

In particular, the synthesis of peroxide **7** establishes this method along with the elegant procedures of the Salomons<sup>15a</sup> and Porter<sup>15b</sup> as a potential method for the synthesis of prostaglandin endoperoxides.

**Acknowledgment.** The authors wish to thank the NSF (Grant No. CHE 76-15343) for financial support, and to express their appreciation to P. S. Engel for helpful suggestions regarding filter solutions, N. A. Porter for kindly providing NMR and IR spectral data for peroxide **7**, and N. J. Turro for freely relating his observations in this area.

## References and Notes

- (1) R. M. Wilson, E. J. Gardner, R. C. Elder, R. H. Squire, and L. R. Florian, *J. Am. Chem. Soc.*, **96**, 2955 (1974); R. M. Wilson and S. W. Wunderly, *Chem. Commun.*, 461 (1974); R. M. Wilson and S. W. Wunderly, *J. Am. Chem. Soc.*, **96**, 7350 (1974); R. M. Wilson, S. W. Wunderly, J. G. Kalmbacher, and W. Brabender, *Ann. N.Y. Acad. Sci.*, **267**, 201 (1976); R. M. Wilson, R. Outcalt, and H. H. Jaffé, *J. Am. Chem. Soc.*, in press; oxygen trapping of 1,4-biradicals derived from aryl ketone addition to olefins has also been observed: R. M. Wilson and Fiona Geiser, unpublished results.
- (2) (a) N. J. Turro, C. A. Renner, W. H. Waddell, and T. J. Katz, *J. Am. Chem. Soc.*, **98**, 4320 (1976); (b) Y. C. Toong, W. T. Borden, and A. Gold, *Tetrahedron Lett.*, 1549 (1975); (c) W. D. K. Clark and C. Steel, *J. Am. Chem. Soc.*, **93**, 6347 (1971); (d) J. A. Berson, C. D. Duncan, and L. R. Corwin, *ibid.*, **96**, 6175 (1974); (e) J. A. Berson, L. R. Corwin, and J. H. Davis, *ibid.*, **96**, 6177 (1974); (f) R. J. Crawford and A. Mishra, *ibid.*, **88**, 3963 (1966); (g) P. S. Engel, *ibid.*, **91**, 6903 (1969); (h) J. A. Kerr, "Free Radicals", Vol. 1, J. K. Kochi, Ed., Wiley, New York, N.Y., 1973, pp 3, 29.
- (3) (a) R. J. Baseman, D. W. Pratt, M. Chow, and P. Dowd, *J. Am. Chem. Soc.*, **98**, 5727 (1976); (b) B. K. Carpenter, R. D. Little, and J. A. Berson, *ibid.*, **98**, 5723 (1976); (c) M. S. Platz, J. M. McBride, R. D. Little, J. J. Harrison, A. Shaw, S. E. Potter, and J. A. Berson, *ibid.*, **98**, 5725 (1976).
- (4) J. A. Berson, R. J. Bushby, J. M. McBride, and H. Tremelling, *J. Am. Chem. Soc.*, **93**, 1544 (1971). These azo compounds were prepared using a modified procedure going through the copper complexes of the azo compounds: P. G. Gassman and K. T. Mansfield, *Org. Syn.*, **5**, 96 (1967).
- (5) R. A. Johnson and E. G. Nidy, *J. Org. Chem.*, **40**, 1680 (1975).
- (6) W. Adam and J. Arce, *J. Am. Chem. Soc.*, **97**, 926 (1975).
- (7) Azo compound **5** was synthesized by the method of Gassman.<sup>4</sup>
- (8) Clark and Steel<sup>2c</sup> have observed the suppression of the hydrocarbon products in the photochemical decomposition of **5**, and speculated that this was due to the oxygen trapping of the biradical. However, they did not report the isolation of any products arising from this trapping.
- (9) S. L. Buchwalter and G. L. Closs, *J. Am. Chem. Soc.*, **97**, 3857 (1975).
- (10) The following filter system is used at present: (a) Oriel glass filter (G774-3550); (b) Oriel infrared-absorbing glass filter (G776-7100); (c) 10-cm cell of 2,7-dimethyl-3,6-diazacyclohepta-1,6-diene perchlorate (0.02 g/10 mL of H<sub>2</sub>O); 1-cm cell of *p*-methoxyacetophenone (0.01 g/10 mL of benzene).
- (11) We thank N. J. Turro and W. Cherry for informing us of this upper limit of the oxygen pressure.
- (12) The chromatography operation is necessary to remove unreacted azo compound **5** and small amounts of peroxide **7** decomposition products, principally, cyclopentenone and levulinolaldehyde.
- (13) The proton NMR and IR spectra of peroxide **7** were kindly provided by N. A. Porter.
- (14) C. Kaneko, A. Sugimoto, and S. Tanaka, *Synthesis*, **12**, 876 (1974); L. N. Owens and P. N. Smith, *J. Chem. Soc.*, 4035 (1952).
- (15) (a) R. G. Salomon and M. F. Salomon, *J. Am. Chem. Soc.*, **99**, 3501 (1977); (b) N. A. Porter and D. W. Gilmore, *ibid.*, **99**, 3503 (1977).
- (16) Formerly Virginia L. Obrock.

