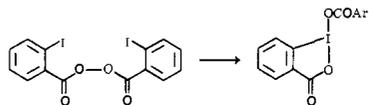
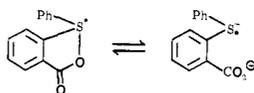


- (1963).  
 (4) R. J. Arhart, Ph.D. Thesis, University of Illinois, 1971.  
 (5) (a) T. W. Koenig and J. C. Martin, *J. Org. Chem.*, **29**, 1520 (1964); (b) J. C. Martin and T. W. Koenig, *J. Am. Chem. Soc.*, **86**, 1771 (1964).  
 (6) T. H. Fisher and J. C. Martin, *J. Am. Chem. Soc.*, **88**, 3382 (1966).  
 (7) The decomposition of bis(2-iodobenzoyl) peroxide in solution was found by J. E. Leffler, R. D. Faulkner, and C. C. Petropoulos, *J. Am. Chem. Soc.*, **80**, 5435 (1958), to result in isomerization to a trivalent iodine species.



- (8) This rearrangement also occurs in the solid state; J. Z. Gougoutas and J. C. Clardy, *J. Solid State Chem.*, **4**, 230 (1972); J. Z. Gougoutas and L. Lessinger, *ibid.*, **9**, 155 (1974).  
 (9) For a recent review, see J. C. Martin and E. F. Perozzi, *Science*, **191**, 154 (1976).  
 (10) J. C. Martin and E. F. Perozzi, *J. Am. Chem. Soc.*, **96**, 3155 (1974).  
 (11) In a chlorobenzene medium containing final products of the decomposition of **1a**, **3** appears at  $\delta$  1.21.  
 (12) The carbonyl stretching frequency is consistent with that expected for **3** from observations on a series of related sulfuranes. A full report is in preparation.  
 (13) *o*-(Phenylthio)benzoic acid prepared by the method of J. Jilek, V. Seidlova, E. Stvatek, and M. Protiva, *Monatsh. Chem.*, **96**, 182 (1965), upon treatment with ozone afforded **6**, mp 164–165 °C, in agreement with **6** reported by W. S. Weedon and H. W. Doughty, *Am. Chem. J.*, **33**, 386 (1905), mp 164 °C.  
 (14) R. J. Arhart and J. C. Martin, *J. Am. Chem. Soc.*, **94**, 5003 (1972).  
 (15) Note that the evidence which was adduced in earlier work<sup>3</sup> for sulfur-oxygen bonding such as that pictured in Scheme II for the intermediate sulfuranyl radical is strictly applicable only to the transition state leading to the radical. The intermediate may well be in equilibrium with an acyclic zwitterionic analogue and in fact the latter may be the preferred formulation. W. A. Pryor and W. H. Hendrickson, *J. Am. Chem. Soc.*, **97**, 1580 (1976), have discussed evidence for an electron-transfer mechanism for the intermolecular reaction between peresters and sulfides to yield radicals.



- (16) B. S. Campbell, D. B. Denney, D. Z. Denney, and L. Shih, *J. Am. Chem. Soc.*, **97**, 3850 (1975). For closely related work see W. A. Pryor and H. T. Bickley, *J. Org. Chem.*, **37**, 2885 (1972).

P. Livant, J. C. Martin\*

Roger Adams Laboratory, University of Illinois  
 Urbana, Illinois 61801

Received August 9, 1976

## Reactions of Magnesium Atoms with Cyclic Ketones

Sir:

In recent years the reactions of metal atoms with organic substrates, through the technique of codeposition at low temperatures, have been an active area of chemical research.<sup>1</sup>

We wish to report the first investigations of the reactions of ketones with metal atoms and to specifically focus on the reactions of magnesium atoms with cycloheptanone for reasons which will be made clear later in this communication. Although reactions of magnesium atoms with water, ammonia, and alkyl halides have been reported previously<sup>2</sup> and very reactive magnesium slurries have been prepared by this codeposition technique,<sup>3</sup> nowhere have the reactions of magnesium atoms with ketones been discussed. It should be pointed out at the outset that products from magnesium atom reactions with ketones reported herein are not found when clean finely divided bulk magnesium<sup>3</sup> is allowed to react with the same ketones; indeed, when this experiment was done only a trace of product, unlike that from the atom reactions, could be detected. A metal atom reactor similar to the one described by Skell and Wescott<sup>4</sup> but modified to use a resistively heated alumina crucible was used.

