Tetrahedron, 1964, Vol. 20, pp. 717 to 722. Pergamon Press Ltd. Printed in Northern Ireland

SOME DERIVATIVES OF DICYCLOPENTADIENE

R. C. COOKSON, N. S. ISAACS and M. SZELKE
Chemistry Department, The University, Southampton

(*Received* 26 *November* 1963)

Abstract—Although 1,8-dioxo-*endo*-dicyclopentadiene reacts preferentially at the 8-carbonyl group with borohydride and with ethylene glycol, it gives the 1-monoxime with hydroxylamine, perhaps by a base-catalysed Cope rearrangement of the 8-monoxime initially formed. 1-Hydroxy-*exo*-dicyclopentadiene does not rearrange under conditions that equilibrate the *endo*-isomers with the 8-alcohols.

endo-*Dicyclopentadiene*

The Woodward-Katz rearrangement[1] of *endo*-dicyclopentadienes takes place particularly rapidly with the 8-ketone,[2] the rearrangement of which is strongly catalysed by acids. The flow of electrons is then illustrated in a simplified form in formula I, where X is from an electrophilic catalyst (e.g. H, $\bar{A}lCl_3$ or $\bar{B}F_3$). The rearrangement of a suitable derivative with a conjugating group at C-8 (e.g. Y = —CHO, —CN, —NO_2, —NO, etc.) might well be catalysed by base, the trend of electron displacement then being indicated in formula II. The structure should be especially favourable when there is an electron-accepting group such as a carbonyl group at C-1.

The oxime III seemed ideally to fulfill the requirements and was expected through its anion to equilibrate with the isomer V *via* the intermediate or transition state IV. The 1-monoxime (V) and diketone (VI) can be made by partial or complete hydrolysis[3] of the dioxime[4,5] (VII). The isomeric 8-monoxime (III) was expected to be available by condensation of the diketone (VI) with hydroxylamine, for the very strained, unconjugated 8-carbonyl group should be the more reactive.

However, under the mildest conditions in which reaction occurred (e.g. hydroxylamine in boiling ethanol with pyridine, in acetic acid with sodium acetate, or in aqueous ethanol with potassium hydroxide) only the 1-monoxime was formed. The diketone also appeared to condense preferentially at C-1 with one equivalent of 2,4-dinitrophenylhydrazine, as shown by the intense band in the IR spectrum of the resulting hydrazone at 1790 cm^{-1} but none near 1700 cm^{-1}.

On the other hand reduction of the diketone (VI) with one equivalent of sodium borohydride gave a high yield of the expected 8-alcohol (VIII; configuration of OH not proved), the conjugated 1-carbonyl group being betrayed by the intense band at 1672 cm^{-1} and λ_{max} 226 mμ, ε 6720. Similarly it condensed with ethylene glycol to form the 8-ketal (IX), with ν_{max} 1692 cm^{-1} and λ_{max} 226 mμ, ε 6100.

A possible route to the required 8-monoxime (III) appeared to be by reduction of

---

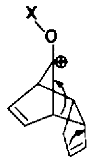
[1] R. B. Woodward and T. J. Katz, *Tetrahedron* **5**, 70 (1959).

[2] R. C. Cookson, J. Hudec and R. O. Williams, *Tetrahedron Letters* No. 22, 29 (1960); see also P. Yates and P. Eaton, *Tetrahedron* **12**, 13 (1961).

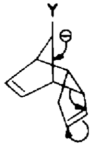
[3] C. H. DePuy and B. W. Ponder, *J. Amer. Chem. Soc.* **81**, 4629 (1959).

[4] J. Thiele, *Ber Dtsch. Chem. Ges.* **33**, 666 (1900).

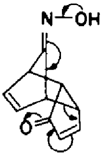
[5] W. v. E. Doering and C. H. De Puy, *J. Amer. Chem. Soc.* **75**, 5956 (1953).



