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Preparation of Dibenzylidenecycloalkanones and Their Mixed Hydride Reductions

JAMES E. PRIVETT, RODGER MILLER and LEON STIDFOLE¹

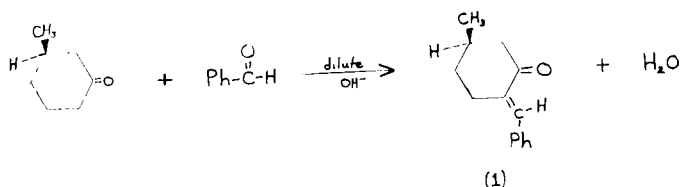
SYNOPSIS: Preparation of dibenzylidenecycloalkanones and their mixed hydride reductions. *Proc. Iowa Acad. Sci.*, 79(2):53-55, 1972. A number of dibenzylidenecycloalkanones were prepared by a base condensation reaction of the cycloalkanone with benzaldehyde or a substituted benzaldehyde. The products were then sub-

jected to a mixed hydride reagent (3 AlCl₃-1 LiAlH₄) to give olefins or tautomeric mixtures depending on the method of reaction.

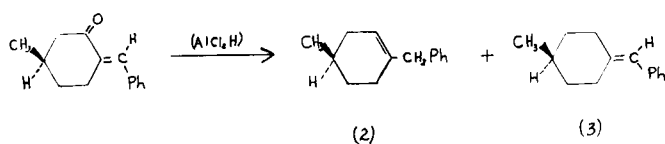
INDEX DESCRIPTORS: Dibenzylidenecycloalkanones.

INTRODUCTION

When benzaldehyde reacts with R-(+)-3-methylcyclohexanone in dilute base (-)-2-benzylidene-5-methylcyclohexanone (1) is produced (Brewster and Privett, 1966).



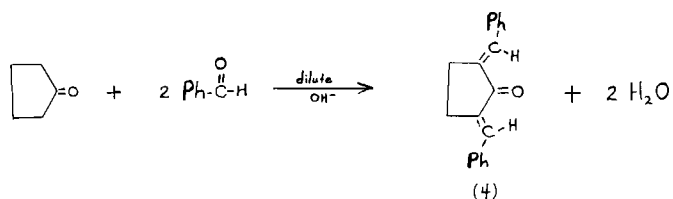
(1) was shown to have the configuration with the vinyl hydrogen *cis* to the carbonyl group. Further, it was shown that (1) reacts with mixed hydride reagent (3 AlCl₃: 1 LiAlH₄, or AlCl₃H) to give two olefins, R-(+)-1-benzyl-4-methylcyclohexene (2) and S-(+)-1-benzylidene-4-methylcyclohexene (3):



These two reactions were shown to be completely stereoselective leading to olefins with the assigned structures. It is the purpose of the present research to utilize this general reaction scheme for the preparation and reduction of dibenzylidenecycloalkanones.

PREPARATION OF DIBENZYLIDENECYCLOALKANONES

The first objective of this research was to prepare 2,5-dibenzylidenecyclopentanone (4) and various derivatives of it by a reaction that would allow assignment of absolute configuration. To this end the reaction below appeared attrac-



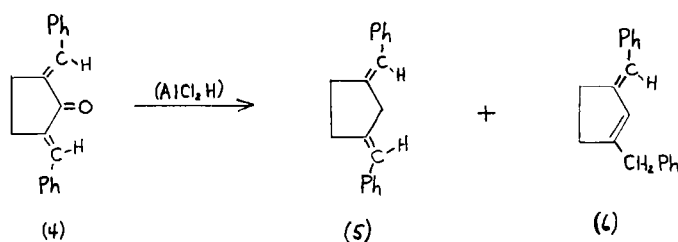
tive. Since 2-benzylidenecyclohexanone was shown to have the configuration with the vinyl hydrogen *cis* to the carbonyl group (Privett, 1965) it seems reasonable to assume that (4) would have the same configuration for the two vinyl hydrogens.

