Table I. Isotopic Distribution in the Products of the Reaction of $Ta[CD_2C(CH_3)_3]_3Cl_2$ with $LiCH_2C(CH_3)_3$ in Hexane or Diethyl Ether

	$Ta[CD_2C(CH_3)_3]_3Cl_2$	$LiCH_2C(CH_3)_3$	neo-d_0	d_1	d_2	d_3	α-d^a
A (hexane)	1	2	15	20	43	22	38
B (hexane)	1	1	11	25	41	23	
C (hexane)[b]	1	10	22	21	46	11	
Theory[c]	1	2	16	24	40	20	44
A′ (ether)	1	2	17	21	43	19	42

[a] This notation refers to the per cent deuteration at the neopentylidene α-carbon in **1**-d_x: theory = 56% $CHC(CH_3)_3$, 44% $CDC(CH_3)_3$. [b] Reaction between **1** and LiC_5H_{11} in pentane (or benzene) is slow as judged by ^1H nmr examination of mixtures. [c] Primary deuterium isotope effect = 2.

of the reaction. These results suggest (respectively) the following: (1) neopentane is formed by abstraction of a neopentyl α-hydrogen by a second neopentyl group in a statistical manner involving *all five* neopentyl moieties with a primary deuterium isotope effect of *ca.* 2 (see theory, Table I); (2)(a) alkyl exchange between $Ta[CD_2C(CH_3)_3]_3Cl_2$ and lithium reagent or intermediate tantalum species is slow and (b) the rate of reaction of $Ta[CD_2C(CH_3)_3]_3Cl_2$ with lithium reagent is the slowest step prior to equilibration of all neopentyl groups; and (3) alkyl exchange between excess lithium reagent and *any* tantalum species is slow on the time scale of the reaction. The simplest and most reasonable postulated mechanism involves rapid formation of a penta(neopentyl) species, **2**, which then "decomposes" by elimination of neopentane to give **1**.[8] If, for example, an intermediate, **3**, is postulated, it is necessary under the experimental conditions employed that the rate of formation of **2** (R_2) be greater than the rate of formation of **3** (R_1), and, since **2** is not the end product, $R_3 \geq R_2$, *viz.*

$$Ta[CH_2C(CH_3)_3]_3Cl_2 \xrightarrow{R_1} \mathbf{3} \xrightarrow{R_2} \underset{\mathbf{2}}{\text{"}Ta[CH_2C(CH_3)_3]_3\text{"}} \xrightarrow{R_3} \mathbf{1}$$

$$R_3 \geq R_2 > R_1$$

A description in terms of rate constants awaits a more detailed study. Although the rate of formation of **1** is apparently greater in diethyl ether the isotopic distribution (run A′) remains essentially unchanged.

An α-hydrogen transfer process related to that which results in the formation of **1** can be observed within **1** itself. The reaction of **1** with $Li(n\text{-}C_4H_9)\cdot L$ (L = *inter alia* *N,N,N′,N′*-tetramethylethylenediamine, 1,2-dimethoxyethane, or *N,N′*-dimethylpiperazine) in aliphatic hydrocarbons yields the pentane soluble lithiated species, **4**. Treatment of **4** with CF_3CO_2D in

$$\mathbf{1} + Li(n\text{-}C_4H_9)\cdot L \longrightarrow \underset{\mathbf{4}}{Ta[CH_2C(CH_3)_3]_3\{C[C(CH_3)_3][Li\cdot L]\}}$$

pentane at −78° yields **1**-d_1 (isolated by sublimation) deuterated to the extent of 90% at the neopentylidene α-carbon. Heating **1**-d_1 at 80° for 24 hr in C_6D_6 scrambles deuterium among the neopentylidene and neopentyl ligands. Essentially no decomposition occurs during this time period. This result should be compared with the more rapid hydrogen transfer process which occurs in $(CH_3)_3P(CH_2)$.[9]

The findings presented here demonstrate clearly that under some conditions (1) complexes of "nonstabilized" carbenoid ligands containing an α-hydrogen, *e.g.*, alkylidenes, are stable and (2) α-hydrogen abstraction is a viable mode of "decomposition" of transition metal alkyl complexes.[10]

(8) Pentamethyltantalum (R. R. Schrock and P. Meakin, *J. Amer. Chem. Soc.*, **96**, 5288 (1974)) has been isolated. Steric factors therefore probably play an important role in the "decomposition" of **2**.

