plexes **5–8**, the observed $\Delta\nu_{C\equiv C}$ (*ca.* 450 cm^{-1}) was demonstrated to be consistent with the assigned platinacyclopropene structures, in that these large $\Delta\nu_{C\equiv C}$ values signify strong acetylene to metal bonding and increased deviation of the acetylene bond from linearity. X-Ray crystallographic studies are planned to elucidate the exact degree of deviation.

Both dissociative[10] and associative[11] mechanisms have been proposed for the exchange reaction between two different acetylenes. The reaction of **5** with di[2-

$$\text{PtL}_2(1) + 4 \underset{5}{\overset{}{\rightleftarrows}} \text{PtL}_2(4) + 1 \atop 8$$
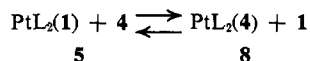
(6-methylpyridyl)]acetylene (**4**) was studied in benzene at 37° by measuring the population of the 6-methyl moiety of the complexed and free ligand (δ 2.16 and 2.56, respectively). At equilibrium, the ratio of complexed to free **4** was 4.5. The initial rate of disappearance of **4** and formation of **8** was found to correspond to a first-order rate constant of 15 × 10^{-4} sec^{-1}. If Cook's interpretation is indeed correct, that is (1) the initial displacement reaction rate is dependent only on the nature of the coordinated acetylene and (2) that the equilibrium constant is essentially the quotient of the rate constants for the forward and reverse reactions, then the calculated first-order rate constant for the dissociation of **8** is 3.2 × 10^{-4} at 37°.

In a typical preparation of the metallabicycle **9**, a solution of anhydrous cobalt(II) chloride in absolute ethanol was added to a stirred benzene solution of **7** under nitrogen. After 2 hr, the mixture was filtered, solvent was removed *in vacuo*, and the residue was recrystallized from benzene–cyclohexane giving the crystalline green metallabicycle **9**:[7] mp 270–280° dec (sealed tube); ν_{max} (KBr 1730 (>C=C<), 1597 (Pyr), 1120, 874, 770 cm^{-1}; uv–visible (EtOH) 610 mμ (ϵ 246), 577 (182), 392 sh (3020). In the crystalline state, **9** was stable indefinitely; however, in solution, **9** slowly decomposed as shown by constant decrease of the extinction coefficient in the visible spectrum (610 mμ). Similarly when complex **8** was treated with cobalt(II) chloride, the resultant green metallabicycle **10** rapidly decomposed during attempted purification.[12] These results indicated that, in both **9** and especially **10**, the cobalt was weakly bonded and underwent apparent dissociation in solution.

From the preliminary X-ray data,[14] the Pt–Co bond distance (*ca.* 4.4 Å), along with the dimensions of the unit cell,[15] indicated that the metallabicycle **9** was flat, or nearly so. Planarity of the pyridyl rings with the platinacyclopropene moiety was also reflected by the $\nu_{max(C=C)}$ stretching frequency (1730 cm^{-1}).

(10) A. D. Allen and C. D. Cook, *Can. J. Chem.*, 41, 1235 (1963); 42, 1063 (1964); J. P. Birk, J. Halpern, and A. L. Pickard, *J. Amer. Chem. Soc.*, 90, 4491 (1968).

(11) C. D. Cook and K. Y. Wan, *Inorg. Chem.*, 10, 2696 (1971); also see J. Halpern and T. A. Weil, *J. Chem. Soc., Chem. Commun.*, 631 (1973).

(12) On warming an ethanolic solution of 10, a color change from green to pale yellow is observed which can be reversed upon cooling. Recently a similar thermochromic change was reported for Ni[(C₆H₅)₃-P]₂(C₂H₄).[13]

(13) P. T. Cheng, C. D. Cook, S. C. Nyburg, and K. Y. Wan, *Inorg. Chem.*, 10, 2210 (1971).

(14) S. F. Watkins, R. Musselman, and B. Gayle, to be submitted for publication.

(15) Preliminary crystal data:[14] PtCoCl₂P₂N₂C₄₈H₃₉; monoclinic; space group P_{2_1}/c; $a = 9.392$ (1), $b = 22.591$ (3), $c = 23.729$ (3) Å; $\beta = 101.41°$; $V = 4935$ Å³; $Z = 4$.

New synthetic routes to, as well as biochemical and crystallographic studies of, metallabicycles and metallatricycles are in progress.