When magnesium is codeposited with cyclopentanone at 77 K we find, among the products, substantial amounts of cy-

cloptene and 1,1'-dihydroxydicyclopentyl. Similarly if one allows magnesium and cyclohexanone to react under these conditions substantial amounts of cyclohexene and 1,1'-dihydroxydicyclohexyl are produced.

The isolation of the olefinic products in these reactions, clearly indicating deoxygenation by the magnesium vapors, led us to suggest a carbene or carbenoid intermediate. Thermodynamic calculations based on bond energies and the heat of vaporization of magnesium oxide<sup>5</sup> suggest that the reaction of magnesium atoms with cyclic ketones to yield carbenacycloalkanes and magnesium oxide should be exothermic by at least 55 kcal mol<sup>-1</sup>. The absence of a product resulting from a reaction unique to carbenes in the aforementioned reactions, however, pointed out the necessity of investigating another system which would yield data on this point.

Friedman and Schechter have reported on the thermolysis of diazocycloalkanes to yield carbenacycloalkanes.<sup>6</sup> In this work they have shown that carbenacyclopentane yields cyclopentene as the only product. Similarly carbenacyclohexane yields only cyclohexene but, on the other hand, carbenacycloheptane yields cycloheptene (82%) and norcarane (18%). The latter product, clearly, is the result of carbon-hydrogen insertion of the divalent carbon, a reaction which is unique to carbene or carbenoid species.

With this background we proceeded to investigate the reaction of atomic magnesium with cycloheptanone. The reaction is carried out using the usual codeposition technique with the reactor immersed in liquid nitrogen.<sup>4</sup> Approximately 200 mg of magnesium was vaporized in a typical run. Upon completion of the codeposition, the liquid nitrogen is removed, and any volatile products and unreacted substrate are pumped into a liquid nitrogen cooled trap from which they can subsequently be removed and analyzed by gas chromatography. The residue in the reactor is then taken up in ether and filtered from the insoluble material and the solution allowed to evaporate. The resulting oil is analyzed by high pressure liquid chromatography.

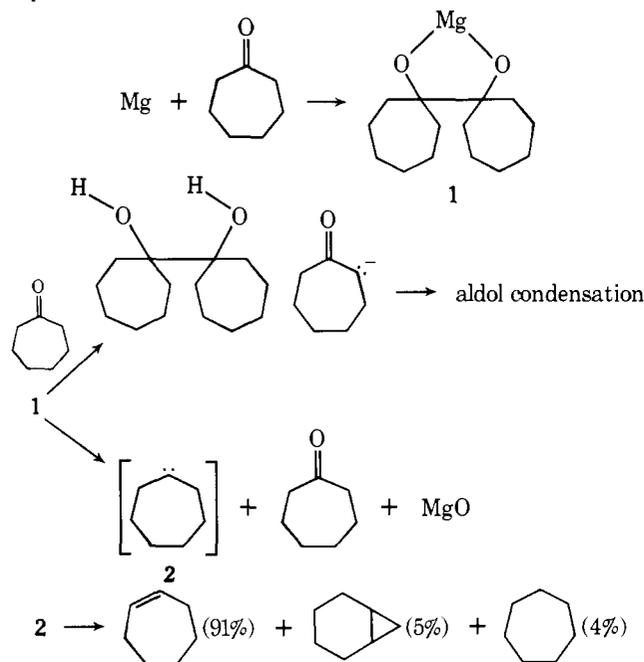
We have found that 13% of the magnesium vaporized can be accounted for as leading to 1,1'-dihydroxydicycloheptyl. Another 13% of the magnesium can be accounted for by the volatile hydrocarbon products. In addition there is considerable gray ether insoluble residue containing unreacted magnesium. Apparently a major portion of the magnesium repolymerizes, a result not uncommon in metal atom chemistry.<sup>1</sup>