R. Marshall Wilson,\* Fiona Geiser<sup>16</sup>

Department of Chemistry, University of Cincinnati  
Cincinnati, Ohio 45221




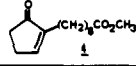



Received November 21, 1977

## Lanthanides in Organic Chemistry. 1. Selective 1,2 Reductions of Conjugated Ketones<sup>1</sup>

Sir:

Although rare earth complexes have enjoyed considerable utility as shift reagents in NMR spectroscopy,<sup>2</sup> there are limited applications of these elements in synthetic chemistry. With the exception of cerium<sup>4+</sup>, which is employed as an efficient oxidation agent,<sup>3</sup> the lanthanides have received only limited uses as catalysts, in petrochemical reactions,<sup>4</sup> epoxide rearrangement,<sup>5</sup> or optical resolution,<sup>6</sup> and an unusual reaction of secondary amines with acetonitrile.<sup>7</sup> Recent reports<sup>8</sup> con-

Table I

Starting material <sup>a</sup>	Lanthanides used	Yields % <sup>b</sup>	Allylic alcohol % <sup>c</sup>	Saturated alcohol <sup>d</sup>
 <b>1</b>	none*	100*	89	11
	Ce	100	100	0
 <b>2</b>	none	100	0	100
	Ce	100	97	3
	Sm	100	94	6
	Eu	100*	93	7
 <b>3</b>	none	95*	38	62
	Sm	96*	96	4
	Ce	100	99	1
 <b>4</b>	none	100	95	5
	Sm	92	100	0
 <b>5</b>	none	100*	51	49
	Sm	98	93	7
	Ce	100	>99	traces
 <b>6</b>	none	98*	90	10
	Ce	100	100	0
 <b>7</b>	none	98*	90	10
	Ce	100	100	0

<sup>a</sup> The following standard procedure was adopted: 1 mmol of starting material is dissolved in 2.5 mL of the 0.4 M LnCl<sub>3</sub>·*n*H<sub>2</sub>O methanol solution and NaBH<sub>4</sub> (1 mmol) is slowly added (2 min) with stirring. The mixture is allowed to react for 3–5 min, followed by hydrolysis and extraction with ether. <sup>b</sup> Isolated yields except in specified cases (asterisk) in which they were obtained by VPC (2 m × 2 mm i.d. Carbowax 20M column on Chromosorb WAW, 15 mL of N<sub>2</sub>/min Carlo Erba Fractovap 1501 chromatograph). <sup>c</sup> Identification of these compounds was made by the usual spectral methods (IR, UV, NMR) and by comparison with authentic samples. <sup>d</sup> The relative percentage of these reduction compounds and their identity were ascertained by TLC and/or VPC.

