and thanks Drs. G. Doyle and M. G. Romanelli for stimulating and fruitful discussions.

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(4) Synthesized by the reduction of $Ru_3(CO)_{12}$ by $Mn(CO)_5^-$ in refluxing diglyme: J. S. Bradley, G. B. Ansell, and E. W. Hill, submitted for publication.

(5) High pressure experiments, up to 20 000 psig, were performed in a 400-cm^3 Hastalloy-lined stirred autoclave equipped with liquid sampling facilities. In a typical run the catalyst solution was pressured into the preheated autoclave containing solvent, and brought quickly to the desired temperature and pressure. Samples for infrared and GLC analysis were taken periodically, via a double block, into a 70-cm^3 bomb and cooled to −50 °C before venting, to prevent loss of volatiles. Gas was added to the reactor as it was consumed, maintaining a reasonably constant pressure. Infrared analysis was performed on a Beckman 4250 spectrophotometer equipped with absorbance accessory; gas–liquid chromatography was performed on a Perkin-Elmer 910 chromatograph using a Chromosorb 102 column.

(6) Rate constant defined as moles of CO hydrogenated/gram-atom of Ru per second.

(7) This inverse dependence of rate on P_{CO} is consistent with similar effects in both cobalt-catalyzed hydroformylation of olefins and also heterogeneous methanation catalysis reflecting the competition for active sites on the catalyst between CO and other reactant molecules.

(8) J. W. Rathke and H. M. Feder, *J. Am. Chem. Soc.*, **100,** 3623 (1978).

(9) The higher figure was suggested as evidence for a free-radical rate-determining step for homogeneous CO hydrogenation in which homolytic cleavage of the cobalt–hydrogen bond and transfer of a hydrogen atom to free CO yields a formyl radical, which then undergoes hydrogenation to the observed products. This novel proposition requires the test of further kinetic investigation.

(10) C. Masters and J. A. Van Doorn (to Shell), German Offen. 2 644 185 (1975).

(11) The solutions were allowed to equilibrate before sampling into precooled receivers; samples were stored in the dark at −78 °C until analysis was performed to preclude photochemical or thermal cluster formation from $Ru(CO)_5$, a reaction which occurs at a rate sufficient to frustrate attempts at quantitative determination of the relative concentrations of the monomeric and trimeric carbonyls.

(12) Water, the byproduct of hydrocarbon formation, was also present, and, since this was the only source of water in the system, water concentration was used as a convenient measure of hydrocarbon formation.

(13) The validity of this correlation was confirmed by recharging the autoclave, after thorough THF washing to remove soluble ruthenium carbonyl, with pure THF and heating to 270 °C under 265 atm of $CO–H_2$. Hydrocarbon synthesis was again observed, but in the absence of added ruthenium carbonyl. Indeed this was used as a test for the adequacy of ruthenium metal removal after each run (a tedious mechanical process) and no attempt to catalyze CO hydrogenation homogeneously was made until a successful blank run was achieved.

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(19) NOTE ADDED IN PROOF. Since the submission of this communication a note has appeared from Shell workers reassessing their earlier claims[10] and confirming our conclusion that hydrocarbon synthesis in this system is heterogeneously catalyzed by deposited ruthenium metal: M. J. Doyle, A. P. Kouwenhoven, C. A. Schaap, and B. Van Oort, *J. Organomet. Chem.*, **174,** C55 (1979).

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Exciplex Isomerization of Dewar Benzenes. Factors Controlling Diabatic and Adiabatic Reaction Paths

Sir:

There are several photosensitized molecular rearrangements[1-5] which may be referred to as *exciplex isomerizations.* These reactions appear to depend on electron transfer (not energy transfer) properties of sensitizer-quencher pairs and are most readily understood in terms of singlet exciplex formation followed by nonradiative decay to photoisomers.

