

pentadienyl carbanions and, with less accuracy, similar carbanion reactions such as carboxylations and reactions with ethylene oxide.³

The studies which most clearly involve the protonation of pentadienyl carbanions were qualitative and complicated by the presence of methoxyl substituents.⁴ In Birch reductions of aromatic compounds, protonation of a pentadienyl carbanion (often free from oxygen-containing substituents) has been postulated to be the last step.^{4a,5} In these reactions, it appears that protonations of U-shaped² pentadienyl carbanions take place faster at the central carbon atom than at the end carbons; it has been suggested that this is due to greater electron density on the central carbon.^{4a} There is some evidence that these anions react with other reagents faster at the central carbon.³ We wish to report quantitative experiments showing how rapidly cyclohexadienyl carbanion (I) protonates at a as compared to b under certain diene isomerization conditions (see Fig. 1).

In separate reactions, 1,2-dihydrobenzene (II) and 1,4-dihydrobenzene (III) were partially isomerized with potassium *t*-amyloxide in *t*-amyl alcohol-O-*d*⁶ for 45 min. at 95°, and the yields of II and III in various states of deuteration were measured (after separation of total II from total III by v.p.c.) by mass spectrometry.⁷ This early in the isomerizations, there was less than 0.3% of di- and polydeuterated II or III. In the isomerization starting from II, the yields of monodeuterated II and monodeuterated III were 5.10 and 1.28%, respectively, indicating, if deuteration of I is indeed the reaction which gives these species, that I deuterates 8 times as fast at a as at each b.⁸ Starting from III, the yields of monodeuterated II and III were 1.49 and 0.37, respectively, again giving a factor of 8 for the rate difference. There is an acute lack of information regarding the nature of the solvation of I, but it is noteworthy that the two experiments give virtually the same rate ratio, a result consistent with the idea that a common intermediate is reacting with deuterated alcohol.

Since the isotope effects for reaction at a and at b in I should be very similar, under these conditions *I* is protonated by solvent 8 times as fast at a as at each b.⁹ This corresponds to an energy difference of 1.52 kcal./mole for the transition states for protonation of I at a (\ddagger_a) and at each b (\ddagger_b), and, with previous data,^{1,2,10}

(3) I. L. Mador and T. S. Soddy, U. S. Patent 2,960,544 (1960) (*Chem. Abstr.*, **55**, 9308 (1961)); D. R. Weyenberg and L. H. Toporcer, *J. Am. Chem. Soc.*, **84**, 2843 (1962). The second carbon dioxide, ethylene oxide, and trimethylchlorosilane are almost certainly reacting with pentadienyl carbanions.

(4) (a) A. J. Birch, *Quart. Rev.*, **4**, 69 (1950); (b) A. J. Birch, E. M. A. Shoukry, and F. Stansfield, *J. Chem. Soc.*, 5376 (1961).

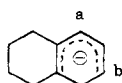
(5) (a) A. P. Krapcho and A. A. Bothner-By, *J. Am. Chem. Soc.*, **81**, 3658 (1959); (b) A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists," John Wiley and Sons, Inc., New York, N. Y., 1961, p. 425.

(6) D. J. Cram and B. Rickborn, *J. Am. Chem. Soc.*, **83**, 2178 (1961). The alcohol used in the current study was 95% deuterated.

(7) We thank Messrs. H. Bondarovich and S. K. Freeman of International Flavors and Fragrances, Inc., for the mass spectral results, and the National Science Foundation (fellowship to R. H. C.) and the Public Health Service (GM-07689, R. B. B. and C. E. S.) for financial support.

(8) Considerable undeuterated II was formed from III and considerable undeuterated III from II, suggesting that the same sort of intramolecular transfer that was found by D. J. Cram and R. T. Uyeda (*J. Am. Chem. Soc.*, **84**, 4358 (1962)) is occurring here.

(9) Experiments in the hexahydronaphthalene series have shown that the rate of protonation of



at a as compared to b is at least 2.5; an upper limit was not established in this case.

