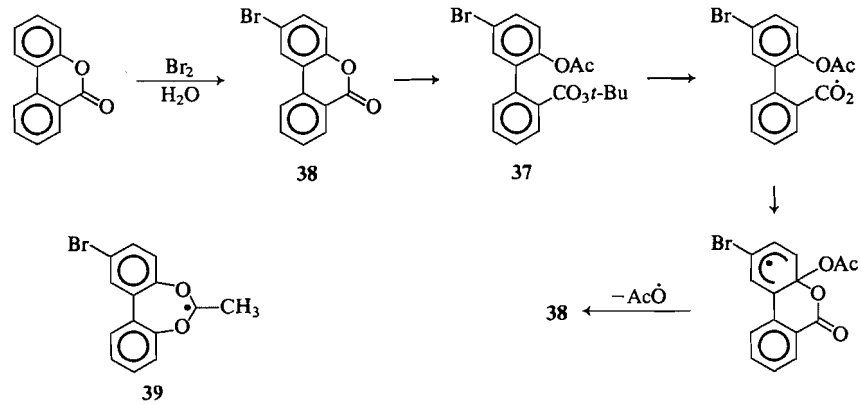
formed then ring opening to form 2 isomeric lactones would have been expected. It may be concluded that the formation of **28** or **39** by an acetoxy cyclization has yet to be convincingly demonstrated. The mechanism of eq. [14] appears likely for the conversion of **29** to **30**, while the intervention of **28** in the conversion of **34** to **30** is possible but is not established.

In summary it is apparent that intramolecular attack on an acetoxy group by an aryl radical is an elusive process, despite the fact that it is apparently favorable thermochemically. Benzo derivatives of 1,3-dioxol-2-yl and 1,3-dioxan-2-yl radicals display some fascinating reactivity, but confirmation of



formation of these species by a rearrangement route must await further more inspired study.

Experimental

Qualitative ir spectra were measured on a Perkin–Elmer 237 instrument. The nmr spectra were recorded on a Varian T-60 spectrometer. Elemental analyses were performed by A. G. Gygli Microanalysis Ltd., Toronto.

Products from tert-*butyl acetylperoxysalicylate (6)*

A solution of **6** (1.02 g, 4.0 mmol) in 10 mL benzene was heated 48 h at 100°C in a sealed tube. In separate experiments the reaction product was esterified with CH_2N_2 or $PhCHN_2$ and the product analyzed by vpc separation and isolation using a 1.5 m × 4 mm SE-30 column. Products were identified by their nmr spectra and, in the case of 2-acetoxybiphenyl, by its mass spectral molecular weight. Product yields (independent of the method of esterification) were phenyl acetate (10%), salicyclic acid (42%), acetylsalicyclic acid (12%), and 2-acetoxybiphenyl (36%). Methyl and benzyl esters of acetic acid were also isolated and it was found that acetylsalicyclic acid formed salicyclic acid and acetic acid under the reaction conditions.

Reaction of 2-bromophenyl acetate (0.43 g) with 0.4 g *n*-Bu_3-SnH (Aldrich) by photolysis in 5 mL ether containing 10 mg *t*-BuOO–*t*-Bu gave a product containing 35% phenyl acetate (isolated by vpc) but no **9**.

2-Methyl-1,3-benzodioxole (9) was originally prepared by a reported procedure (*7a*) utilizing pyrocatechol and paraldehyde but the reaction was highly irreproducible and gave low or nil yields of product. Therefore a modification of a reported (*7b*) method for preparation of acetals of *o*-dihydroxyaromatics was utilized. A solution of pyrocatechol (11.0 g, 0.10 mol), 1,1-dichloroethane (11.2 g, 0.11 mol), CuO (1.6 g), and K_2CO_3 (41.4 g, 0.30 mol) in 120 mL DMF was flushed with N_2 and heated at 125°C overnight. The mixture was cooled, poured into ice water, extracted with ether, and the ether layer was extracted once with 3% HCl, eight times with 20% K_2CO_3 solution, and once with water. The ether layer was dried with Drierite and evaporated and the product separated by vpc using a 1.5 m × 4 mm 10% SE-30 column at 160°C to give 2.3 g (0.017 mol, 17%) **9** with nmr (CCl_4) δ: 1.75 (d, 6, J = 5 Hz, CH_3), 6.20 (q, 1, J = 5 Hz, C*H*Me), 6.78 (s, 4, Ar).

