The rapid rates of back electron transfer indicate the Ag^0 and Ag_2^+ species generated via electron transfer in solutions are extremely reactive reagents which should be capable of reacting with a variety of substrates that are either inert or sluggishly reactive toward metallic silver. The measured quenching rates permit an assessment of the energetics of the silver ion reduction if we assume that the retardation of the rate below the diffusion controlled limit is attributable to a free energy of activation equal to the endoergonicity of the quenching step (eq 1).[15-17] Thus for the reduction (eq 7) we

$$Ag_{(solv)}^+ + e \rightarrow Ag_{(solv)}^0 \qquad (7)$$

obtain potentials of -1.05 to -1.11 V in acetonitrile and -0.96 to -1.02 V in water.[15] Comparing these values to the measured Ag^+ metal reduction potentials indicates that the metal is more stable than the reduced soluble species by 31-44 kcal/mol. The values thus estimated are considerably below the sublimation energy of ~60 kcal/mol[18,19] indicating that solvation by water or acetonitrile stabilizes the metal atom to at least some extent.[20] Interestingly, related experiments on the photoinduced reduction of complexed Ag^+ ions suggest that the stability of Ag^0 complexes can cause profound changes in its redox reactivity toward reagents such as $Ru(bpy)_3^{3+}$.[21]

The results obtained in the photolysis study are somewhat related to recent investigations of silver ion reduction in solution initiated by pulse radiolysis (γ-radiation or electrons).[13,18,22] However, in the present study the reduced silver species can be generated under very mild conditions and in the presence of reagents which might not survive in radiolysis experiments. The use of scavengers to avert the back-reaction provides the possibility of increasing the lifetime of the reactive reduced species and to allow its interception by other substrates. The utility of reactive metal species in a number of synthetic applications has been demonstrated by Rieke,[23] Skell,[24] and Klabunde[25] using very different methods of generation. The general techniques used in the present study should be useful for reducing a number of monovalent metal ions to reactive atomic or subaggregate species, including those from copper, thallium, and mercury.

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Photochemical or Photomimetic Fossil Triterpenoids in Sediments and Petroleum

Sir:

During a study of the sediments deposited in the delta of the Mahakam river, off the east coast of Borneo, we have encountered a series of fossil triterpenoids, the nature of which discloses the operation of a novel mechanism of early geochemical maturation: decay of excited ketones.

Precise structural characterization of products of the transformation or degradation of biological molecules has proven quite useful in the elucidation of the origin of the geological organic matter and of the (geo)chemical processes occurring in sediments at various stages of their maturation.[1,2] These processes, which start in the recent sediment, lead over geological periods to the formation of fossil energy sources, such as petroleum, gas, and coal.[3,4]

Most of the complex alicyclic molecular fossils identified so far in sediments (including petroleums, coals, shales etc.) are derivatives of the 3-deoxyhopane triterpene family, of microbiological origin.[5] Other triterpenoids, derived from 3-hydroxy constituents of higher plants, are sometimes found, and are considered as indicators of continental influences.[6,7] One such derivative of β-amyrin (**1**) has recently been identified in several recent and ancient sediments and crude oils.[8] The process leading to the loss of ring A, in **1**, was mysterious. Results described below appear to explain it.

Off the coast of as densely forested an island as Borneo, in the deltaic recent sediments (2-30% organic carbon) of a large river, dating from the present to a few thousand years at the most, continental impact should be large, and this is reflected by the isolation of a series of triterpene ketones in the nonpolar neutral fraction by our standard procedure.[9] Friedelin, α-amyrenone, β-amyrenone, and lupenone are frequent constituents of higher plants, notably of tree barks, or could have been formed by trivial oxidation of the corresponding 3-alcohols, ubiquitous in green plants. However, these ketones are accompanied, in particular in the same fraction or in the acidic and hydrocarbon fractions, by a homogeneous genetic family of products, *obtainable by photochemical decomposition of the 3-ketones*[10,11] (Figure 1). Indeed this is the way we have prepared most of the authentic reference samples to identify these products (Figure 2). A quantitative comparison of the results of the photochemical reaction with the relative abundance of the fossil substances is, in this case, meaningless, as

