Table II. Isotopic Distribution of Products in the H_2–D_2 Equilibration, and the Reaction of 1,3-Butadiene with a Mixture of $H_2 + D_2$ over MgO at 0 °C

Reactant	Reaction time, min	Product	% each product	% of each isotopic species			
				d_0 or H_2	d_1 or HD	d_2 or D_2	d_3-d_8
$H_2 + D_2$	0	H_2, HD, D_2		46.9	0.5	52.6	
	60	H_2, HD, D_2		47.4	1.2	51.4	
1,3-Butadiene + H_2 + D_2	0	H_2, HD, D_2		32.7	0.9	66.4	
	60	H_2, HD, D_2		31.9	0.9	67.2	
		1,3-Butadiene	1.2	100.0	0	0	0
		1-Butene	3.3	31.3	1.5	67.2	0
		trans-2-Butene	60.8	34.1	1.5	64.4	0
		cis-2-Butene	34.7	26.1	1.0	72.9	0

during which H_2 (or D_2) maintained its molecular identity; that is, both H (or D) atoms in a H_2 (or D_2) molecule are incorporated into one hydrogenated molecule. A maintenance of molecular identity of hydrogen, though it is not frequently observed, is one of the characteristics which distinguish a nonmetal heterogeneous catalyst from a metal catalyst. This characteristic has been observed in the hydrogenation of ethylene over Cr_2O_3,[1-3] ZnO,[3] and Co_3O_4[4] and in the hydrogenation of 1,3-butadiene over ZnO[5] and MoS_2.[6] Over these catalysts, products were limited to those that resulted from an addition of two H (or D) atoms to the original doube bond. This fact, combined with the fact that all the hydrogenation catalysts were active for H_2–D_2 equilibration, has left unsolved the problem as to whether a hydrogen molecule participates in the addition process in its molecular form by one step or in its dissociatively adsorbed form by two steps.

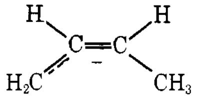
It was reported that MgO showed a high activity for H_2–D_2 equilibration when heated at 500–750 °C but it lost the activity when heated to very high temperatures.[7] However, MgO evacuated at 1100 °C shows a new catalytic property for hydrogenation, which does not involve the above question.

The hydrogenation of 1,3-butadiene with D_2, or a mixture of H_2 and D_2, and the H_2–D_2 equilibration were carried out at 0 °C in a recirculation reactor having a volume of about 1510 ml, 0.4 g of a MgO catalyst being used. The catalyst was prepared by evacuating $Mg(OH)_2$ at 1100 °C for 2 hr. $Mg(OH)_2$ was a guaranteed reagent of Knato Chemical Co. 1,3-Butadiene, H_2, and D_2 were purified by passage through 4A molecular sieves at −78 °C. The molar ratio of H_2 (or D_2) to 1,3-butadiene was 3.0. Composition of H_2, HD, and D_2 was determined by mass spectrographic analysis. Butenes and 1,3-butadiene were gas chromatographically separated and subjected to mass spectrographic analysis. The positions of D atoms in the products were determined by NMR.

Distributions of D atoms in the products of the reaction of 1,3-butadiene with D_2 are listed in Table I. Preferential formation of *cis*-2-butene containing two D atoms was observed. The NMR spectrum of *cis*-2-butene showed that the intensity ratio of methyl hydrogens to olefinic hydrogens was 2.02, and that peaks of olefinic hydrogen exhibited a 1:2:1 triplet. This indicates that two D atoms in *cis*-2-butene are located at carbon atoms 1 and 4.

In Table II are shown the results of the H_2–D_2 equilibration and the reaction of 1,3-butadiene with a mixture of H_2 and D_2. The butenes consist substantially of d_0 and d_2 isotopic species even at the high conversion of 98.9%. These results clearly demonstrate that MgO evacuated at 1100 °C does not catalyze the H_2–D_2 equilibration but catalyzes the hydrogenation of 1,3-butadiene by a process in which a hydrogen molecule maintains its molecular identity.

Since D atoms attack carbon atoms 1 and 4, D_2 must be adsorbed dissociatively. Since π-allyl carbanion is most stable in the cis form,[8] preferential formation of *cis*-2-butene indicates that a π-allyl carbanion mechanism is involved with the present catalyst. The mechanism for the deuteriogenation of 1,3-butadiene is suggested to be as follows. Deuterium adsorbs heterolytically to form D^+ and D^-. At first, D^- attacks a terminal carbon atom to form π-allyl carbanion as a half hydrogenated state. Since the electron density in a π-allyl carbanion is highest at the other terminal carbon atom, D^+ selectively attacks the carbon atom to form *cis*-2-butene-*1,4*-d_2. Both D^+ and D^- on one set of active sites must be assumed not to migrate to other sites, and, therefore, it is suggested that each set of active sites is isolated from the others.



