observed in radiolyzed CH_4 at 4°K[9] but are never found in hydrocarbons at 77°K, implying that they are sufficiently mobile to migrate to trapped electrons. It is plausible that the hydride ion should remain in the trap originally occupied by the electron, precluding the trapping of another electron.

Reactions 1 and 3 cannot be important because trapped radicals in these media have half-lives much too long to allow significant migration to trapped electrons. Reaction 2, which might occur if positive charge moves through the matrix by a chain of proton transfers, would produce H atoms which would diffuse out of the trapping sites. (It can only explain the observations if the energy of neutralization destroys the sites.) Dielectron formation (4) in these nonpolar media seems to be excluded by coulombic repulsion.

To test whether trapped free radicals affect electrons produced during subsequent irradiation, we have irradiated a sample of MCH glass at 77°K to a dose of 1.4×10^{20} eV g^{-1}, which produced the maximum electron esr signal. This signal was then removed by tungsten light, with no change in the free-radical esr signal. A subsequent 1.4×10^{20} eV g^{-1} irradiation doubled the intensity of the free-radical signal and produced a new electron signal approximately equivalent to that produced by the first irradiation. This shows that, within the sensitivity of detection, neither mobile electrons produced by photobleaching nor those produced by γ-irradiation react significantly with the prevailing concentration of trapped radicals to form anions.

To determine whether the species formed in removing the trapped electrons, and which preempts the trapping sites, can be removed by light, with regeneration of the traps, W. G. French of our laboratory has irradiated a sample of MCH to a dose of 4.4×10^{20} eV g^{-1}, at which point only a very small electron esr signal remained. The sample was then exposed to the light of a 150-W tungsten lamp at 25 cm for 15 min (<10 sec exposure would have bleached a full electron signal). An additional 8×10^{19} eV g^{-1} γ-irradiation did not produce a new electron signal, indicating that the inactivated traps are not regenerated by such illumination.

The transmission of MCH at 77°K from 11,500 to 16,000 Å as a function of γ dose has been determined by A. C. Ling, of our laboratory. These tests indicate a rise to a maximum in electron concentration followed by a decrease at higher doses similar to that observed by esr.

Assuming $G(e^-) = 0.7$ during the initial linear portion of the growth curves in the hydrocarbons, the trapped-electron concentrations at the maxima are about 10^{-4} mole fraction. In a preprint kindly sent to us while the present work was in progress, Lin, Tsuji, and Williams[5c] show that the electron concentration in γ-irradiated 3-methylhexane at 77°K reaches a maximum at a dose of about 8.5×10^{19} eV g^{-1} and a concentration of about 10^{-4} mf. Limited data indicate an apparent decrease in concentration at higher doses.

The electron esr signal in γ-irradiated methyltetrahydrofuran (MTHF) reaches a plateau at 2×10^{20} eV g^{-1} which shows no decrease up to at least 5.6×10^{20} eV g^{-1}. This indicates either that many more electron trapping sites are available in this more polar medium than in the hydrocarbons (possibly the electron can be trapped in a polarized envelope anywhere in the medium) or that the entity which removes e_t^- in hydrocarbons cannot do so in MTHF.

In contrast to the electron signals, the free-radical esr signals from MCH, 3MP, 3MO, and MTHF matrices grow linearly with dose to at least 4×10^{20} eV g^{-1}. C_2H_5 radicals produced by dissociative electron capture during γ-irradiation of 1.5 mole % C_2H_5 in 3MP or MCH show a still different pattern;[10] at a dose rate of 2×10^{18} eV g^{-1} min^{-1} their concentration approaches a steady state at 4×10^{20} eV g^{-1}. The decrease in G value with increasing dose must result from radiation-catalyzed[8,10] removal processes.