Compound (4) and its derivatives were prepared by a method similar to that of Yeh (1957). Some of the properties of these substances in addition to other dibenzylidene compounds are given in Table 1. All of these compounds were prepared and analyzed in our laboratory. The reference column indicates whether the compound is new or prepared at an earlier date. The new compounds are presently being further characterized and the data for the other compounds are in agreement with reported information.

The infrared spectra of all of the prepared compounds showed a stronger olefinic absorption than carbonyl absorption. The locations of the peaks are close to what is expected for ring structures with long conjugation. Shifts in frequencies have been related to ring strain, length of the conjugated system and degree of coplanarity of the conjugated system (Schwartz, 1964). By analogy with the well-established 2-benzylidene-5-methylcyclohexanone structure one can reasonably assume that the structure of each dibenzylidene compound has the vinyl hydrogen *cis* to the carbonyl group.

MIXED HYDRIDE REDUCTION OF THE DIBENZYLIDENE KETONES

The mixed hydride treatment of the dibenzylidenecycloalkanones was expected to give a mixture of olefins according to the reaction scheme shown below (Privett, 1965).



Assignment of the structures (5) and (6) is based on an analogy of this reduction with that of 2-benzylidene-5-methylcyclohexanone. Since the latter reduction led to preservation of configuration around the olefinic system it was assumed that reduction of (4) would lead to similar results.

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TABLE 1. PROPERTIES OF DIBENZYLIDENECYCLOALKANONES

Compound	1 $\nu_{C=O}$ (cm^{-1})	1 $\nu_{C=C}$ (cm^{-1})	2 ν	MP	Reference
2,5-Dibenzylidenecyclopentanone	1700	1600	3.0	191-2	Mayer, Gebhardt
2,5-Di-(4-methylbenzylidene)cyclopentanone	1700	1600	2.0	234(d)	Maccioni, Marongiu
2,5-Di-(2-methylbenzylidene)cyclopentanone	1680	1580	2.9	195-7	new
2,5-Di-(1-naphthylidene)cyclopentanone	1685	1620	3.5	177-80	new
2,6-Di-(2-methylbenzylidene)cyclohexanone	1660	1570	3.1	134-5	Rapson, Shuttleworth
2,6-Dibenzylidenecyclohexanone	1660	1560	3.0	112-4	YEH et al.
2,6-Di-(3-methylbenzylidene)cyclohexanone	1660	1570	3.2	76-7	new
2,6-Di-(1-naphthylidene)cyclohexanone	1660	1570	3.1	206-7	new
2,6-Di-(4-methylbenzylidene)cyclohexanone	1660	1560	3.0	165-8	new
2,8-Dibenzylidenecyclooctanone	1680	1600	2.5	265(d)	
2,8-Di-(2-methylbenzylidene)cyclooctanone	1680	1600	2.7	255(d)	Cornubert, et al. new

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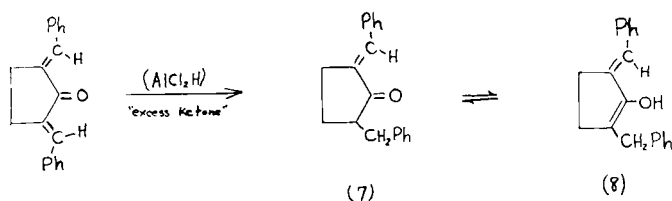
2 ν = absorbance of $C=C$
absorbance of $C=O$

When (4) was added to the mixed hydride reagent in anhydrous ether one compound was obtained which was identified as olefin (6). Evidence for this structure came from analysis of its IR, NMR, and UV spectra. The yield of product was very low (20%). Compound (5) was not produced.

Addition of the mixed hydride reagent to (4) produced a compound different from olefin (6). The following list shows some of the physical properties of this compound.