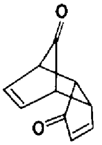
I



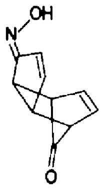
II



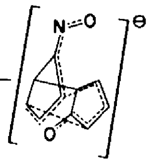
III



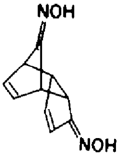
VI



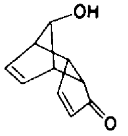
V



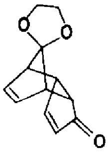
IV



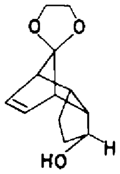
VII



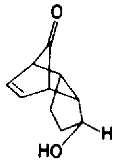
VIII



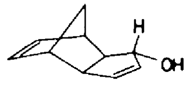
IX



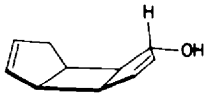
X



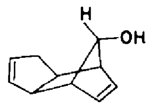
XI



XII



XIII



XIV

the carbonyl group in the ketal (IX), hydrolysis, oximation and re-oxidation (although it would perhaps have been too optimistic to hope to avoid premature rearrangement during the later stages[2]); but this was frustrated at the very first step by the susceptibility of the 2,3-double bond to reduction. Complete reduction of the carbonyl group required an excess of borohydride in boiling methanol. The resulting hydroxy-ketal contained only one double bond, and its structure (X) was confirmed by oxidation to a ketone with ν_{max} 1736 cm^{-1} and only end-absorption in the UV spectrum.

Hydrolysis of the hydroxy-ketal (X) led to the hydroxy-ketone (XI), the 8-carbonyl group of which was revealed by the strong band at 1786 cm^{-1}. Oxidation of XI gave a diketone, with bands at 1786 and 1739 cm^{-1} and no intense UV absorption, also formed by hydrolysis of the oxidation product of X. Similarly reduction of the diketone (VI) with borohydride gave a diol containing only one double bond.

It is at least possible that in all three cases (formation of IV, VII and IX) equilibration by the Woodward–Katz rearrangement occurred under the conditions of reaction, so that the same product would have been isolated whichever carbonyl reacted first. To establish this would need the use of less symmetric compounds.

exo-Dicyclopentadiene

It has been recognised for many years that cyclic, molecular reactions like the Cope rearrangement[6] proceed so readily because they pass through transition states where the electrons involved are in delocalized orbitals, allowing their redistribution with the minimum energy: the cost of breaking the old bonds is partly paid by making the new ones. An essential feature of the Cope rearrangement, then, is the simultaneous breaking and making of the bonds between the ends of the two allyl groups, as in the Woodward–Katz rearrangement.

Nevertheless it seemed worth testing whether any rearrangement could be detected in a rigid diallyl system where the unlinked (olefinic) ends of the two allyl groups were held away from one another so that a completely concerted rearrangement was impossible, although the groups were in parallel planes. *exo*-Dicyclopentadiene represents such a system. We therefore studied the 1-hydroxy derivative (XII), the *exo*-isomer of the *endo*-compound of Woodward and Katz.[1] For example, rearrangement of the α-epimer (XII) to eventually join opposite ends of the two double bonds, in the way analogous to the rearrangement of the *endo*-isomers, would lead to XIV by rotation of the two cyclopentadiene units by 120° around the unbroken bond C_7—C_{7a}. Completion of a bond half way through such a double allylic shift would give the cyclobutane isomer (XIII).

Although the configuration of the hydroxyl group in the 1-hydroxy-*exo*-dicyclopentadiene made by oxidation of the hydrocarbon with selenium dioxide[7] has not been proved, the hindrance of one side of C-1 by the 8-methylene group makes that drawn in the formula (XII) very likely (Ref. 1).

Conditions that caused equilibration of the pairs of 1- and 8-alcohols in the *endo*-series[1] (e.g. distillation at 140°) induced no detectable rearrangement in the *exo*-compound (XII). Indeed, apart from polymerisation, the latter was stable up to 190°. Correspondingly, whereas *endo*-dicyclopentadiene dissociated to cyclopentadiene at 140°, the *exo*-isomer, with unsaturated centres remote from one another, boiled unchanged at 170°.

Evidently, rearrangement of the *exo*-isomers would cost an energy of activation something like that needed to separate two allyl radicals (cf.[8] the 47 kcal/mole for $PhCH_2CH_2Ph \rightarrow 2PhCH_2\cdot$) rather than the much lower value ($<$30 kcal/mole[9]) for a Cope rearrangement proceeding through a cyclic transition state.

