excellent yields of products are obtained within 5 min. Provided its concentration is <5%, water has little effect on selectivity. 2-Cyclopentenone produces cyclopentenol in 95 and 91% yield, respectively, when reduced in methanol solution with 10 and 15% water. This allows use of the lanthanide chlorides in the commercially inexpensive hexahydrate form. Steric hindrance has no detectable effect on the rate of the reduction: 3-methylene 2-norbornanone **8** undergoes exclusively the 1,2 reduction with the same rate as with sodium borohydride, and the PGA$_2$ derivative **9** yields the 9-OH Δ-10 compounds (91% isolated yield of the 1:1 mixture of epimers) within minutes. We obtained extremely slow reductions of **8** and **9** with 9-BBN (>24 h at room temperature), and, with NaBH$_4$, **9** yields only saturated alcohols.
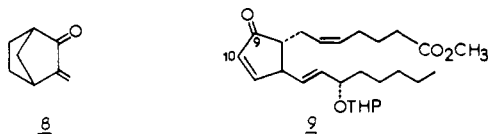
The mechanism of the reaction process has not yet been extensively studied, but does not involve a catalytic role for the lanthanide since reduction of 2-cyclopentenone in the presence of 0.1 equiv of Sm^{3+} gave a 1:4 mixture of cyclopentenol and cyclopentanol. A complex reduction scheme via the +2 oxidation state of the rare earth[15] also seems unlikely for in this state the lanthanides are only slightly reactive with ketones.[8] Reduction by a lanthanide borohydride, formed in situ[16] (at least as a transient species), might explain the observed regioselectivity according to the hard and soft acids bases theory.[17] Another possible hypothesis is that a reduction by NaBH$_4$ of a carbonyl compound–rare earth complex[18] is occurring. Although the NMR and UV spectra of cyclohexenone in methanol solution with or without cerium trichloride are quite similar, this possibility cannot be excluded in the absence of precise kinetic data. Further investigation of the mechanism and stereochemistry of the reductions is in progress. Reductions of various terpenoid, steroid, and prostanoid α-enones will be published in a next paper.[19]

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Equilibrium Geometry of Trimethylenemethane and the Absence of an Adjacent Secondary Minimum on the Triplet Potential Energy Surface

Sir:

In a very recent communication, Dowd and Chow have reported[1] that there may exist a second triplet electronic state of trimethylenemethane, energetically accessible and of symmetry lower than D_{3h}, such that the second state becomes populated as the temperature is raised. Their conclusion was based on the fact that, when the temperature of the matrix-isolated $C(CH_2)_3$ is raised from −196 to −140 °C, some rather startling changes in the ESR spectrum occur. Although several other possible explanations of the ESR temperature dependence were noted, the "second state" hypothesis appeared to be the most reasonable to Dowd and Chow.

The fact that rapid equilibration or averaging occurs near −150 °C implies a very small energy separation, certainly no more than 2 kcal, between the two states. Dowd and Chow suggest that the "second state" is of $^3B_2$ symmetry; i.e., there is a secondary minimum associated with the molecule's distortion from D_{3h} to C_{2v} symmetry. More specifically, they note that, if the expected transformation occurs via an E' vibration, this would entail not only contraction of the central bond angle, but also lengthening of the opposing carbon–carbon bond. They concluded that "this symmetry-breaking step would add a bizarre new dimension to the chemical and spectroscopic attributes of trimethylenemethane".

As noted by Dowd and Chow, although several ab initio quantum mechanical studies[2-5] have appeared in the literature, none of them is specifically pertinent to the question of a secondary minimum on the $^3B_2$ potential surface. For example, the first ab initio study, that of Yarkony and Schaefer,[2] assumed the triplet equilibrium geometry to be D_{3h}, with $r(CC)$ = 1.43 Å, $r(CH)$ = 1.10 Å, and $\theta(HCH)$ = 120°. In the most reliable theoretical study to date, Davis and Goddard[4] adopt a similar procedure. To the best of our knowledge, the only such study to report[6] more than a single point on the triplet potential energy surface is that of Borden and Davidson.[5a] As noted in their footnote 12, they actually did observe a distortion, of the type hypothesized by Dowd and Chow, at the minimum basis set, self-consistent-field (SCF) level of theory. However, this distortion vanished after configuration interaction was allowed.[7]

Here we report a complete geometry optimization for triplet trimethylenemethane and a rather thorough search for the proposed secondary minimum. As in previous work,[2] SCF theory was used with a standard contracted gaussian double zeta basis set: C(9s5p/4s2p) H(4s/2s).[8] A wealth of previous experience[9] suggests the reliability of this approach to the
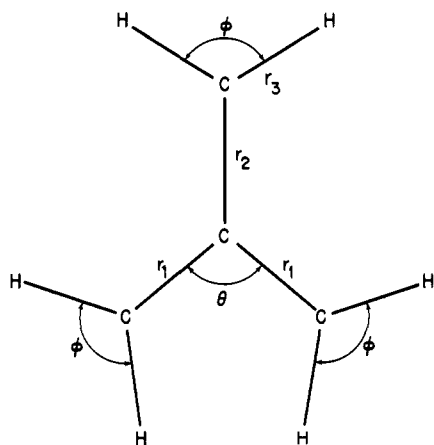
Figure 1. Degrees of freedom investigated for planar triplet trimethylenemethane.

