Rapid Intramolecular 1,4-Hydride Transfer across a Rigid 4-Hydroxycycloheptanone

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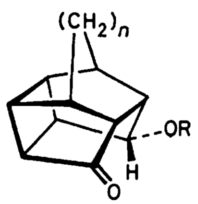
The n.m.r. spectrum of the sodium salt (4; R = Na) was found to be temperature dependent and this behaviour has been associated with a rapid degenerate rearrangement involving intramolecular hydride transfer from alkoxide to carbonyl. Dynamic ^{13}C n.m.r. measurements gave a barrier of 13.7 (4 °C) kcal mol^{-1} for the rearrangement. A much slower competing process leading to the hemiacetal (5) was also found. The *X*-ray crystal structure of (4; R = *p*-nitrobenzoyl) has been determined and the ketonic carbonyl shows some pyramidalization.

We have recently determined barriers for the degenerate rearrangements of the sodium alkoxides of the cage hydroxy-ketones (1)—(3), in which hydride migrates across the six-membered ring between the oxygen-bearing carbon atoms.[1] Barriers decrease in the order (1) > (2) > (3), and the results of a structural investigation showed that there was a qualitative correlation between the barriers and the magnitude of the H · · · C=O non-bonded repulsion energy. Inspection of the structures shows that the angular relationships at the reaction sites in (1)—(3) do not differ significantly, and the variation of barrier in this series therefore provided no information on angular preference in the reaction, or on the internuclear distances at which angular preferences become energetically demanding.

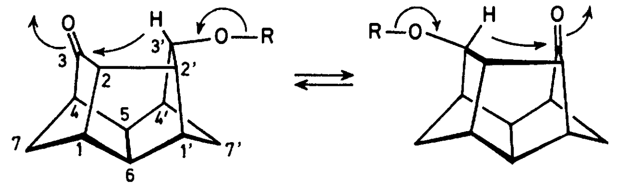


(1) n=1; $\Delta G_{100°}$ = 21.7 kcal mol^{-1}
(2) n=2; $\Delta G_{100°}$ = 19.0 kcal mol^{-1}
(3) n=3; $\Delta G_{72°}$ = 17.3 kcal mol^{-1}

Structures of (1)—(3) (R = H) and barriers to hydride transfer in (1)—(3) (R = Na)

Investigation of these factors requires examination of hydroxy-ketones with significantly different angular arrangements, and these can only be achieved by incorporating the reacting groups into rings larger than six-membered. The structure[2] and reactivity[3] of *exo*-7-hydroxybicyclo[3.3.1]nonan-3-one, in which the hydride migrates 1,5 across an eight-membered ring, have been described, and in this paper we report the results of our investigation of the hydroxy-ketone (4) in which the reacting sites are common to a seven-membered ring held in a cage framework. As with our earlier substrates, the proposed hydride transfer reaction is degenerate, with exchange of five pairs out of the twelve carbon sites in the molecule.

The substrate (4; R = H), a known compound first described by Woodward and Fukunaga[4] as an intermediate in their triquinacene synthesis, was prepared by the published procedure. Material thus obtained had analytical, physical, and spectral properties in full agreement with those reported and with the indicated structure.



(4)(R = H, Na, Ac, p-$NO_2C_6H_4CO$)

The ^1H n.m.r. spectrum of (4; R = H) showed a one-proton singlet ($W_{\frac{1}{2}}$ 5.0 Hz) at δ 4.19 assigned to the alcohol methine hydrogen, the width of the signal being consistent with the near 90° dihedral angles[5] between this hydrogen and those at adjacent (2′ and 4′) bridgehead sites. Doublets at δ 1.58, 1.67, 1.86, and 2.23 were assigned to the methylene hydrogens at C(7) and C(7′), and double-resonance experiments showed that those at δ 1.58 and 1.86 were coupled (J_{gem} 10.9 Hz), forming one AB pair, while those at δ 1.67 and 2.23 formed the second AB pair (J_{gem} 10.0 Hz). The remainder of the spectrum was not fully resolved at 300 MHz.

