and co-workers for gymnomitrol (**2**)[1] as well as those shifts observed by Coates and co-workers for the two alcohols produced upon reduction of the diastereomer of ketone **8.**[17]

Hydroboration of alkene **8** with excess disiamylborane in THF, followed by oxidation with basic hydrogen peroxide, gives diol **9** in 80% yield.[18] Oxidation of diol **9** with Jones reagent[19] and esterification of the resultant keto acid afford keto ester **10** in 84% yield. The tricyclic structure of **2** now requires a Claisen condensation on keto ester **10.** The rationale for performing a modified Claisen condensation on keto ester **10** is as follows: (1) differentiation between the two potential carbonyl moieties, (2) selective and stereoselective reduction of the cyclopentanone carbonyl, and (3) ease of protection of the resultant cyclopentanol and unmasking of the silylated cyclohexanone. Addition of keto ester **10** to a solution of 2.0 equiv of lithium bis(trimethylsilyl)amide[20] in anhydrous THF-hexane (95:5) at reflux over a period of 20 min, followed by continued heating at reflux for 2.25 h, cooling to 0 °C, addition of HMPT, and enolate anion trapping with *tert*-butyldimethylsilyl chloride,[21,22] affords tricyclic ketone **11** in 65% yield. Stereoselective reduction of ketone **11** with sodium borohydride in 100% ethanol at 0 °C to room temperature for 6 h gives alcohol **12** in 87% yield containing a small amount of the diastereomeric alcohol.[21,23]

Sequential treatment of silyl enol ether alcohol **12** with 2-methoxypropene in the presence of a catalytic amount of phosphorus oxychloride[24] at room temperature for 16 h, followed by the addition of tetra-*n*-butylammonium fluoride[21] in THF and stirring at room temperature for an additional 10 h, produces keto ketal **13** (R = $-C(CH_3)_2OCH_3$) in 74% yield along with the isomeric keto ketal in 5% yield.[23] Finally, a Wittig reaction on keto ketal **13** with methylenetriphenylphosphorane[25] in anhydrous dimethyl sulfoxide at 75 °C for 16 h and methanolysis in the presence of a catalytic amount of 5% hydrochloric acid solution at room temperature for 0.5 h afford (±)-gymnomitrol (**2**) in 87% yield. Synthetic **2** was found to be identical with a sample of the natural substance with respect to NMR, IR, GLC, and TLC data.

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(26) Professors R. M. Coates (University of Illinois) and G. Büchi (Massachusetts Institute of Technology) and their respective co-workers have recently synthesized (±)-gymnomitrol by independent routes. We congratulate them on their synthetic achievements. See the two accompanying communications in this issue.

(27) After submission of this manuscript we learned that Professor L. A. Paquette and co-worker also have synthesized (±)-gymnomitrol. See Paquette, L. A.; Han, Y.-K., *J. Org. Chem.*, in press. We congratulate them on their successful synthesis.

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Photoactivation of Cobalt Carbonyl Catalysts: Generation of Reactive Mononuclear Fragments from Dinuclear, Metal–Metal Bonded Complexes

Sir:

Metal–metal bonded complexes are generally photosensitive with respect to cleavage of the metal–metal bond,[1] and certain dicobalt complexes are known[2] to be hydroformylation catalyst precursors under thermal conditions. We report herein our preliminary results concerning the photogeneration of catalytically active mononuclear cobalt carbonyl fragments from dinuclear, metal–metal bonded complexes. The results illustrate the potential utility of photoinduced metal–metal bond cleavage in probing catalytic mechanisms and in initiating catalytic chemistry under thermal conditions where there would be no reaction without light activation. The complexes studied thus far are $[Co_2(CO)_6L_2]$ ($L = P(n\text{-}Bu)_3, P(OPh)_3$) and $[Fe(\eta^5\text{-}C_5H_5)(CO)_2Co(CO)_3(P(OPh)_3)]$,[3] and the catalytic probe chemistry has been reaction of 1-pentene-$HSiEt_3$ mixtures. The cobalt systems have been chosen for study be-