---

[6] W. v. E. Doering and W. R. Roth, *Tetrahedron* **18**, 67 (1962), and refs. given there.

[7] K. Alder, F. H. Flock and P. Janssen, *Chem. Ber.* **89**, 2689 (1956).

[8] T. L. Cottrell, *The Strengths of Chemical Bonds* (2nd Edition) p. 195. Butterworths, London (1958).

[9] H. Levy and A. C. Cope, *J. Amer. Chem. Soc.* **66**, 1684 (1944), and earlier papers.

EXPERIMENTAL

When not contradicted, UV spectra were measured in ethanol and IR spectra in nujol.

1,8-*Dioximino*-endo-*dicyclopentadiene* (VII), made by Doering and DePuy's modification[5] of Thiele's method,[4] was obtained in a slightly improved yield (84%), m.p. 174 (dec), λ_{max} 240 mμ (ε 9150). (Reported[5] m.p. 178–180 (dec), λ_{max} (EtOH) 261 mμ (ε 2500).)

1-*Oximino*-endo-*dicyclopentadien*-8-*one* (V) was obtained by hydrolysis of the dioxime (VII) with HCl aq. in the presence of laevulinic acid at room temp,[3] as colourless prisms from benzene (61%), m.p. 157–158° (dec), λ_{max} 237 mμ (ε 10500), ν_{max} 1779 cm^{-1}. (Reported[3] m.p. 158–159°.)

endo-*Dicyclopentadien*-1,8-*dione* (VI) was obtained by hydrolysis either from the dioxime (VII) or from the monoxime (V).[3] One-step hydrolysis of the former at 100° with a mixture of 1 N HCl–laevulinic acid (1:10) yielded the diketone as a fawn crystalline solid (74%), m.p. 99–100·5°. It crystallized from di-isopropyl ether in colourless prisms, m.p. 101·5–103°, λ_{max} 215 mμ (ε 7150), ν_{max} 1776 and 1701 cm^{-1}. (Reported[3] m.p. 100–101·5°.)

The 1-2′,4′ -*dinitrophenylhydrazone* was formed by treatment of the diketone with one equivalent of the reagent under mild conditions.[10] It crystallized from chloroform–light petroleum (1:1) as red platelets, m.p. 193·5–194° (dec). (Found: N, 16·7; O, 23·5. $C_{16}H_{12}N_4O_5$ requires: N, 16·45; O, 23·5%). ν_{max} 1790 cm^{-1}. No absorption at 1700 cm^{-1}. The 1,8-*bis*(2′,4′-*dinitrophenylhydrazone*) was obtained by using an excess of the reagent. The deep orange prisms (from dioxan) had m.p. 226–226·5° (dec). (Found: C, 50·75; H, 3·15; N, 21·35. $C_{22}H_{16}N_8O_8$ requires: C, 50·75; H, 3·1; N, 21·5%). No absorption in the carbonyl region of the IR spectrum. (After our work was finished[11] a compound decomposing at 192–193° was assigned the same structure.[12])

Reaction of the diketone (VI) *with hydroxylamine.* The diketone (0·16 g, 0·001 mole) was dissolved in methanol (3 ml), hydroxylamine hydrochloride (0·07 g, 0·001 mole) and pyridine (0·5 ml) were added and this mixture was refluxed for 30 min, followed by the evaporation of the solvent. The residue was taken up in water (5 ml), made alkaline with 2 N NaOH (1·1 ml) and extracted with ether to remove starting material. The aqueous solution was acidified with 2 N HCl (1·3 ml) and extracted with ether. This extract was dried and evaporated to leave a yellow crystalline solid (0·14 g, 78%, m.p. 151–153° (dec). Recrystallisation from benzene afforded colourless prisms, m.p. and mixed m.p. with a sample of the 1-monoxime (V), 154–156°. The IR spectrum was identical with that of the 1-oxime.

Treatment of the 1-*monoxime* (V) *with hydroxylamine.* To the monoxime (0·18 g, 0·001 mole) in a mixture of ethanol (2 ml) and pyridine (0·5 ml) was added hydroxyammonium chloride (0·21 g, 0·003 mole) and the resultant solution was heated under reflux for 50 min. It was evaporated and the residue was dissolved in water (5 ml) and acidified with acetic acid. After saturation with NaCl the solution was extracted with ether, to give a pale yellow solid (0·05 g, 26%), m.p. 165–172°, identified through its IR spectrum as the dioxime.