(10) The rate constant for the conversion of II to III used in this diagram was 2.19×10^{-4} sec.⁻¹, taken from a reaction in which 21 mg. of potassium

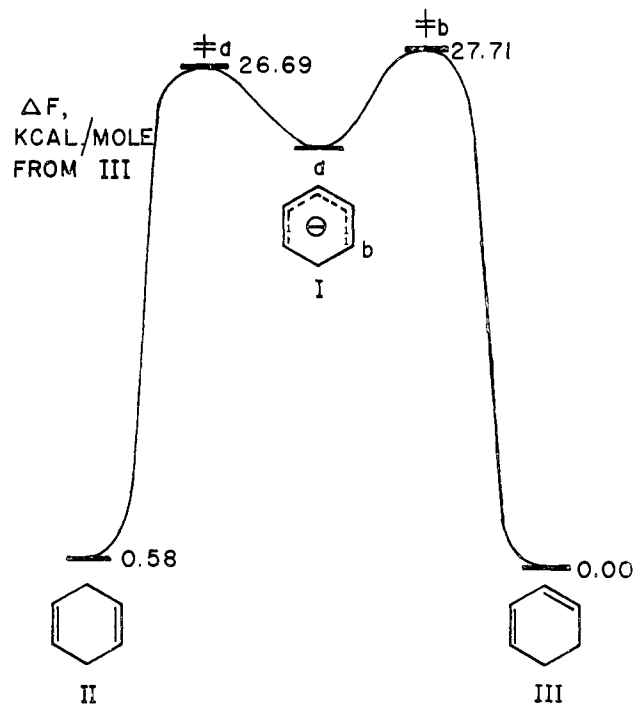


Fig. 1.—Energy diagram for the interconversion of II and III at 95.0°, without statistical corrections.

allows the assignment of numerical values to four of the five extremes in the energy diagram for the isomerization of II to III (see Fig. 1).

It is interesting that under certain conditions^{5a,11} the ratio of protonation of I at a as compared to b appears to be larger than what we have found, and under other conditions, transfer of a hydride ion to a hydroxylic species occurs faster than abstraction of a proton.¹²

was treated with 257 mg. of *t*-amyl alcohol, 906 mg. of II was added, and the ampoule was sealed and immersed in a 95° bath.

(11) W. von E. Doering, G. Schroeder, K. Trautner, and S. Staley, 144th National Meeting of the American Chemical Society, Los Angeles, California, April, 1963, p. 14M.

(12) R. Paul and S. Tchelitcheff, *Compt. Rend.*, **239**, 1222 (1954); G. Wittig and D. Wittenberg, *Ann.*, **606**, 1 (1957). This competing hydride transfer may be a serious problem with cyclohexadienyl carbanions, but will not be with most other types of pentadienyl carbanions.

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On the Photochemical Cyclization of Saturated Ketones and Aldehydes to Cyclobutanols¹

Sir:

The photochemical formation of cyclobutanols from saturated ketones possessing γ -hydrogen atoms has provided a convenient synthetic tool in numerous cases.²⁻⁴ A stepwise mechanism^{2a} has been proposed for this reaction postulating γ -hydrogen abstraction and subsequent cyclization of the intermediate diradical (eq. 1). Available experimental data, how-

(1) Photochemical Reactions, Part 23; Part 22: *Helv. Chim. Acta*, **46**, 1599 (1963).

(2) (a) N. C. Yang and D. H. Yang, *J. Am. Chem. Soc.*, **80**, 2913 (1958); (b) *Tetrahedron Letters*, **4**, 10 (1960).