- Infrared Spectrum** (CCl_4):
3400 (v.w., broad), 3100 (w), 3080 (w), 3020 (w), 2940 (w), 2880 (w), 1725 (s), 1638 (s), 1625 (m), 1500 (m), 1455 (m), 1190 (m), 1155 (m), 1035 (w), 930 (w), 950 (w), 700 (s), 690, cm^{-1} .
- NMR** (CCl_4):
1.0-3.4 δ (7H); 7.4 δ (11 H).
- Mass Spectrum**:
 m/e = 262, 246, 172, 129, 128, 117, 115, 116, 101, 91, 84, 77, 72, 69, 68, 66, 51, 28 (main peaks).
- Analysis**. Calcd. for $\text{C}_{19}\text{H}_{18}\text{O}$; C, 87.02; H, 6.87. Found: C, 85.97; H, 6.75.¹
- Ultraviolet Spectrum** (100% ethanol): 265 nm (ϵ 29,200), 315 nm (ϵ 29,900).

These data are in agreement with a mixture of tautomers (7) and (8).



Evidence for the enol form is based mainly on the infrared spectrum and the ferric chloride test, but supportive evi-

dence is obtained from the mass spectrum and NMR spectrum.

A broad weak -OH peak (3400 cm^{-1} in combination with the olefin peak (1640 cm^{-1}) have been demonstrated for similar enol structures (Schwartz, 1964). The ferric chloride test was positive indicating the presence of the enol form. The NMR showed complex C-H and CH_2 regions indicative of a tautomeric mixture. The vinyl hydrogen peak is located under the aromatic hydrogen peak (Privett, 1965). Minor peaks in the mass spectrum at m/e = 130, 131 indicate fragments of both the enol and keto forms. The carbon analysis is off by substantially more than normal experimental error. After analysis was completed the experimenter noted a damp character to the sample. The sample was shown to contain some benzaldehyde evidently formed by reverse condensation. This compound would lower the experimental carbon value.

Mixed hydride reduction of several other dibenzylidenecycloalkanones led to similar results. In all cases a product was formed which had an infrared spectrum revealing a broad weak peak centered near 3400 cm^{-1} (enol OH), a strong peak at 1640 cm^{-1} (olefin), and another peak as a shoulder on the 1640 cm^{-1} peak (olefin).

The tautomeric mixture was also obtained when the ketone was added to partially decomposed mixed hydride reagent or weaker solutions of mixed hydride reagent. Evidently an excess of ketone always leads to the tautomeric mixture and an excess of strong active mixed hydride reagent leads to reduction involving the removal of the carbonyl function.

Further research is in progress to investigate the nature of the mixed hydride reduction mechanism for dibenzylidenecycloketones. More evidence is being accumulated to show the nature of the intermediates during reduction.

¹ Purdue University Analysis Laboratory

EXPERIMENTAL

2, 5-Dibenzylidenecyclopentanone. A mixture of 49 g of cyclopentanone and 107g of benzaldehyde was added to a reflux flask containing 20 g NaOH, 150 ml H₂O and 150 ml ethanol. The mixture was heated for two hours at 70°C. The yellow solid that separated was vacuum filtered and recrystallized from pet ether. An 89% yield of yellow plates, mp 191-2°C, was obtained. Other dibenzylidenecycloalkanones reported in this paper were prepared in a similar manner. Purification techniques varied with the compound produced.

Preparation of Mixed Hydride Reagent. The mixed hydride reagent was prepared in a manner similar to that reported by Bayer (1961). Solutions of 82g of aluminum chloride in 400 ml of anhydrous ether and 8.3 of lithium aluminum hydride in 400 ml of anhydrous ether were cooled to -10°C. They were mixed and this mixture was allowed to stand six hours at 0°. The reagent was filtered into a dry flask and was stored at -10°C.

General Procedure for Mixed Hydride Reductions.

Procedure A (excess hydride): The 3:1 mixed hydride reagent was added to a three-neck round bottom flask containing a reflux condenser and a dropping funnel to which the ketone in anhydrous ether was added. The ketone solution was added dropwise to the mixed hydride reagent maintaining a temperature below reflux. After completion of the reaction the excess hydride was destroyed by slow addition of

H₂O. After all the solids dissolved the ether layer was separated and washed several times with water. The ether was distilled and the residue purified depending on its physical state.

Procedure B (excess ketone): the procedure was similar to A except the ketone solution and mixed hydride reagent exchanged places. The hydride reagent was added to the ketone solution.

ACKNOWLEDGMENTS

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