Table I. Photocatalyzed 1-Pentene Reaction Using Dinuclear Co Complexes as Catalyst Precursors

catalyst precursor (concn)	conditions[a]	irrdn time, h	analysis, %[b]			
			n-pentane	1-pentene	*trans*-2-pentene	*cis*-2-pentene
$[Co_2(CO)_6(P(n\text{-}Bu)_3)_2]$	3.6 M 1-pentene	0		99.7	0.20	0.0_3
(2.64×10^{-3} M)	in *n*-octane	94		99.7	0.2_3	0.0_9
		thermal control		99.7	0.2_1	0.0_6
	1.0 M 1-pentene	0		99.7	0.1_8	0.1_6
	+ 1.6×10^{-2} M $P(OMe)_3$	72	0.1_3	95.5	2.6_9	1.7_2
	in *n*-octane	thermal control		99.6	0.2_2	0.1_8
$[Co_2(CO)_6(P(OPh)_3)_2]$	1.0 M 1-pentene	0		99.3	0.2_8	0.3_8
(8.97×10^{-4} M)	in benzene	76	0.2_8	92.0	5.0_5	2.6_5
		thermal control		99.3	0.4_0	0.3_0

[a] All experiments were run at 25 °C using 1.0-mL samples freeze-pump-thaw degassed in at least four cycles and hermetically sealed in Pyrex ampules. Irradiation was with a GE Blacklite with principal output at 355 ± 20 nm providing 1.6×10^{-6} einstein/min incident on the sample. [b] Analysis of C_5 mixture by VPC against *n*-hexane as an internal standard.

Table II. Photocatalyzed 1-Pentene Reaction in the Presence of $HSiEt_3$[a]

catalyst precursor (concn)	conditions	irrdn time, h	analysis, %			
			n-pentane	1-pentene	*trans*-2-pentene	*cis*-2-pentene
$[Co_2(CO)_6(P(n\text{-}Bu)_3)_2]$	3.6 M $HSiEt_3$ +	0	0.0_1	99.6	0.27	0.1_4
(2.65×10^{-3} M)	3.6 M 1-pentene	94	3.1_0	3.30	74.5	18.0
	(neat)	thermal control	0.6_4	97.9	1.0_7	0.3_6
	1.0 M $HSiEt_3$ +	52	0.93	94.0	3.61	1.51
	1.0 M 1-pentene					
	in *n*-octane					
	1.0 M $HSiEt_3$ +	52	5.44	16.5	58.7	19.4
	1.0 M 1-pentene +					
	5.3×10^{-3} M $P(OMe)_3$					
	in *n*-octane					
$[Co_2(CO)_6(P(OPh)_3)_2]$	1.0 M $HSiEt_3$ +	0		99.6	0.28	0.20
(8.97×10^{-4} M)	1.0 M 1-pentene	5	3.07	46.0	37.0	13.9
	in benzene	thermal control	0.1_2	97.8	1.2_9	0.7_8
$[(\eta^5\text{-}C_5H_5)Fe(CO)_2\text{-}$	1.0 M $HSiEt_3$ +	0		99.6	0.2_2	0.2_0
$Co(CO)_3(P(OPh)_3)]$	1.0 M 1-pentene	7	2.74	7.46	76.2	13.6
(1.79×10^{-3} M)	in benzene	thermal control	0.0_2	99.1	0.6_5	0.2_2
$[(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_4]$	3.6 M $HSiEt_3$ +	0	0.0_4	99.6	0.1_9	0.1_4
(2.65×10^{-3} M)	3.6 M 1-pentene	96	0.77	98.3	0.6_0	0.3_5
	(neat)	thermal control	0.0_4	99.3	0.4_1	0.2_5

[a] See notes for Table I.

cause it is believed that the dinuclear $[Co_2(CO)_6(P(n\text{-}Bu)_3)_2]$ actually forms mononuclear $[HCo(CO)_3(P(n\text{-}Bu)_3]$ under hydroformylation conditions.[2] The ability to photogenerate $[Co(CO)_3L]$ under mild thermal conditions offers an opportunity to gain insight into the mechanisms of cobalt carbonyl catalyzed reactions.