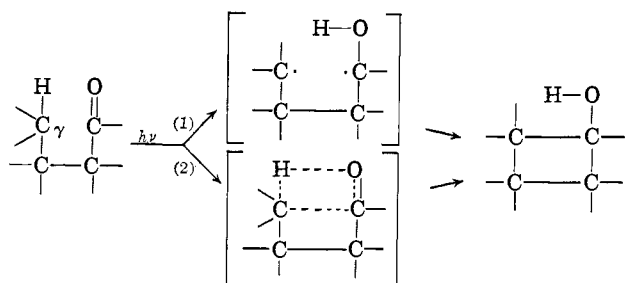
(3) (a) P. Buchschacher, M. Cereghetti, H. Wehrli, K. Schaffner, and O. Jeger, *Helv. Chim. Acta*, **42**, 2122 (1959); (b) M. Cereghetti, H. Wehrli, K. Schaffner, and O. Jeger, *ibid.*, **43**, 354, 367 (1960); (c) H. Wehrli, M. Cereghetti, K. Schaffner, J. Urech, and E. Vischer, *ibid.*, **44**, 1927 (1961); (d) H. Wehrli, M. S. Heller, K. Schaffner, and O. Jeger, *ibid.*, **44**, 2162 (1961); **45**, 1261 (1962); (e) J. Iriarte, K. Schaffner, and O. Jeger, *ibid.*, in press.

TABLE I
 PERCENTAGE RETENTION OF CONFIGURATION IN THE PHOTOCHEMICAL CYCLIZATION

Product	Specific rotations, ^a deg.				Optical activity, ^b %
	578 m μ	546 m μ	436 m μ	405 m μ	
(R)-Lactone 8 ^{c,e}	+9.35	+11.42	+19.35	+23.48	28.6 \pm 5
(S)-Lactone 7 ^{d,e}	-3.04	-3.19	-5.62	-6.35	
<i>t</i> -Cyclobutanol 2					21.0 \pm 5
from cyclobutanone 6 ^{d,f}	+4.83	+5.62	+10.40	+12.36	
from methyl ketone 1 ^{d,f}	+3.64	+4.16	+7.27	+9.35	
<i>t</i> -Cyclobutanol 3					16.9 \pm 5
from cyclobutanone 6 ^{d,f}	-5.50	-6.42	-11.01	-12.84	
from methyl ketone 1 ^{d,f}	-3.69	-3.93	-6.19	-7.37	

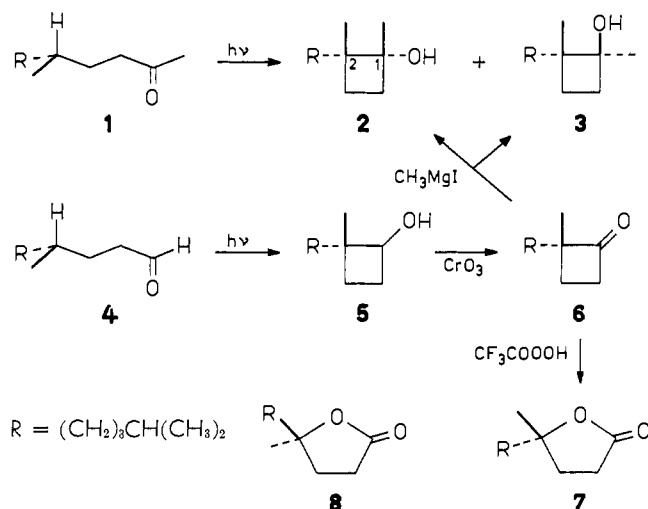
^a Measured as solutions in chloroform. ^b Mean value calculated from rotation at each wave length. ^c Corrected rotations based on 81.1% optical activity of the (R)-linalool used as starting material [reported maximum value taken as 100%: $[\alpha]^{20}_D -21.63^\circ$, Y. R. Naves, *Helv. Chim. Acta*, **29**, 553 (1946)]. ^d Uncorrected rotations based on 100% optical activity of the (R)-citronellal used as starting material [maximum value reported in this work]. ^e c 3.3-3.5. ^f c 1.8-2.2.

ever, do not exclude a concerted (insertion) mechanism^{3a} as a possible alternative (eq. 2).



