Table I. Formation of Deuterated Esters and Ketones by the Reaction of Diazo Derivatives with Organoboranes in the Presence of Deuterium Oxide

Olefin[a]	Diazo compound	Product	Yield, %[b]	Deuterium, %[c] d_1	Deuterium, %[c] d_2
1-Hexene	$N_2CHCOOC_2H_5$	Ethyl 2-deuteriooctanoate	98	100[d,e]	
Cyclopentene	$N_2CHCOOC_2H_5$	Ethyl α-d_1-cyclopentylacetate	97	100[d]	
1-Hexene	$N_2CHCOCH_3$	3-Deuterio-2-nonanone	99	94[d]	
1-Hexene	$N_2CHCOC_6H_5$	α-Deuterioheptyl phenyl ketone	100	95[d]	
1-Hexene	$N_2CDCOCH_3$	3,3-Dideuterio-2-nonanone	100		96[d]
1-Hexene	$N_2CDCOOC_2H_5$	Ethyl 2,2-dideuteriooctanoate	98		100[d,e]

[a] Each olefin was converted to the corresponding trialkylborane according to the method described in ref 1. The mole ratio of organoborane:diazo compound:deuterium oxide was 1.5:1:10, although we have not established that these excesses are necessary. Deuterium oxide, 99.7%, was obtained from Columbia Organic Chemicals Co., Inc. [b] Based on diazo compound and established by glpc analysis. [c] Established by mass spectroscopy (accurate to ±2%), and 100-MHz nmr spectroscopy (*ca.* ±4%). [d] By nmr spectroscopy. [e] By mass spectroscopy.

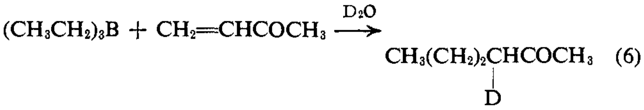
materials.[7] Utilization of these reagents in this synthesis providesa unique and convenient route to dideuteriomethylene ketones and α,α-dideuterio esters. For example, treatment of a mixture of trihexylborane and deuterium oxide with diazoacetone-d_1 produced an essentially quantitative yield of 3,3-dideuterio-2-nonanone (5). The results are summarized in Table I.

$$(C_6H_{13})_3B + N_2CDCOCH_3 \xrightarrow{D_2O} n\text{-}C_6H_{13}CD_2COCH_3 \qquad (5)$$

The procedure illustrated for the preparation of ethyl 2-deuteriooctanoate is representative. A solution of trihexylborane (60 mmol) in tetrahydrofuran was prepared by the hydroboration[1] of 1-hexene. To the magnetically stirred solution was added 7.2 ml (400 mmol) of deuterium oxide, followed by the dropwise addition (2 hr) of a solution of 4.56 g (40 mmol) of ethyl diazoacetate in 25 ml of tetrahydrofuran. The reaction temperature was maintained below 20° by means of an ice bath. After stirring for an additional hour at 25°, the nitrogen evolution was quantitative. At this stage, glpc analysis indicated a 98% yield of product. The solution was concentrated, D_2O (3 ml) was added, and the mixture was extracted with pentane (three 20-ml portions). The extract was dried (Na_2SO_4), and the residue that remained after removal of solvent was distilled to afford 5.32 g (77%) of ethyl 2-deuteriooctanoate, bp 95–97° (17 mm), n_D^{25} 1.4158, spectroscopically identical with a sample independently synthesized by the reaction of deuteriodiazoacetic ester with trihexylborane in the presence of H_2O.

It has recently been demonstrated that trialkylboranes react with methyl vinyl ketone,[8] cyclic α,β-unsaturated ketones,[9] acrolein,[10] and 2-bromo- and 2-methylacrolein.[11] These reactions produce intermediates, presumably enol borinates, which are also readily cleaved by water to yield the corresponding alkylated carbonyl derivatives.

We examined the reaction of methyl vinyl ketone with triethylborane in the presence of deuterium oxide. A quantitative yield of 3-deuterio-2-hexanone (93% d_1 by nmr) was obtained (6). This result is in keeping with



$$(CH_3CH_2)_3B + CH_2{=}CHCOCH_3 \xrightarrow{D_2O} CH_3(CH_2)_2\underset{\displaystyle D}{\underset{|}{C}}HCOCH_3 \qquad (6)$$

the suggestion of a vinyloxyborane intermediate,[10] and by analogy with mechanistically related processes should render readily available α-deuterio-α-alkylated cyclic ketones, α-deuterio aldehydes, α-deuterio-α-bromo aldehydes, and α-deuterio-α-methylated aldehydes, materials which at present would be accessible with considerable difficulty.

