were removed by successive Clemmensen and Wolff–Kishner reductions to afford 26-hydroxycholesterol (**1b**), mp 175–177 °C (lit.[7] 177–178 °C), which was transformed into the corresponding ditosylate.[8] Selective hydrolysis[9] of the ester group at C-3 yielded the 26-monotosylate,[10] which after treatment with lithium aluminium deuteride afforded 26-deuteriocholesterol,[11] mp 144–146 °C. Proper application of the sequence rules,[12] in combination with the recently proposed nomenclature[2] for cholesterol (**1a**), shows that kryptogenin is a (25*R*)-27-hydroxy steroid and that the transformation of its derived (25*R*)-27-tosylate affords (25*S*)-27-deuteriocholesterol (**1c**), even though, during all these reactions, the C-25 chiral center is never touched.

We found the C-26 and C-27 peaks of cholesterol (**1a**) at 22.54 and 22.78 ppm in the ^{13}C NMR spectrum. In the deuterated sample (Figure 1) the lower field peak at 22.78 ppm was not observed owing to the quadrupole moment and the spin–spin coupling of the directly attached deuterium atom and corresponds, therefore, to the (*pro-S*)-methyl groups (C-27). The signal at 22.54 ppm remains unchanged and is due to the (*pro-R*)-methyl group (C-26). These assignments are in agreement with those made from the biosynthetic experiments[2] and, therefore, it is now clear that no rearrangements occur when cholesterol is oxidized by *Mycobacterium smegmatis*.[3] The side-chain carbon atoms of cholesterol (**1a**) show chemical shifts similar to those of the dihydroperezone (**3**) side chain[13] with the obvious exception of the carbon directly bonded to the rings (Table I). This allows also the assignment of the isopropyl methyl groups in the sesquiterpene. An analogous situation is found between the side chains of perezone (**4a**) and desmosterol (**2**), thus allowing also the definitive assignment of individual methyl groups.

Although several hundred steroids[14] have been analyzed by ^{13}C NMR, surprisingly no data appear to be available for desmosterol (**2**) and its spectrum was therefore recorded. It shows (Figure 1) the ring carbons and angular methyl groups[15] at essentially the same values found for cholesterol (**1a**), while the side-chain carbons appear (Table I) as in perezone (**4a**). The isopropylidene methyl groups are assigned unambiguously using a sample of deuterioperezone (**4b**) obtained by a regioselective synthesis.[16] The *trans*-methyl groups appears at 25.65 ppm, while the *cis*-methyl is found at 17.61 ppm.

The chiral center of dihydroperezone (**3**) has the same *R* configuration as C-20 in the steroids and this appears to be the main factor controlling the chemical shift difference between the isopropyl methyl groups which is observed[1a] even in 2,6-dimethyloctane where the rings are replaced by a methyl group. Future biosynthetic studies on the hydrogenation of isopropylidene residues might be followed by deuterium labeling and ^{13}C measurements.

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The Unlikelihood of an Electron-Transfer (Haber–Weiss) Reaction between Superoxide and Peroxides

Sir:

While an increasing number of investigations have recently been directed toward the reactions of superoxide ion ($O_2^{-}\cdot$) with a range of molecules,[1-3] its fundamental reactivity is yet poorly understood. It has recently been proposed, and shown for at least one case, that ultimate products in mixtures of $O_2^{-}\cdot$ with many molecules are the result of $O_2^{-}\cdot$ *decomposition products* acting as oxidizing species or as very strong bases.[4] We report here on a very simple, but centrally important system, $O_2^{-}\cdot$ in the presence of peroxides. It is found that, while *tert*-butyl hydroperoxide acts solely as a proton source toward $O_2^{-}\cdot$ in toluene and pyridine, attack upon solvent by the peroxide anion occurs in acetonitrile, leading ultimately to products of peroxide decomposition. Additional studies, together with precedents from the literature, show that experimental support is lacking for the assumed electron-transfer process between $O_2^{-}\cdot$ and peroxides.