The ^{13}C n.m.r. spectrum showed only eleven of the expected twelve signals (see Table 1), but with added Eu(fod)$_3$[6] the highest field line split into a distinct doublet. Carbonyl and alcohol carbon signals were assigned on the basis of their chemical shifts. In the off-resonance decoupled spectrum, all high-field signals were doublets except for the composite line at δ 37.0 which appeared as a clear triplet allowing its assignment to both methylene carbons at C(7) and C(7′). Comparison of the spectra of (4; R = H) and (4; R = Ac) shows that acetylation has caused significant upfield shifts in only two signals and these can therefore be assigned to sites adjacent to the alcohol function [C(2′) and C(4′) or C(4′) and C(2′)].[7] Full assignment of the remainder of the spectrum has not been carried out but the simplicity of the ^{13}C n.m.r. spectrum strongly indicated the use of this method in measurement of reaction rates. The further assignments in Table 1 follow from the observation of coalescences of exchanging pairs of signals in the dynamic n.m.r. experiments described below.

Solutions of the sodium salt (4; R = Na) in [$^2H_6$]DMSO were prepared using previously described procedures [1] and examined by ^{13}C n.m.r. At 45 °C only six non-solvent lines were found with the notable absence of any signal above δ 60. At 90 °C these signals were unchanged in width and chemical shift, but a new broad signal ($W_{\frac{1}{2}}$ *ca.* 125 Hz) appeared at δ 146.

TABLE 1

^{13}C N.m.r. data for (4) at 20.1 MHz

Substrate–solvent	Chemical shift (δ) and assignment [a] C(3) (A)	C3′ (A)	C(5) or C(6)	C(2) or C(4) (B)	C(2′) or C(4′) (B)	C(4) or C(2) (C)	C(1) or C(1′) (D)	C(4′) or (C2′) (C)	C(6) or C(5)	C(1′) or C(1) (D)	C(7) + C(7′) (E)
(4; R = H)–CDCl$_3$	217.5	75.1	52.9	51.1	50.2	49.4	45.1	43.5	43.2	43.1	37.0, 37.0
(4; R = H)–pyridine	215.5	74.9	53.3	51.4	50.8	49.7	45.5	44.3	43.5	43.5	37.7, 37.2
(4; R = Ac)–pyridine [b]	214.3	78.6	53.1	51.2	47.7	49.5	45.5	41.8	43.3	43.1	37.8, 36.9
(4; R = Na)–pyridine [c]	215.7	78.9	53.1	51.3	56.0	49.5	45.1	47.5	43.3	43.1	37.5

[a] Exchanging pairs are denoted A—E. [b] Signals from CH_3CO not listed appeared at δ 169.7 and 21.1 p.p.m. [c] Low-temperature spectra.

This behaviour can be reconciled with a fast hydride transfer of the type shown which would exchange C(1) and C(1′), C(2) and C(2′), C(3) and C(3′), C(4) and C(4′), and C(7) and C(7′). Since C(5) and C(6) lie on the symmetry plane of the degenerate rearrangement, in the fast exchange limit, only seven signals are expected. Ionization of simple alcohols has been shown to cause downfield shifts of 4—6 p.p.m. in the alcohol carbon signal and of *ca.* 5 p.p.m. in signals from bridgehead sites β to the alcohol.[1] The maximum separation of signals of exchanging carbon sites in the hydrocarbon part of the molecule cannot therefore be more than 400 Hz (at 20.1 MHz), but for the carbonyl and alkoxide carbon pair, the expected separation is *ca.* 2 800 Hz. An exchange rate of *ca.* 10^4 s^{-1} would be expected to give full coalescence of all but the widely separated pair, and signals from these sites could well be broadened sufficiently to be unobserved above baseline noise.[8] The appearance of the broad signal at δ 146, almost exactly the mean of the expected chemical shifts of the carbonyl and alkoxide, when the temperature is raised, is nicely consistent with this interpretation. The width of the new signal allows a crude estimate [9] of k_{ex} 10^5 s^{-1} at 90 °C.

Since DMSO (m.p. 18—20 °C) is too viscous below *ca.* 30 °C (4; R = Na) was also prepared by addition of one equivalent of [$^2H_6$]dimsyl sodium in [$^2H_6$]DMSO to a solution of (4; R = H) in [$^2H_5$]pyridine. The resulting mixed solvent system remained clear and mobile down to —30 °C. At —20 °C, the ^{13}C n.m.r. spectrum of this solution showed eleven lines (see Table 1), and the highest-field line, partially obscured by signals from solvent, was noticeably broadened. We assign this line to signals from the C(7) and C(7′) methylene groups, already coalesced by exchange at this temperature because of their small separation. Carbonyl and alkoxide signals are apparent at δ 215.7 and 78.9, respectively, and comparison with the spectrum of (4; R = H), in the same solvent, shows that ionization has induced a downfield shift of δ 4.0 p.p.m. in the alcohol carbon signal, consistent with quantitative formation of the salt.[1] In the remainder of the spectrum there is a good match between the chemical shifts in the alcohol and its salt, with the exception of those signals assigned to C(2′) and C(4′) (β to the alcohol) which have moved downfield on ionization, in agreement with the pattern found in earlier investigations.