8-*Hydroxy*-endo-*dicyclopentadien*-1-*one* (VIII). A solution of $NaBH_4$ (0·17 g, 0·018 equiv.) in water (10 ml) and methanol (5 ml) was added dropwise to a stirred solution of the diketone (VI) (2·4 g, 0·015 mole) in methanol (25 ml). After evaporation and treatment with acid, it was extracted with ether to give a pale yellow solid (2·21 g, 91%). Two recrystallizations from methylcyclohexane afforded colourless prisms, m.p. 94–97°. (Found: C 73·75; H, 6·2; O, 20·15. $C_{10}H_{10}O_2$ requires: C, 74·05; H, 6·2; O, 19·75%), λ_{max} 226 mμ (ε 6720), ν_{max} 3322, 1672 and 1575 cm^{-1}. The 2,4-*dinitrophenylhydrazone*, made by Shine's technique,[10] formed deep red elongated prisms (from 90% ethanol), m.p. 221–223°. (Found: C, 56·2; H, 4·3; N, 16·35; O, 23·5. $C_{16}H_{14}N_4O_6$ requires: C, 56·14; H, 4·15; N, 16·35; O, 23·4%). The 3,5-*dinitrobenzoate* crystallized from ethanol as pale yellow prisms, m.p. 180–182°.

Treatment of the hydroxyketone with ethylene glycol in boiling benzene, in the presence of toluene-*p*-sulphonic acid, failed to give a ketal. After 4 hr the starting material was recovered; more prolonged reaction time (2 days) led to the formation of dark resins.

1,8-*Dihydroxy*-2,3-*dihydro*-endo-*dicyclopentadiene.* To a stirred solution of the diketone (VI, 0·4 g, 0·0025 mole) in methanol (5 ml) was added to a solution of $NaBH_4$ (0·1 g, 0·0026 mole) in a

---

[10] H. J. Shine, *J. Org. Chem.* **24**, 252 (1959).

[11] M. Szelke, Ph.D. Thesis, Southampton, 1961.

[12] K. Hoffner and K. Goliasch, *Chem. Ber.* **94**, 2909 (1961).

mixture of water (5 ml) and methanol (2·5 ml). After being stirred at 22° for 2 hr, the solution was heated under reflux for another 2 hr. Methanol was removed (red. press.) and the aqueous residue was acidified with 2 N HCl (1·3 ml). It was saturated with NaCl and extracted with ether to give, after evaporation, a pale yellow oil (0·4 g) which crystallized. Recrystallization from ethyl acetate afforded prisms, m.p. 167–168°. (Found: C, 71·7; H, 8·3. $C_{10}H_{14}O_2$ requires: C, 72·25; H, 8·5%), ν_{max} 3268, 1570 and 742 cm^{-1}. End-absorption in the ultraviolet. The product absorbed 112% of the hydrogen calculated for one double bond.

endo-*Dicyclopentadien*-1,8-*dione 8-ethylene ketal* (IX). The diketone (VI, 0·8 g, 0·005 mole) was dissolved in benzene (25 ml), ethylene glycol (0·31 g, 0·005 mole) and toluene-*p*-sulphonic acid hydrate (20 mg) were added and this mixture was heated under reflux for 20 hr. in an apparatus provided with a Dean-Stark trap. After washing with 2 N Na_2CO_3, the solvent was removed (red. press.) to leave a pale yellow oil (0·86 g, 84%) which crystallized. It was dissolved in hot pet. ether (b.p. 60–80°, 45 ml), the clear solution was decanted from a brown oil and cooled to furnish a white crystalline solid (0·62 g, 61%), m.p. 90–92°. It was recrystallized from hexane as colourless prisms, m.p. 93–93·5°. (Found: C, 70·4; H, 5·85; O, 23·5. $C_{12}H_{12}O_3$ requires: C, 70·55; H, 5·9; O, 23·5%), λ_{max} 226 mμ (ε 6100), ν_{max} 1692, 1580, 1110 and 1066 cm^{-1}. The 2,4-*dinitrophenylhydrazone* made by Shine's method[10] crystallized from methanol–chloroform (1:1) as glistening red prisms, m.p. 229·5–230·5°. (Found: C, 56·2; H, 4·5; N, 14·3; O, 25·1. $C_{18}H_{16}N_4O_6$ requires: C, 56·25; H, 4·2; N, 14·55; O, 25·0%).