All three complexes studied here undergo efficient photochemical cleavage of the metal-metal bond, as reflected in the photochemistry that we find:

$$[Mn_2(CO)_{10}] + [Co_2(CO)_6L_2] \xrightleftharpoons[\substack{L = P(n\text{-}Bu)_3 \\ \text{benzene}}]{h\nu} 2[Mn(CO)_5Co(CO)_3L] \qquad (1)$$

$$[Fe_2(\eta^5\text{-}C_5H_5)_2(CO)_4] + [Co_2(CO)_6L_2] \xrightleftharpoons[\substack{L = P(OPh)_3 \\ \text{benzene}}]{h\nu} 2[Fe(\eta^5\text{-}C_5H_5)(CO)_2Co(CO)_3L] \qquad (2)$$

$[Mn_2(CO)_{10}]$[4] and $[Fe_2(\eta^5\text{-}C_5H_5)_2(CO)_4]$[5] are known to undergo efficient metal-metal bond cleavage, and the photoinduced formation of heterodinuclear complexes is believed to result from coupling of two different 17-valence electron radicals. The forward and reverse photoreactions represented in equations 1 and 2 are chemically clean, and quantum yields for near-ultraviolet-light-induced cleavage of the metal-metal bonds are all >0.1.

Irradiation of $[Co_2(CO)_6L_2]$ in the presence of 1-pentene in benzene or *n*-octane solution results in little net reaction of any kind. The disappearance of the Co-Co bonded species is very slow, particularly for L = $P(n\text{-}Bu)_3$. Presumably, the Co-Co bond is cleaved efficiently, but recoupling of the $[Co(CO)_3L]$ fragments obtains to result in little net chemical change. Irradiation of the Fe-Co bonded species under the same conditions results in the redistribution reaction shown in equation 2. Table I shows the effect on 1-pentene by irradiating the $[Co_2(CO)_6L_2]$ species. For L = $P(n\text{-}Bu)_3$ there is no detectable reaction in 94 h, but for L = $P(OPh)_3$ there is considerable alkene isomerization and a small amount of *n*-pentane forms. Further, adding $P(OMe)_3$ to a 1 M 1-pentene solution containing $[Co_2(CO)_6(P(n\text{-}Bu)_3)_2]$ results in photocatalytic activity comparable with that found for the $[Co_2(CO)_6(P(OPh)_3)_2]$ complex.

Addition of $HSiEt_3$ to the 1-pentene solutions dramatically affects the photocatalytic activity (Table II). Under the same conditions, except for the presence of $HSiEt_3$, the photolysis of $[Co_2(CO)_6(P(n\text{-}Bu)_3)_2]$ essentially completely equilibrates the linear pentenes to the thermodynamic ratio,[6] whereas no reaction obtains in the absence of the $HSiEt_3$. A significant amount of *n*-pentane is formed and small quantities of Si-containing products are also detectable but have not been analyzed quantitatively. The addition of $P(OMe)_3$ further accelerates the photocatalytic activity of the $P(n\text{-}Bu)_3$ complex. The effect of added $HSiEt_3$ on the photocatalytic activity of the $[Co(CO)_3P(OPh)_3]$ precursors is equally striking. The heterodinuclear Fe-Co complex is about as active as the homodinuclear precursor. Note that the $[Fe_2(\eta^5\text{-}C_5H_5)_2(CO)_4]$ is essentially nonactive and is, of course, the homodinuclear source of the 17-valence electron radical $[Fe(\eta^5\text{-}C_5H_5)(CO)_2]$. However, the related radical, $[Fe(\eta^3\text{-}C_3H_5)(CO)_3]$, is active as an isomerization catalyst.[7]