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(7) Diazoacetone-d_1 was prepared by the reaction of dideuteriodiazomethane with acetyl chloride. Deuteriodiazoacetic ester was synthesized by the heterogeneous exchange (D_2O–ether) of ethyl diazoacetate using potassium carbonate as catalyst, followed by extraction with methylene chloride. We wish to thank Professor S. Masamune and Mr. K. Hojo for kindly providing the details of this efficient exchange procedure.

(8) A. Suzuki, A. Arase, H. Matsumoto, M. Itah, H. C. Brown, M. M. Rogić, and M. W. Rathke, *J. Amer. Chem. Soc.*, **89**, 5708 (1967).

(9) H. C. Brown, M. W. Rathke, G. W. Kabalka, and M. M. Rogić, *ibid.*, **90**, 4166 (1968).

(10) H. C. Brown, M. M. Rogić, M. W. Rathke, and G. W. Kabalka, *ibid.*, **89**, 5709 (1967).

(11) H. C. Brown, G. W. Kabalka, M. W. Rathke, and M. M. Rogić, *ibid.*, **90**, 4165 (1968).

(12) University of Alberta Postdoctoral Research Fellow.

Vibrational Quenching of Triplet States

Sir:

During the course of triplet counting experiments with *cis*-piperylene,[1] we observed that 1,4-cyclohexadiene (D) reduced without chemical reaction the quantum yield for *cis–trans* isomerization of piperylene using acetophenone (**1**) or β-chloropropiophenone (**2**) as sensitizers.

The triplet energy of 1,4-cyclohexadiene can be estimated at >80 kcal[2] while the triplet energy of β-chloro-

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(1) A. A. Lamola and G. S. Hammond, *J. Chem. Phys.*, **43**, 2129 (1965). All experiments were run using 0.01 *M* sensitizer in benzene and variable concentrations of piperylene and D.

(2) The triplet energy of planar ethylene was measured by Evans to be 82 kcal/mole, and he reports that alkyl substituents had little effect on the triplet energy levels of unsaturated compounds.[3] The unconju-

propiophenone is 75.1 kcal/mole[4] and of acetophenone is 73.6 kcal/mole.[5] Triplet energy transfer from the lowest aromatic ketone triplet to 1,4-cyclohexadiene is at least 5 kcal/mole endothermic and should be very slow.[6]

In addition, the 1,4-cyclohexadiene triplet would also be quenched by piperylene, yielding no effect of the additional quencher on the rate of isomerization, unless one does assume a highly effective radiationless decay of the same excited state.

Yang[7] has reported that n,π* ketones can be quenched by olefins of higher energy through interaction with a geometry of the olefin different from its ground state. However, lowering of the triplet energy of the olefin by twisting about the axis connecting the two carbons of the double bond appears to be prohibited in 1,4-cyclohexadiene owing to constraint of the ring.

Recently several cases of reactions from upper triplet states have been reported.[8–11] If D is reacting with an upper triplet state or an excited singlet state of the ketone, the Stern–Volmer relationship (eq 1) can be derived

$$\Phi_{\mathrm{C}\rightarrow\mathrm{T}}{}^0/\Phi_{\mathrm{C}\rightarrow\mathrm{T}} = 1 + kq^{\pm}T[\mathrm{D}] \qquad (1)$$

where T is the lifetime of the excited state in the absence of D. Piperylene then serves as a counter for the number of excited molecules which reach the lowest triplet state. From eq 1 $kq^{\pm}T$ can be obtained from the slope of the lines in Figure 1. Assuming a diffusion-controlled quenching rate of 6.6×10^9 M^{-1} sec^{-1} in cyclohexane[12] as an upper limit, a lifetime for the quenchable excited states of **1** and **2** of 0.24 and 0.32 nsec, respectively, can be calculated. These numbers are within an order of magnitude of calculated singlet lifetimes for aryl ketones,[13] and are comparable to rates for internal conversion in the triplet manifold.[14] However, the same arguments used against quenching the lowest triplet state are also valid for this case.