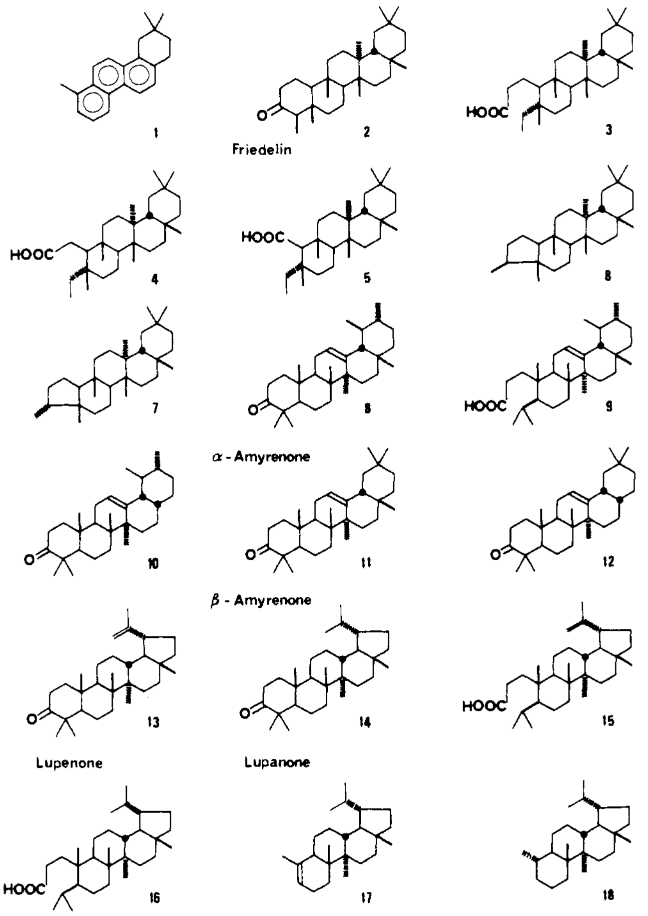

Figure 1. Fossil triterpenoids identified in the deltaic recent sediments of the Mahakam river (Indonesia).[21]

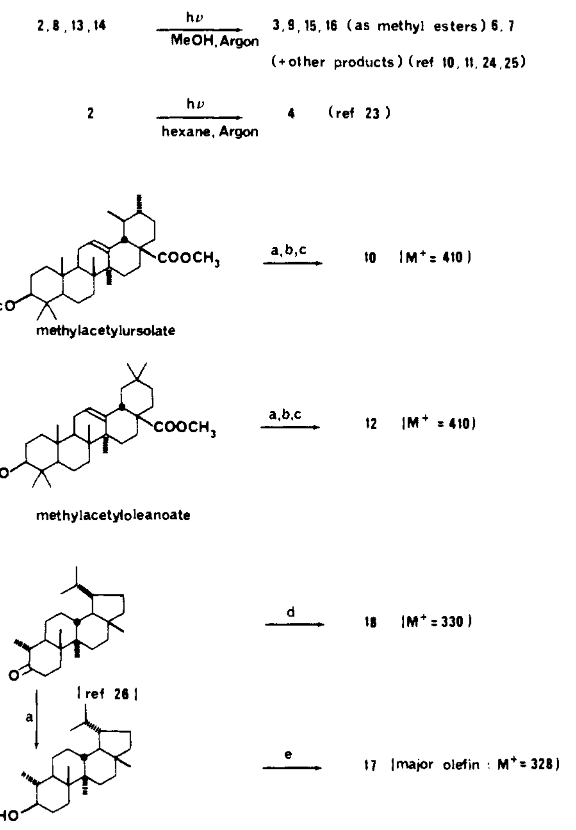

Figure 2. Preparation of the reference compounds used for the identification of the fossil triterpenoids:[22] a, $LiAlH_4$; b, CrO_3, Py; c, $(Ph_3P)_3RhCl$, PhCN, 160 °C, d, Wolff-Kishner; e, $POCl_3$, Py.