In order to study the mechanism of the photochemical cyclization, aliphatic optically active starting materials with a single asymmetric carbon atom in γ position to the carbonyl group were chosen. In particular, (5R)-5,9-dimethyldecan-2-one (1), $[\alpha]^{22}_D +0.712^\circ$ (liq.), $d^{22} 0.828$,⁵ and (4R)-4,8-dimethylnonan-2-one (4), $[\alpha]^{20}_D +0.98^\circ$ (liq.),⁶ were prepared from (R)-citronellal, $[\alpha]^{20}_D +12.86^\circ$ (liq.).⁷ Both compounds were irradiated in pentane at room temperature with a high pressure mercury lamp. From each reaction mixture the alcoholic fractions were separated by chromatography on alumina. Subsequent fractionation by gas chromatography led to the isolation of the pure cyclobutanols. Thus, two optically active *t*-cyclobutanols, 2, $[\alpha]^{21}_D +3.67^\circ$ (liq.), $d^{20} 0.870$, and 3, $[\alpha]^{20}_D -2.47^\circ$ (liq.), $d^{20} 0.881$ (yields 8.5% each), were obtained from irradiation of the methyl ketone 1.⁸ Photolysis of analogous aldehydes is also found to yield cyclobutanol derivatives. Thus, from aldehyde 4 one of the two possible optically active *sec*-cyclobutanols 5, $[\alpha]^{18}_D +2.38^\circ$ (liq.), $d^{20} 0.859$ (yield 20%), was isolated. Oxidation of 5 gave the cyclobutanone 6, $[\alpha]^{18}_D +13.06^\circ$ (liq.), $d^{20} 0.859$, $\nu_{\max}^{\text{liq}} 1775 \text{ cm}^{-1}$. Reaction of this ketone with methylmagnesium iodide in ether furnished a 3:4 mixture of the *t*-cyclobutanols 2 and 3, with trifluoroacetic acid in methylenechloride, the partially racemized (-)-lactone 7. By v.p.c. analysis, infrared, n.m.r., and mass spectra, 7 is con-

stitutionally identical with the (R)-lactone 8, $[\alpha]^{22}_D +8.81^\circ$ (liq.), $d^{20} 0.941$, $\nu_{\max}^{\text{liq}} 1768 \text{ cm}^{-1}$, synthesized from (R)-linalool, $[\alpha]^{19}_D -17.54^\circ$ (liq.).⁷



Comparison of the absolute specific rotations of the two lactones 7 and 8 (see Table I) shows that the partially racemized product possesses at least 24% of the expected optical activity for 7. Similar comparisons show that 2 and 3 obtained by photolysis possess at least 16 and 12%, respectively, of the corresponding optically pure compounds. These values demonstrate a partial retention of configuration during photochemical cyclobutanol formation from the methyl ketone 1 and the aldehyde 4. The partial insertion character of these reactions cannot be explained either by a stepwise reaction mechanism alone, if this involves a long-lived free radical, or by a concerted mechanism alone. The results could, of course, be interpreted by competitive participation of both mechanisms, but they are just as compatible with the production of a short-lived intermediate diradical whose rates of racemization (or, less probably, inversion) and of cyclization are of the same order of magnitude.

Recent photochemical investigations by Yang and co-workers⁹ have shown that with the unsaturated compound 6-hepten-2-one γ -hydrogen abstraction can generate an intermediate resonance-stabilized allyl radical. By analogy, these authors have postulated for the photocyclization of saturated ketones a stepwise mechanism involving a free diradical.

Acknowledgment.—Financial support of this work from the Schweiz. Nationalfond zur Förderung der

(4) E. J. Corey, R. B. Mitra, and H. Uda, *J. Am. Chem. Soc.*, **85**, 362 (1963), footnote 6.

(5) The purity of all products was controlled by gas chromatography. Satisfactory analyses and spectroscopic data (infrared, nuclear magnetic resonance, and mass spectra) of the new compounds have been obtained.

(6) B. Riniker, D. Arigoni, and O. Jeger, *Helv. Chim. Acta*, **37**, 546 (1954); for 4 $[\alpha]_D +1.16 \pm 0.10^\circ$ (liq.) is given.

(7) Full experimental details of these preparations will be forthcoming.