While none of the systems exhibit significant thermal activity on the same time scale as used in the photochemical experiments, long thermal reaction time at 25 °C does result in similar catalytic chemistry, and the effects of added $HSiEt_3$ or $P(OMe)_3$ are similar. The most thermally active species is the $[Co_2(CO)_6(P(OPh)_3)_2]$; the $[Fe(\eta^5\text{-}C_5H_5)(CO)_2Co(CO)_3(P(OPh)_3)]$ is qualitatively less active, but the least active complex is $[Co_2(CO)_6(P(n\text{-}Bu)_3)_2]$.

The data suggest that the 17-valence electron radicals $[Co(CO)_3L]$ (L = $P(n\text{-}Bu)_3$, $P(OPh)_3$) or $[Fe(\eta^5\text{-}C_5H_5)(CO)_2]$ are not themselves active catalysts for alkene isomerization. However, these species apparently can react with $HSiEt_3$, a hydride source, to give mononuclear hydride catalysts for isomerization and alkene reduction. The enhanced catalytic activity, *n*-pentane formation, and formation of Si-containing products strongly implicate such a role for the $HSiEt_3$. Irradiation of metal-metal bonded compounds in the presence of silicon hydrides is known to result in the formation of silyl and hydride complexes.[8] Note that $[M_2(CO)_8H_2]$ (M = Mn, Re) can be formed via photolysis of $[M_2(CO)_{10}]$ in the presence of H_2.[9] IR and UV-visible spectral changes in our system containing $HSiEt_3$ reveal conversion into mononuclear Co complexes, and catalytic activity persists when all metal-metal bonded compounds are exhausted. Molecular H_2 at 2 atm does appear to serve as a source of hydride for $[Co_2(CO)_6(P(OPh)_3)_2]$, but the catalytic activity in the presence of 1 M 1-pentene is not so great as that found with $HSiEt_3$. A priori H_2 should be less active as a hydride source, since the H-H bond is stronger than the Si-H bond. Whether mononuclear hydrides are responsible for reaction in the absence of H_2 or Si-H sources (Table I) is not clear. Our studies of this low activity situation have not been definitive to date.

Mononuclear Co-hydride complexes possibly arise from reaction of 15-valence electron Co-containing species[10] with $HSiEt_3$ followed by hydrogen abstraction according to reactions 3-6, not unlike the processes proposed for the photochemical formation of $[M_2(CO)_8H_2]$.[9,11] That reaction 4 is crucial is consistent with our finding that 10 psi of CO pressure effectively supresses photocatalytic activity.

$$[{>}M\text{-}Co(CO)_3L] \xrightarrow{h\nu} {>}M\cdot + [Co(CO)_3L] \qquad (3)$$

$$[Co(CO)_3L] \overset{\Delta}{\rightleftarrows} [Co(CO)_2L] + CO \qquad (4)$$

$$[Co(CO)_2L] + HSiEt_3 \xrightarrow{\Delta} [Co(CO)_2(H)(SiEt_3)L] \qquad (5)$$

$$[Co(CO)_2(H)(SiEt_3)L] + [Co(CO)_3L] \xrightarrow{\Delta} [HCo(CO)_3L] + [Co(CO)_2(SiEt_3)L] \qquad (6)$$