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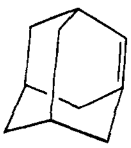
Short-Lived Intermediates. 6. Cyclization of the 1,4-Diradical in Ester Photochemistry. Completion of an Analogy Found Wanting

Sir:

It has been well established that ketones having a γ-hydrogen atom undergo photorearrangement yielding a 1,4-diradical which potentially can (a) return the hydrogen atom to the γ-carbon, (b) eliminate to form an alkene and an enol, or (c) cyclize to form a cyclobutanol.[1] The extensive ketone results would seem to provide an ideal analogy for the structurally and electronically related carboxylate esters. There are, in fact, some examples of esters which undergo reverse γ-hydrogen abstraction to regenerate the original or isomeric ester,[2,3] and many examples of esters which undergo the type II process to yield alkenes and carboxylic acids.[2-8] Heretofore, however, this analogy has been flawed by the striking lack of any recorded examples of ester photochemistry involving cyclization of the 1,4-diradical. The following first report of a 1,4-diradical cyclization in carboxylate esters is, in fact, the most prominent photochemical reaction in the systems studied. Thus, the analogy is completed. This discovery has also led to the first useful photochemical synthesis involving alkyl ester carboxylates. This synthesis represents the most direct and efficient route known to date to many 1,2-disubstituted adamantanes.

In the midst of continuing studies of adamantene,[9,10] **1**, generated in small amounts in the type II photoelimination reaction of adamantyl esters,[10] it was observed that the major product in the photolysis (254 nm, methanol) of 2-adamantyl trifluoroacetate, **2**, was a material heretofore overlooked. Medium pressure liquid chromatography of the photolyzate on silica gel followed by recrystallization from hexane yielded large quantities of a highly crystalline solid: mp 80–81.5°; ir (CCl$_4$) ν 3630, 2905, 1743, 1195, 1145, 1135 cm^{-1}; Raman (solid) ν 1737 cm^{-1}; mass spectrum *m/e* (M$^+$) 248; uv (MeOH) 282 (ϵ 69), 209 (ϵ 1150) nm; ^{1}H NMR (CDCl$_3$, Me$_4$Si) δ 4.22 (br s, 1 H, CHOH), 1.35 (s, 1 H, disappears on shaking with D$_2$O, OH), 1.3–2.5 (m, 13H) ppm; ^{19}F NMR (CFCl$_3$, CFCl$_3$) δ +73 (COCF$_3$) ppm; ^{13}C NMR (CDCl$_3$, Me$_4$Si) δ 26.8, 26.9, 29.8, 30.5, 34.3, 35.7, 36.1, 37.2, 50.6 (C-COCF$_3$), 73.0 (C-OH), ~125 (CF$_3$), 194 (COCF$_3$ $J_{^{13}\mathrm{CF}}$ = 35 Hz) ppm; Anal. (C$_{12}$H$_{15}$F$_3$O$_2$) C, H.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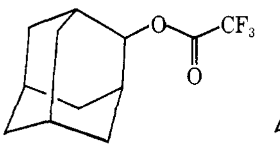

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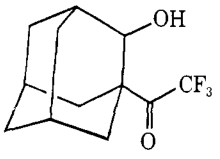
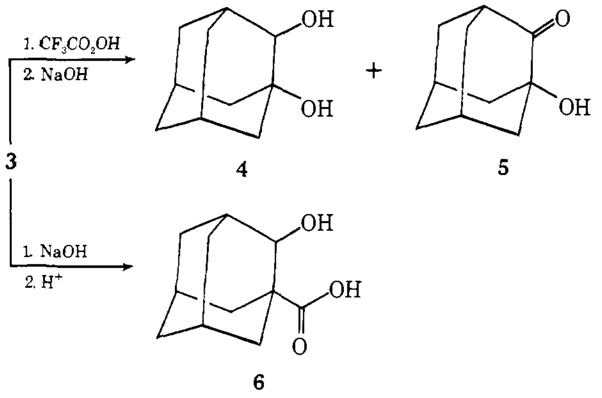


3

These data, along with chemical analogy (vide infra), are nicely accommodated by 1-trifluoroacetyl-2-hydroxyadamantane, **3**. The mass spectrum and analytical data verify that **3** is isomeric with **2**. Infrared, ^{13}C, and ^{19}F NMR[11] data establish the presence of the hydroxyl and trifluoroacetyl functional groups. ^{1}H NMR indicates one substituent on a secondary position. ^{13}C NMR (73.0 ppm) shows this substituent to be the hydroxy group (2-adamantanol C-OH, 74.3 ppm; 1-adamantanol C-OH, 67.5 ppm).[12] A 1,2-disubstituted adamantane seemed reasonable (vide infra) even though no intramolecular hydrogen bonding was evident in the infrared spectrum. An unsymmetrically multisubstituted adamantane is also consistent with the appearance of all ten carbon atoms in the ^{13}C NMR spectrum.