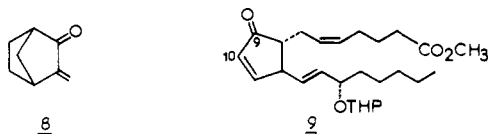
cerning the synthetic potential of lanthanides prompt us to communicate our preliminary results using rare earth halides and sodium borohydride for the selective conversion of  $\alpha,\beta$ -unsaturated ketones to allylic alcohols.

Treatment of an equimolar amount of a ketone (2-hexanone, cyclohexanone, acetophenone) and samarium chloride hexahydrate in ethanol<sup>9</sup> with sodium borohydride (1 molar equiv) produces an evolution of hydrogen coupled with a quantitative yield of the corresponding alcohol in 5–10 min. Application of this procedure (in methanol<sup>9</sup>) to  $\alpha,\beta$ -unsaturated ketones produced high yields of the corresponding allylic alcohols, in many cases uncontaminated with the 1,4 reduction product. Several representative examples are presented in Table I.

Such selectivity has been noted with other reducing systems,<sup>10</sup> but the previous methods usually suffer from limitations. Thus, of the recently developed reagents, NaBH<sub>3</sub>CN,<sup>11</sup> is unreliable with certain cyclic enones, giving mixtures resulting from 1,2 and 1,4 additions. 9-Borabicyclonane (9-BBN) has a decreased reactivity with sterically hindered carbonyl groups,<sup>12</sup> which requires long reaction times and/or refluxing solvent for reduction. Diisobutylaluminum hydride (Dibah) is not selective for carbonyl groups<sup>13</sup> and must be used at low temperature. The last two reagents are expensive and require anhydrous conditions in an inert atmosphere.

Of the lanthanides tested, samarium and cerium appear to offer the best combination of yield and selectivity (Table I). The method evidently offers the following advantages. First, nearly exclusive selective 1,2 reduction is obtained under conditions which do not affect carboxylic acids, esters, amides, halides, and cyano and nitro groups.<sup>14</sup> Even 2-cyclopentenone, which is especially prone to undergo the 1,4 addition reaction, can be reduced to 2-cyclopentenol with a selectivity as high as 97%. Furthermore, the reactions may be conducted at room temperature, without special exclusion of air or moisture, and

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<sub>2</sub> derivative **9** yields the 9-OH  $\Delta$ -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<sub>4</sub>, **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<sup>3+</sup> gave a 1:4 mixture of cyclopentenol and cyclopentanol. A complex reduction scheme via the +2 oxidation state of the rare earth<sup>15</sup> also seems unlikely for in this state the lanthanides are only slightly reactive with ketones.<sup>8</sup> Reduction by a lanthanide borohydride, formed in situ<sup>16</sup> (at least as a transient species), might explain the observed regioselectivity according to the hard and soft acids bases theory.<sup>17</sup> Another possible hypothesis is that a reduction by NaBH<sub>4</sub> of a carbonyl compound-rare earth complex<sup>18</sup> 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  $\alpha$ -enones will be published in a next paper.<sup>19</sup>

**Acknowledgment.** The author thanks Professor P. Crabbé for encouragement and stimulating discussions and Drs. A. E. Greene and A. F. Orr for valuable suggestions.