(8) The configuration at C-1 indicated in the two formulas is based solely on interpretation of field positions of n.m.r. signals assigned to the methyl group at C-2. Whereas the 2-CH₃ singlet occurs at 0.95 δ in 2 (1-CH₃ at 1.20 δ), it is shifted downfield to 1.13 δ in 3 (1-CH₃ at 1.29 δ), suggesting *trans* attachment of the hydroxyl group relative to the methyl group at C-2 in 2 and *cis* attachment in 3. (N.m.r. data were measured in carbon tetrachloride at 60 Mc.; shifts are expressed as p.p.m. from tetramethylsilane as internal standard.)

(9) N. C. Yang, A. Morduchowitz, and D. H. Yang, *J. Am. Chem. Soc.*, **85**, 1017 (1963).

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Nature of Niobium(V) Fluoride Species in Solution

Sir:

We have unequivocally established the existence of the NbF_6^- ion in solution and find that it shows little tendency to interact with F^- to generate the seven-coordinate NbF_7^{2-} anion in solution.¹

The Nb^{93} n.m.r. spectrum of NbF_6^- , the first high resolution niobium spectrum, consists of a septet showing that six equivalent fluorine atoms are bound to the niobium atom (Fig. 1). Consistently, the F^{19} spectrum

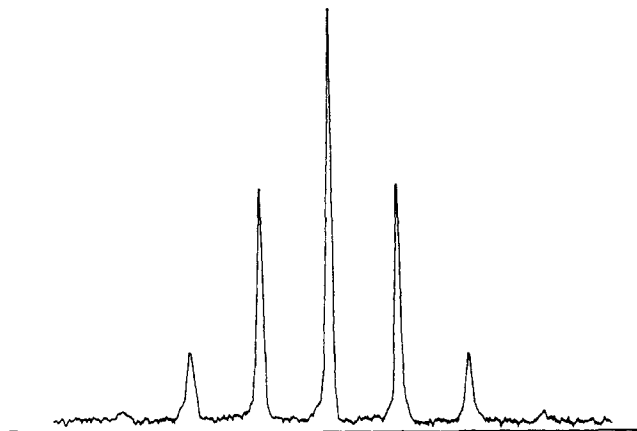


Fig. 1.—The Nb^{93} n.m.r. spectrum of the NbF_6^- ion at 14.2 Mc.

is a decet; the ten lines arise from coupling with the niobium nucleus which has a spin quantum number of $9/2$. There is a symmetrical variation in the line widths in this spectrum (Fig. 2). This is a consequence of the predominant relaxation process for the Nb^{93} nucleus, namely, the interaction of its quadrupole moment with the fluctuating electric field gradients in the ion. The theoretical spectrum for a nucleus of spin $1/2$ coupled to a nucleus of spin $9/2$ was calculated, using the treatment of Pople.² The agreement between the observed and calculated line intensities is very good, as shown in Fig. 2.

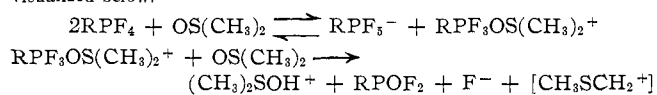
The n.m.r. spectra of NbF_6^- were obtained from acetonitrile solutions of the reaction product (A) of NbF_5 with dimethylformamide.³ Previously characterized metal salts of NbF_6^- are too insoluble for n.m.r. solution studies (AgNbF_6 , *vide infra*, is an exception).

The following observations bear on the reactivity of the NbF_6^- anion. Addition of water, saturated

(1) O. L. Keller, Jr., in an article (*Inorg. Chem.*, **2**, 783 (1963)) appearing after submission of this manuscript, reports on a Raman study of hydrofluoric acid solutions of Nb^V and concludes that NbF_7^{2-} is not an important species in solution.

(2) J. A. Pople, *Mol. Phys.*, **1**, 168 (1958).

(3) Another niobium species must be formed and is identified with a very broad resonance in the F^{19} spectrum of A in acetonitrile. Water rapidly hydrolyzes this species; thus an F^{19} spectrum (Fig. 2) free of this resonance can be obtained. In related work, we have established that RPF_4 compounds react with $(\text{CH}_3)_2\text{SO}$ to give RPF_5^- , RPOF_2 , and Me_2SOH^+ as visualized below.



and a similar sequence is suggested for the NbF_5 system.