The experimental methods used in this work were similar to those described earlier.[5b]

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Stereoelectronic Requirements for the Type II Cleavage of *cis*- and *trans*-4-*t*-Butylcyclohexanones[1,2]

Sir:

Intramolecular type II photoeliminations, whereby a ketone or aldehyde possessing hydrogen on a γ-carbon atom yields an olefin and carbonyl compound,[3] have been the topic of much recent work.[4-7] It is now known that both singlet and triplet states of branched alkyl ketones may participate in this reaction.[4,6] Although there has been much speculation on the geometry and electronic structure of the excited n,π^* states of ketones, only recently have the stereoelectronic requirements for reactions of these states been investigated.[1] We wish to report such a study of the type II cleavage of *cis*- and *trans*-4-*t*-butylcyclohexanones.

Irradiation of cyclohexane solutions of *cis*- and *trans*-2-*n*-propyl-4-*t*-butylcyclohexanones (**1** and **2**) results in strikingly different photochemistry, both qualitatively and quantitatively. Thus, vapor chromatography of the reaction mixtures indicates that the major intramolecular path for photodecomposition of **1** results in formation of 4-*t*-butylcyclohexanone, while photolysis of **2** yields **1** as the major product, presumably as the result of α cleavage followed by epimerization.[8]

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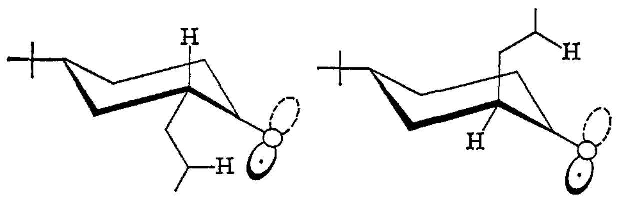
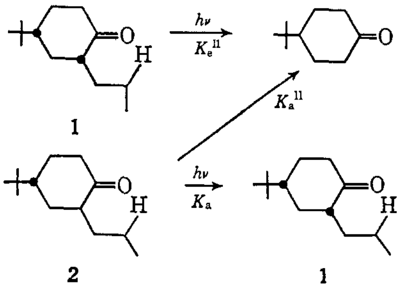


1 2

Figure 1. Most probable excited-state conformation for **1** and **2**. Notice that for **1** the formation of a cyclic six-membered transition state for hydrogen abstraction by the half-vacant n orbital is easy to achieve, while for **2** the hydrogen to be abstracted lies close to the nodal plane of the half-vacant n orbital.

A remarkable difference in the rate constants for photolysis of **1** and **2** is revealed by studies of the quenching of reactions 1 and 2 by 1,3-pentadiene.[9] Thus, reaction 1 is unaffected by addition of up to 0.9 *M* 1,3-pentadiene, which implies that either (a) nearly all of the type II split for **1** occurs in the singlet state (which is not quenched by piperylene[9]) or (b) the type II split occurs in the triplet state with a rate constant[10,12] greater than $\sim 8 \times 10^{10}$ sec^{-1}. On the other hand, the conversion of **2** to **1** is strongly quenched by 1,3-pentadiene ($k/k_\alpha \sim 60$).



(1)

(2)

We propose that the striking contrast in the photochemistry of **1** *and* **2** *results from a stereoelectronic requirement for the type II split and that this requirement probabably also exists in all photochemical hydrogen abstraction reactions by the* n,π* *states of alkyl ketones.*[14] It is clear from models of **1** that the hydrogen on the γ carbon can facilely form a six-membered transition state (for the type II split) in which the C-H bond axis is directed toward the half-vacant n orbital of the carbonyl oxygen atom (see Figure 1). It is generally assumed that the reactivity[15–17] toward hydrogen abstraction for the n,π* states of alkyl ketones derives from the electrophilic nature of the localized half-vacant n orbital. If so, then **1** should experience minor restrictions because of the relatively unrestrained approach of the n orbital by the γ-H for type II reaction and proceed faster than the analogous process for **2**, *which cannot achieve the required transition state for hydrogen abstraction without severe molecular deformations or conversion into a higher energy boat construction.*