As expected, the spectrum was temperature dependent. The carbonyl and alkoxide signals broaden and disappear into baseline noise as the temperature is raised. The behaviour of the high-field signals (Figure 1) is clearly consistent with the exchange process. Lines at δ 53.1 and 43.3 remain sharp throughout and can be assigned to the non-exchanging sites at C(5) and C(6) [or C(6) and C(5)]. The highest-field line sharpens with increasing temperature, and the remaining six lines behave as three coalescing pairs. We have localised the coalescence temperature for the δ 49.5 and 47.5 pair to 4 ± 3 °C and the derived exchange rate and barrier [10] at this temperature are 89 s^{-1} and 13.7 (±0.2) kcal mol^{-1}, respectively.

Variable-temperature ^1H n.m.r. spectroscopy of this solution gave comparable results. The spectrum of the salt, like that of the alcohol, is complex at 300 MHz and was spectacularly temperature dependent with multiple overlapping coalescences. It was possible, however, to identify doublets at δ 1.63 and 1.70 as arising from an exchanging pair of hydrogens attached to C(7) and C(7′). These signals coalesce at -8 ± 3 °C giving k_{ex} and a barrier of 40 s^{-1} and 13.5 (±0.2) kcal mol^{-1}, respectively,[11] at that temperature.

Aqueous quench followed by ether extraction and crystallization of the mixed solvent samples gave 85% recovery of (4) and t.l.c. examination of the crude extract failed to reveal any new compounds. Mass spectral analysis of the recovered (4) showed that there had been no incorporation of deuterium under the reaction conditions, firmly excluding a homoenolization mechanism [12] for the observed exchange.

In contrast, similar quench and extraction of the DMSO solutions which had been heated at 90 °C for over 30 h gave a 76% recovery of a mixture of (4; R = H) and a new compound (5; R = H) in 35 : 65 ratio. Mass spectral and elemental analysis established that (5) was isomeric with (4). I.r. spectroscopy of (5; R = H) showed a strong band at 3 400 cm^{-1} but no absorption in the carbonyl region. Absence of any signal below δ 120 in its ^{13}C n.m.r. spectrum confirmed loss of carbonyl, but the singlet and doublet at δ 113.8 and 84.0, respectively, were consistent with the presence of acetal- and alcohol-type carbons.[13] In the rest of the spectrum, signal multiplicities indicated the presence of eight methine and two methylene sites. The ^1H n.m.r. spectrum was again complex, but showed a clear one-proton doublet of doublets centred at δ 4.45 with splittings of 7.2 and 3.6 Hz. We assign the hemiacetal structure to (5) on the basis of these observations. The δ 4.45 signal in the ^1H n.m.r. spectrum is assigned to the ethereal methine hydrogen and the observed splittings are consistent with the dihedral angles of 25 and 55° to the adjacent hydrogens at C(2) and C(4) bridgehead sites.

