Aust. J. Chem., 1995, 48, 1827-1834

Clemmensen Reduction. XI* Fragmentation Reactions of Some 3-Acetylcycloalkanones

Karen E. Bailey^A and Brian R. Davis^{A,B}

 ^A Department of Chemistry, University of Auckland, Private Bag 92019, Auckland, New Zealand.
^B Author to whom correspondence should be addressed.

Abstract

Clemmensen reduction of a series of 3-acetylcycloalkanones yields, as the major product, an acyclic unsaturated ketone, the product of fragmentation. Some normal carbonyl-methylene reduction also occurs. A mechanistic rationale for the fragmentation is advanced.

Previous work in this series,¹ and work by other groups,^{2–5} has shown that the Clemmensen (Zn/Hg-HCl) reduction of 1,4-diketones yields a variety of products dependent largely on the structural environment of the two carbonyl groups. When conformational mobility allows these two groups to approach one another, saturated and unsaturated alcohols are the major products. When the two carbonyl groups are held in a syn- or anti-periplanar arrangement, Grob-type fragmentation occurs. On rare occasions, cyclobutane-1,2-diol formation is observed. Reduction of one or both of the carbonyl groups to methylene is seen, to varying extents, in many such reduction processes.

In order to define more closely the parameters of these processes, we chose to study the reduction of a series of 3-acetylcycloalkanones. Fragmentation and alcohol formation should both be possible in terms of our previous hypotheses. Conformational mobility could allow the formation of tetrahydrofuran-type intermediates or could allow an antiperiplanar arrangement of the diketone or some reduction intermediate.

The diketones were synthesized by oxidation of the corresponding γ -nitro ketone, obtained, in turn, by Michael addition of the anion from nitroethane to

* Part X, Aust. J. Chem., 1992, 45, 865.

¹ Buchanan, J. G. St. C., and Davis, B. R., *J. Chem. Soc.*, 1967, 1340; Davis, B. R., Rewcastle, G. W., Stevenson, R. J., and Woodgate, P. D., *J. Chem. Soc.*, *Perkin Trans.* 1, 1977, 2148; Crump, D. R., and Davis, B. R., *J. Chem. Soc.*, *Chem. Commun.*, 1970, 768; Buchanan, J. G. St. C., Crump, D. R., and Davis, B. R., *J. Chem. Soc.*, *Perkin Trans.* 1, 1979, 2826.

² Wenkert, E., and Yoder, J. E., J. Org. Chem., 1970, 35, 2986.

 ³ Dekker, J., Dekker, J. J., Fourie, L., and Martins, F. J. C., J. S. Afr. Chem. Inst., 1976, 29, 114; Dekker, J., Fourie, L., Dekker, J. J., and Burger, J., S. Afr. J. Chem., 1977, 30, 83.
⁴ Martins, F. J. C., Fourie, L., Venter, H. J., and Wessels, P. L., Tetrahedron, 1990, 46, 623.
⁵ Martins, F. J. C., Viljoen, A. M., Coetzee, M., Fourie, L., and Wessels, P. L., Tetrahedron, 1991, 47, 9215.

Manuscript received 19 June 1995

0004-9425/95/111827\$05.00

a cycloalkenone. The diketones were reduced by reaction with amalgamated zinc and boiling 6 M hydrochloric acid. The products of reduction were removed, as formed, by steam distillation. Reduction is reasonably rapid and the diketones are comparatively involatile under these conditions. The organic steam distillate represented some 50% of the mass of the diketone. Percentages quoted here are based on g.l.c. analysis of the steam distillate.

The cycloalkenones were synthesized by standard procedures. The Michael addition of the anion from nitroethane was performed in two ways. For less hindered enones, the ketone and nitroethane in acetonitrile were treated with 1,1,3,3-tetramethylguanidine,⁶ while for compounds having a methyl group on the β -carbon of the enone, or having a methyl group in a 1,3-diaxial relationship with that centre, a phase transfer catalyst and potassium carbonate as base were employed.⁷ The nitro ketones were, in all cases, mixtures of diastereomers and were characterized as such by the usual spectral techniques. The conversion of the nitro group into carbonyl was effected by permanganate oxidation of the nitronate anion, produced by base treatment of the nitro compound.⁸ The diketones were characterized by combustion analysis or high-resolution mass spectrometry and by spectroscopic methods.