Table I. Photochemical and Photophysical Data for HMDB (HMB) Quenching and Isomerization[a]

sensitizer	k_q(HMDB) × 10^{-9} M^{-1} s^{-1}	k_q(HMB) × 10^{-9} M^{-1} s^{-1}	$k_q\tau_0$, M^{-1} [b]	i/s, M^{-1} [c]
1,4-dicyanobenzene (DCB)	10.4	13.2		
1-cyanonaphthalene (CN)	3.2	4.4	84.0	85.6
9,10-dicyanoanthracene (DCA)	7.3	8.7	112	119
9-cyanoanthracene (CA)	0.13	2.6		

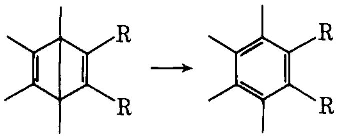
[a] Cyclohexane solution, room temperature. [b] Stern–Volmer constants for quenching sensitizer fluorescence. [c] Intercept/slope ratios for plots of reciprocal HMDB isomerization quantum yield vs. 1/[HMDB].

Table II. Singlet Sensitizer Properties, HMB Exciplex-Excitation Energies, and Preference for Adiabatic HMDB Rearrangement

sensitizer	τ_f, ns[a]	$E_{1/2}^*$(red), V[b]	E_{00}(exc), kcal/mol	P
CN	26	2.1	77	20 ± 2
DCB	13	2.7	73	32 ± 2
CA	9	1.4	64	
DCA	15	2.1	57	50 ± 3

[a] Fluorescence lifetimes in hydrocarbon solvents from the literature: M. Yoshida, H. Sakuragi, I. Tanaka, K. Tokumaru, and N. Morikawa, *Bull. Chem. Soc. Jpn.*, **48**, 2399 (1975); M. E. R. Marcondes, V. G. Toscano, and R. G. Weiss, *J. Am. Chem. Soc.*, **97**, 4485 (1975); E. Vander Donckt, M. R. Barthels, N. Antheunis, and M. Swinnen, *Mol. Photochem.*, **8**, 121 (1977); ref 1b. [b] $E_{1/2}^*$(red) = $E_{1/2}$(red) + sensitizer singlet energy; sensitizer ground-state reduction potentials (vs. SCE, CH_3CN) are reported: E. A. Chandross and J. Ferguson, *J. Chem. Phys.*, **47**, 2557 (1967); D. R. Arnold and A. J. Maroulis, *J. Am. Chem. Soc.*, **98**, 5901 (1976).

The most unusual of these isomerizations is the rearrangement of hexamethyl(Dewar benzene) (HMDB) to hexamethylbenzene (HMB). Evans reported[4] that the isomerization which results from quenching the fluorescence of aromatics by HMDB in polar solvents has a quantum efficiency well exceeding unity. A chain reaction involving radical ions was proposed. Taylor found,[5] on the other hand, that the quenching of 1-cyanonaphthalene (CN) emission by HMDB in relatively nonpolar solvents resulted in a new emission identical with the fluorescence of HMB exciplexes. To our knowledge this important observation of sensitized decomposition of HMDB in nonpolar media is the only example of adiabatic exciplex isomerization (an exciplex → exciplex rearrangement).[6] We report herein a study of Dewar benzene excited complexes in which some of the features which control exciplex formation and the efficiency of diabatic and adiabatic isomerization have been identified.



HMDB
DHD

HMB
DTP

$R = CH_3$
$R = CO_2CH_3$

Fluorescence quenching efficiencies of HMDB and HMB toward four aromatic nitriles were measured in cyclohexane. Quenching rate constants (Table I) were computed from Stern–Volmer plots using literature data for sensitizer fluorescence lifetimes (Table II). The parallel between quenching rate and redox properties (similar oxidation potentials for HMDB and HMB[4] and varied reduction potentials for the