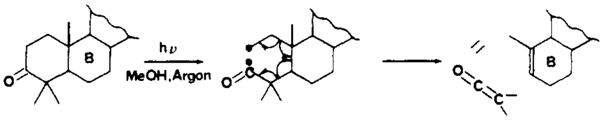

Figure 3. Proposed mechanism for the photochemical fragmentation leading to hydrocarbon **17**.

the distribution of the photoproducts themselves vary with experimental conditions, and as the primary products may well be further altered in the sediment, in a manner depending on the burial conditions.

The tropical origin of the samples studied conjures up the hypothesis of sun-drenched sediments, the ketones of which would undergo photolysis. However, at least some of the same substances have been isolated also in other sediments, where active sunlight appears less likely: hydrocarbons **17** and **18** had already been found (but not identified then) in a Baltic sea sediment;[12] **18** in the Messel oil shale;[13] substances **3**, **5**, **17**, and **18** in the dark, contemporary surface muds of temporary ponds near Strasbourg;[14] and acids **3** and **16** in a Nigerian crude oil.[15] Furthermore, hydrocarbon **1**, which is also present as a major compound in the aromatic hydrocarbons of the Mahakam delta sediments, has been found in various other geological sources.[8] It is derivable from the equivalent of hydrocarbon **17**, in the oleanane series, by aromatization, a known geochemical maturation process, which is probably induced by microorganisms in this case.

It is possible that some of the decay reactions leading to these compounds do already take place in a previous stage in the precursor plant material since acids formed by 3,4 cleavage of ring A of triterpenes have been detected in higher plants,[16] as well as at least one de-A derivative of a triterpene.[17] Another possibility which we would like to suggest is that these substances may well not be *photochemical*, but *photomimetic*[18] products, formed by microorganisms through biochemical reactions leading to the 3-ketones in their excited state (either by energy transfer or by oxidation of the 3-alcohol to the excited ketone). These hypotheses are now being checked.

Be it as it may, the fact remains that many molecular fossils appear to have been formed from their obvious precursors by another process, photochemical or photomimetic, than the ones known up till now, i.e., hydrogenation, dehydrogenation,[1] and carbenium ion evolution.[19] The main value of such a result is of course its heuristic character: it can now be used to predict (and later check) structures of other molecular fossils.

The substances isolated derive from lupane, oleanane, ursane, and friedelane but not from hopane. Yet, these sediments are no exception to the ubiquitous presence of hopanoids;[5] however these, in sediments, are never oxygenated in ring A, and could therefore not serve as precursors for the cleaved or ring-contracted derivatives described here.

It is amusing to note that we had postulated a photochemical/photomimetic origin for the hydrocarbons **17** and **18**, despite the fact that they (or their equivalents) had not previously been detected in the many photochemical studies of 3-ketones. A reasonable fragmentation mechanism can be postulated (Figure 3). We have now found that it is indeed operative, albeit with a very low efficiency, in the photolysis of lupanone in methanol which does give hydrocarbon **17**. Cyclohexanone, in the gas phase, is similarly photofragmented.[20]

Note Added in Proof. All naturally occurring 3:4-seco triterpene acids previously known[16] were oxidation products of the 3-ketones, and carried at C-5 an isopropenyl group. The very recent isolation[27] from a fresh living plant, a *Cistus*, of two 5-isopropyl 3:4-seco acids analogous to those described here suggests that they could be products of the normal photolysis of leaf triterpene ketones. This point is being checked.

