Tetrahedron Vol 23, pp 4143 to 4145 Pergamon Press Ltd 1967 Printed in Great Britain

A CYCLOHEXANE RING CONTRACTION

C. J. R. Adderley, G. V. Baddeley[1] and F. R. Hewgill

Department of Organic Chemistry, University of Western Australia, Nedlands, W.A.

(*Received* 11 *January* 1967; *accepted for publication* 26 *January* 1967)

Abstract—The magnesium enolate (II) derived from 2-methylcyclohex-1-enyl acetate (I) reacts with chloroacetone to give the unexpected product (IV).

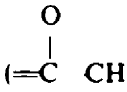
DISCUSSION

As part of a series of experiments designed to evaluate the directed α-substitution of cyclic ketones *via* their magnesium enolates, methylcyclohexanone was converted into the enolate II through the enol acetate I.

The enol acetate I was prepared by acid catalysis[2] as a 95% component of the acetylation mixture (IR and NMR spectroscopy, analytical VPC) and was readily purified by distillation. The NMR spectrum[3] showed a singlet at 126 c/s due to the coincident signals from the vinylic and acetoxyl methyl groups.

The enol acetate I reacted with methyl magnesium iodide (2 molar equiv) in ether to give the magnesium enolate II. This salt reacted with chloro-acetone in ether and the reaction was terminated by acidification.

The product, isolated by steam-distillation and in 33% yield (from enol acetate), was not the expected γ-diketone III. The physical and chemical properties support the isomeric structure, 1-(1-methylcyclopentyl)butan-1,3-dione (IV) which we allocate to this product.

Elemental analysis was consistent with the formula $C_{10}H_{16}O_2$. The IR spectrum showed a broad absorption at 1600 cm^{-1}. The NMR spectrum showed resonances at 72 (tertiary methyl), 134 (CO—CH_3) and 220 c/s (—CO—CH_2—CO—) consistent with the formulation IV and at 124  $(=\overset{\overset{\displaystyle O}{|}}{C}—CH_3)$, 339 (—CO—CH=) and 950 c/s (=C—OH) expected[4] for the hydrogen-bonded enol form V. The spectrum integral indicated ca. 80% enolization. The signal at 950 c/s was removed by exchange with deuterium oxide.

Support for the formulation as a β-diketone was provided by a strong ferric chloride reaction and the formation of a blue, crystalline copper chelate from which the diketone was regenerated upon acidification.

Chemical confirmation of structure IV was given by the alkaline cleavage of the

---

[1] To whom inquiries should be addressed: School of Chemistry, The University of New South Wales, P.O. Box 1, Kensington, N.S.W., Australia.

[2] *inter alia*, H. O. House and V. Kramer, *J. Org. Chem.* **28**, 3362 (1963).

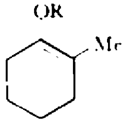
[3] NMR spectra were recorded on a Varian A60 spectrometer for $CDCl_3$ solns with TMS as internal reference. Chemical shifts are expressed in cycles per second downfield from the reference signal.

[4] J. L. Burdett and M. T. Rogers, *J. Am. Chem. Soc.* **86**, 2105 (1964).

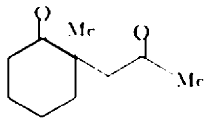
β-diketone which afforded both the acid VI identified as its anilide and the ketone VII identified as its semicarbazone whose m.p. was undepressed on admixture with an authentic specimen.

The NMR spectrum of the ketone showed singlets at 73 and 130 c/s due to the two methyl groups and the IR spectrum showed a sharp absorption at 1705 cm^{-1}.

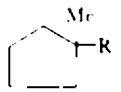
We offer the mechanism depicted in Fig. 1 to account for the formation of the β-diketone IV. Further work is in hand to test this mechanism and to ascertain the generality of the ring contraction since transformation *via* Favorskii reaction intermediates is possible.



I: R = Ac
II: R = MgI



III



IV R = MeCOCH$_2$CO –
V R = MeC(OH) = CHCO–
VI R = CO$_2$H
VII R = Ac

FIG. 1

EXPERIMENTAL

M.ps and b.ps are uncorrected. Refractive indices were determined with an Abbe refractometer model G. Analyses were by the Australian Micro-analytical Service, Melbourne.