(9) H. Schmidbaur and W. Tronich, *Chem. Ber.*, **101**, 604 (1968).

(10) See, for example, M. C. Baird, *J. Organometal. Chem.*, **64**, 289 (1974).

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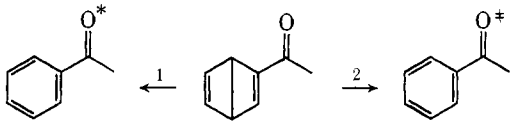
Chemiexcitation of Acetophenone *via* the Nonadiabatic Thermal Rearrangement of Dewar Acetophenone

Sir:

Bicyclo[2.2.0]hexadienes have been observed to produce electronically excited state products upon thermolysis.[1] The previous studies were restricted in scope by the lack of established reactions of the benzene excited triplet state and by energetic constraints on the production of excited singlet benzene. We have pursued the investigation of this interesting family of nonadiabatic valence isomerization with the study of Dewar acetophenone (**1**),[2] eq 1 and 2. The Dewar acetophenone–acetophenone system possesses several *important* and *fundamentally different features* from the previously studied cases: (1) both the S_1 and T_1 states of the valence isomer product correspond to n, π^* configurations; (2) both the S_1 and T_1 states of the valence isomer product possess a lower energy content than the transition state for thermal rearrangement; (3) the essential chemistry occurs (Dewar benzene to benzene) on atoms which are spatially distinct from the expected final site of chemiexcitation (the carbonyl function). Thus, a study of the thermolysis of **1** to acetophenone offers an opportunity to evaluate several intriguing aspects of a simple unimolecular chemiexcitation process.



The thermolysis of Dewar acetophenone is anticipated to release *ca.* 90 kcal/mol in activation enthalpy, and reaction enthalpy.[1] This amount of energy is sufficient[3] to produce either singlet or triplet acetophenone (Figure 1). The photochemistry of acetophenone is well understood.[4]

(1) P. Lechtken, R. Breslow, A. H. Schmidt, and N. J. Turro, *J. Amer. Chem. Soc.*, **95**, 3025 (1973).

(2) Compound **1** was prepared by the addition of cyclobutadiene (released from its iron carbonyl complex) to 3-butyne-2-one. The material was handled after distillation, in solution since attempts at purification resulted in rearrangement to acetophenone. Our samples contained acetophenone as the sole impurity detectable by nmr.

(3) A. A. Lamola and N. J. Turro, "Energy Transfer and Organic Photochemistry," Wiley, New York, N. Y., 1969, p 198.

(4) For example, see H. Lutz, M.-C. Duval, and E. Breheret, and L. Linqvist, *J. Phys. Chem.*, **76**, 821 (1972), and references therein.

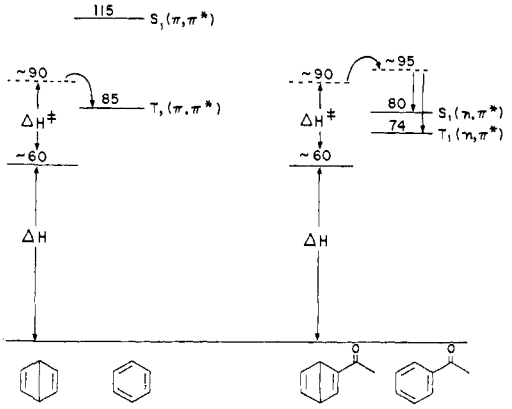


Figure 1. Energy diagram for conversion of "Dewar" to "Kekule" structures.

Thermolysis of **1** in benzene or acetonitrile solution leads to a readily detectable indirect chemiluminescence,[5] with 9,10-dibromoanthracene (DBA) as acceptor. The total rate of disappearance of **1** was determined by monitoring the indirect chemiluminescence of added fluorescent acceptors.[5] It was found that the disappearance of **1** was first order for at least four half-lives. The activation parameters for the total disappearance of **1**, Table I, are comparable to those found for other bicyclo[2.2.0]hexadienes which have been investigated.[1,6] Nmr analysis revealed that acetophenone was the only detectable product obtained from thermolysis of **1**.