The products of Clemmensen-type reduction of the diketones were analysed by g.c.m.s. and the major products isolated by column chromatography and characterized by i.r., ¹H n.m.r. and mass spectrometry and by comparison of these data with literature values. An unsaturated ketone was shown to be a major product in each case and was related to the parent dione by the general form of Scheme 1.



G.c.m.s. analysis showed the reduction product mixture to be complex; the predominant product comprised less than 50% of the mixture and was usually accompanied by cyclic products of partial reduction, whereby one of the ketones had been reduced to methylene. An array of unidentified compounds, each of which comprised no more than 2 or 3% of the total product, completed the mass balance. In no cases were alcohols identified among the reaction products and there was no evidence for their presence, in significant amounts, from the i.r. and ¹H n.m.r. spectra of the total reduction products.

The mass spectra of the unsaturated ketone products provided diagnostic structural evidence and, as expected, showed consistent fragmentation patterns (Table 1).

⁶ Ono, N., Kamimura, A., Miyake, H., Hamamoto, I., and Kaji, A., *J. Org. Chem.*, 1985, **50**, 3692.

⁷ Parfenov, E. A., Bekker, A. R., and Kostereva, G. F., *J. Org. Chem. USSR*, 1981, 17, 1412. ⁸ Steliou, K., and Poupart, M.-A., *J. Org. Chem.*, 1985, **50**, 4971.



Table 1. Mass spectra of unsaturated ketone products

3-Acetyl-5,5-dimethylcyclohexanone gave 5,5-dimethyloct-7-en-2-one⁹ (18%) whose spectral properties accorded closely with those reported. A minor product (9%) was tentatively identified (mass spectrum) as 3-acetyl-5,5-dimethylcyclohexene or an isomer. 3-Acetyl-3-methylcyclohexanone gave 3-methyloct-7-en-2-one¹⁰ (i.r., ¹H n.m.r., m.s.) (45%) and another ketone (30%) probably 1-acetyl-1-methylcyclohexane (¹H n.m.r., m.s.). In the reduction of 3-acetyl-2-methylcyclohexanone, the above patterns indicate the possibility of E and Z isomers in the alkene and spectroscopic analysis confirmed this expectation. The major product (24%) showed a medium absorption in the infrared spectrum at 967 cm⁻¹ which suggested an E configuration in the double bond. The ¹H n.m.r. and mass spectra were consistent with the assignment as (E)-non-7-en-2-one.¹¹ The minor products were tentatively identified by their mass spectral fragmentation patterns. One (6%) had a mass spectrum very similar to that of the alkene above and was assumed to be the Z isomer.^{11,12} The other (8%) was probably 1-acetyl-2-methylcyclohexane by comparison of its mass spectrum with that published for this compound.¹³ 3-Acetylcyclohexanone gave oct-7-en-2-one as the major product, identified by its mass spectrum.¹⁴ A similar pattern was observed with two cyclopentanones. 3-Acetylcyclopentanone gave hept-6-en-2-one (36%) identified by its mass spectrum which was identical with the published spectrum.^{14,15} The other two products were tentatively identified from their mass spectra as the products of partial reduction, acetylcyclopentane (15%)

⁹ Cockerill, G. S., Kocienski, P., and Treadgold, R., J. Chem. Soc., Perkin Trans. 1, 1985, 2101.

¹⁰ Rouessac, F., Le Perchec, P., and Conia, J.-M., Bull. Soc. Chim. Fr., 1967, 818.

¹¹ Marvell, E. N., and Rusay, R., J. Org. Chem., 1977, 42, 3336.

¹² Molanders, G. A., and McKie, J. A., J. Org. Chem., 1995, **60**, 872.

¹³ House, H. O., Chu, C.-Y., Wilkins, J. M., and Umen, M. J., J. Org. Chem., 1975, 40, 1460.

¹⁴ Dias, J. R., Sheikh, Y. M., and Djerassi, C., J. Am. Chem. Soc., 1972, 94, 473.