*Reaction of 9 with di-*tert-*butyl peroxyoxalate (DBPO) in benzene-*d_6

A solution of **9** (0.2 g, 1.5 mmol) in 2 mL C_6D_6 with DBPO (0.5 g, 2 mmol) was degassed and sealed in a glass tube and allowed to stand at 25°C for 3 days. The mixture was separated by vpc (4 mm × 2 m 10% SE-30 column) and the products identified by nmr, **9** (40% d_0 and 24% d_1 by nmr, see Fig. 1), **10** (23%); nmr ($CDCl_3$) δ: 2.48 (s, 3, CH_3CO), 5.60 (broad s, 1, OH), 7.1 (m, 4, Ar). The identifications of **11***a–c* are tentative and depend on mass spectral data (M^+ peaks for **11***a* and **11***c*, an $M^+ - t$-Bu peak for **11***b*) and an nmr of **11***b* contaminated with **6**; nmr **11** ($CDCl_3$) δ: 1.28 (s, 9, *t*-Bu), 1.68 (s, 3, Me), 6.76 (s, 4, Ar).

2-Methyl-1,3-benzodioxan (12)

1,1-Dichloroethane (7.5 g, 0.074 mol) was added to a solution obtained by adding 9.3 g (0.075 mol) *o*-hydroxybenzyl alcohol (Aldrich) in 50 mL DMF to an ice-cooled mixture of 3.6 g (0.15 mol) pentane-washed NaH in 200 mL dry DMF. The resulting solution was heated overnight at 100°C, cooled, poured into ice water, and extracted with ether. The ether layer was washed repeatedly with 10% KOH solution, once with 10% HCl, dried over $MgSO_4$, and evaporated. Separation by vpc gave 0.25 g (1.7 mmol, 2%) **12**, identified by nmr ($CDCl_3$) δ: 1.54 (d, 3, J = 5 Hz, CH_3), 4.85 (center of AB quartet of CH_2), 5.10 (q, 1, J = 5 Hz, CHMe), 6.7–7.1 (m, 4, Ar).

Reaction of 2-acetoxytoluene (16) with DBPO was carried out analogously to the reaction of **9** using C_6D_6 as solvent. Formation of 12% **17** was indicated by gc/ms.

2,4,4-Trimethyl-1,3-benzodioxan (18) was prepared in 3–5% yields by the same procedure used for **12** from *o*-hydroxycumyl alcohol prepared by reacting excess MeLi in ether with *o*-hydroxyacetophenone. The product **18** was purified by vpc (1.5 mm × 4 m SE-30 at 140°C) and identified by nmr ($CDCl_3$) δ: 1.50 (d, 3, J = 5 Hz, $CHCH_3$), 1.60 (s, 6, CMe_2), 5.16 (q, 1, J = 5 Hz, $CHCH_3$), 6.7–7.3 (m, 4, Ar).

Reaction of 18 with DBPO

A C_6H_6 solution of **18** (0.18 g, 1.0 mmol) and 0.18 g DBPO (0.75 mmol) in dry benzene was sealed in an evacuated tube and let stand at 25°C for 2 days. Analysis of the product by gc/ms revealed the presence of 73% unreacted **18** and 27% *o*-acetoxycumene (**20**).

o-*Acetoxycumene 20* was prepared by reaction of 13.6 g (0.1 mol) *o*-hydroxycumene with 10 mL pyridine and 78 g (1 mol) acetyl chloride in 150 mL ether at 0°C. After one day the reaction mixture was poured into ice water, extracted with ether, and the ether layer washed with 10% HCl, 10% KOH, dried over $MgSO_4$, and evaporated. The product was identified by nmr ($CDCl_3$) δ: 1.10 (d, 6, J = 7 Hz, $CH(CH_3)_2$), 2.32 (s, 3, CH_3CO), 3.00 (heptet, 1, J = 7 Hz, $CHMe_2$), 7.0–7.4 (m, 4, Ar).