Table I. Activation Energies for the Thermal Rearrangement of **1** to Acetophenone Measured by Variation of Rate Constant and Temperature Jump

Temp, °C	Solvent	Rate constant × 10^4 sec^{-1}	Activation energy (kcal/mol)
49.6	Benzene[a]	3.86 ± 0.58[b]	
52.1	Benzene	5.09 ± 0.28	
54.5	Benzene	6.65 ± 0.31	
57.1	Benzene	9.26 ± 0.27	
58.4	Benzene	10.4 ± 0.31	24.8 ± 0.8
50.2	CH_3CN[c]	5.45 ± 0.13	
53.8	CH_3CN	8.00 ± 0.22	
56.1	CH_3CN	9.31 ± 0.35	
59.6	CH_3CN	13.0 ± 0.32	
61.8	CH_3CN	17.8 ± 0.42	23.0 ± 1.4
Temp jump	Benzene[d]	DBA Activated	27.6 ± 2.4[e]
Temp jump	Benzene[f]	DPA Activated	28.9 ± 3.2
Temp jump	CH_3CN[g]	DBA Activated	28.7 ± 1.5[e]
Temp jump	CH_3CN[h]	DPA Activated	30.6 ± 1.8

[a] [**1**] = 4.60 × 10^{-3} *M*, [DBA] = 3.07 × 10^{-3} *M*, air saturated solutions. [b] All rate constants and activation energies are least-squares values, all errors are standard deviations. [c] [**1**] = 4.60 × 10^{-3} *M*, [DBA] = 2.08 × 10^{-4} *M*, air saturated solutions. [d] [**1**] = 2.08 × 10^{-3} *M*, [DBA] = 1.55 × 10^{-4} *M*, nitrogen purged. [e] Corrected for the decrease in DBA fluorescence quantum yield and acetophenone triplet lifetime as temperature increases. [f] [**1**] = 4.60 × 10^{-3} *M*, [DPA] = 1.15 × 10^{-3} *M*, nitrogen purged. [g] [**1**] = 4.60 × 10^{-3} *M*, [DBA] = 2.08 × 10^{-4} *M*, air saturated. [h] [**1**] = 4.60 × 10^{-3} *M*, [DPA] = 8.18 × 10^{-4} *M*, nitrogen purged.

Two methods were employed in an attempt to determine the absolute yield of acetophenone electronically excited states produced from thermolysis of **1** (eq 1). The first was "chemical titration" with *trans*-dicyanoethylene (*t*-DCE).[7] Acetophenone triplet was found to effect the isomerization of *t*-DCE to *cis*-dicyanoethylene (*c*-DCE).[8] Since intersystem crossing in acetophenone is a very fast process ($k_{ST} \sim 10^9$ sec^{-1}),[3] determination of the triplet yield of acetophenone should suffice to measure the total yield of excited state products. Benzene solutions of **1** (0.15 *M*) and *t*-DCE (0.05–0.25 *M*) were thermolyzed and then analyzed for *c*-DCE by glpc. No *c*-DCE above that in control samples was found. An *upper* limit on the yield of excited state species of *ca.*2 % is estimated from this result. The second method for measuring the yield of excited acetophenone was then employed, namely comparison of the integrated indirect chemiluminescent intensity[5] of tetramethyldioxetane (**2**) and **1**. Carbonyl triplet states are capable of producing the excited singlet state of DBA.[5,9] Comparison of the integrated chemiluminescent intensity of **1** and **2** extrapolated to infinite DBA concentration allows the yield of excited products from **1** to be calculated.[7] Application of this method to benzene solutions of **1** and **2** produces an excited state yield from **1** of 0.1–0.3 %.

A kinetic identification of the excited state species produced from **1** was then attempted. The chemiluminescence of **1** activated by DBA could be quenched with *trans,trans*-2,4-hexadiene (**3**). The usual Stern–Volmer analysis gave a straight line from which a value of $k_q\tau$ = 750 could be extracted (41°, [DBA] = 1.5 × 10^{-3}). With the assumption of diffusion controlled quenching by the diene, this value is consistent with comparable data reported for acetophenone triplet in benzene.[10]