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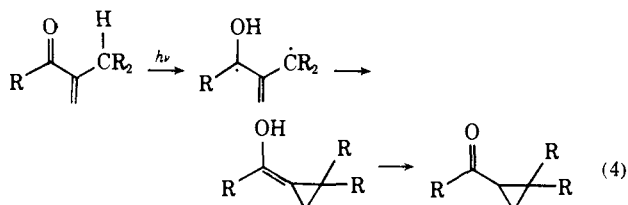## Singlet Biradical Intermediates in the Photochemistry of α-Methylene Ketones

Sir:

We recently described[1] photochemical isomerization of a variety of α-methylene ketones to form primarily cyclobutyl ketones, accompanied in some cases by the related cyclopropyl compounds and methylenecyclobutanols. Typical examples are shown in eq 1 and 2.
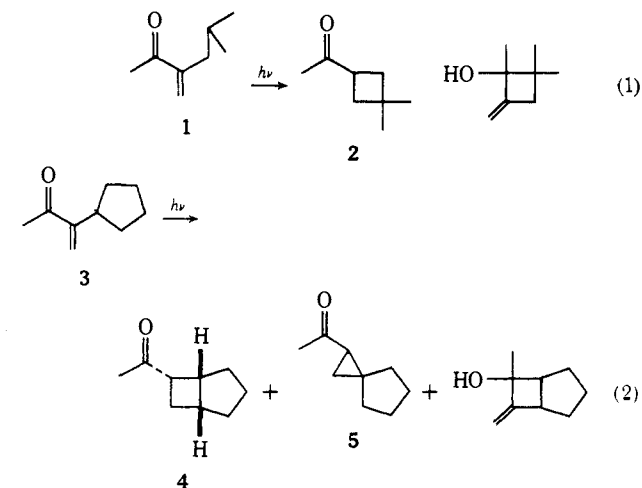
We now present evidence that these ketones arise through carbonyl abstraction of γ (for cyclobutanes) or β (for cyclopropanes) hydrogen, closure to enol, and subsequent ketonization, as illustrated in eq 3 and 4. In addition we report quenching and sensitization experiments which suggest that these reactions occur from an excited singlet state.

Specifically labeled ketones **1-D**, **2-D**, and **3-D** were

(1) R. A. Cormier, W. L. Schreiber, and W. C. Agosta, *J. Amer. Chem. Soc.*, 95, 4873 (1973).

Scheme I

Equations (3) and (4) (reaction schemes shown at top left)
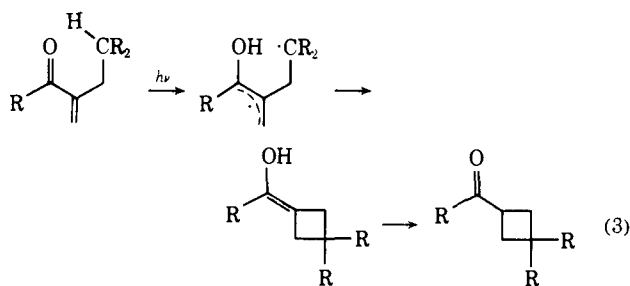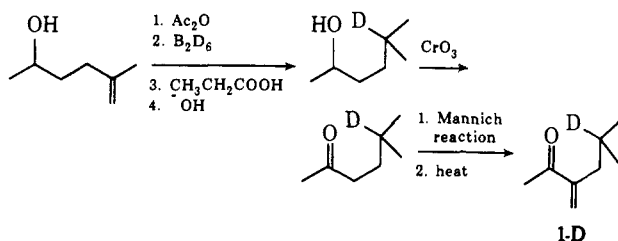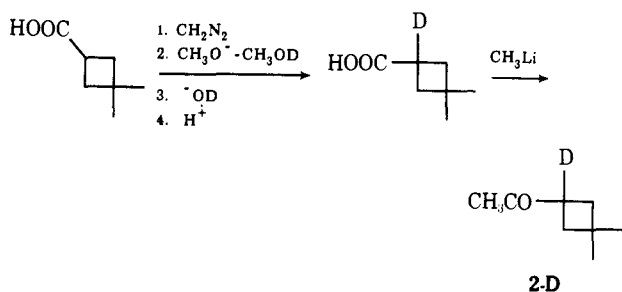
prepared as summarized in Schemes I, II, and III.[2]