¹⁵ Agosta, W. C., Bowen, D. V., Brodsky, L., Rennekamp, M. E., and Field, F. H., *J. Org. Chem.*, 1976, **41**, 136.

and 3-ethylcyclopentanone¹⁶ (40%). 3-Acetyl-3-methylcyclopentanone gave, as the sole major product, the unsaturated ketone 3-methylhept-6-en-2-one (43%), separated by flash chromatography and having the expected i.r., ¹H n.m.r. and mass spectrum, identical with published values.^{12,17}



A consistent pattern emerges in these reductions as shown in Scheme 1. Thus a 3-acetylcycloalkanone undergoes fragmentation to yield an unsaturated ketone, whereby C1-C2 becomes a double bond, C2-C3 is cleaved and the acetyl group is, in the end, unchanged. This result can be rationalized by postulating the formation of an organozinc intermediate which, in acid solution, fragments to yield the observed major product (Scheme 2). Both the five- and six-membered ring ketones can adopt a conformation that allows for the antiperiplanar arrangement of the appropriate bonds. The reason for the observed regioselectivity of the reaction is not clear.

Experimental

Microanalyses were carried out by the Microanalytical Laboratory, University of Otago, New Zealand. I.r. spectra were recorded by means of a Perkin–Elmer 1600 Fourier-transform infrared spectrometer. ¹H n.m.r. spectra were recorded on a Varian T60 (60 MHz) or a Bruker AM-400 (400 MHz) spectrometer and ¹³C n.m.r. spectra on the Bruker instrument at 100 MHz. Mass spectra were determined on a VG 70-SE mass spectrometer. Analytical G.l.c. was carried out on a Hewlett–Packard 5980 Series II gas chromatograph.

Synthesis of Cycloalkenones

The cycloal kenones, if not commercially available, were synthesized by methods described in the literature: 3-methylcyclopent-2-enone,¹⁸ 2-methylcyclohex-2-enone,¹⁹ 3-methylcyclohex-2-enone,²⁰ 5,5-dimethylcyclohex-2-enone.²¹

Synthesis of 3-(1-Nitroethyl)cycloalkanones

(a) Using Tetramethylguanidine

(i) 2-Methylcyclohex-2-enone (18.858 g, 0.171 mol), nitroethane (65.01 g, 0.866 mol) and 1,1,3,3-tetramethylguanidine (2.01 g, 0.017 mol) were reacted in acetonitrile (100 ml) for 3 days. Workup and distillation gave 2-methyl-3-(1-nitroethyl)cyclohexanone (19.57 g, 62%), Kugelrohr b.p. 174–176°/3 mmHg (Found: C, 58.1; H, 8.2. C₉H₁₅NO₃ requires C, 58.4; H, 8.2%). I.r. $\nu_{\rm max}$ (neat) 1712, 1548, 1456m, 1393 cm⁻¹. N.m.r. $\delta_{\rm H}$ (CDCl₃, 400 MHz)

¹⁶ Reinfried, R., Belluš, D., and Schaffner, K., Helv. Chim. Acta, 1971, 54, 1517.

¹⁷ Brocard, J., Moinet, G., and Conia, J.-M., Bull. Soc. Chim. Fr., 1973, 1711; Clarke, T. C., and Bergman, R. G., J. Am. Chem. Soc., 1974, **96**, 7934.

¹⁸ Acheson, R. M., and Robinson, R., J. Chem. Soc., 1952, 1127.

¹⁹ Warnhoff, E. W., Martin, D. G., and Johnson, W. S., Org. Synth., 1957, 37, 8.

²⁰ ApSimon, J. W., Badripersaud, S., Nyugen, T. T. T., and Pike, R., Can. J. Chem., 1978, 56, 1646.

²¹ Frank, R. L., and Hall, H. K., Jr, J. Am. Chem. Soc., 1950, 72, 1645.