9,10-Diphenylanthracene (DPA) singlet states are not efficiently produced by excited carbonyl triplet states.[5,9] Thus, chemiluminescence activated by DPA is usually considered evidence for the intervention of singlet excited states. When DPA is added to benzene solutions of **1** at 50°, DPA luminescence is observed. The chemiluminescence is very much weaker than DBA activated chemiluminescence of **1**, even though DPA photoexcitation of fluorescence is *ca.* 20 times more efficient than DBA fluorescence under these conditions. Stern–Volmer quenching of benzene solutions of **1** plus DPA by **3** gave a value of $k_q\tau$ = 550 (50°, [DPA] = 3.5 × 10^{-3} *M*). This value is inconsistent with DPA excitation from the excited singlet state of acetophenone. Since it was found that the intensity of DPA activated chemiluminescence varied linearly with the concentration of **1**, it appears that the small amount of luminescence observed from DPA results from triplet to singlet energy transfer to that dye. It is estimated that triplet–singlet transfer to DBA is more than 10^3 times faster than to DPA.[5,9]

Chemiluminescent reactions are somewhat unique

(5) N. J. Turro, P. Lechtken, G. Schuster, J. Orell, H. C. Steinmetzer, and W. Adam, *J. Amer. Chem. Soc.*, **96**, 1627 (1974); H. C. Steinmetzer, P. Lechtken, and N. J. Turro, *Justus Liebigs Ann. Chem.*, 1984 (1973).

(6) J. F. Oth, *Recl. Trav. Chim. Pays-Bas*, **87**, 1185 (1968); H. C. Volger and H. Hoogeveen, *ibid.*, **86**, 830 (1967).

(7) N. J. Turro, P. Lechtken, N. E. Schore, G. Schuster, H. C. Steinmetzer, and A. Yekta, *Accounts Chem. Res.*, 7, 97 (1974).

(8) For other examples of this photosensitized cis–trans isomerization, see J. C. Dalton, P. A. Wriede, and N. J. Turro, *J. Amer. Chem. Soc.*, **92**, 1318 (1970).

(9) R. F. Vasilev, *Progr. React. Kinet.*, **4**, 305 (1967).

(10) H. Lutz and L. Lindqvist, *Chem. Commun.*, 493 (1971); W. D. K. Clark, A. D. Litt, and C. Steel, *J. Amer. Chem. Soc.*, **91**, 5413 (1969); L. Giering, M. Bergen, and C. Steel, *ibid.*, **96**, 953 (1974).

in that it is possible to determine the temperature profile of those reactions leading to chemiluminescence even if they are a very small fraction of the total reaction pathway. Thus, by determination of the instantaneous chemiluminescence intensity at several temperatures, the conglomerate activation energy of the sequence leading to chemiluminescence can be determined.[11,12] Results of application of this temperature jump method to the DPA and DBA activated chemiluminescence of **1** are shown in Table I. It is seen that the path leading to activated emission of the dyes requires *ca.* 4–6 kcal/mol more activation energy than the main pathway leading to reaction of **1**. This excess activation energy necessary to produce excited state products may account for the very low chemiluminescence yield from **1**.

An *upper* limit for the yield of acetophenone excited singlet can be estimated from the unquenched activated DPA chemiluminescence at 10^{-2} *M* diene. A conservative calculation indicates that the singlet yield is *below* 1% of the triplet yield, *i.e.*, the estimated upper limit for the singlet acetophenone yield is 3×10^{-4}%.

We have considered the possibility that, as in the case of 1,2-dioxetanes,[13] a catalytic pathway might be responsible for the low value of E_a as measured by the standard methods involving the disappearance of **1**. However, the experimental indistinguishability of E_a in CH_3CN and benzene (Table I) is good evidence against such a complication. Furthermore, the comparable excitation efficiencies of **1** and Dewar benzene itself argue against an unknown catalytic pathway. Finally, the activation entropy for disappearance of **1** is within experimental error of 0 eu, a value which is inconsistent with a bimolecular catalytic pathway for reaction.

In summary, the thermal rearrangement of Dewar acetophenone to acetophenone represents the first example of an electrocyclic reaction of a "Dewar" structure for which it is energetically feasible to populate both a singlet or triplet electronically excited state of the product. The system is of special theoretical interest because the key bond breaking and making processes are expected to be located mainly on the benzene moiety whereas the final excited states are localized on the carbonyl moiety. This dislocation of the incipient location of bond energy release may require more activation than that for the major path for rearrangement. Thus, the final location of electronic excitation starts off "π,π^*-like" but must finish "n, π^*-like;" however, the n, π^* states may not come into operation during the lifetime of the transition state of the chemiexcitation step. This molecular feature may be responsible for the extra activation energy and hence the low efficiency of excited state production from thermolysis of **1**.