Hydrides like that indicated in equation 6 are known catalysts for alkene reactions.[12] Independent preparation[13] of $[HCo(CO)_3P(OPh)_3]$ by addition of $HBF_4{\cdot}Et_2O$ to $Na[Co(CO)_3P(OPh)_3]$ in tetrahydrofuran (THF) solution has been carried out, and we find thermal catalytic chemistry (isomerization and alkene reduction at 25 °C in $HSiEt_3$-1-pentene, 1.4 M each, in THF), and the distribution of products is similar to that found from irradiating $[Co_2(CO)_6(P(OPh)_3)_2]$ under the same conditions. We find that the $[HCo(CO)_3P(OPh)_3]$ has an intense IR absorption at 1992 cm^{-1} (THF), and that at 25 °C the complex decomposes[13] to form $[Co_2(CO)_6(P(OPh)_3)_2]$ (1978 cm^{-1}) in THF solution. Further, the catalytic activity of our THF solutions of $[HCo(CO)_3P(OPh)_3]$ is enhanced (factor of ~3 in rate) by near-UV irradiation. This last result would indicate that our photocatalytic experiments beginning with $[Co_2(CO)_6L_2]$ likely have a component of light-accelerated catalysis by mononuclear compounds. Consistent with this conclusion we find that ~15 min of irradiation of $[Co_2(CO)_6(P(OPh)_3)_2]$ followed by dark reaction yields catalytic chemistry at a rate substantially lower than with continuous irradiation. Comparison of relative dark and light rates accords well with the dark vs. light rates when $[HCo(CO)_3P(OPh)_3]$ is used.

Preliminary results using 1:1 $DSiEt_3$-1-pentene with $[Co_2(CO)_6P(OPh)_3)_2]$ as the photocatalyst reveals the rapid formation of $HSiEt_3$ (detected by ^1H NMR and GC-MS) accompanying formation of pentane and *cis*- and *trans*-2-pentene. The deuterium is found in all of the hydrocarbons. This experiment confirms an important role for the Si-H(D) system and adds further to the understanding of the mechanism. Thus a Co species containing alkene, hydride, and the trialkylsilyl group is implicated in the catalytic cycle. Inasmuch as we do observe significant amounts of alkane product, it is reasonable that a key species is in fact $[H_2Co(CO)_2(SiEt_3)L]$ from oxidative addition of $HSiEt_3$ to $[HCo(CO)_3L]$ or from disproportionation of the 17-valence electron species $[HCo(CO)_2(SiEt_3)L]$ indicated in equation 5.

Data in Tables I and II reveal that the ordering of the activity of the three 17-valence electron radicals is $[Co(CO)_3P(OPh)_3] > [Co(CO)_3P(n\text{-}Bu)_3] > [Fe(\eta^5\text{-}C_5H_5)(CO)_2]$. The lower thermal activity of the Fe-Co system compared with that of $[Co_2(CO)_6(P(OPh)_3)_2]$ is logically a consequence of the more inert metal-metal bond. The effect of added $P(OMe)_3$ on the activity of the $P(n\text{-}Bu)_3$ complex is in accord with the notion that the photogenerated $[Co(CO)_3L]$ radicals are substitution labile,[10] and the various substituted radicals will have a different reactivity toward $HSiEt_3$.[14] The activity of the systems studied do not seem to be great under the conditions employed, but we note that the observed quantum yields (molecules of product/photon incident) are essentially unity for the alkene isomerization in the presence of $HSiEt_3$ using $[Co_2(CO)_6(P(OPh)_3)_2]$. Increased light intensity increases the observed rates, and we find that the linear pentenes can be equilibrated to the thermodynamic ratio in <3 h for a neat 1:1 $HSiEt_3$-1-pentene solution. The turnover rate thus exceeds (3×10^2)/h, and may be much higher at higher intensities. If a 1:1 $HSiEt_3$-1-pentene is exposed to 10 psi of H_2 and illuminated at high intensities, the turnover number for pentane formation exceeds 10^2/h. Finally, at the high intensities, large yields of hydrosilation products are observable on the time scale of experiments detailed in Table II. Further data concerning these optical effects on turnover rate will be included in the full paper.