Analysis of the volatile products shows that they consist of cycloheptene (91%), norcarane (5%), and cycloheptane (4%). The ether soluble nonvolatile oil contains 37% 1,1'-dihydroxydicycloheptyl, the balance being a mixture of aldol condensation products. The hydrocarbon products were identified by comparing their gc retention times (Carbowax 20 M and S. E. 30) and mass spectra to those of authentic samples. The 1,1'-dihydroxydicycloheptyl was identified by comparing its HPLC retention time (Corasil II, 60/40 volume/volume *n*-heptane/chloroform) to that of an authentic sample prepared according to the procedure of Greidinger and Ginsburg.<sup>7</sup> In addition, crystals were isolated from the oil (mp 76–78 °C, reported 78 °C) by adding cold *n*-hexane and allowing the solution to stand overnight at 5 °C. These crystals gave an IR spectrum identical with the authentic sample and when mixed with the authentic sample, caused no depression of its melting point.

The isolation of norcarane among the hydrocarbon products requires the intervention of a carbene or carbenoid species and the formation of cycloheptane suggests a certain amount of triplet carbenacycloheptane. Although the aldol condensation products were not individually isolated and identified, the oil, in addition to the 1,1'-dihydroxydicycloheptyl, shows a distribution of products by HPLC which bear a striking resemblance to the aldol condensation products obtained from cy-

cloheptanone when the latter is subjected to aldol condensation conditions as described by Grignard and Colonge.<sup>8</sup> One should also note that although the aldol condensation of cycloheptanone is inadequately described in the literature, the aldol condensation of cyclohexanone is well known to yield a variety of products depending on reaction conditions.<sup>9</sup> For this reason a rigorous analysis of the balance of the oil was not attempted.

In light of these facts, we should like to suggest the following mechanism for the reaction of magnesium atoms with cycloheptanone.



Actually it is unlikely that **2** is a free species but is probably a highly complexed carbenoid. The ratio of cycloheptene to norcaradiene does not suggest a free carbene in light of the Friedman and Schechter work.<sup>6</sup>

We are extending our studies to other metals and other carbonyl compounds and shall report these results in due course.

**Acknowledgment.** K.J.K. and L.D.W. would like to acknowledge support of the National Science Foundation (GP-42326) which supported L.D.W. on a summer visiting professorship at UND. We also thank Research Corporation for the purchase of vacuum equipment.

## References and Notes

- (1) K. J. Klabunde, *Acc. Chem. Res.*, **8**, 393 (1975).
- (2) P. S. Skell and J. E. Girard, *J. Am. Chem. Soc.*, **94**, 5518 (1972).
- (3) K. J. Klabunde, H. F. Efner, L. Satek, and W. Donley, *J. Organomet. Chem.*, **71**, 309 (1974).
- (4) P. S. Skell, L. D. Wescott, Jr., J. P. Golstein, and R. R. Engel, *J. Am. Chem. Soc.*, **87**, 2829 (1965).
- (5) C. A. Alexander, J. S. Ogden, and A. Levy, *J. Chem. Phys.*, **39**, 3057 (1963).
- (6) L. Friedman and H. Schechter, *J. Am. Chem. Soc.*, **83**, 3159 (1961).
- (7) D. S. Greidinger and D. Ginsburg, *J. Org. Chem.*, **22**, 1406 (1957).
- (8) V. Grignard and J. Colonge, *C. R. Acad. Sci.*, **194**, 929 (1932).
- (9) A. C. Cope et al., Ed., *Org. React.*, **16**, 115 (1968).