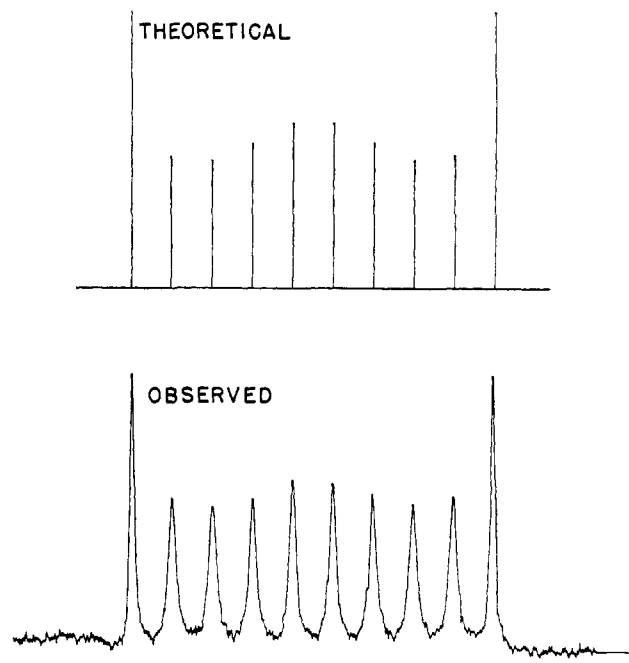


Fig. 2.—Comparison of the theoretical F^{19} n.m.r. spectrum of NbF_6^- with that observed at 56.4 Mc. $J_{\text{NbF}} = 334$ c.p.s. and $\delta_{\text{F}} = -178$ p.p.m. (CF_3COOH reference).

aqueous ammonium fluoride, or 48% hydrofluoric acid to the acetonitrile solution of A caused some broadening of the Nb^{93} septet but no shift or collapse. A solution of A in water gave a single broad Nb^{93} resonance unshifted from the resonance observed for the acetonitrile solution.

Dissolution of A in water or in 48% hydrofluoric acid followed by rapid evaporation and then redissolution in acetonitrile yielded the F^{19} decet in the n.m.r. experiment. The F^{19} spectrum of A in 48% hydrofluoric acid was identical with that of A in acetonitrile except that there was a high field fluoride ion resonance and sufficient broadening that the decet fine structure for NbF_6^- was not discernible. Addition of water, saturated aqueous ammonium fluoride, or 48% hydrofluoric acid to the acetonitrile solution of A resulted in a broadening, but no collapse, of the $\text{NbF}_6^- \text{F}^{19}$ decet and the slow appearance of two overlapping broad resonances at higher field. The intensities of the two higher field peaks increased with time showing a slow irreversible hydrolysis of NbF_6^- to $\text{NbO}_x\text{F}_y^{2-}$ species. Even after several hours, an aqueous acetonitrile solution of NbF_6^- still showed the $\text{NbF}_6^- \text{F}^{19}$ decet although increase in intensity of the higher field peaks was observable indicating continuing hydrolysis. The hydrolyzed species eventually separate from solution; these show strong OH infrared stretching absorption and are rich in oxygen by analyses.

The line-width dependence of the Nb^{93} and F^{19} spectra of NbF_6^- on medium is ascribed to a solvent dependence of nuclear relaxation times and not to an exchange process.⁴ Exchange is ruled out by the observations that additions of 48% hydrofluoric acid to acetonitrile solutions of A cause broadening of the F^{19} and Nb^{93} spectra, yet solutions of A in 48% hydrofluoric acid show a resonance which, although broad, occurs at precisely the same position as for the acetonitrile solutions. If fluorine exchange were responsible for the initial broadening, then the solution of A in 48%

(4) We have found another example of this dependence of quadrupole relaxation on medium in the F^{19} n.m.r. spectrum for the hexafluoroarsenate anion; line width and shape are grossly altered by large changes in dielectric constant and the nature of the cation.