Quenching of singlet excited states without electronic energy transfer has recently been well documented.[15–18] This quenching probably degrades electronic to vibrational energy.[16] Vibrational quenching of triplet states must also be considered as a mechanism. If the assumption of competitive triplet quenching of the lowest triplet by *cis*-piperylene (c-P) (electronic) and 1,4-cyclohexadiene (D) (vibrational) is made, the Stern–Volmer relationship represented by eq 2 can be derived, where

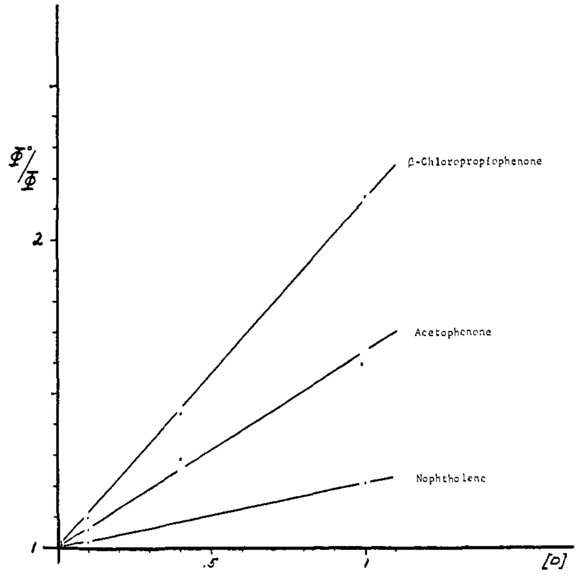

Figure 1.

$$\frac{\Phi_{\mathrm{C}\rightarrow\mathrm{T}}{}^0}{\Phi_{\mathrm{C}\rightarrow\mathrm{T}}} = 1 + \frac{k_{\mathrm{q}'}[\mathrm{D}] + k_{\mathrm{d}}}{k_{\mathrm{q}}[\mathrm{c\text{-}P}]} \qquad (2)$$

$\Phi_{\mathrm{C}\rightarrow\mathrm{T}}{}^0$ and $\Phi_{\mathrm{C}\rightarrow\mathrm{T}}$ are the quantum yields for isomerization of *cis*-piperylene in the absence and presence of D, respectively, k_{q} and $k_{\mathrm{q}'}$ are the quenching rates for piperylene and D, respectively, k_{d} is the unimolecular decay rate for the excited state of the sensitizer, and [D] and [c-P] represent the concentrations of 1,4-cyclohexadiene and *cis*-piperylene, respectively. A plot of $\Phi_{\mathrm{C}\rightarrow\mathrm{T}}{}^0/\Phi_{\mathrm{C}\rightarrow\mathrm{T}}$ *vs.* [D] for **1** and **2** at a constant *cis*-piperylene concentration of 0.01 M is linear with a slope of 1.6 M^{-1} for **1** and of 2.1 M^{-1} for **2** (Figure 1).[19] Since k_{q} is greater than 10^9 M^{-1} sec^{-1} for piperylene,[1] $k_{\mathrm{q}'}$ must be greater than 10^7 M^{-1} sec^{-1}, larger than one would predict if endothermic energy transfer is occurring. A plot of $1/\Phi_{\mathrm{C}\rightarrow\mathrm{T}}$ *vs.* 1/[c-P] for **2** at a constant 1,4-cyclohexadiene concentration of 0.01 M is also linear with a slope of 8.5×10^{-3} M^{-1}. Rearranging eq 2 and assuming values for k_{q}, k_{d}, and $\Phi_{\mathrm{C}\rightarrow\mathrm{T}}{}^0$ of 10^9 M^{-1} sec^{-1},[19] 2×10^5 sec^{-1},[19] and 0.55,[1] respectively, give a value of 2.5×10^7 M^{-1} sec^{-1} for $k_{\mathrm{q}'}$, in good agreement with the value calculated above.

In order to check the accuracy of our triplet-counting technique, the rate at which D quenches naphthalene singlets was measured using eq 1 and compared with the rate measured by fluorescence quenching.[15] From triplet counting a rate of 6.5×10^5 M^{-1} sec^{-1} was measured which compares favorably with 5.9×10^5 M^{-1} sec^{-1} obtained from fluorescence quenching.

Extraneous quenching by decomposition of the sensitizer, hydrogen abstraction from D, or oxetane forma-

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gated diene, 1,4-cyclohexadiene, should have a triplet energy comparable to a simple olefin and the six-membered ring should prevent stabilization of the triplet owing to rotation about the excited double bond.

[3] D. F. Evans, *J. Chem. Soc.*, 1735 (1960).