1-*Hydroxy*-2,3-*dihydro*-endo-*dicyclopentadien*-8-*one ethylene ketal* (X). A solution of $NaBH_4$ (0·4 g, 0·01 mole) in a mixture of methanol (6 ml) and water (12 ml) was added to a stirred solution of the 8-ketal (2·58 g, 0·0126 mole) in methanol (30 ml), causing the temp. to rise slightly. After stirring at room temp. for 1 hr, the clear solution was boiled for 3 hr. Methanol was removed and the aqueous residue was extracted with ether to leave, on evaporation, a viscous oil (2·58 g). Part of this (2·06 g) was fractionated *in vacuo* to give a colourless syrup (1·65 g), b.p. 104°/5·10^{-4} mm. (Found: C, 68·5; H, 7·7; O, 23·55. $C_{12}H_{16}O_3$ requires: C, 69·2; H, 7·75; O, 23·05%), ν_{max} (neat) 3472, 3086, 1580, 1119, 1085 and 1055 cm^{-1}. UV spectrum: end-absorption. The substance, in the presence of Adams platinum catalyst, absorbed 102% of the amount of hydrogen calculated for one double bond. The 3,5-*dinitrobenzoate* crystallized from ethanol as fine needles, m.p. 147–147·5°. (Found: C, 56·85; H, 4·7; N, 6·9; O, 31·55. $C_{19}H_{18}N_2O_8$, the dinitrobenzoate of X, requires: C, 56·7; H, 4·5; N, 7·0; O, 31·8%).

1-*Hydroxy*-2,3-*dihydro*-endo-*dicyclopentadiene*-8-*one* (XI). The ketal (X, 3·27 g) was dissolved in 50 vol% acetic acid (120 ml) and heated on the steam bath for 40 min. After cooling it was neutralized ($NaHCO_3$) and extracted with ether. Evaporation of the solvent left a yellow semi-crystalline mass (2·38 g). It was fractionated *in vacuo* to give a colourless product, b.p. 112°/0·15–0·2 mm, consisting of soft wax-like crystals (1·87 g) melting between 88–93° (Found: C, 72·3; H, 7·35; O, 20·2. $C_{10}H_{12}O_2$ requires: C, 73·15; H, 7·35; O, 19·5%), ν_{max} 3460, 1786 and 1085 cm^{-1}. UV spectrum: end-absorption. 130% of the amount of hydrogen calculated for X was absorbed by the substance on hydrogenation in the presence of Adams catalyst.

When a sample of this substance (540 mg) was chromatographed on "Florisil" (20 g) in benzene, 75% of the material (405 mg) was recovered from a fraction eluted with ether, to give a waxy solid melting between 89–93°, its IR spectrum being identical with that of the crude material or that of the sample purified by distillation.

Compound X furnished a 2,4-*dinitrophenylhydrazone*, which crystallized from ethanol as large orange needles, m.p. 152–153° (Found: C, 55·65; H, 5·1; N, 15·95; O, 23·2. $C_{16}H_{16}N_4O_7$ requires: C, 55·8; H, 4·7; N, 16·25; O, 23·25%). Treatment with hydroxylamine in pyridine–ethanol at 100° for 1 hr yielded no oxime; 88% of the starting material was recovered. The 3,5-*dinitrobenzoate* (prisms from ethanol) had m.p. 131·5–133·5°. (Found: C, 56·55; H, 4·25; N, 7·95. $C_{17}H_{14}N_2O_7$ requires: C, 56·95; H, 4·0; N, 7·85%).

2,3-*Dihydro*-endo-*dicyclopentadien*-1,8-*dione 8-ethylene ketal* was obtained as a colourless oil by oxidation of X with chromic anhydride–pyridine complex at room temp. for 36 hr ν_{max} (neat) 3077, s 1736, 1580, 1099 and 1073 cm^{-1}. UV spectrum: end-absorption.