Scheme I

1. Ac$_2$O
2. B$_2$D$_6$
3. CH$_3$CH$_2$COOH
4. $^-$OH

1. Mannich reaction
2. heat

1-D

Scheme II

HOOC

1. CH$_2$N$_2$
2. CH$_3$O$^-$-CH$_3$OD
3. $^-$OD
4. H$^+$

HOOC — CH$_3$Li

CH$_3$CO

2-D

Scheme III

1. LiAlD$_4$
2. TsCl, pyridine

acetoacetic ester

C$_2$H$_5$O$^-$

1. glycol, H$^+$
2. LiAlH$_4$
3. H$^+$

CO$_2$C$_2$H$_5$

3-D
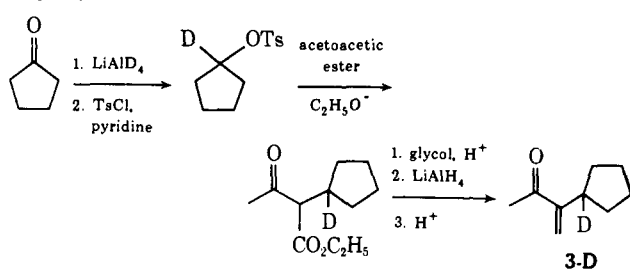
These deuterated compounds along with unlabeled **1** and **3** were irradiated as noted below; products were isolated and purified by preparative vapor phase chromatography, and extent of labeling was estimated from 220-MHz nmr spectra. Irradiation[3] of an approximately 0.0082 M pentane solution of **1-D** yielded **2-D** with dry pentane as solvent and a 9:1 mixture of **2** and **2-D** when pentane saturated with water was used.

Similarly, photolysis of unlabeled **1** in pentane saturated with deuterium oxide gave a 1:1 mixture of **2** and **2-D**. Appropriate controls showed that deuterium was neither scrambled nor exchanged in or out of recovered starting material or product under the conditions employed. Analogous results were obtained on irradiation of approximately 0.0072 M benzene solutions of **3** and **3-D**. In benzene saturated with deuterium oxide, **3-D** yielded **5-D** and **6**, while in water-saturated benzene the products were **5** and **7**. Starting with unlabeled **3**, benzene–deuterium oxide gave **5-D** and **8**, and *tert*-butyl alcohol-O-d^4 as solvent gave **5-D**, **8**, and a small amount of the labeled exo isomer **9**.[1,5] Again controls assured that recovered starting material and products were unaffected by the reaction conditions. These results require that the γ-hydrogen of **1** and the β-hydrogen of **3** become readily[6] exchangeable with solvent protons at some intermediate stage in the isomerizations to **2** and **5**, respectively, and that these hydrogen atoms ultimately appear in the α position of the prod-

5-D

6, X = Y = D
7, X = H; Y = D
8, X = D; Y = H

9
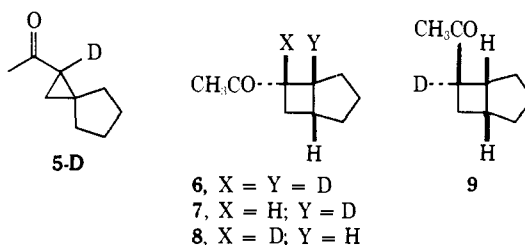
ucts. The enols of eq 3 and 4 nicely fulfill this requirement, and the results thus provide strong support for these pathways.[7]

The isomerization of **1**, **3**, and also **10** proceeded equally well in benzene and in benzene containing 4 M 2,3-dimethyl-1,3-butadiene. Similarly there was no quenching of these processes by 0.05 M *cis*-piperylene, although *trans*-piperylene was formed.[8] No isomerization of *cis*-piperylene occurred in an appropriate control. Attempts to sensitize the reactions of **1** and **3** using propiophenone were unsuccessful;[9] in the case of **10** propiophenone sensitization led only to formation of the [2 + 2] adduct **11**.[10] This result indicates that triplet energy is indeed transferred from propiophenone to the α-methylene carbonyl chromophore of **10** but that this triplet leads only to **11**. These various experiments point to an excited singlet species as the source of all the reactions of eq 1, 2, and 5 occurring on direct irradiation and suggest that, apart from formation of **11**, triplet species are inactive in these processes.

(2) For the preparation of unlabeled cyclopentylacetoacetic ester adapted in Scheme III see W. R. Vaughan and K. S. Andersen, *J. Amer. Chem. Soc.*, **77**, 6702 (1955). All other transformations follow methods either well known or described in ref 1.

(3) Photolyses were carried out at 15–20° under nitrogen in oven-dried quartz apparatus using a Rayonet RPR-100 reactor equipped with 16 RPR-3500-Å lamps. Solutions were flushed with dry nitrogen before irradiation.

(4) M. Morton, J. A. Cala, and I. Piirma, *J. Amer. Chem. Soc.*, **78**, 5394 (1956).