1.11, d, J 6.5 Hz, 3H, 2-Me; 1.50, m, 1H, H 4eq; 1.60, d, J 6.9 Hz, 3H, CHNO₂CH₃; 1.70, m, 1H, H 5eq; 2.05, m, 1H, H 4ax; 2.10, m, 1H, H 5ax; 2.30, m, 1H, H 2ax; 2.38, m, 1H, H 3ax; 2.40, m, 1H, H 6eq; 4.67, m, 1H, CHNO₂CH₃. N.m.r. $\delta_{\mathbb{C}}$ (CDCl₃) 11.8, 2-CH₃; 16.5, CHNO₂CH₃; 24.3, C5; 24.6, C4; 40.9, C6; 44.9, C2; 48.1, C3; 83.1, CHNO₂CH₃; 210.8, C1 (major diastereomer).

(ii) 3-(1-Nitroethyl)cyclopentanone was prepared in a similar manner and had b.p. 112–120°/3·7 mmHg. I.r. ν_{max} 1740, 1552, 1391 cm⁻¹. N.m.r. $\delta_{\rm H}$ (CDCl₃, 60 MHz), 1·4–1·7, m, 3H, CH₃; 1·7–2·7, m, 7H, CH₂, CH; 4·3–4·6, m, 1H, CHNO₂. Lit.²² b.p. 102–107°/1·3 mmHg.

(iii) 3-(1-Nitroethyl)cyclohexanone was prepared in a similar manner and had b.p. 118-124°/4 mmHg. I.r. $\nu_{\rm max}$ 1711, 1549, 1390 cm⁻¹. Lit.²³ b.p. 101-102°/0.01 mmHg.

(b) Using Phase Transfer Catalysis, K₂CO₃

(i) 3-Methyl-3-(1-nitroethyl)cyclopentanone.—3-Methylcyclopent-2-enone (82·80 g, 0.862 mol) was added to nitroethane (193·68 g, 2·58 mol) and benzyltriethylammonium chloride (18·69 g, 0.082 mol) in benzene (803 ml). Potassium carbonate (119 g, 0.861 mol) was added and the mixture stirred rapidly under nitrogen for 4 days. Workup gave 3-methyl-3-(1-nitroethyl)cyclopentanone (75·59 g, 51·0%), b.p. 96–100°/0.8 mmHg, as two diastereomers (Found: C, 56·0; H, 7·6. C₈H₁₃NO₃ requires C, 56·1; H, 7·6%). I.r. ν_{max} 1744, 1552, 1452, 1393 cm⁻¹. N.m.r. $\delta_{\rm H}$ (CDCl₃, 400 MHz) 1·13 and 1·15, 2s, 3H, 3-Me; 1·56 and 1·57, 2d, J 6·8 Hz, CHNO₂CH₃; 1·88, m, 1H, H4; 2·13, m, 1H, H4; 2·45, m, 4H, (H2)₂, (H5)₂; 4·63, m, 1H, CHNO₂CH₃. N.m.r. $\delta_{\rm C}$ (CDCl₃) 14·1, 14·7, 3-CH₃; 20·5, CHNO₂CH₃; 32·5, 32·6, C4; 36·0, C5; 42·8, C3; 49·2, 49·7, C2; 215·9, C1.

(ii) 3-Methyl-3-(1-nitroethyl)cyclohexanone was prepared in a similar manner and was obtained as a mixture of diastereomers, b.p. $102-126^{\circ}/6$ mmHg. I.r. ν_{max} 1712, 1548, 1456, 1392 cm⁻¹. N.m.r. $\delta_{\rm H}$ (CDCl₃, 400 MHz) 0.97, 0.99, s, 3H, 3-Me; 1.49, d, J 6.8 Hz, 3H, CHNO₂CH₃; 1.57-2.38, m, 8H, (H2)₂, (H4)₂, (H5)₂, (H6)₂; 4.49, m, 1H, CHNO₂CH₃. N.m.r. $\delta_{\rm C}$ (CDCl₃) 13.5, 13.6, CHNO₂CH₃; 19.9, 20.0, 3-CH₃; 21.1, 21.2, C5; 32.4, 32.6, C4; 40.5, 40.5, C6; 48.6, 49.8, C2; 90.3, 91.4, CHNO₂CH₃; 209.3, C1.