Since the simple model of a planar n,π* suffices to explain these data, an important implication of the results reported here is that the geometry of the n,π* is not severely distorted from planarity.[18]

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[9] 1,3-Pentadiene has been shown to quench only triplet states of ketones: see ref 6 and G. S. Hammond, P. A. Leermakers, and N. J. Turro, *J. Am. Chem. Soc.*, 83, 2396 (1961); however, 1,3-dienes are known to quench singlet states of nonketonic compounds: L. M. Stephenson, D. G. Whitten, G. F. Vesley, and G. S. Hammond, *ibid.*, **88**, 3665 (1966).

[10] 2-Hexanone, an open-chain model for the type II split for **1** and **2**, undergoes cleavage with a rate constant[6] of 1×10^9 sec^{-1} from the triplet and 10^7–10^8 sec^{-1} from the singlet (assuming an intersystem rate constant of 10^7–10^8 for 2-hexanone[11]). A small amount of unquenchable type II cleavage also apparently occurs from **2**.

[11] R. F. Borkman and D. R. Kearns, *J. Chem. Phys.*, **44**, 945 (1965); *J. Am. Chem. Soc.*, **88**, 3467 (1966).

[12] Value calculated assuming the rate constant for diffusion-controlled quenching[13] in cyclohexane is 8×10^{10} l./mole sec^{-1}.

[13] F. W. Wilkinson, *Quart. Rev.* (London), **20**, 403 (1966).

[14] (a) Stereochemical requirements for the "McLafferty rearrangement," the mass spectral analog of the Type II split, have also been noted: H. Budzikiewicz, C. Fensilau, and C. Djerassi, *Tetrahedron*, 22, 1391 (1966). (b) We have found the mass spectra of **1** and **2** to be essentially identical at 75 and 12 eV. However, the source temperature (200°) unfortunately may be sufficiently high to equilibrate the molecular ions of **1** and **2** before decomposition. Experiments at lower source temperature and measurements of ionization potentials are in progress.

[15] For example, see C. Walling and M. Gibian, *J. Am. Chem. Soc.*, **87**, 3361 (1965); A. Pawda, *Tetrahedron Letters*, 3465 (1964).

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[18] Independent evidence for this conclusion is difficult to obtain. Formaldehyde is severely puckered and has a pyramidal shape in its n,π* states.[19] However, a substantial degree of this bending probably originates from H-H *bonding* in the n,π* state.[20]

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Fluorinated Organocopper Compounds

Sir:

We have isolated several fluorinated organocopper compounds and found that they are highly soluble in organic solvents, more thermally stable than their hydrocarbon analogs, and useful synthetic intermediates.

We have prepared solutions of fluorinated arylcopper(I) compounds by the metathetical reaction of Grignards with cuprous halide in ether. The magnesium salts are removed as their insoluble dioxane complexes and the arylcoppers isolated by concentration in an inert atmosphere.

$$C_6F_5MgX + CuX \longrightarrow \underset{\mathbf{1}}{C_6F_5Cu} + MgX_2$$

By this method, pentafluorophenylcopper (**1**) is isolated in 70% yield as colorless 1:1 and 2:1 dioxane complexes which are freed of dioxane by heating at 130° (1 μ) for 5 hr.

Anal. Calcd for C_6F_5Cu: C, 31.3; F, 41.2; Cu, 27.6. Found: C, 31.2; F, 39.8; Cu, 27.8.

1 dissolves in most aprotic solvents except alkanes, hydrolyzes and oxidizes slowly in moist air, and decomposes above 200° to form decafluorobiphenyl and copper metal. For comparison, phenylcopper,[1] a colorless solid, is difficult to obtain in pure state,[2] complexes weakly with ether,[2] is soluble in the presence of strong complexing agents,[1a,3] is very difficult to handle,[2]

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