Lyle D. Wescott, Jr.,\* Clint Williford, Frank Parks  
Margaret Dowling, Susan Sublett

Department of Chemistry, Christian Brothers College  
Memphis, Tennessee 38104

Kenneth J. Klabunde

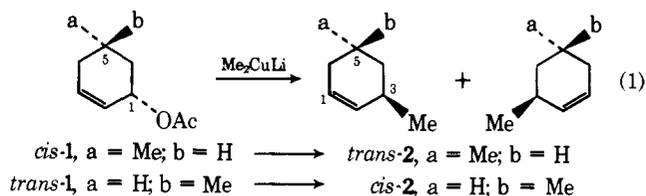
Department of Chemistry, University of North Dakota  
Grand Forks, North Dakota 58202

Received July 19, 1976

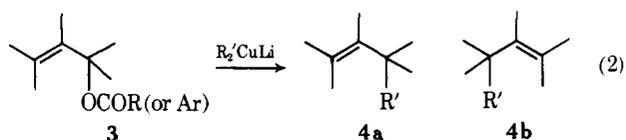
## On the Stereochemistry of Conversion of Allylic Esters to Olefins with Lithium Dialkylcuprates

Sir:

We wish to report that conversion of *cis*- and *trans*-5-methyl-2-cyclohexenyl acetate (**1**) to 3,5-dimethylcyclohexene (**2**) with lithium dimethylcuprate ( $\text{Me}_2\text{CuLi}$ ) is stereospecific; *cis*-**1** gives *trans*-**2** and *trans*-**1** gives *cis*-**2**. Thus substitution occurs on the side of the ring opposite from the replaced acetate group. The two allylic positions become equivalent as shown by eq 1.

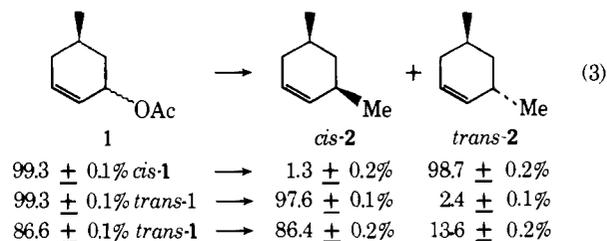


The conversion of allylic esters (**3**) to olefins by coupling with lithium dialkylcuprates was first reported by Crabbé and co-workers<sup>1</sup> and has been a key step in several subsequent investigations.<sup>2,4</sup> Coupling can occur at either end of the allylic system to give unrearranged (**4a**) or rearranged (**4b**) products.<sup>3</sup> Mixtures are generally formed; however, in some cases single isomers, either rearranged<sup>1,2</sup> or unrearranged,<sup>4</sup> are obtained. In one case isomeric allylic acetates gave essentially the same product distribution<sup>2b</sup> and it was concluded that the transformation involves formation of allylic radicals and subsequent transfer of an alkyl radical.<sup>2b</sup>



Recently Corey and Mann<sup>3</sup> reported a case in which a cyclopentenyl allylic lactone reacts without rearrangement and with complete inversion to give the desired product. However, the system was designed to give the observed result and alternatives are precluded for steric reasons.

In this work we have converted the isomeric 5-methyl-2-cyclohexenyl acetates (**1**)<sup>5a</sup> to 1,3-dimethylcyclohexene (**2**). Configurations of the isomeric acetates were established previously.<sup>5</sup> Lithium dimethylcuprate was prepared by addition of methyl lithium to a cold (0 °C) suspension of methylcopper (prepared from a butyl sulfide-copper iodide complex)<sup>6</sup> in ether. Reaction of **1** with 2 equiv of  $\text{Me}_2\text{CuLi}$  in ether at 0 °C for 24 h resulted in 90–95% conversion to **2**. The olefin was isolated by preparative GC and configurations were established by hydrogenation to the corresponding 1,3-dimethylcyclohexanes which were identified by comparison with authentic samples.<sup>7</sup> The pertinent data are summarized under eq 3. These data are averages of two to seven independent experiments. Isomeric compositions were determined by capillary GC (200 ft SE-30 for **2** and 300 ft UCON polar for **1**) which gave baseline resolution.



The conversion of  $\alpha$ - and  $\gamma$ -deuterio-**1** to **2** was investigated to determine the amount of allylic rearrangement in this un-