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(11) The oxidative addition of H_2 to Co(0) in the equilibrium $H_2 + N_2Co(PPh_3)_3 \rightleftharpoons N_2 + H_2Co(PPh)_3$ may be via 15-e$^-$ species: Speier, G.; Marko, L. *Inorg. Chim. Acta* **1969**, *3*, 126. However, direct abstraction of H· from $HSiEt_3$ by the 17-e radical *may* be possible if there is ligand redistribution to produce $[Co(CO)_nL_{4-n}]$ species. See also Kidd, D. R.; Brown, T. L. *J. Am. Chem. Soc.* **1978**, *100*, 4103.
(12) For discussion of various catalytic reactions of alkenes using cobalt carbonyl precursors, see Taqui Khan, M. M.; Martell, A. E. "Homogeneous Catalysis by Metal Complexes"; Academic Press: New York, 1974; Vol. II.
(13) (a) Hieber, W.; Lindner, E. *Chem. Ber.* **1961**, *94*, 1417. (b) Wender, I.; Pino, P. "Organic Syntheses via Metal Carbonyls"; Interscience: New York, 1968; pp 188–189. (b) Piacenti, F.; Bianchi, M.; Benedetti, E. *Chim. Ind.* (*Milan*) **1967**, *49*, 245.
(14) A reviewer suggested that $[CoL_4(olefin)]^+$ may represent an actual catalyst involved here. Small quantities of very active species are of course difficult to rule out, but $[CoL_4]^+$, though a reactive species, has a short lifetime and gives decomposition to $[CoL_5]^+$ and Co(0) under catalytic conditions: Muetterties, E. L.; Watson, P. L. *J. Am. Chem. Soc.* **1978**, *100*, 6978. Note too that we find photocatalytic formation of 3,3-dimethylpentane when $[Co_2(CO)_6(P(OPh)_3)_2]$ is irradiated in the presence of $HSiEt_3$-3,3-dimethyl-1-pentene, evidencing catalytic activity for alkenes incapable of easy π-allyl-hydride formation believed to be important in the $[CoL_4]^+$ catalyzed isomerization. Use of $DSiEt_3$ results in the formation of $HSiEt_3$ and deuterated hydrocarbon alkane and alkene product.

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α-Hydroxynitrosamines: Transportable Metabolites of Dialkylnitrosamines

Sir:

We report herein evidence demonstrating that α-hydroxynitrosamines (**1**), the proposed critical metabolites in dialkylnitrosamine carcinogenesis,[1] (a) decompose via an alkyldiazotic acid (**2**), as previously postulated;[1] and (b) may be the "transportable" metabolic forms[2] responsible for alkylation of nuclear DNA upon in vivo administration of nitrosamines.[3] The instability of **1** has to date prevented their isolation and spectroscopic characterization; however, they can be studied by in situ preparation via the alkaline- or enzyme-catalyzed hydrolyses of the corresponding α-acetoxynitrosamine (**3**).[2,4]

$$\underset{\textbf{1}}{RN(NO)CH_2OH} \quad \underset{\textbf{2}}{RN{=}NOH} \quad \underset{\textbf{3}}{RN(NO)CH_2OAc}$$

$$\underset{\textbf{4}}{RN(NO)CO_2Et} \quad \underset{\textbf{5}}{RNHCO_2Et}$$

a, R = $PhCH(CH_3)$
b, R = $CH_2{=}CHCH_2$
c, R = CH_3CH_2
d, R = $PhCH_2$

To elucidate the decomposition pathway of **1**, *l*-(−)-acetoxymethyl(1-phenylethyl)nitrosamine (**3a**)[5] was prepared by the method of Saavedra,[4] and the stereochemical outcome of its alkaline (pH 8.5) and esterase hydrolyses was studied. These results were compared with the alkaline (pH 8.5) hydrolysis of *l*-(−)-ethyl *N*-(1-phenylethyl)nitrosocarbamate (**4a**), a compound, which under basic conditions reacts via **2a**.[6] The results shown in Table I demonstrate that the optical purity of the product, 1-phenylethanol, is virtually identical in all three hydrolyses.[7] Thus **2a** is an intermediate in the hydrolysis of **1a**, as expected.[1]