2-Bromobenzyl acetate (26) and n-Bu_3SnH

A solution of 2.3 g (10 mmol) **26** (obtained from reaction of Aldrich 2-bromobenzyl bromide and NaOAc) and 3.2 g (11 mmol) *n*-Bu_3SnH (Alfa) in 8 mL benzene with 0.2 g azoisobutyronitrile was heated in a sealed tube at 90°C for 48 h. Distillation of the benzene and then the product showed benzyl acetate as the only volatile product.

2-Chlorocumyl acetate (27) was obtained by reaction of

o-chloroacetophenone with methyllithium, followed by treatment of the isolated 2-chlorocumyl alcohol with KH and acetyl chloride in ether. This was reacted with n-Bu_3SnH as described for **26**, and gc/ms analysis of the product showed cumyl acetate as the major volatile product.

*2-Methyl dibenzo[*d,f*][1,3]dioxepin (29)* was prepared in 6% yield by the same procedure used for **12** from *o,o'*-biphenol (Aldrich). The material was purified by vpc separation on a 6 m SE-30 column, mp 48–49°C, and was identified by nmr ($CDCl_3$) δ: 1.62 (d, 3, J = 5 Hz, CH_3), 5.78 (q, 1, J = 5 Hz, C*H*Me), 7.0–7.8 (8, m, Ar).

Products from 29 and DBPO

The reaction was carried out with 70 mg (0.5 mmol) **29** and 120 mg (0.5 mmol) DBPO in 1 mL C_6D_6 as described for **9**.

2-Acetoxy-2'-tert-*butylpercarboxylbiphenyl (35)* was prepared by adding to the known (13) acid chloride of 2-acetoxy-2'-biphenylcarboxylic acid (1.37 g, 5 mmol), in 150 mL ether stirred at 0°C, a solution of 1.0 g (11 mmol) *t*-BuOOH and 1 mL pyridine in 30 mL ether. The mixture was stirred overnight, poured into water, extracted into ether, washed with 10% NaOH and then 10% HCl, dried, and the solvent evaporated. The crude product was chromatographed on a 20 cm silica gel column with 1:1 pentane/ether to give 0.52 g **35** (1.6 mmol, 32%); nmr ($CDCl_3$) δ: 1.12 (s, 9, *t*-Bu), 1.96 (s, 3, CH_3CO), 7.2 (m, 8, Ar).

Products from 35

Solutions of **35** (0.165 g, 0.5 mmol) in 2 mL of solvent were sealed in evacuated Pyrex tubes and decomposed either thermally (40 h at 110°C) or photochemically (72 h irradiation with a Hanovia medium pressure Hg lamp). The products were analyzed by gas chromatography as shown (±5%):

	Photochemical		Thermal
Product	Benzene	Toluene	Benzene
o-Acetoxybiphenyl	2	9	2
2-(2'-Acetoxyphenyl)benzoic acid	14	11	2
30	80	80	90

2-Acetoxy-5-bromo-2'-tert-*butylpercarboxybiphenyl (37)* was obtained by a route analogous to **35** beginning with **38** (14), which on reaction with NaOH and Ac_2O gave 2-(2'-acetoxy-5'-bromophenyl)benzoic acid (mp 126–127°C), which on reaction with $SOCl_2$ followed by *t*-BuOOH/pyridine gave **37** as an oil; nmr ($CDCl_3$) δ: 1.23 (s, 9, *t*-Bu), 2.03 (s, 3, Ac), and 7.0–8.0 (m, 7, Ar). *Anal.* calcd. for $C_{19}H_{19}BrO_5$ (mol. wt. 407.27): C 56.03, H 4.70, Br 19.62; found: C 56.52, H 4.36, Br 19.46. Product studies on **37** carried out analogously to **35** gave **38** as the only lactonic product detected, as identified by nmr and mass spectroscopy.

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Appendix

The $\Delta\Delta H_f^0$ for the conversion of **4*a*** to **5*a*** at 25°C may be derived from the ΔH_f^0 values for phenyl acetate (−51.4 kcal/mol) and **9** (−55.7 kcal/mol, not corrected for ring strain) calculated by the method of group equivalents (15) and the estimated C—H bond dissociation energies of phenyl acetate to form **4*a*** (110 kcal/mol) and of **9** to form **5*a*** (93 kcal/mol) (16). The latter value applies to H—$CH(OH)CH_3$ and the actual value is probably less.