(5) R. Granger, J. Boussinesq, J.-P. Girard, and J.-C. Rossi, *Bull Soc. Chim. Fr.*, 2801 (1969).

(6) The solubility of water in benzene at 20° is 0.021 M [G. G. Joris and H. S. Taylor, *J. Chem. Phys.*, **16**, 45 (1948)] and in pentane at 15° is 0.0021 M [C. Black, G. G. Joris, and H. S. Taylor, *ibid.*, **16**, 537 (1948)].

(7) A theoretically interesting alternative is that these reactions are concerted [$_\sigma$2 + $_\pi$2] cycloadditions of the γ C–H bond with the olefin. To satisfy the present data such a mechanism would require that **2** and **5** be formed in an excited state in which rapid exchange between α-hydrogen and solvent protons occurs before demotion to the inert ground state. This seems unlikely.

(8) G. S. Hammond, P. A. Leermakers, and N. J. Turro, *J. Amer. Chem. Soc.*, **83**, 2396 (1961).

(9) Typical conditions were 0.096 M propiophenone and 0.0094 M ketone **1** in benzene; propiophenone absorbs approximately 90% of the radiation at 3500 Å.

(10) As reported in ref 1, the yield of **11** on direct irradiation is only 8%. The sensitized reaction provides a synthetically attractive route to this product.

O O

10   CH=CHCH₃ +

cis and trans

O O HO

cis and trans   +   +   +   (5)

O=

11
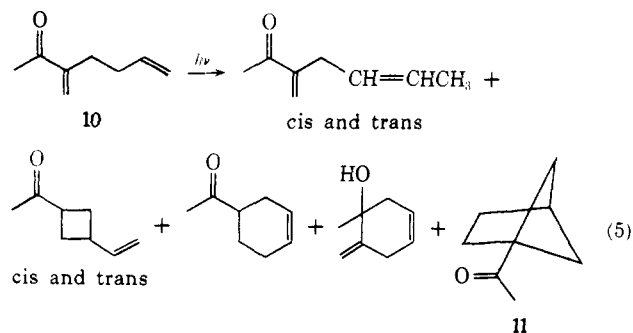
From these observations we conclude that the rearrangements of α-methylene ketones generalized in eq 3 and 4 involve singlet biradical intermediates.[11] For the γ-hydrogen abstraction leading to cyclobutyl ketones these intermediates must have a lifetime sufficient to permit the rotation about the α,β carbon–carbon bond required for ring closure. It is noteworthy in this regard that evidence is on record favoring short-lived biradical intermediates in the singlet γ-hydrogen abstraction reactions of saturated alkanones[12] and also implicating longer-lived singlet biradicals as intermediates in the related abstraction processes of β,γ-unsaturated ketones.[13,14]

(11) A theoretical discussion detailing the oversimplifications inherent in use of simple structures for such species is given by L. Salem and C. Rowland, *Angew. Chem.*, **84**, 86 (1972); *Angew. Chem., Int. Ed. Engl.*, 11, 92 (1972).

(12) L. M. Stephenson, P. R. Cavigli, and J. L. Parlett, *J. Amer. Chem. Soc.*, **93**, 1984 (1971); C. P. Casey and R. A. Boggs, *ibid.*, **94**, 6457 (1972).

(13) J. C. Dalton and H.-F. Chan, *J. Amer. Chem. Soc.*, **95**, 4085 (1973). See also P. S. Engel and M. A. Schexnayder, *ibid.*, **94**, 9252 (1972).

(14) Grateful acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.
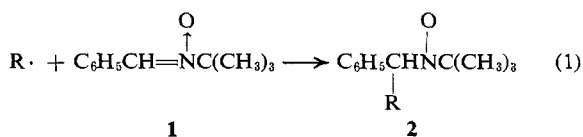
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Application of Spin Trapping to the Detection of Radical Intermediates in Electrochemical Transformations

Sir:

Radicals are postulated as intermediates in many electrochemical transformations.[1] Because many of the radicals so generated are too short-lived to be observed directly by electron spin resonance (esr) spectroscopy, most of these postulates are based upon n values and product analyses. We now report development of a new approach that permits direct spectroscopic detection and characterization of electrochemically generated free radicals and circumvents the laborious product analyses required in previous methods.