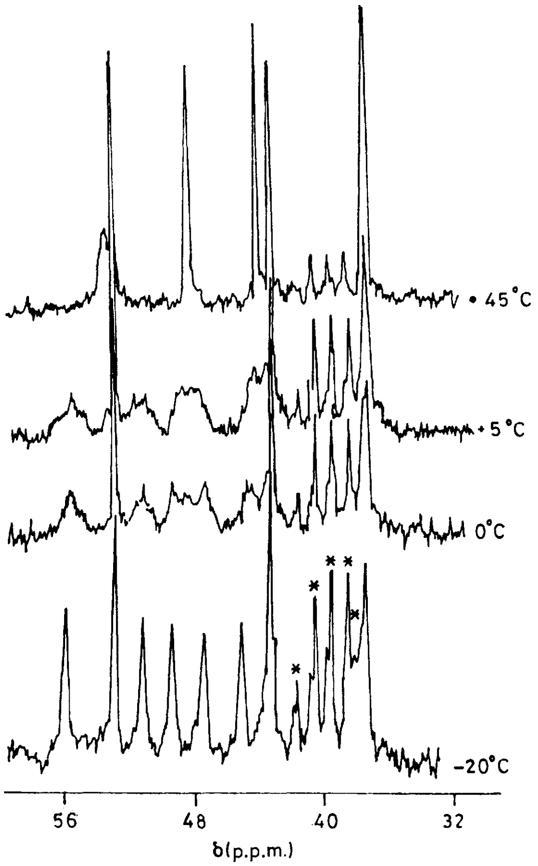
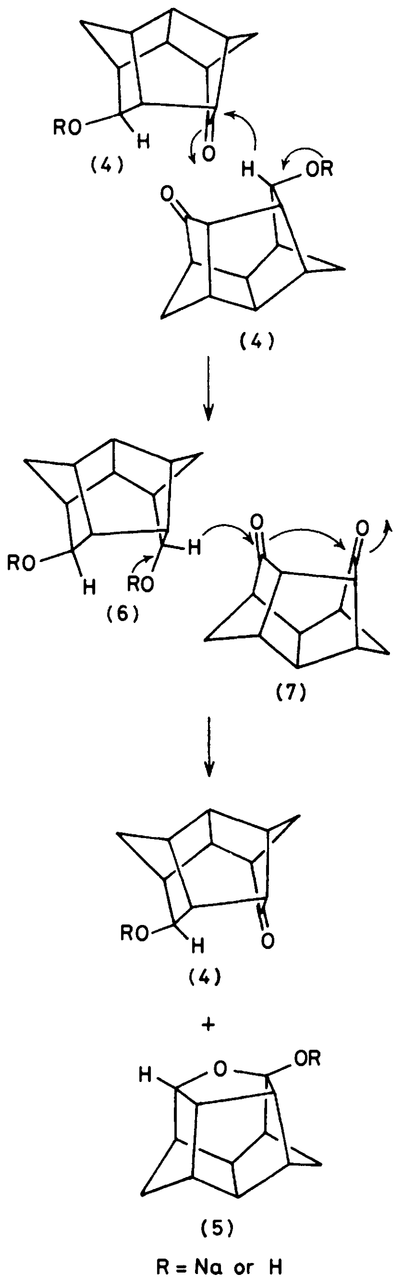


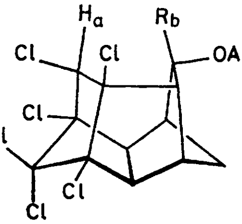
FIGURE 1 Temperature-dependent high-field region of ^{13}C n.m.r. spectra of (4; R = Na) in [$^2H_5$]pyridine-[$^2H_6$]DMSO. * = signals from [$^2H_6$]DMSO

Epimerization of the alcoholic oxygen function in (4) is the first competing reaction we have found in any of our studies and may be the result of an intermolecular hydride transfer giving, initially, the diol (6) and the dione (7) (Scheme). A second intermolecular transfer from the more hindered alkoxide of (6) to the outside face of a carbonyl in (7) would give the hemiacetal as its salt under the strongly basic conditions. Examination by t.l.c. and g.l.c. of the crude extract has, however, failed to reveal more than 0.05% of any material other than (4) and (5). This speculative sequence is sterically improbable, but the reaction was only 65% complete after 30 h at 90 °C, and so the epimerization process must



SCHEME Possible mechanism for formation of (5) *via* (6) and (7) be *ca.* 10^{10}-fold slower than the intramolecular reaction. There is, however, a substantial driving force for the formation of (5), since non-bonded interactions across the reaction sites are relieved, and the acetal type hydroxy-group is expected to be *ca.* 5 pK_a units[14] more acidic than a simple secondary hydroxy-group.

Transfer of hydride across the constrained seven-membered ring in (4; R = Na) thus occurs *ca.* 10^3 times more rapidly than the corresponding shift in the most reactive of the rigid six-membered ring series (3). Most simply, the variation of reactivity in the cage compounds examined to date can be related to relief, in the hydride transfer transition states, of high ground-state strain associated with non-bonded interactions between functionalised carbon atoms. Acid-induced rearrangements involving hydride transfer across these positions in the molecular framework of (4) have been noted previously,[15] and Anet[16] has recently described a steric isotope effect on the chemical shift of H_a in the isotopomers (8; R = H or D), and has estimated, from ^1H and ^{13}C T_1 measurements, that the $H_a \cdots H_b$ distance is only 1.6 ± 0.05 Å.