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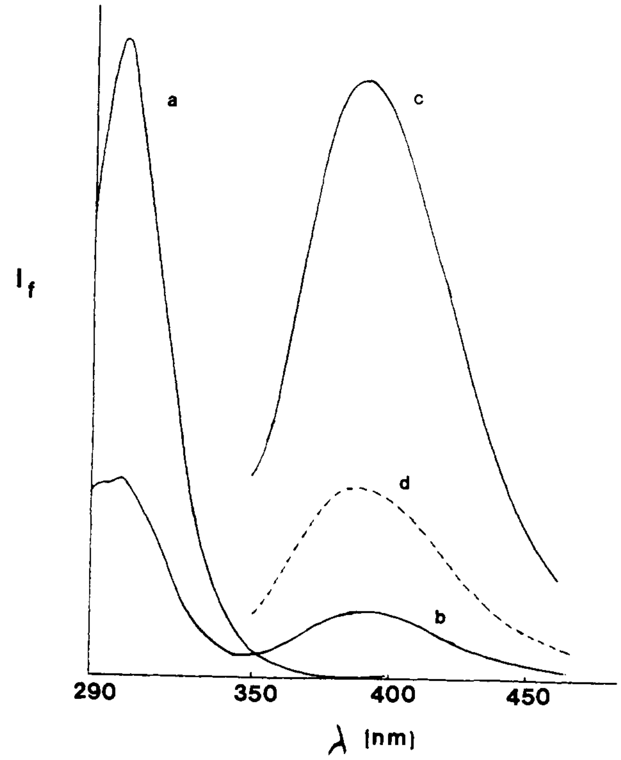

Figure 1. 1-Cyanonaphthalene fluorescence quenching by HMB and HMDB in cyclohexane: (a) CN fluorescence; (b) exciplex emission on addition of HMB; (c) exciplex emission on addition of HMB (×10); and (d) exciplex emission on addition of HMDB (×10).

sensitizers, Table II) is similar to that found for quenching in methanol solution.[4]

Efficient HMDB → HMB rearrangement accompanied the quenching of aromatic nitrile fluorescence in cyclohexane. Plots of reciprocal quantum yield vs. reciprocal HMDB concentration were linear for CN and DCA.[7] Their intercepts yielded limiting quantum efficiencies ($\phi = 0.98$), and intercept/slope ratios compared favorably with Stern-Volmer $k_q\tau$ values obtained from fluorescence quenching (Table I). These results implicate aromatic nitrile singlets as the sensitizing species.

The most unusual findings of Taylor[5] concerning exciplex fluorescence of CN pairs were reproduced in our study for other sensitizers. In all cases exciplex emission was observed on quenching by HMDB or HMB. The long-wavelength fluorescence resulting from HMDB quenching was weaker but clearly superimposed on the emission obtained with HMB (Figure 1).[9] A buildup of HMB (fluorimeter photolysis) that might have been responsible for the similarity of exciplex emission spectra was ruled out by careful GLC analysis of fluorimeter samples.[10] The lifetime of the apparently common exciplex fluorescence was estimated from the results of three-component quenching experiments.[11] 2,5-Dimethyl-2,4-hexadiene (DMH) was an efficient quencher of CN-HMB exciplex emission ($k_q\tau = 59\ \mathrm{M}^{-1}$). At low concentrations of HMDB,[12] a similar value ($k_q\tau = 49\ \mathrm{M}^{-1}$) was found for CN-HMDB exciplex fluorescence quenching by DMH.