Table I. Distortions of Triplet Trimethylenemethane from Its D_{3h} Equilibrium Geometry, Given in the Text. Energies Are Given in Kilocalories/Mole Relative to That of the Equilibrium Structure, -154.82948 hartrees. Here the CH Distance and HCH Angle Were Kept at Their Predicted Equilibrium Values

$\Delta\theta(CCC)$, deg	$\Delta r_1(CC)$, Å	$\Delta r_2(CC)$, Å	ΔE, kcal
0	0	0	0.00
-10	-0.025	$+0.025$	$+5.36$
-10	-0.050	$+0.025$	$+7.84$
-10	-0.025	$+0.050$	$+6.21$
-10	-0.050	$+0.050$	$+8.45$
0	-0.025	$+0.025$	$+0.61$
0	-0.050	$+0.025$	$+2.48$
0	-0.025	$+0.050$	$+1.13$
0	-0.050	$+0.050$	$+2.83$
0	$+0.025$	-0.025	$+0.52$
-10	$+0.025$	-0.025	$+3.72$
0	0	$+0.025$	$+0.27$
-10	0	$+0.025$	$+4.48$
0	-0.025	0	$+0.57$
-10	-0.025	0	$+5.06$
-20	-0.025	$+0.025$	$+21.14$
-20	-0.050	$+0.025$	$+24.97$
-20	-0.025	$+0.050$	$+22.08$
-20	-0.050	$+0.050$	$+25.78$
$+10$	0	0	$+3.36$
-10	0	0	$+3.96$
-10	$+0.050$	-0.050	$+4.21$
-10	$+0.025$	$+0.025$	$+4.94$
-10	0	$+0.050$	$+5.41$
-5	$+0.025$	-0.025	$+1.13$
-15	$+0.025$	-0.025	$+8.73$

prediction of hydrocarbon (even for severely strained hydrocarbons) equilibrium geometries. The coordinate system adopted is seen in Figure 1. The predicted equilibrium geometry lies in the D_{3h} point group, as expected: $\theta(CCC) = 120°$; $\phi(CH) = 117.6°$; $r_1(CC) = r_2(CC) = 1.413$ Å; $r_3(CH) = 1.073$ Å. The most interesting structural feature is that the carbon–carbon bond distance is somewhat closer to that of a double (1.34 Å) than a single (1.54 Å) bond. The HCH angle is similar to that (116.6°) in ethylene,[10] and the CH distance is a bit smaller than in ethylene (1.076 Å).

Given the predicted equilibrium geometries, a number of excursions were considered to examine the possibility of a secondary minimum. Initially the E' direction (θ decreased, r_2 increased) was considered, but other C_{2v} possibilities were evaluated as well. Our results are summarized in Table I, where it is seen that there is no adjacent triplet secondary minimum for planar $C(CH_2)_3$. Thus it appears that an alternative explanation of the ESR spectrum is required.[11]

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A Simple Method for Obtaining X-Ray Photoelectron Spectra of Species in Liquid Solution

Sir:

In x-ray photoelectron spectroscopy, it is important to prevent sample vapors from interfering with the flight path of the photoelectrons in the electron energy analyzer chamber. The study of liquid samples by XPS is usually ruled out because most liquids have vapor pressures which are too high. Even if the vapor pressure of a liquid is low enough to avoid interference in the electron analyzer, the vapor pressure directly over the liquid is generally so high that photoelectrons from the liquid are masked and the observed XPS spectrum corresponds to that of the vapor, not the liquid. Using a "liquid beam" technique, Siegbahn et al. obtained XPS spectra of formamide, ethylene glycol, benzyl alcohol, and a solution of potassium iodide in formamide.[1-3] Later, a liquid-coated moving wire system was developed by the same group to study ethylene glycol.[4] Recently Delahay et al.[5] have obtained ultraviolet photoelectron spectra of various liquids using an apparatus in which the liquid is carried into the irradiation zone by a rotating disk which is partially immersed in a refrigerated bath of the liquid. All these methods require complicated experimental apparatus and are therefore unlikely to be widely applied.

We have found that high quality x-ray photoelectron spectra can be readily obtained for compounds dissolved in glycerin[6] and that aqueous solutions can be converted into glycerin solutions which give good XPS spectra of the solutes. This technique is adaptable to most commercial x-ray photoelectron spectrometers, with little instrument modification.

Glycerin has a very low vapor pressure (2×10^{-4} Torr) at room temperature.[7] Many ionic compounds can be dissolved in glycerin in high concentrations. These factors make glycerin