## References and Notes

- Contribution 23 of the Laboratoire de Chimie Organique (CERMO). For 22 see P. Crabbé, J. M. Dollat, J. Gallina, J. L. Luche, M. Maddox, E. Velarde, and L. Tökés, *J. Chem. Soc., Perkin Trans. 1*, in press.
- R. E. Sievers, Ed., "Nuclear Magnetic Resonance Shift Reagents," Academic Press, New York, N.Y., 1973.
- (a) M. Fieser and L. Fieser, "Reagents for Organic Synthesis", Vol. 5, Wiley, New York, N.Y., 1975; (b) Tse Lok Ho, *Synthesis*, 347 (1973).
- Inter alia: (a) D. Kruzikova, J. M. Beruk, J. Obloj, R. Chojnacki, M. Popowicz, W. Tecza, and Z. Linicki, *Pol. 78336 (Chem. Abstr., 85, 10781z (1976))*; (b) T. Saito, T. Kikuchi, T. Awano, and G. Sato, *Japan Kokai*, **76**, 36429 (*Chem. Abstr.* **85**, 77874a (1976)).
- B. M. Trost and M. J. Bogdanowicz, *J. Am. Chem. Soc.*, **95**, 5321 (1973).
- B. T. Golding, P. J. Sellars, and A. K. Wong, *J. Chem. Soc., Chem. Commun.*, 570 (1977).
- J. H. Forsberg, T. M. Balasubramanian, and J. T. Spaziano, *J. Chem. Soc., Chem. Commun.*, 1060 (1976).
- (a) J. L. Namy, P. Girard, and H. B. Kagan, *Nouv. J. Chim.*, **5** (1977), and references cited; (b) P. Girard and H. B. Kagan, *Tetrahedron Lett.*, 4513 (1975).
- In contrast to  $\alpha,\beta$ -unsaturated ketones, saturated ketones and aldehydes and  $\alpha,\beta$ -unsaturated aldehydes easily form ketals in methanolic lanthanide chlorides solution. This ketalization does not occur in ethanol. These findings will be discussed in a future paper.
- Inter alia: (a) H. O. House, "Modern Synthetic Reactions", Benjamin, Menlo Park, Calif., 1972; (b) E. R. H. Walker, *Chem. Soc. Rev.*, **15**, 23 (1976); (c) M. R. Johnson and B. Rickborn, *J. Org. Chem.*, **35**, 1041 (1970).
- R. O. Hutchins and D. Kandasamy, *J. Org. Chem.*, **40**, 2530 (1975).
- (a) H. C. Brown, S. Krishnamurthy, and N. M. Yoon, *J. Org. Chem.*, **41**, 1778 (1976); (b) S. Krishnamurthy and H. C. Brown, *ibid.*, **42**, 1197 (1977).
- E. Winterfeldt, *Synthesis*, 617 (1975).
- Inter alia, diethyl malonate, ethyl heptanoate, 5-bromopentanoic acid, 3,3-dimethylacrylic acid, benzyl bromide, 1-iodoundecane, *p*-bromonitrobenzene, *o*-nitrophenol, *N*-benzoylglycine, *N*-acetylucine, and benzonitrile remain unaffected under the specified conditions.
- L. B. Asprey and B. B. Cunningham, *Prog. Inorg. Chem.*, **8**, 267 (1960).
- (a) T. J. Marks and J. R. Kolb, *Chem. Rev.*, **77**, 263 (1977); (b) A. Bruckl and K. Rossmann, *Monatsh. Chem.*, **90**, 481 (1959).
- (a) For a review, see Tse Lok Ho, *Chem. Rev.*, **75**, 1 (1975). (b) J. Bottin, O. Eisenstein, C. Minot, and Nguyen Trong Anh, *Tetrahedron Lett.*, 3015 (1972).
- Such a complexation may explain the enhanced solubility of substrates in methanol in the presence of lanthanides halides. Even glucose and saccharose can be dissolved under these conditions in concentrations as high as 0.2 M.
- J. L. Luche, L. Rodriguez-Hahn, and P. Crabbé, unpublished work.

Jean-Louis Luche

Laboratoire de Chimie Organique  
Université Scientifique et Médicale, CERMO  
Boîte Postale No. 53, 38041 Grenoble, France

Received October 13, 1977

## 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<sup>1</sup> 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<sub>2</sub>)<sub>3</sub> 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<sup>2-5</sup> 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,<sup>2</sup> assumed the triplet equilibrium geometry to be  $D_{3h}$ , with  $r(CC) = 1.43$  Å,  $r(CH) = 1.10$  Å, and  $\theta(HCH) = 120^\circ$ . In the most reliable theoretical study to date, Davis and Goddard<sup>4</sup> adopt a similar procedure. To the best of our knowledge, the only such study to report<sup>6</sup> more than a single point on the triplet potential energy surface is that of Borden and Davidson.<sup>5a</sup> 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.<sup>7</sup>

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