Both hydrogen peroxide and organic hydroperoxides undergo electron transfer from Fe^{2+} (and other reduced metals) via

$$ROOH + Fe^{2+} \rightarrow RO\cdot + HO^- + Fe^{3+} \qquad (1)$$

R = H or alkyl

The evidence for this reaction is quite strong, and it has been studied in detail.[5,6] By analogy, it has been generally accepted that a similar process occurs with $O_2^{-}\cdot$ as the electron donor:[2,3,7,8]

$$HOOH + O_2^{-}\cdot \rightarrow HO\cdot + HO^- + O_2 \qquad (2)$$

Both eq 1 and 2 have been discussed in terms of biological effects of H_2O_2 (and its destructiveness in systems in which it is produced) by generating the reactive $HO\cdot$ radical.[8,9]

Noting the absence of direct evidence for reaction 2, Peters and Foote recently examined the reaction of *t*-BuOOH with $O_2^{-}\cdot$ in acetonitrile.[10] They observed rapid O_2 evolution and

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Table I. Stability of *tert*-Butyl Hydroperoxide with KO_2 (or KOH) and Crown Ether in Various Solvents[a]

entry	solvent, (mL)	reagent[b]	time, min[c]	results[d] *t*-BuOOH remaining, %	results[d] *t*-BuOH + acetone, %	results[d] other
1	$C_6H_5CH_3$ (2)	KO_2	3	44[e]	0	*t*-$BuOO^-$ formed
2	$C_6H_5CH_3$ (2)	KO_2	14	11[e]	0	
3	$C_6H_5CH_3$ (4)	KO_2	41 h	95	10	
4	C_5H_5N (2)		96 h	99	5	
5	C_5H_5N (4)	KO_2	10 h	81	12	
6	CH_3CN (2)		96 h	100	0	
7	CH_3CN (4)	KO_2	2	92	7	
8	CH_3CN (4)[f]	KO_2	15	3	72	14% CH_3CONH_2 + 10% HOAc
9	CH_3CN (4)[f]	KO_2	25	0	50	25% CH_3CONH_2 + 10% HOAc
10	CH_3CN (4)	KO_2	15	57	30	6% CH_3CONH_2
11	CH_3CN (4)	KO_2	1 h	0	105	13% CH_3CONH_2 + 29% HOAc
12	CH_3CN (4)[f]	KOH	25	0	55	18% CH_3CONH_2 + 0% HOAc
13	CH_3CN (4)	KOH	15	27	69	
14	CH_3CN (4)	KOH	25	16	84	5% CH_3CONH_2 + trace of HOAc

[a] All runs contain 1.0 mmol of distilled *tert*-butyl hydroperoxide. Except for entries 1 and 2, after the mixture was stirred in the dark for the time indicated, 1 equiv (to KO_2 or KOH, i.e., 3.0 mmol) of concentrated HCl was added and the mixture stirred and centrifuged before removing a sample for gas chromatographic analysis. [b] If KO_2 or KOH were added, 3.0 mmol of KO_2 or KOH were ground with solvent containing 0.1 mmol of 18-crown-6 ether before adding the hydroperoxide. A blank indicates that no KO_2 or KOH and CE were added. [c] Except where noted otherwise. [d] Analysis was carried out on Carbowax 20M (Teflon column). Yields are based on initial *t*-BuOOH; the sum of *tert*-butyl alcohol and acetone is given (see text). [e] In these runs (entries 1 and 2) the reaction mixture was not neutralized; a small sample was directly injected into the gas chromatograph. [f] These runs, typical of those done first, were performed without temperature control. Runs 10, 11, 13, and 14 were done in a 25 °C water bath.

obtained excellent evidence for the formation of *tert*-butoxy radicals, implying that reaction 3 occurred.

$$t\text{-BuOOH} + O_2^{-}\cdot \rightarrow t\text{-BuO}\cdot + HO^- + O_2 \qquad (3)$$

Virtually simultaneously we had reported, as part of another study, that both *tert*-butyl hydroperoxide and di-*tert*-butyl peroxide in toluene are apparently inert toward $O_2^{-}\cdot$.[11] The dialkyl peroxide result was confirmed by Peters and Foote.[10,12] Since others have accepted eq 2 and 3 as written,[3,13] we addressed ourselves to this discrepancy in the hydroperoxide results.