The similar electron donor properties of HMDB and HMB[4,5] make possible a coincidence of exciplex characteristics (emission wavelength and lifetime). The definitive experiment in support of adiabatic photochemistry is the demonstration that the fluorescent state produced on HMDB quenching of sensitizer emission is not a precursor to HMDB-HMB rearrangement. Thus the quenching of exciplex fluorescence and exciplex isomerization by DMH was compared. For the CN-HMDB system, exciplex emission was reduced substantially ($k_q\tau = 23\ \mathrm{M}^{-1}$ at 0.22 M HMDB[12]) for DMH concentrations where exciplex isomerization was hardly diminished ($k_q\tau = 5.3\ \mathrm{M}^{-1}$).[13]

The proportion (P) of exciplex isomerization which is the adiabatic path (Scheme I) was determined from relative emission yields. The ratio of exciplex/monomer emission was recorded as a function of % of monomer sensitizer emission quenched by HMDB and HMB. At five levels of sensitizer quenching, for each of three sensitizers, the fraction P ($P = I_{\mathrm{exc}}/I_{\mathrm{mon}}(\mathrm{HMDB})/I_{\mathrm{exc}}/I_{\mathrm{mon}}(\mathrm{HMB})$) was computed (Table II).

Scheme I

$$\mathrm{HMDB} + \mathrm{S}^* \longrightarrow [\mathrm{HMDB}\text{--}\mathrm{S}]^*$$

$$[\mathrm{HMDB}\text{--}\mathrm{S}]^* \xrightarrow{\mathrm{P}} [\mathrm{HMB}\text{--}\mathrm{S}]^* \longrightarrow \mathrm{HMB} + \mathrm{S}$$

$$\xrightarrow{\mathrm{1\text{-}P}} \mathrm{HMB} + \mathrm{S}$$

In summary, the evidence for adiabatic exciplex isomerization of HMDB includes the identity of product exciplex emission wavelengths and emission lifetimes. In a nonpolar solvent the sum of limiting exciplex isomerization quantum yield and exciplex fluorescence yield appear to exceed unity.[14] The product (HMB) exciplex emission can be quenched in lieu of HMDB exciplex isomerization quenching, showing that the emitting state is reached after HMDB rearrangement. The quantum efficiency of exciplex isomerization is not significantly dependent on an initially strong EDA interaction (large quenching constant; i.e., a high limiting yield obtains for a weak—CA-HMDB—pair). Most importantly, the adiabatic portion of exciplex isomerization of HMDB sensitized by the aromatic nitriles is principally a function of product exciplex excitation energy (note E_{00}(exc) and P values in Table II).

This dependence on product exciplex properties (which is a function of the sensitizer in this case) parallels the solvent effect on relative emission yield observed by Taylor for CN-HMDB.[5] Whereas Dewar benzene rearrangements are remarkable in preserving excitation energy during isomerization,[16] HMDB exciplexes are sensitive to storage requirements of the excited surface, so that adiabatic rearrangement is favored when reaction leading to excited product is least endothermic. If the excited surface for HMDB exciplex isomerization resembles the potential curves for Dewar benzene or Dewar naphthalene rearrangement,[17] then the thermodynamics (the energy release) for the adiabatic path are probably reflected in the barrier which separates excited product from the pericyclic minimum near the rearrangement midpoint.

In related studies we have found that quenching of biacetyl fluorescence and phosphorescence and of CN phosphorescence by HMDB does not lead to rearrangement. Also, readily oxidizable aromatics sensitize the rearrangement of a Dewar pththalate derivative (DHD → DTP), but no exciplex emission is observed in parallel with sensitized isomerizaton.[18] We are currently studying further the meaning of these limitations.

Acknowledgments. We thank Professors P. M. Maitlis and C. C. Wamser for providing samples of hexamethyl(Dewar benzene). This work was supported by the U.S. Department of Energy.

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(9) Exciplex fluorescence maxima for quenching by HMDB or HMB in cyclohexane are as follows: DCB, 392; CN, 373; DCA, 500; CA, 450 nm. The CA–HMDB exciplex emission is very weak and poorly resolved; the corresponding CA–HMDB exciplex fluorescence is not detectable.

(10) HMB was not detected (<0.5%) in purified samples of HMDB before or after fluorescence measurements. Since quenching efficiencies for HMDB and HMB are similar (Table I), the portion of the observed emission on HMDB quenching which is due to competitive HMB quenching must be negligible.