(iii) 5,5-Dimethyl-3-(1-nitroethyl)cyclohexanone was prepared in a similar manner and had b.p. 112–136°/7 mmHg (Found: C, 60·0; H, 8·7; N, 7·1. $C_{10}H_{17}NO_3$ requires C, 60·3; H, 8·6; N, 7·0%). I.r. ν_{max} 1712, 1548, 1458, 1391, 1369 cm⁻¹. N.m.r. $\delta_{\rm H}$ (CDCl₃, 400 MHz) 0·90, 0·92, s, 3H, 5-Me; 1·10, 1·12, s, 3H, 5-Me; 1·54, d, J 6·7 Hz, 3H, CHNO₂CH₃; 1·57, d, J 6·7 Hz, 2H, (H4)₂; 2·04–2·56, m, 5H, (H2)₂, H3, (H6)₂; 4·50–4·58, m, 1H, CHNO₂CH₃. $\delta_{\rm C}$ (CDCl₃) 16·2, 16·3, CHNO₂CH₃; 25·3, 25·5, CHNO₂CH₃; 31·75, 31·8, 5-CH₃; 34·4, C5; 38·4, C3; 39·95, 40·6, C4; 42·1, 42·7, C2; 53·9, C6; 87·3, 87·45, 5-CH₃; 208·6, 208·7, C1. Mass spectrum m/z 199 (M), 184, 169, 152, 137, 123, 109, 97, 83, 69, 55, 41.

Oxidation of γ -Nitro Ketones

Typical Procedure

To a mechanically stirred solution of 3-methyl-3-(1-nitroethyl)cyclopentanone (28.90 g, 0.168 mol) in methanol (1 litre), in an ice-salt bath and under nitrogen, was added dropwise over 45 min a freshly prepared solution of methanolic (900 ml) potassium hydroxide (85%; 14.33 g, 0.217 mol). After 15 min additional stirring, a freshly prepared aqueous solution of potassium permanganate (22.79 g, 0.144 mol) and magnesium sulfate (19.18 g, 0.159 mol) was added dropwise. The mixture was stirred at room temperature for 1 day, heated under reflux for 12 h and filtered through Celite. Workup, drying and solvent removal gave 3-acetyl-3-methylcyclopentanone (11.43 g, 49%), b.p. 108-132°/2.5 mmHg (Found: M⁺, 140.0842. C₈H₁₂O₂ requires M⁺, 140.0837). I.r. ν_{max} 1744, 1703 cm⁻¹. N.m.r. $\delta_{\rm H}$ (CDCl₃, 400 MHz) 1.34, s, 3H, 3-Me; 1.82-1.90, m, 1H, H4; 2.00, d, J 18 Hz, 1H, H2; 2.10-2.36, m, 3H, H4, (H5)₂; 2.19, s, 3H, COCH₃; 2.69, d, J 18 Hz, 1H, H2. N.m.r. $\delta_{\rm C}$ (CDCl₃) 23.3, 3-CH₃; 24.9, CO**C**H₃; 32.3, C4; 36.5, C5; 47.7, C2; 52.3, C3; 210.7, C1; 216.5, **C**OCH₃:

²² Kádas, I., Morvai-Kádas, V., and Tóke, L., Acta Chim. Hung., 1983, 113, 303.
²³ McCoubrey, A., J. Chem. Soc., 1951, 2931.

3-Acetyl-3-methylcyclohexanone

Oxidation of the nitro ketone in a similar manner gave 3-acetyl-3-methylcyclohexanone, Kugelrohr b.p. $90-94^{\circ}/0.4$ mmHg (Found: M⁺, 154.1001. C₉H₁₄O₂ requires M⁺, 154.0994). I.r. ν_{max} 1708 cm⁻¹. N.m.r. $\delta_{\rm H}$ (CDCl₃, 400 MHz) 1.21, s, 3H, 3-Me; 1.68–1.78, m, 2H, H4eq, H5ax; 1.82–1.93, m, 1H, H5eq; 1.97–2.05, m, 1H, H4ax; 2.10, d, J 14.4 Hz, 1H, H2eq; 2.13, s, 3H, COCH₃; 2.19–2.33, m, 2H, (H6)₂; 2.67, d, J 14.4 Hz, 1H, H2ax. N.m.r. $\delta_{\rm C}$ (CDCl₃) 21.8, C5; 23.4, 3-CH₃; 24.6, COCH₃; 33.3, C4; 40.1, C6; 49.2, C2; 52.0, C3; 209.6, C1; 211.3, COCH₃. N.m.r. spectral assignments were confirmed by ¹H–¹³C correlation and ¹H–¹H cosy experiments. Mass spectrum m/z 154, 126, 111, 97, 83, 69, 55, 43.