The addition of *tert*-butyl hydroperoxide to a solution of 18-crown-6 ether (CE) in the presence of KO_2 in all solvents investigated leads to rapid evolution of gas (assumed to be O_2). In toluene or pyridine, direct analysis of the reaction mixture shows rapid (but not instantaneous) loss of the hydroperoxide peak on GC (minutes; Table I, entries 1 and 2). Analysis after neutralization reveals almost total recovery of hydroperoxide and only *very slow net loss of initial hydroperoxide* (days; Table I, entries 3–5). These results (rapid O_2 evolution and reversible *t*-BuOOH disappearance) most reasonably indicate the occurrence of reactions 4 and 5, removal of a proton from *t*-BuOOH followed by the well-known disproportionation reaction of $O_2^{-}\cdot$ with $\cdot O_2H$.[14-16]

$$t\text{-BuOOH} + O_2^{-}\cdot \rightleftharpoons t\text{-}BuOO^- + \cdot O_2H \qquad (4)$$

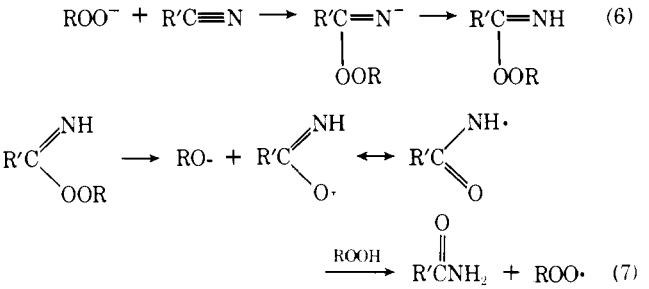
$$\cdot O_2H + O_2^{-}\cdot \rightarrow {}^{-}O_2H + O_2 \qquad (5)$$

In agreement with the earlier report,[10] in acetonitrile we observe rapid O_2 evolution and irreversible loss of *t*-BuOOH upon reaction with KO_2 (Table I, entries 6–11). Peters and Foote reported quantitative formation of the sum of *tert*-butyl alcohol and acetone; we concur with this result, although, when the reactions are not run in an ambient temperature water bath, noticeable heating occurs and yields of these products are lower.

The effect of KOH (replacing KO_2) in these systems is rather revealing. In acetonitrile, *t*-BuOOH is rapidly decomposed by KOH (Table I, entries 12–14), but in toluene and pyridine only anion (or salt) formation occurs and the hydroperoxide is recovered after neutralization. The *t*-BuOH/acetone product ratio in acetonitrile is the same for KO_2 and KOH (22).

This profoundly different stability of the hydroperoxide anion in toluene and pyridine as opposed to acetonitrile suggested possible actual reaction of the latter solvent. Reasoning from earlier work,[19-20] we looked for, and found, acetamide (along with varying, usually smaller, amounts of acetic acid) as a product in this reaction (Table I).[21]

That hydroperoxides (including *tert*-butyl) undergo *free-radical chain* decomposition in the presence of nitriles and base was shown conclusively by Denney[19] following the original work by Kharasch.[17] The reaction (run at room temperature in benzene with nitrile, base, and excess ROOH) involves nucleophilic addition to the cyano group (eq 6) followed by breakdown via eq 7 to yield amides. Berger[15] was able to trap



(6)

(7)

the α-imino peroxide itself by the addition of HCl at the time of maximum velocity. The resultant alkoxy and peroxy radicals initiate a normal *t*-BuOOH chain decomposition

$$RO\cdot + ROOH \rightarrow ROH + ROO\cdot$$

$$2ROO\cdot \rightarrow 2RO\cdot + O_2 \qquad (8)$$

yielding *tert*-butyl alcohol, acetone (by β scission), and O_2. In the absence of nitrile, only strong base and much higher temperatures produce reaction. Denney also showed, using ^{18}O, that the amide oxygen in the product derives from the ROOH.