[4] The triplet energy was assigned as the average of the 0–0 bands from phosphorescence and singlet triplet absorption spectra (ethyl iodide solvent) of 2.

[5] W. G. Herkstroeter, A. A. Lamola, and G. S. Hammond, *J. Am. Chem. Soc.*, **86**, 4537 (1964).

[6] W. G. Herkstroeter and G. S. Hammond, *ibid.*, **88**, 4769 (1966). Energy transfer from sensitizers with triplet energies 5 kcal/mole below that of stilbene and 1,2-diphenylpropene occurs with rates on the order of 10^6 M^{-1} sec^{-1}.

[7] N. C. Yang, J. I. Cohen, and A. Shani, *ibid.*, **90**, 3264 (1968).

[8] N. C. Yang, R. Loschen, and D. Mitchell, *ibid.*, **89**, 5466 (1967).

[9] P. de Mayo, J. P. Pete, and M. Tchu, *ibid.*, **89**, 5712 (1967).

[10] O. L. Chapman, T. H. Koch, F. Klein, P. J. Nelson, and E. L. Brown, *ibid.*, **90**, 1657 (1968).

[11] R. S. H. Liu and J. R. Edman, *ibid.*, **91**, 1492 (1969).

[12] J. G. Calvert and J. N. Pitts, Jr., "Photochemistry," John Wiley and Sons, Inc., New York, N. Y., 1966, p 627.

[13] N. J. Turro, "Molecular Photochemistry," W. H. Benjamin, Inc., New York, N. Y., 1965, p 75.

[14] Liu[11] estimates a rate for $T_2 \rightarrow T_1$ conversion in 9,10-dibromoanthracene of 2.2×10^{-10} sec.

[15] L. M. Stephensen, D. G. Whitten, and G. S. Hammond, "The Chemistry Ionization and Excitation," Taylor and Francis, Ltd., London, 1967, p 35, and references cited therein.

[16] S. Murov and G. S. Hammond, *J. Phys. Chem.*, **72**, 3797 (1968).

[17] R. S. Cooke and G. S. Hammond, *J. Am. Chem. Soc.*, **90**, 2958 (1968).

[18] S. D. Andrews and A. C. Day, *Chem. Commun.*, 477 (1967).

[19] This plot is linear because k_{d} is small relative to $k_{\mathrm{q}'}$[D]. Cohen[20] has measured a value of $k_{\mathrm{d}} \sim 2 \times 10^{-5}$ sec^{-1} for acetophenone.

[20] S. G. Cohen, D. A. Laufer, and W. Sherman, *J. Am. Chem. Soc.*, **86**, 3060 (1964).

tion between sensitizer and D were eliminated as possibilities by observing that neither sensitizer nor D was consumed on prolonged irradiation under quenching conditions.

Because published data on singlet lifetimes of aryl ketones and rates of radiationless decay for olefins are few and of limited accuracy, a clear distinction between the proposed mechanisms cannot be made. We strongly tend to support the hypothesis of vibrational quenching, and work is continuing on this problem.

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Some Unusual Acid-Catalyzed Rearrangements of Glycidic Esters

Sir:

The acid-catalyzed rearrangement of glycidic esters usually results in the formation of pyruvic esters,[1] the only exception being an earlier report by Tiffeneau and Levy[2] who claimed to have obtained ethyl α-formylphenylacetate (IIIa) from ethyl β-phenylglycidate (Ia). However, they also reported that ethyl β-methyl-β-phenylglycidate (Ib) yielded the pyruvic ester IIb. Following these apparently anomalous results, House, *et al.*,[1] reinvestigated both reactions using boron trifluoride and convincingly proved the structure of the rearranged product from Ia to be ethyl phenylpyruvate (IIa), not the reported aldehyde IIIa. Although the rearrangement of Ib was repeated by these authors, the structure of the product was not questioned since it was in harmony with the established pattern of behavior for glycidic esters.

We wish to report that the structure for the rearranged product from Ib was in error and that an unprecedented skeletal rearrangement with carbethoxy migration had in fact taken place, yielding ethyl α-formyl-α-methylphenylacetate (IIIb).[3] In our hands, exposure of Ib to boron trifluoride resulted in a product, mol wt 206 (mass spectroscopy), having the properties reported by House, *et al.*,[1] and ascribed to IIb (2,4-dinitrophenylhydrazone melting at 161° and semicarbazone at 161–63°). The nmr spectrum in CCl_4 displayed, in addition to the aromatic and ester protons, a methyl signal at δ 1.6 as well as an aldehyde signal at δ 10.8, both appearing as sharp singlets. These signals were also present in the spectrum of the 2,4-DNP derivative at δ 1.9 and 8.0, respectively. The above data unequivocally support structure IIIb for the rearranged product from Ib.