(11) R. A. Caldwell, D. Creed, and H. Ohta, *J. Am. Chem. Soc.*, **97,** 3246 (1975).

(12) HMDB was found to be a quencher of CN–HMB exciplex fluorescence ($k_q\tau$ = 35 M^{-1}). Indeed the CN–HMDB-derived emission reaches a limiting value and diminishes at high concentrations of HMDB. Values of $k_q\tau$ for DMH quenching of the CN–HMDB derived emission were obtained at several concentrations of HMDB and extrapolated to [HMDB] = 0 to obtain the value of 49 M^{-1}.

(13) Relative quantum yields for isomerization in the presence of DMH were corrected for the amount of quenching due to interception of CN singlets, (DMH quenching of CN fluorescence). The residual isomerization quenching ($k_q\tau$ = 5.3 M^{-1} after correction) appears to be real and can be associated with DMH interception of the apparently shorter lived CN–HMDB exciplex which is responsible for rearrangement. Taylor has obtained spectroscopic evidence for the CN–HMDB exciplex in low temperature experiments.[5]

(14) (a) Relatively low yields of HMB exciplex emission do not allow a decisive test. The quantum yield of exciplex fluorescence for CN–HMB is 0.1. The adiabatic fluorescence yield then for the CN–HMDB pair is 0.02. Absolute fluorescence yields for the other exciplex pairs are similarly low. (b) We believe it unlikely that radical-ion formation (and the chain propagation of rearrangement observed in methanol[4]) is important in cyclohexane. The solvent dependent behavior of exciplexes of HMB (which has electron-donor properties similar to HMDB) provides support. HMB exciplexes are highly emissive in cyclohexane but nonemissive in acetonitrile showing a resistance to ionic photodissociation[15] in the nonpolar solvent. Geminate sensitizer–HMDB radical-ion pairs capable of rearrangement and back-electron transfer in a solvent cage cannot be excluded.

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(17) J. Michl, *Photochem. Photobiol.*, **25,** 141 (1977).

(18) For example, 1,4-dimethoxyanthracene (DMA) is a DHD → DTP sensitizer ($\phi_{lim} \simeq 0.2$). Quenching of DMA fluorescence by DTP results in exciplex fluoresence (λ_{max} 460 nm). This emission is not observed on quenching DMA by DHD.

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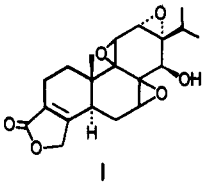
Isodehydroabietenolide

Sir:

In synthetic approaches to the promising anti-leukemic agent triptolide (**1**), as well as other natural products with the novel 18(4→3)*abeo*-abietane skeleton,[1a] such as stemolide,[1b] lactone **2** (or a close relative thereof) is anticipated to be a pivotal intermediate, pathways to which can be rocky because of the greater thermodynamic stability of the A/B cis arrangement in this system.[2] Herewith we describe two, distinctly dissimilar routes to this A/B trans tetracyclic prototype ("isodehydroabietenolide"): one features an electrocyclic reaction involving transformation of an allylic sulfonium methylide to a butenyl sulfide, and the other depends on a polyene cyclization initiated by a β-keto ester unit, a new version of this reaction type.



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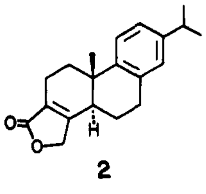

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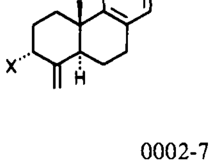
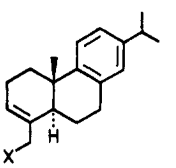
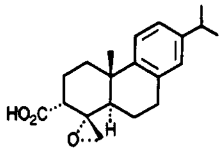