The quantities of acetamide found here (Table I) are in accord with the chain nature of the nitrile reaction. To further demonstrate the acetonitrile dependence of the KO_2 process, we allowed KO_2, *t*-BuOOH, and CE to react for 30 min in varying ratios of pyridine/acetonitrile. As apparent in Table

Table II. Reaction of *tert*-Butyl Hydroperoxide with Acetonitrile in KO_2/Pyridine[a]

pyridine, mL	acetonitrile, mL (mmol)	results[b] *t*-BuOOH remaining, %	results[b] *t*-BuOH + acetone, %
3.95	0.05 (1.0)	95	10
3.79	0.21 (4.0)	69	21
3.48	0.52 (10)	18	54
2.96	1.04 (20)	15	61
1.91	2.09 (40)	trace (<2)	62
0.00	4.00 (76.6)	0	75[c]

[a] All runs have 1.0 mmol of *t*-BuOOH, 3.0 mmol of KO_2, and 0.1 mmol of CE and were treated exactly as described in Table I (with workup) for 30-min reaction times. Temperature was not controlled. [b] Results (percent yield) are in each case based on the initial concentration (from an initial point by GC) of *t*-BuOOH. [c] Worked up after reacting 15 min.

II, there is a direct correspondence between the acetonitrile concentration and the loss of hydroperoxide after neutralization.

From the dramatic difference in *t*-BuOOH stability in the solvents investigated, the effect of KOH, the observation of significant quantities of acetamide, the mixed solvent work, and ample literature precedents, it seems clear that reaction 3 does not occur under the conditions of this or the prior[10] study, but rather that eq 4 and 5 take place, followed by eq 6 in acetonitrile. In an earlier report we had shown that hydroperoxide ion is highly reactive to dimethyl sulfoxide, giving dimethyl sulfone and the corresponding alcohol.[11] Apparently neither Me_2SO nor CH_3CN is an inert solvent in these kinds of systems.

In conclusion, we must comment on the unlikelihood of reaction 2 for superoxide and H_2O_2. Neither dialkyl peroxides nor alkyl hydroperoxides act as electron acceptors from $O_2^{-}\cdot$ (vide supra). The energetics of the H_2O_2 molecule are very similar to those of the organic peroxides, and the pK_a of HOOH and *t*-BuOOH are quite close. Indeed, several recent studies fail to observe the occurrence of reaction 2 under conditions in which it might have been an important process. In 1976 McClune and Fee, studying $O_2^{-}\cdot$ reactions by a stopped-flow method, showed that reaction 2 does not compete with a number of other elementary $O_2^{-}\cdot$ processes, and it is at best extremely slow.[22,23] They also cite earlier literature on this point that has been generally ignored. Taken together, it would seem that a Haber–Weiss-type process for $O_2^{-}\cdot$ has not been demonstrated, and that $O_2^{-}\cdot$ does indeed give solutions that act as if they were strongly basic.

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Polar Substituent Effects in Triplet Quenching. Excitation Transfer and Cycloaddition

Sir:

Rate constants for quenching of sensitizer triplets by excitation acceptors are sensitive to the triplet excitation energy gap, E_T(acceptor) − E_T(sensitizer), when transfer is endothermic.[1,2] The slope of a plot of log k_Q vs. E_T(sensitizer) is roughly the theoretical value of 0.73 decade/kcal, i.e., $(2.3RT)^{-1}$, in favorable cases,[2] which value derives from spectroscopic excitation energies, the assumption of vertical[3] excitation transfer, and the consequent requirement that vertical energy deficits be made up thermally. The quenching of ketone triplets by simple alkenes, however, often leads ultimately to cycloadduct[4] via a polar triplet exciplex[5,6] and a 1,4 biradical, and such rates correlate instead with the energetics of electron transfer.[5-7] Quenching of triplet ketones by amines[8] has also been interpreted on the basis of charge transfer (CT).

Cycloaddition and excitation transfer have only occasionally been observed simultaneously with the same triplet donor–acceptor pair.[9] We now report a study of the kinetics of one such series. We find that, although triplet excitation transfer apparently dominates triplet quenching, sensitizer triplet excitation energies are much inferior to a blend of excitation energy and electron-transfer effects as predictors of rate. The CT contribution to k_Q clearly does not simply correspond to the cycloaddition pathway.

The quenching of cyanophenanthrene triplets bearing remote polar substituents by *trans*-β-methylstyrene and by *trans*-anethole (*p*-methoxy-β-methylstyrene) leads to efficient trans–cis isomerization in the four cases that we studied (Table

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