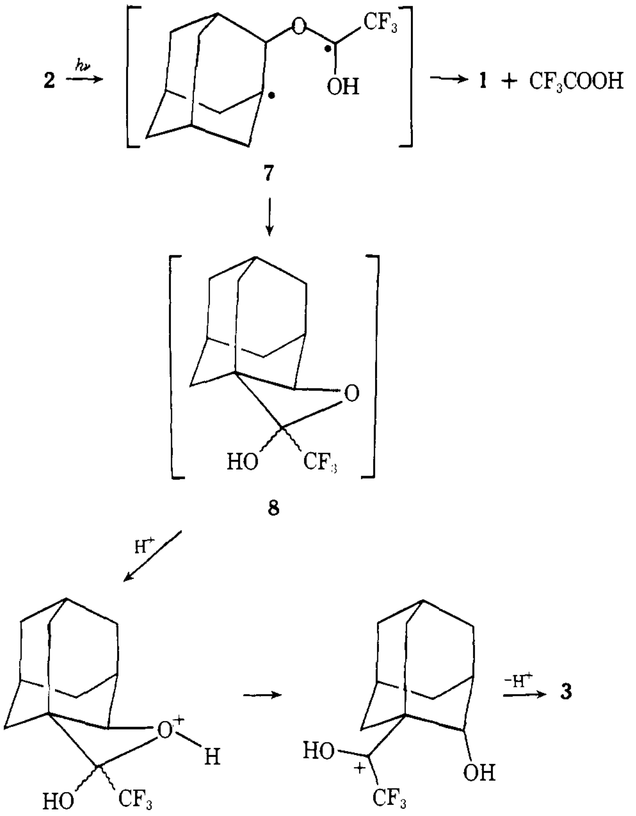
Final proof of the structure of **3** was obtained by chemical degradation. Baeyer–Villager oxidation[13] of **3** with trifluoroperacetic acid followed by hydrolysis of the intermediate esters led to a good yield of a mixture of the known alcohols 1,2-dihydroxyadamantane,[14] **4**, and 1-hydroxy-2-ketoadamantane,[15] **5**. Treatment of **3** with 10% sodium hydroxide in an iodoform-like reaction provided a quantitative yield of the known 1-carboxy-2-hydroxyadamantane,[16] **6**.



6

A mechanism which nicely explains the formation of **3** involves initial 1,4-diradical, **7**, formation from the ester excited state. This diradical then cleaves to yield adamantene, **1**, and trifluoroacetic acid or it cyclizes to yield **8**, a cyclic hemiacetal. The hemiacetal **8** is not expected to survive the reaction conditions, and, likely by acid catalysis, is converted to **3**. It should be noted that the formation of **3** provides some of the strongest evidence to date for the intermediacy of a 1,4-diradical in ester photochemistry.[2,4,17] This is the first reported example of cyclization occurring from such a diradical. Even in a case where a precise mass balance was determined, no products corresponding to a cyclization reaction were reported.[18]

In general, the syntheses of 1,2-disubstituted adamantane derivatives are difficult, lengthy processes.[14-16,19,20] The above cyclization to form **3** occurred in 60–90% yield depending on the reaction conditions. In addition, 1-adamantyl trifluoroacetate and 1-adamantyl acetate underwent the cyclization reaction with comparable ease. In the limited number of reactions studied to date, our preparations of these, 1,2-disubstituted adamantane derivatives are synthetically much simpler and more facile than the published syntheses.[14-16,20]



It is interesting to note the photolysis of an analogous ketone, 1-adamantylacetone, produced nearly a quantitative yield of cyclization products, cyclobutanols, with no products corresponding to a type II photoelimination process being detected.[21] Although slightly lower yields of cyclization products were obtained in the photolyses of adamantyl esters, a 3–6% yield of the photoelimination product, adamantene, **1**, trapped as 1-methoxyadamantane by the methanol solvent,[10] was isolated in all cases studied. Thus a partial explanation for the absence of other examples of ester 1,4-diradical cyclization seems to be a greater tendency for them to fragment rather than cyclize as compared to corresponding ketones. A recent report[22] indicates that α-fluorines greatly enhance the amount of cyclization occurring in the type II photoreaction of ketones. This fact does not appear to be applicable in our cases since cyclization products are formed in large quantitites in these adamantyl esters whether α-fluorine are present or absent.