3-Acetyl-5, 5-dimethylcyclohexanone

Oxidation of the correspondeing nitro ketone as described above gave 3-acetyl-5,5-dimethylcyclohexanone, Kugelrohr b.p. 59–63°/0·4 mmHg (Found: M⁺, 168·1191. C₁₀H₁₆O₂ requires M⁺, 168·1150). I.r. $\nu_{\rm max}$ 1709 cm⁻¹. N.m.r. $\delta_{\rm H}$ (CDCl₃, 400 MHz) 0·95, s, 3H, 5-Me; 1·12, s, 3H, 5-Me; 1·60, dd, J 13·0, 13·0 Hz, 1H, H 4ax; 1·80–1·85, m, 1H, H 4eq; 2·21, s, 3H, COCH₃; 1·99–2·48, m, 4H, (H2)₂, (H6)₂; 2·93–3·02, m, 1H, H3. N.m.r. $\delta_{\rm C}$ (CDCl₃) 25·3, 5-CH₃; 28·2, CO**C**H₃; 31·6, 5-CH₃; 35·6, C5; 40·3, C4; 41·5, C2; 47·3, C3; 53·9, C6; 208·3, C1; 210·1, **C**OCH₃. N.m.r. spectral assignments were confirmed by ¹H–¹³C correlation spectra and ¹H–¹H cosy experiments. Mass spectrum m/z 168, 153, 132, 125, 111, 98, 83, 69, 55, 43.

3-Acetyl-2-methylcyclohexanone

Oxidation of the corresponding nitro ketone gave 3-acetyl-2-methylcyclohexanone, b.p. 86–100°/5 mmHg. I.r. ν_{max} 1712 cm⁻¹. N.m.r. $\delta_{\rm H}$ (CDCl₃, 400 MHz) 0.95, d, J 6.4 Hz, 3H, 2-Me; 1.70, m, 1H, H4eq; 1.72, m, 1H, H5eq; 2.03, m, 1H, H4ax; 2.15, m, 1H, H5ax; 2.20, s, 3H, COCH₃; 2.35, m, 1H, H6eq; 2.42, m, 1H, H6ax; 2.65, m, 1H, H3; 2.75, m, 1H, H2ax. N.m.r. $\delta_{\rm C}$ (CDCl₃) 12.4, 2-CH₃; 26.0, C5; 28.5, C4; 29.7, CO**C**H₃; 41.0, C6; 45.6, C2; 58.4, C3; 208.9, C1; 211.6, **C**OCH₃.

3-Acetylcyclopentanone

Oxidation of the nitro ketone gave 3-acetylcyclopentanone,^{22,24} b.p. 118–130°/5·2 mmHg. I.r. ν_{max} 1744, 1710 cm⁻¹. N.m.r. δ_{H} (CDCl₃, 400 MHz) 2·19, s, 3H, COCH₃; 1·90–2·46, m, 6H, (H 2)₂, (H 4)₂, (H 5)₂; 3·22, tt, J 8·1, 8·1 Hz, 1H, H 3.

3-Acetylcyclohexanone

Oxidation of the nitro ketone gave 3-acetylcyclohexanone, 23,25 b.p. 122–130°/4 mmHg. I.r. $\nu_{\rm max}$ 1712 cm⁻¹. N.m.r. spectra accorded with literature data.²⁵