3 X = H
9 X = $CH_2SC_6H_5$
10 X = CHO
11 X = COOH

In the first approach, which requires isolation and purification of only three intermediates, the known dehydroabietene **3** serves as the starting material, accessible by a totally synthetic route terminating with cyclization of a polyene ketone,[3] or better by a previously described pathway starting from dehydroabietic acid.[6] On treatment with *i*-Pr_2NAlEt_2[7] in benzene–petroleum ether at 50 °C for 2 days, the known[8] α-epoxide of **3** was converted into the allylic alcohol **4**: 60-MHz NMR (CCl_4), inter alia, δ 3.98 (dd, J = 14 Hz, 2 H, 19-CH_2), 5.63 (s, 1 H, 3-CH). The Lees reagent (n-Bu_3P–CCl_4) was used for formation of allylic chloride **5**, which was transformed by means of $LiSC_6H_5$ in THF at room temperature to thioether **6** (78% from **3**, without isolation of intermediates). The product of S-methylation ($Me_3O^+BF_4^-$ in CH_3CN at 0 °C), sulfonium salt **7**, was deprotonated (BuLi in THF, −78 → 0 °C) to give the corresponding methylide (**8**) which, via a [2,3]-sigmatropic shift,[9] isomerized to the butenylic thioether **9** (86% from **6**). After monochlorination of the *S*-methylene moiety (*N*-chlorosuccinamide in CCl_4), exposure to methanol at 0 °C followed by $I_2/NaHCO_3$ in dioxane-water resulted in formation of aldehyde **10** (63% from **9**).



4 X = OH
5 X = Cl
6 X = SC_6H_5
7 X = $(CH_3SC_6H_5)^+$
8 X = $CH_2{=}SC_6H_5$



12

The synthesis can be completed without further isolation of intermediates. After oxidation of **10** to acid **11** ($NaClO_2$/NH_2SO_3H in dioxane-water at room temperature)[10] (NMR (CCl_4), inter alia, β 3-CH, δ 3.30 ($w_{h/2}$ = 7 Hz)), 3,5-dinitroperbenzoic acid[11] in methylene dichloride at room temperature was employed for conversion into epoxy acid **12**. The corresponding methyl ester, through the action of lithium diisopropylamide (THF, −78 °C → room temperature), suffered β-elimination and lactonization, providing (50% from **10**) lactone **2** as a viscous oil: M$^+$ 296; IR^{NaCl} 1748 (C=O), 1669 cm^{-1} (conjugated C=C); NMR (CCl_4), inter alia, δ 1.02 (s, 3 H, 20-CH_3), 1.20 (d, J = 6.5 Hz, 6 H, 16-CH_3 and 17-CH_3), 4.65 (m, 2 H, 19-CH_2), 6.80–7.30 (m, 3 H, aromatic); ^{13}C NMR ($CDCl_3$) δ 70.1 (C-19), 124.4 (C-3), 162.6 (C-4), 173.5 (C-18); UV λ_{max} 216 nm (EtOH, ϵ 19 900). In respect to the lactone and A-ring moieties, the IR, UV, and ^1H NMR spectra of **2** thus compare favorably with those of triptolide itself:[1a] IR^{KBr} 1773 (C=O), 1686 cm^{-1} (C=C); NMR ($CDCl_3$) δ 4.78 (m, 2 H, 19-CH_2); λ_{max} 218 nm (EtOH, ϵ 14 000). Similarly, the ^{13}C NMR correlates impressively with that of stemolide:[1b] δ 70.2 (C-19), 124.3 (C-3), 162.0 (C-4), 173.5 (C-18). Isodehydroabietenolide obtained as described above was identical in all respects with A/B trans material and dissimilar to the A/B cis isomer, both obtained from dehydroabietic acid by entirely independent means currently being developed and improved in this laboratory.

In preliminary studies involving a fundamentally different synthetic approach, the substituted acetoacetic ester **13** was constructed and subjected to carbocyclization conditions. Reaction of the Grignard reagent (Mg/THF) of *m*-isopropyl-β-phenethyl bromide[12] with α-methylcyclopropane car-