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Models for NADH Dependent Enzymes. Solvent Effects in Dihydronicotinamide Reductions

Sir:

As part of a study to examine the hypothesis that some of the rate acceleration caused by an enzyme may be imitated by different solvent effects, we have examined the rates of reduction of trifluoroacetophenone (**2**)[1] by propyldihydronicotinamide (**1**) in various solvents and solvent mixtures as a model for the reduction of a carbonyl by an NADH dependent enzyme. Although it has been noted[2] that these kinds of reactions are sensitive to the polarity of the medium, in this communication we wish to report the dramatic effect of the protic nature of the solvent on the rate of reduction.

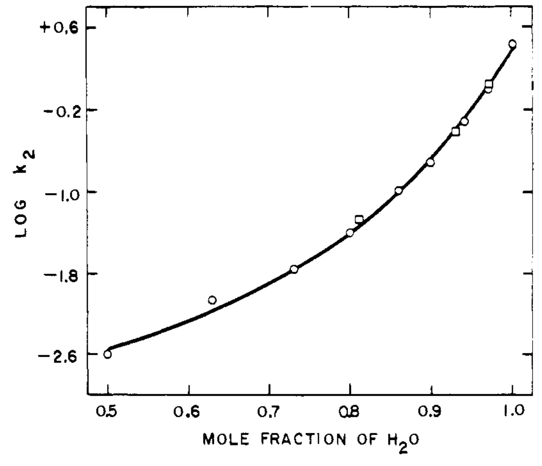
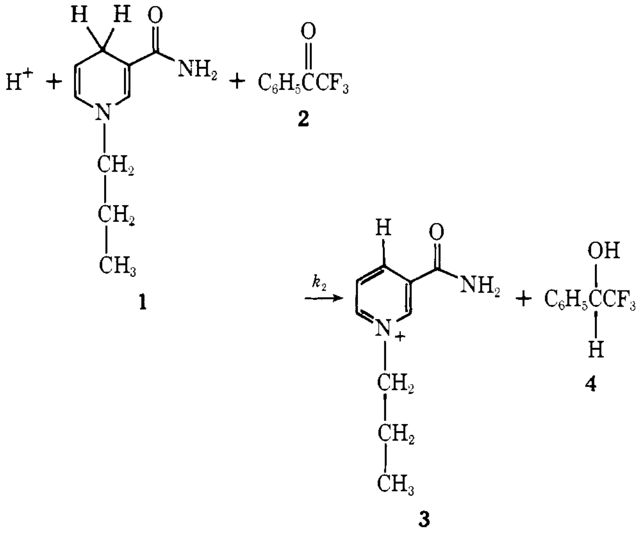


Figure 1. Dependence of log k_2 on the mole fraction of water present during the reduction of trifluoroacetophenone with propyldihydronicotinamide at 50.0 ± 0.1° in: (a) water–dimethyl sulfoxide mixture containing 0.01 M sodium carbonate–sodium bicarbonate (pH 9.9) buffer (○); (b) water–isopropyl alcohol mixtures containing 0.001 M solution dihydrogen phosphate–sodium hydrogen phosphate (pH 7.2) buffer (□).



The reductions were studied in the appropriate buffered solvent or solvent mixture maintained at 50.0 ± 0.1°. In the presence of an excess of trifluoroacetophenone, the disappearance of the dihydronicotinamide (**1**) monitored spectrophotometrically at 355 mμ follows first-order kinetics.[1a] The variation of the pseudo-first-order rate constant, k_{obsd}, with increasing concentration of trifluoroacetophenone is linear and provides the second-order rate constant for the reduction of **2** through the following equation:

$$k_{\text{obsd}} = k_{\text{dec}} + k_2[\mathbf{2}] \qquad (1)$$

All rate constants were evaluated by computer via the method of least squares. Product analyses were carried out by high pressure liquid chromatography.[3]

The reduction of **2** in several solvent mixtures is independent of pH over the range 7.2–9.9. Moreover, the rate of reduction of **2** at 50.0° in a solution consisting of 25% (v/v) isopropyl alcohol–water (pH 7.2) is independent of the ionic strength. No significant change occurs in the second-order rate constant when the ionic strength is varied from 0.002 to 0.5 by the addition of $LiClO_4$.

The very slow reduction of **2** in dimethyl sulfoxide or acetonitrile occurs with a second-order rate constant of approximately 6×10^{-4} M^{-1} min^{-1}. The addition of small quantities