Reduction of Diketones with Amalgamated Zinc-Hydrochloric Acid

Typical Procedure

3-Acetyl-5,5-dimethylcyclohexanone (0·99 g, 6 mmol), amalgamated zinc wool (3·92 g, 60 mmol), concentrated hydrochloric acid (2·5 ml, 21 mmol) and water (1·9 ml) were heated together and the mixture was subjected to steam distillation over 1·5 h. G.l.c. analysis of the total steam distillate showed the presence of two products (18·3 and 8·8%) along with some starting material (4·6%). Other reduction products each constituted less than 2% of the total mixture. Column chromatography yielded 5,5-dimethyloct-7-en-2-one with spectral properties identical to those reported by Kocienski *et al.*⁹ I.r. ν_{max} 1716, 913 cm⁻¹. N.m.r. $\delta_{\rm H}$ (CDCl₃, 400 MHz) 0·86, s, 6H, 5,5-Me₂; 1·49, m, 2H, (H4)₂; 1·95, d, J 7·43 Hz, 2H, (H6)₂; 2·15, s, 3H, (H1)₃; 2·39, m, 2H, (H3)₂; 5·02, m, 2H, (H8)₂; 5·80, m, 1H, H7.

²⁴ Monte, W. T., Baizer, M. M., and Little, R. D., J. Org. Chem., 1983, 48, 803.
²⁵ Degl'Innocenti, S., Ricci, A., Mordini, A., Reginato, G., and Colotta, V., Gazz. Chim. Ital., 1987, 117, 645; Corey, E. J., and Crouse, D., J. Org. Chem., 1968, 33, 298; Söderberg, B. C., York, D. C., Hoye, T. R., Rehberg, G. M., and Suriano, J. A., Organometallics, 1994, 13, 4501.

Mass spectrum m/z 154, 139, 113, 95, 83, 69, 55, 43. The minor product had mass spectrum m/z 152, 137, 119, 109, 93, 77, 67, 55, 43, and was tentatively assigned the structure 3-acetyl-5,5-dimethylcyclohexene.

Reduction of 3-Acetyl-3-methylcyclohexanone

The diketone (0.50 g, 3 mmol), amalgamated zinc wool (2.1 g, 32 mmol), concentrated hydrochloric acid (2.63 ml, 32 mmol) and water (2.8 ml) were reacted as above to give an oil (0.2 g) which was subjected to g.l.c. analysis to reveal the presence of two major products (45 and 30%). Chromatography on silica gave 3-methyloct-7-en-2-one.¹⁰ I.r. ν_{max} 1713 (C=O), 997, 911 cm⁻¹ (-CH=CH₂). N.m.r. $\delta_{\rm H}$ (CDCl₃, 400 MHz) 1.06, d, J 7 Hz, 3H, Me; 1.24-2.48, m, 6H, (H4)₂, (H5)₂, (H6)₂; 2.10, s, 3H, (H1)₃; 4.95, m, 2H, (H8)₂; 5.75, m, 1H, H7. The other product was tentatively assigned the structure 1-acetyl-1-methylcyclohexane. N.m.r. $\delta_{\rm H}$ (CDCl₃; 400 MHz) 1.37, s, 3H, 1-Me; 2.22, s, 3H, COMe; 1.05-2.80, m, 10H, CH₂. Mass spectrum m/z 140, 125, 97, 81, 72, 55, 43, 32.

Reduction of 3-Acetyl-2-methylcyclohexanone

The diketone (1.45 g, 0.010 mol) was added to amalgamated zinc (5.98 g, 0.092 mol), concentrated hydrochloric acid (7.3 ml, 0.089 mol) and water (7.9 ml). The mixture was heated and the products were collected by codistillation over 45 min. Workup gave an oil (0.94 g). G.l.c. analysis showed the presence of three compounds in yields of 20.2, 7.8 and 6.3% (based on total reduction product). Purification by flash chromatography on silica gave a mixture of (E)- and (Z)-non-7-en-2-one.^{11,12} I.r. ν_{\max} 1716 (C=O), 967 $(E-CH=CH-) \text{ cm}^{-1}$. N.m.r. $\delta_{\rm H}$ (CDCl₃, 400 MHz) 1.23-1.70, m, 4H, (H5)₂, (H4)₂; 1.57, m, (H9)₃ (E); 1.62, m, (H9)₃ (Z); 1.94-2.21, m, 2H, (H3)₂; 2.11, s, 3H, (H1)₃; 2.36-2.44, m, 2H, (H6)₂; 5.35-5.46, m, 2H, H7, H8. Mass spectrum m/z 140, 125, 122, 111, 97, 85, 82, 71, 67, 58, 55, 43. The mass spectrum of the 7.8% fraction had m/z 140, 125, 122, 111, 97, 85, 82, 71, 55, 43, 29, and was assigned structure 1-acetyl-2-methylcyclohexane.¹³ The fraction accounting for 6.3% of the product mixture was assigned structure (Z)-non-7-en-2-one on the basis of the similarity of its mass spectrum to that of the E isomer.