2-Methylcyclohex-1-enyl acetate (I). 2-Methylcyclohexanone (100 g) was treated with Ac$_2$O (130 g) and perchloric acid (60%; 1·5 ml) for 2·5 hr at room temp. The soln was diluted with ether (150 ml) and gently agitated with excess sat NaHCO$_3$aq. After the evolution of CO$_2$ had ceased, the organic layer was washed with 5% NaHCO$_3$aq (50 ml), water (50 ml), dried (Na$_2$SO$_4$) and distilled to give I, b.p. 92–94°/30 mm, n_D^{25} 1·4560 (lit. b.p. 85°/20 mm,[5] n_D^{25} 1·4560[2]), ν_{max} 1760 cm^{-1}.

Reaction of the enol acetate (I) *with methyl magnesium iodide*. Mg powder (6·5 g; 0·27 mole) was treated slowly with MeI (43 g; 0·30 mole) in dry ether (60 ml). After the addition the mixture was heated under reflux for 30 min, after which the Grignard reagent was decanted. The enol acetate (20 g; 0·13 mole) was added so as to gently boil the mixture and the mixture was heated at reflux for 1 hr to give a suspension of II.

Reaction of the magnesium enolate (II) *with chloro-acetone*. Chloro-acetone (14 g; 0·21 mole) in ether (20 ml) was added slowly to the suspension II (prepared as above) during 30 min. The mixture was heated at reflux for 5 hr and the reaction was then terminated by the addition of ice-cold 10% HCl (100 ml). The mixture was neutralized by NaHCO$_3$ and steam-distilled to give an oil which was redistilled to give 1-(*1-methylcyclopentyl*)*-butan-1,3-dione* (7·25 g; 33%), b.p. 77°/0·4 mm, 108–109°/9 mm. (Found: C, 71·0; H, 9·6. C$_{10}$H$_{16}$O$_2$ requires: C, 71·4; H, 9·6%.)

The *copper chelate* was prepared by treatment with cupric acetate and formed blue prisms (from MeOH), m.p. 103–103·5° (Found: C, 60·4; H, 7·7. C$_{20}$H$_{30}$CuO$_4$ requires: C, 60·4; H, 7·6%.)

---

[5] M. Mousseron, R. Jacquier, R. Henry and M. Canet, *C.R. Acad. Sci., Paris*, **233**, 1625 (1951).

Acidification of the copper chelate regenerated the diketone.

Cleavage of the diketone (IV) *by alkali.* The diketone (384 mg) was heated under reflux with NaOH (4 g) in MeOH–water (1 : 1 ; 20 ml) during 2 hr. The soln was cooled and extracted by ether. The organic layer was washed with 5% $NaHCO_3$aq (4 × 5 ml), 2% NaOHaq (5 × 5 ml) and water (2 × 5 ml). The soln was then dried (Na_2SO_4) and slowly evaporated to leave a yellow oil which formed the semicarbazone of 1-methylcyclopentyl methyl ketone (39 mg), m.p. 140·5–141° (lit.[6] m.p. 140·5–141°). The mixed m.p. with a sample prepared after pinacol rearrangement of *cis*-1,2-dimethylcyclohexane-1,2-diol[7] showed no depression and the IR spectra of the two samples were identical.

The alkaline aqueous layer and the aqueous washings were combined, acidified and extracted with ether. The ether was cautiously removed and the residue was treated successively with $SOCl_2$ and aniline. The resultant anilide was extracted by ether and the organic layer was washed with 2NHCl and filtered through activated charcoal to give, after evaporation, the anilide of VI, m.p. 103–104·5° (lit.[8] m.p. 104–105°).

---

[6] S. Nametkin and N. Delektorsky, *Ber. Dtsch. Chem. Ges.* **57B**, 583 (1924).

[7] H. Meerwein, *Liebig's Ann.* **542**, 123 (1939).

[8] M. Mousseron, R. Jacquier and A. Fontaine, *Bull. Soc. Chim. Fr.* 767 (1952).