Acknowledgment. The authors at CU thank the Air Force Office of Scientific Research (Grant AFOSR-74-2589) and the National Science Foundation (Grants NSF-GP-26602x and NSF-GP-40330x) for their generous support of this work. The authors at UT thank the National Science Foundation, the Army Office of Scientific Research, and the Robert A. Welch Foundation for their support.

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Received June 18, 1974

Isotope Effects in the Hydroxylation of Phenylethylamine by Dopamine β-Hydroxylase

Sir:

Dopamine β-hydroxylase (EC 1.14.17.1) (3,4-dihydroxyphenylethylamine, ascorbate:oxygen oxidoreductase (β-hydroxylating)) catalyzes the hydroxylation of phenylethylamine derivatives such as 3,4-dihydroxyphenylethylamine (Dopamine)[1] at the benzylic position. The reaction, which is the final step in the biosynthesis of norepinephrine, has been shown[2] to proceed according to eq 1.

$$\text{Dopamine} + O_2 + \text{ascorbate} \longrightarrow (R)\text{-norepinephrine} + \text{dehydroascorbate} + H_2O \quad (1)$$

The enzyme from bovine adrenal glands is a tetrameric protein[3,4] containing about 4% carbohydrate,[3] variable amounts of copper (4–7 mol per mole of enzyme), and a constant amount of Cu(II) (2 mol per mole of enzyme).[5] Although it is not known whether the carbohydrate is essential for enzymatic activity, it is known that the copper is required. Apoenzyme devoid of copper has no hydroxylase activity.[5] Furthermore, it has been shown that the first step[5] in the hydroxylation sequence is the reduction by ascorbate of most of the protein-bound Cu(II) to Cu(I).

There has been a great deal of speculation as to how the oxygen might be activated to bring about the hydroxylation in mixed function oxidases. The schemes usually invoke either an "oxenoid"[6] or an electrophilic species[7] as the active hydroxylating agent. Although inversion at the hydroxylated center has been reported, the hydroxylations normally proceed with a net retention at the hydroxylated center.[8] It has recently been demonstrated that the hydroxylation of *d*-amphetamine by Dopamine β-hydroxylase takes place with a net retention of configuration at the benzylic center.[9]

In order to evaluate various mechanistic speculations put forth concerning the mechanism of action of

(1) Abbreviations used in this paper: Dopamine, 3,4-dihydroxyphenylethylamine; Dopamine β-hydroxylase, 3,4-dihydroxyphenethylamine β-hydroxylase.

(2) E. Y. Levin, B. Levenberg, and S. Kaufman, *J. Biol. Chem.*, **235**, 2080 (1960).
(3) E. F. Wallace, M. J. Krantz, and W. Lovenberg, *Proc. Nat. Acad. Sci. U. S.*, **70**, 2253 (1973).
(4) J. E. Craine, G. H. Daniels, and S. Kaufman, *J. Biol. Chem.*, **248**, 7838 (1973).
(5) S. Friedman and S. Kaufman, *J. Biol. Chem.*, **240**, 4763 (1965).
(6) G. A. Hamilton, *Advan. Enzymol. Relat. Areas Mol. Biol.*, **32**, 55 (1969).
(7) S. Bergstrom, S. Lindstredt, S. Samuelson, E. J. Corey, and G. Gregoeiou, *J. Amer. Chem. Soc.*, **80**, 2337 (1958).
(8) W. C. Wildman and N. E. Heimer, *J. Amer. Chem. Soc.*, **89**, 5265 (1967); I. T. Bruce and G. W. Kirby, *Chem. Commun.*, 207 (1968).
(9) K. B. Taylor, *J. Biol. Chem.*, **249**, 454 (1974).

(11) T. Wilson and A. P. Schaap, *J. Amer. Chem. Soc.*, **93**, 4126 (1971).
(12) H. C. Steinmetzer, A. Yekta, and N. J. Turro, *J. Amer. Chem. Soc.*, **96**, 282 (1974).
(13) T. Wilson, M. E. Landis, A. L. Baumstack, and P. D. Bartlett, *J. Amer. Chem. Soc.*, **95**, 4765 (1973).