Reduction of 3-Acetylcyclohexanone

The diketone (0.226 g, 1.6 mmol) was added to amalgamated zinc (1.97 g, 0.030 mol), concentrated hydrochloric acid (2.1 ml) and water (1.9 ml). The mixture was heated and the products were collected by codistillation over c. 35 min. Workup gave an oily liquid (0.178 g). I.r. ν_{max} 1714, 911, 720 cm⁻¹. G.l.c. analysis revealed the presence of three major products comprising 44, 10 and 14% of the total mixture and in order of increasing polarity. All three were found to be significantly less polar than the starting material. From mass spectral data, these were identified as follows. (i) Oct-7-en-2-one¹⁴ (44%): m/z 126 (M), 111, 108, 97, 83, 71, 68, 58, 55, 43 (100%), 41, 39. (ii) Acetylcyclohexane²⁶ (10%): m/z 126 (M), 111, 108, 97, 93, 71, 67, 55 (100%), 43, 41, 39. (iii) Cyclohex-3-enyl methyl ketone²⁶ (14%): m/z 124 (M), 109, 106, 95, 91, 81, 79, 77, 66, 53, 51, 43 (100%), 41, 39.

Reduction of 3-Acetylcyclopentanone

A mixture of the diketone (1.43 g, 0.011 mol), amalgamated zinc wool (6.54 g, 0.10 mol), concentrated hydrochloric acid (2.5 ml, 0.03 mol) and water (6.2 ml) was heated, and the products were collected by codistillation. Workup gave an oily liquid analysed by g.c.m.s., and the products were identified from mass spectral fragmentation patterns as follows. (i) Hept-6-en-2-one (36%):^{14,15} m/z 112, 97, 94, 83, 71, 69, 58, 43. (ii) Acetylcyclopentane (15%): m/z 112, 97, 84, 79, 71, 69, 43, 41. (iii) 3-Ethylcyclopentanone¹⁶ (40%): m/z 112, 97, 94, 83 (100%), 70, 56, 55, 42, 41.

²⁶ McLafferty, F. W., and Stauffer, D. B., (Eds) 'Wiley/NBS Atlas of Mass Spectral Data' Vol. 1 (John Wiley: New York 1989).

Reduction of 3-Acetyl-3-methylcyclopentanone

The diketone (0.65 g, 5 mmol), amalgamated zinc wool (5.23 g, 80 mmol), concentrated hydrochloric acid (5.8 ml, 70 mmol) and water (2.1 ml) were heated together, and the organic products collected by codistillation over 2 h. G.l.c. analysis revealed only one predominant product of reduction (43% of mixture). Chromatography on silica (ether/hexane, 1:1) gave 3-methylhept-6-en-2-one.^{12,17} I.r. ν_{max} 1713, 996, 912 cm⁻¹ (-CH=CH₂). N.m.r. $\delta_{\rm H}$ (CDCl₃, 400 MHz) 1.09, d, J 7.0 Hz, 3H, 3-Me; 1.37-2.16, m, 4H, (H4)₂, (H5)₂; 2.14, s, 3H, (H1)₃; 2.52-2.58, m, 1H, H3; 4.95-5.07, m, 2H, (H7)₂; 5.72-5.83, m, 1H, H6. $\delta_{\rm C}$ (CDCl₃, 100 MHz) 16.0, C1; 28.2, C3; 31.2, 31.7, C4,5; 46.2, Me; 115.0, C7; 137.9, C6; 212.5, C2.

Acknowledgment

We thank the University of Auckland Research Committee for grants, Professor P. Kocienski for the supply of spectral data and Mr Nausad Ali for assistance with the preparation of some starting materials.