Janzen has reported that short-lived free radicals can be trapped by reaction with a nitrone to yield stable nitroxide radicals (eq 1) which can be identified by esr

$$R\cdot + C_6H_5CH{=}\overset{O}{\overset{\uparrow}{N}}C(CH_3)_3 \longrightarrow C_6H_5CH\overset{O}{\overset{|}{N}}C(CH_3)_3 \quad (1)$$
$$\overset{|}{R}$$

1   2

(1) A. P. Tomilov and M. Ya. Fioshin, *Russ. Chem. Rev.*, **32**, 30 (1963).

spectroscopy.[2] It appeared likely that this approach to spin trapping could be extended to electrochemically generated radicals assuming (1) that the technique was successful in solvents compatible with electrochemistry and (2) that the nitrone and nitroxides were electroinactive in useful potential ranges.

The potential of this trapping procedure was tested in an electrochemical environment by thermally decomposing phenylazotriphenylmethane, a source of the short-lived phenyl radical, in acetonitrile containing 0.1 M tetrabutylammonium perchlorate (TBAP) and α-phenyl-N-$tert$-butylnitrone (PBN, **1**). A six-line esr spectrum was obtained ($a_N = 14.72$ G, $a_H = 2.72$ G) which closely matches that reported for **2** (R = C_6H_5) ($a_N = 14.48$ G, $a_H = 2.17$ G) in benzene.[3] The slightly larger coupling constants in acetonitrile are to be expected.[4] Spin trapping thus is feasible in an electrochemical solvent.

The electrochemical limits imposed by oxidation or reduction of PBN and the resulting nitroxide, **2**, are gratifyingly minor. Cyclic voltammetry indicated that PBN is electroinactive between 1.5 and -2.4 V (*vs.* sce). Although electrochemical data on the nitroxide **2** were not as definitive, cyclic voltammetry of solutions of it prepared in various ways as well as recent reports[5] indicated that the nitroxide resulting from phenyl radical trapping should be electroinactive between 0.7 and -2.0 V.[6]

The electrochemical reduction of aryl diazonium salts was chosen for our initial studies. This reaction has been postulated to proceed *via* a free-radical intermediate, using the criteria of n value and product analyses, both in aqueous[7,8] and in aprotic[9-13] media. For example, reduction of various diazonium tetrafluoroborates in sulfolane afforded n values near unity;[8] reduction in acetonitrile containing an aromatic substrate gave biaryls which had isomer ratios and partial rate factors which agreed well with those from thermal decomposition of benzoyl peroxide and N-nitrosoacetanilide, established sources of phenyl radical.[10]

Phenyldiazonium tetrafluoroborate (0.01 M) was reduced in acetonitrile containing 0.1 M TBAP at a stirred mercury pool cathode using a platinum auxiliary electrode (fritted compartment) and an aqueous sce reference electrode (fritted compartment) in the presence of PBN (0.01 M).[14] The solution was cooled in an

(2) E. G. Janzen, *Accounts Chem. Res.*, **4**, 31 (1971), and references cited therein.

(3) A. L. Bluhm and J. Weinstein, *J. Org. Chem.*, **37**, 1748 (1972). The coupling constants originally reported by E. G. Janzen and B. J. Blackburn, *J. Amer. Chem. Soc.*, **91**, 4481 (1969), have been corrected to give comparable values (E. G. Janzen, personal communication).

(4) Y. Takaya, G. Matsubayashi, and T. Tanaka, *Inorg. Chim. Acta*, **6**, 339 (1972). The coupling constants obtained by us for the trapping experiment in benzene are identical with those reported.[3] The increase is apparently due only to a solvent effect.

(5) M. Tsunga, C. Iwakura and H. Tamura, *Electrochim. Acta*, **18**, 241 (1973).

(6) Our data on 2,2,6,6-tetramethyl-4-acetamidopiperidine-1-oxyl agree with those for the unsubstituted compound.[5]

(7) J. K. Kochi, *J. Amer. Chem. Soc.*, **77**, 3208 (1955).

(8) R. M. Elofson, *Can. J. Chem.*, **36**, 1207 (1958).

(9) R. M. Elofson and F. F. Gadallah, *J. Org. Chem.*, **34**, 854 (1969).

(10) F. F. Gadallah and R. M. Elofson, *J. Org. Chem.*, **34**, 3335 (1969).

(11) R. M. Elofson, F. F. Gadallah, and K. F. Schulz, *J. Org. Chem.*, **36**, 1527 (1971).

(12) R. M. Elofson and F. F. Gadallah, *J. Org. Chem.*, **36**, 1769 (1971).

(13) F. F. Gadallah, A. A. Cantu, and R. M. Elofson, *J. Org. Chem.*, **38**, 2386 (1973).