The above rearrangement is not exceptional since we observed that β-phenylglycidic esters having α- and/or β-alkyl substituents behave similarly. For example, when ethyl α-methyl-β-phenylglycidate (Ic) was rearranged in hexane, it yielded ethyl α-phenylacetoacetate (IIIc) which was identified by nmr and mass spectroscopy and by comparing the melting point and mixture melting point of its 2,4-DNP derivative with an authentic sample. Similarly, Id gave IIId when treated with boron trifluoride in benzene.

Although the nature of the substituents at either the α or the β position does not explain why Ia behaved normally to give a pyruvate, while Ib, Ic, and Id rearranged with the migration of a carbethoxyl, it is clear that a carbonium ion character at the β position (after protonation and epoxide ring opening) accounts for these as well as all the known acid-catalyzed isomerizations of glycidic esters. The location of a carbonium ion adjacent to a carbonyl is usually prohibited, but we found that the electrostatic repulsion of adjacent positive charges can be overcome by substantially stabilizing the carbonium ion adjacent to the ester, for instance with a phenyl substituent.[6] This represents a second synthesis of esters having a β-carbonyl function from glycidic esters, this time without involving a carboethoxy migration. For instance, ethyl α-phenylglycidate (Ie) and ethyl β-methyl-α-phenylglycidate (If) gave the "abnormal" products IVe and IVf, respectively. However, the β-dimethyl-α-phenylglycidate Ig gave the normal product, the pyruvate IIg.

All these rearrangements took place very cleanly upon bubbling boron trifluoride through a benzene solution of the glycidic ester for 30 min at room temperature. After decomposition of the BF_3 complex with aqueous sodium chloride and evaporation of the solvent, a carbon tetrachloride extract of the residue gave an nmr spectrum which, with one exception,[9] was that of the compounds reported above, in pure state.

These results indicate that, while a benzylic carbonium ion adjacent to a carbethoxy is favored over an aliphatic β-carbonium ion which is primary or secondary, it is not favored over one which is tertiary. Finally, our results indicate that the migratory aptitude to a carbonium ion in this series follows the order phenyl > carbethoxy > methyl.[10] While all three groups migrate individually in preference to it, the position of hydrogen in this sequence remains to be ascertained since its transfer from the α to the β position may take place through deprotonation–protonation as well as through hydride shift.

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(1) H. O. House, J. W. Blaker, and D. A. Madden, *J. Am. Chem. Soc.*, **80**, 6386 (1958).

(2) M. Tiffeneau and J. Levy, *Anales Soc. Quim. Argentina*, **16**, 144 (1928).

(3) The preferential acid-catalyzed migration of a carbalkoxy group over an alkyl substituent has already been observed, but only in aromatization reactions.[4,5]

(4) S. Inayama and M. Yanagita, *J. Org. Chem.*, **27**, 1465 (1962).

(5) D. E. McGreer and Y. Y. Wigfield, *Can. J. Chem.*, **47**, 2095 (1969).

(6) A similar situation exists in the α,β-epoxyketone series and has been discussed by House, *et al.*,[7] However, in contrast to some epoxy ketones, all the isomeric *cis* and *trans* glycidic esters which we studied[8] yielded the same rearrangement product, thus providing additional support to the intermediacy of a carbonium ion.

(7) H. O. House, D. J. Reif, and R. L. Wasson, *J. Am. Chem. Soc.*, **79**, 2490 (1957).

(8) Glycidic esters Ib, Ic, and Id were prepared by the Darzens reaction, while Ie, If, and Ig were obtained by epoxidation of the corresponding α,β-unsaturated esters with *m*-chloroperoxybenzoic acid.

(9) The isolated yield of IVe (as the 2,4-DNP derivative) from the rearrangement of Ie was only 20%.

(10) The migration of dialkylphosphono group in the acid-catalyzed reaction of α,β-epoxyalkylphosphonates has recently been described.[11] The same order of migratory aptitudes was found in that series.

(11) C. E. Griffin and S. K. Kundu, *J. Org. Chem.*, **34**, 1532 (1969); M. Sprecher and D. Kost, *Tetrahedron Letters*, 703 (1969), and references therein cited.