2,3-*Dihydro*-endo-*dicyclopentadiene*-1,8-*dione*, a colourless oil, was prepared from the 1-alcohol in a manner similar to that described in the preceding experiment. It could also be obtained from the 8-ketal by prolonged treatment with 80% acetic acid at 100°. ν_{max} (neat) 3086, s 1786 and s 1739 cm^{-1}. UV spectrum: end-absorption only.

1α-Hydroxy-exo-*dicyclopentadiene* (XII). *Exo*-dicyclopentadiene[18] (2·3 g, 0·0175 mole) was dissolved in 10% aqueous dioxan (10 ml) containing KH_2PO_4 (0·25 g). The mixture was refluxed and stirred vigorously and freshly sublimed SeO_2 (1·0 g, 0·009 mole) was added, while heating and stirring were continued for 3 hr. After filtration of the precipitated Se, the solution was diluted with ether, washed with 10% Na_2CO_3 aq. and dried (Na_2SO_4). Distillation yielded 1α-*hydroxy*-exo-*dicyclopentadiene*, b.p. 82°/0·5 mm, n_D^{18} 1·5352, as a colourless oil (yield 1·2 g). The complex IR spectrum contained bands at 3320, 3010, 2900, 1618, 1570, 1340, 1035 and 780 cm^{-1}. The alcohol formed a *phenylurethane*, m.p. 127° (from petrol). (Found: C, 76·5; H, 6·5; N, 5·4. $C_{17}H_{17}O_2N$ requires: C, 76·3; H, 6·4; N, 5·2%). (Reported[7] m.p. 130–132°).

exo-*Dicyclopentadiene*-1-*one*. XII (5·0 g, 0·034 mole) was oxidized by CrO_3 (4·5 g) in acetic acid at −5°. After having warmed up to room temp. the solvent was removed at 50° and 12 mm and the residue was extracted with ether from saturated $NaHCO_3$ solution. Distillation gave the ketone as a colourless oil smelling of lavender, b.p. 60°/0·4 mm (yield 3·5 g). ν_{max} 1710 cm^{-1}, no band at 3500 cm^{-1}.

Reduction. The ketone (2·5 g, 0·017 mole) in ether was added to a solution of $LiAlH_4$ (0·5 g, 0·013 mole) in ether and the mixture refluxed 1 hr. After treatment with NH_4Cl aq. and drying (Na_2SO_4), distillation yielded a colourless, viscous oil, b.p. 70°/1 mm. This was further purified by column chromatography through alumina, eluting with 10% benzene in light petrol. After standing at 0° for several days, the product crystallized and was obtained as large, colourless plates, m.p. 63–67° (after crystallization at low temp., from petrol). The IR spectrum was similar to but quite distinct from that of XII. The compound formed a *phenylurethane*, m.p. 86° from petrol. (Found: C, 76·1; H, 6·7; N, 5·3. $C_{17}H_{17}O_2N$ requires: C, 76·3; H, 6·4; N, 5·2%). The NMR spectrum of this urethane indicated that the 2,3-double bond had probably been reduced.

Attempted thermal isomerization of hydroxy-exo-*dicyclopentadiene* The hydroxy-*exo*-dicyclopentadiene (XII) in 1 g quantities were separately distilled slowly through a 10 cm Vigreux column, jacketed with xylene vapour at 140° and with the press. adjusted so as to permit a variation in the distillation temp. of the alcohol between 140° and 160° (heating bath at temp. up to 190°). In all cases, the distillate was identical with the starting material, as shown by its IR spectrum and m.p. of the phenylurethane, the yield decreasing from around 80% at the lower temp. to half that figure at the higher one, while an increasing amount of undistillable polymer remained in the flask.

Acknowledgments—We acknowledge with thanks a special grant from the D.S.I.R. M. S. is indebted to John Wyeth and Brother Ltd. for generous facilities and to Dr. A. B. A. Jansen for advice and encouragement. We thank also Dr. J. Hudec for helpful discussions.

[18] A. A. Oswald and F. Noel, *J. Org. Chem.* **26**, 3948 (1961).