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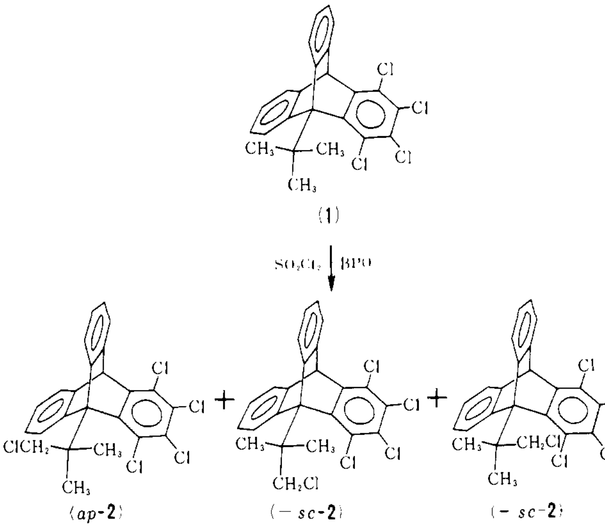
Differential Reactivity of the Methyls in a *tert*-Butyl Group[1]

Sir:

Chemically identical ligands in a group of local C_{3v} symmetry, such as the hydrogen atoms in a methyl group or the methyl substituents in a *tert*-butyl group, are usually treated as nondistinguishable in organic chemistry, because in most circumstances they are interchanged rapidly on the laboratory time scale by rotation. In principle, however, the methyls in the *tert*-butyl group of a molecule $(CH_3)_3CCXY_2$ can exhibit different reactivities to give diastereoisomers, since their environments are not equivalent. Although rapid internal rotation will prevent realization of this difference, it should become recognizable if the rotation is frozen: the compound will then produce two kinds of diastereoisomers on substitution at the *tert*-butyl group with two different reaction rates. We report in this communication that this situation is realized in 9-*tert*-butyl-1,2,3,4-tetrachlorotriptycene (**1**).



(1)

When **1** in chlorobenzene was treated with sulfuryl chloride under reflux for 1 h with a small amount of benzoyl peroxide, the chromatographic fraction of the monochlorinated products (**2**) showed an ±*sc*/*ap* ratio of 3.2:1 according to the ^{1}H NMR spectrum. Although the separation of the *ap* and ±*sc* isomers was tedious, it was found that the ±*sc* forms were destroyed by chromatography on alumina. The pure *ap*-**2** eluted by hexane-benzene (6:4) had the following properties: mp 251.2–252.5 °C; ^{1}H NMR (CCl_4) δ 2.38 (6 H, s), 4.51 (2 H, s), 6.02 (1 H, s), 6.8–8.0 (8 H, m).[2]

The formation ratio (3.2:1) of the ±*sc* to the *ap* forms was reproducible; yet the negligibility of isomerization during the reaction must be established. The rates of isomerization represented by eq 2 were measured at two temperatures: $k_1 = 1.21 \times 10^{-4}$ and $k_{-1} = 1.28 \times 10^{-4}\ s^{-1}$ at 208 °C, $k_1 = 2.49 \times 10^{-5}$ and $k_{-1} = 2.60 \times 10^{-5}\ s^{-1}$ at 185 °C. Thus a rough estimate of the rates of isomerization at the boiling point of chlorobenzene (132 °C) is possible: it takes 14 days for effecting the conversion of 5% of the materials which is considered to be no more than the error limit of the integration in NMR spectroscopy.

$$ap\text{-}\mathbf{2} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \pm sc\text{-}\mathbf{2} \tag{2}$$

The preferential attack on the ±*sc* methyls over the *ap* by the factor of 1.6 is caused by the presence of the chloro group in 1 position. This conclusion is drawn because 9-*tert*-butyl-1-chlorotriptycene afforded chlorination products in a 2.6:1 ±*sc*:*ap* ratio, whereas 9-*t*ert-butyl-2,3-dichlorotriptycene gave a mixture of monochlorinated products with a 2:1 ratio of the ±*sc* and the *ap* forms, which is the statistical value.

Two explanations are possible for the observed preference of the ±*sc* methyls in the reaction. One is to ascribe the phenomenon to a steric effect. Since X-ray analysis of **1** has revealed that the *tert*-butyl group is tilted against the *peri*-chloro group,[3] the *ap* methyl is pushed into the triptycyl moiety. This might make the ±*sc* methyls more exposed to the attack of chlorine atoms. The other is to consider the participation of the chloro group in the 1 position: a chloro group is known to facilitate radical formation, although not to a very extensive degree.[4]

Photobromination of hydrocarbons is known to give better