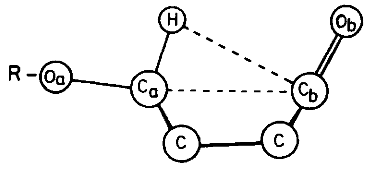
(8) R = H or D

Table 2, with its accompanying diagrams, compares details of the reaction site geometries and non-bonded interactions in (3) and (4) (R = H) found by empirical force field calculations,[17] and there are three obvious differences in the structures. First, the H ••• C=O non-bonded distance in (4) is 0.07 Å smaller, resulting in a larger contribution from this interaction to the total steric energy. Secondly, the arrangement of the reacting atoms is ' flatter ' in (4), as shown by the difference in the C–H ··· C angles [82.5° in (3), 92.5° in (4)] or by the ratios of the $C_a \cdots C_b$ distance to the $O_a \cdots O_b$ distance [0.546 in (3), 0.657 in (4)]. Thirdly, while both oxygen atoms in (3) are within 0.1 Å of the C–H ··· C plane, the arrangement in (4) is bent such that the alcoholic and ketonic oxygen-atoms are both above this plane by 0.277 and 0.316 Å respectively. In our earlier work[1] we noted that with the rigid compounds (1)—(3) there was a good qualitative correlation between the barriers and the magnitude of the H ··· C=O non-bonded repulsion in their calculated structures. This term is 1.87 kcal mol^{-1} in (4; R = H) [*cf.* 1.44 kcal mol^{-1} in (3; R = H)] and the correlation does not break down when this datum is included, despite the rather different angular relationship of the functional groups in (4). With the currently available data, a more detailed analysis of correlations between reactivity and various geometrical parameters is not permissible.

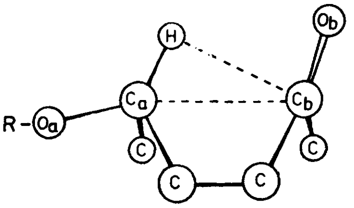
The empirical force field calculations afford a useful first basis for comparison of the structures of (1)—(4) but *X*-ray crystal structures of suitable derivatives are being determined and we report here the structure of the *p*-nitrobenzoate ester of (4). Figure 2 shows a stereoscopic view of the molecule and indicates the numbering system used in the Tables of structural data included in the Experimental section.

TABLE 2

Reaction site geometries in (3; R = H), (4; R = H), and (4; R = p-$NO_2C_6H_4CO$)



(3)



(4)

	(3; R = H) (calc.)	(4; R = H) (calc.)	(4; R = p-$NO_2C_6H_4CO$ (*X*-ray)
Interatomic distances (Å)			
$C_a \cdots C_b$	2.516	2.635	2.583 (5)
C_a–H	1.101	1.100	0.97 (4)
C_a–O_a	1.429	1.431	1.463 (4)
$C_a \cdots O_b$	3.295	3.172	3.233 (6)
$C_b \cdots$ H	2.410	2.343	2.18 (4)
C_b=O_b	1.222	1.223	1.203 (5)
$C_b \cdots O_a$	3.938	4.021	3.949 (6)
$O_a \cdots O_b$	4.629	4.377	4.403 (6)
Interatomic angles (°)			
H–C_a–O_a	102.1	103.0	106 (3)
H $\cdots$ C_b=O_b	93.5	80.7	91 (3)
C_a–H $\cdots$ C_b	82.5	92.5	103 (3)
Out-of-plane displacement (Å) [a]			
$C_b(O_bCC)$	0.015	0.033	0.074
$C_a(O_aCC)$	0.530	0.532	0.560

[a] Perpendicular displacement of central carbon from plane of its non-hydrogen ligands. The direction of displacement is always towards H.

Details of the reaction site geometry in the crystal structure are also included in Table 2 for comparison with those derived from the empirical force field calculations, which reproduce the general features of the experimentally determined structure rather well, but with a tendency to underestimate the proximity of the two functional groups.

The most interesting feature of the structure, from the viewpoint of the hydride transfer, is the substantial (0.074 Å) displacement of the carbonyl carbon (C_b, see

Table 2) from the plane of its attached carbons and the carbonyl oxygen (O_b).

Displacements of this size do not appear to be a general feature of recognisable partial structures imbedded in the framework of (4). For example, a search[18] of the CCDC file for molecules containing the cycloheptanone fragment [C(3), C(2), C(2′), C(3′), C(4′), C(5), C(4), and O in (4)] yielded 36 structures for which crystallographic data were available. Of these, only four contained carbonyls[19] with displacement greater than 0.04 Å and all but one[20] of these had electronegative substituents α to the carbonyl. A similar search for the bicyclo[2.2.1]-heptan-2-one fragment [C(3), C(2), C(1), C(6), C(5), C(4), C(7), and O of (4)] yielded 14 structures, and only two[21] of these contained carbonyls with displacements greater than 0.04 Å. Again, the large displacements were associated with electronegative substituents at the position α to the carbonyl.