Table I. Hydrolysis of **3a** and **4a**

compd	reaction conditions[a]	$t_{1/2}$, h	α°D (temp, °C)[b]	% net[c,d] inversion
3a	ph 7.0	41		
4a	pH 7.0	13		
3a	pH 7 + esterase[e]	0.25	+13.60 (25)[f]	31.2[i]
3a	pH 8.5	8.3	+12.75 (25)[g]	29.2[j]
4a	pH 8.5	5.0	+12.50 (24)[h]	28.6[j]

[a] All reactions were carried out at 37 °C in 0.05 M phosphate buffer, at ~2 mM concentration of nitroso compounds. [b] Reaction product 1-phenylethanol was diluted with pure racemic alcohol to obtain optical measurements. [c] Initial 1-phenylethylamine used in syntheses has α_D (26 °C) of −38.95°, 99% optically pure. [d] Optically pure 1-phenylethanol has α_D (25 °C) of +43.70°: Burwell, Jr., R. L.; Shields, A. D.; Hart, H. *J. Am. Chem. Soc.* **1954**, *76*, 908–909. Control experiments show that the 1-phenylethanol is stereochemically stable to reaction conditions. [e] Hog liver esterase concentration = 2.53 × 10^{-7} M; molar ratio of **3a**:esterase, 4400. [f] Dilution factor, 4.75. [g] Dilution factor, 5.30. [h] Dilution factor, 5.43. [i] Yield of alcohol, 80%. [j] Yield of alcohol, 90%.

Table II. Inhibition of Hog Liver Esterase Activity

compd[a]	mole ratio of compd:esterase[b]	% inhibition[c]
3a	10:1	0
4a	11:1	95
	10:1	90[d,e]
	6:1	64
	3:1	48
	1:1	30
4b	10:1	51[d]
4c	10:1	28[d]
4d	10:1	100[d]
4a + 5d	10:10:1	52[f,g]
5a	10:1	80[f]
5b	10:1	79[f]
5d	10:1	88[f]

[a] Note 5. [b] Mole ratios are based on enzyme molecular weight of 164 000: Krisch, K. *Enzymes* **1971**, *5*, 43–69. Esterase concentration, 9 × 10^{-6} M. [c] *N*-Acetyl-L-tyrosine ethyl ester assay method: Birk, Y. *Methods Enzymol.* **1976**, *45*, 716–718. Phosphate buffer of pH 7.0 (0.05 M) was used. [d] After extensive dialysis against pH 7.0 (0.05 M) phosphate buffer, the esterase activity remained inhibited to the same extent. [e] Control experiments were carried out to demonstrate that the product(s) of reaction were not responsible for the observed inhibition. [f] Control experiments with the unnitrosated carbamates showed that these compounds all reversibly inhibit the esterase at a level of ~80%. This inhibition, which is readily removed by dialysis, is attributed to formation of a carbamyl-enzyme (ENZ-OH → ENZ-OCONHR) which is slowly hydrolyzed back to free enzyme: Erlanger, B. F.; Cohen, W., *J. Am. Chem. Soc.* **1963**, *85*, 348–349. [g] Conditions: preincubation with **5d** for 2 h (footnote *f*) followed by incubation with **4a** for 2 h, followed by extensive dialysis.

The results of the enzymatic hydrolysis of **3a** also indicate that the collapse of **1a** to **2a** occurs away from the enzymic environment. If the collapse takes place within the enzyme's active site we would expect (a) a difference in the stereochemistry of the 1-phenylethanol product caused by a change in the solvation of **2a** compared with that in free solution;[6,7] and (b) the irreversible inhibition of the esterase due to alkylation at, or near, the active site.[8,9]

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