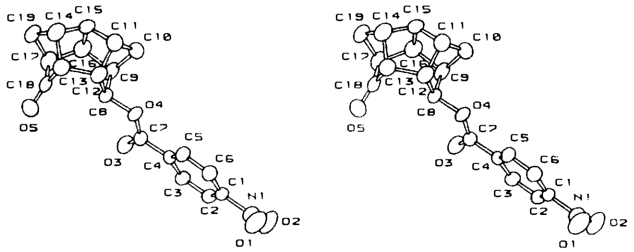


FIGURE 2 Stereoscopic view of (4; R = p-$NO_2C_6H_4CO$)

The out-of-plane distortion at the carbonyl may be regarded as a response to steric compression of the alcohol and carbonyl groups. However, Bürgi *et al.*[22] have examined crystal structures in which there is close approach of a formally non-bonded nitrogen to carbonyl, and have been able to associate the range of geometries found with a preferred pathway for approach of this nucleophilic atom. A similar pattern has been found for addition of the weaker oxygen nucleophiles,[23] although the picture is less clear. The rearrangement studied in this work involves addition of hydride to carbonyl[24] (and its reverse) and, although the migrating hydrogen can have little hydridic character in (4; R = p-nitrobenzoyl), the pyramidalization at the carbonyl could be viewed as a geometric response to approach of this nucleophile.

One interesting consequence of this response is the apparent enlargement of the H · · · C=O angle; behaviour reminiscent of that found in the structures of 1-acetyl-8-dimethylaminonaphthalene[25] and 7-methyl-7-azabicyclo[3.3.1]nonan-3-one[26] and rationalized as allowing more favourable angles of approach of potential nitrogen nucleophiles to carbonyl.

At present, the lack of structural data does not allow comparative study. Only crystallographic examination of other derivatives of (4)[27] and other molecules, such as (1)—(3), will show whether ‘ the principle of structural correlation ’[28] can be applied to the $H^- + \rangle C{=}O$ reaction.

EXPERIMENTAL

I.r. spectra were recorded on a Perkin-Elmer 457G spectrophotometer. Routine ^1H n.m.r. spectra were determined at 90 MHz on a Perkin-Elmer R32 or at 300 MHz on a Varian SC 300 instrument. ^{13}C N.m.r. spectra were recorded on a Brüker WP 80 spectrometer at 20.1 MHz. Mass spectra were determined on an AEI MS 9 instrument. Analytical g.l.c. used a 1.7 m × 2 mm glass column with 3% Dexsil on Supelcoport 100—200 as the stationary phase at 230 °C with nitrogen at an inlet pressure of 20 lb in^{-2} as carrier gas. Silica gel GF_{254} was used for analytical t.l.c. and PF_{254} for preparative t.l.c. Light petroleum refers to the fraction boiling between 40 and 60 °C. A locally adapted version of the program STRAIN was used for the empirical force field calculations.

exo-9-*Hydroxypentacyclo*[6.2.1.1^{3,6}.0^{2,7}.0^{4,10}]*dodecan-5-one* (4; R = H).—This material was prepared by the method of Woodward and Fukunaga.[4] Recrystallization from ether–light petroleum gave crystals, m.p. 190—195 °C (sublimes) (lit.,[4] 190—192 °C), $\nu_{max.}$ (CCl_4) 3 650, 3 470, 2 990, 2 900, 1 752, 1 475, 1 295, 1 060, and 918 cm^{-1}, δ_H ($CDCl_3$) 1.58 (1 H, d, J 10.9 Hz), 1.67 (1 H, d, J 10.0 Hz), 1.65 (1 H, s, removed on addition of D_2O), 1.86 (1 H, d, J 10.9 Hz), 2.23 (1 H, d, J 10.0 Hz), 2.27br (1 H, s), 2.34 (2 H, m), 2.55 (3 H, m), 2.61br (1 H, s), 2.70br (1 H, s), and 4.19 (1 H, s, $W_{\frac{1}{2}}$ 5.0 Hz), δ_C, see Table 1, m/e 105(100%), 95(84), 96(80), 124(71), 79(64), 43(62), 67(44), 77(38), and 91(37) (Found: C, 75.6; H, 7.3; M^+, 190.0991. $C_{12}H_{14}O_2$ requires C, 75.8; H, 7.4%; M^+, 190.0994).

endo-9-*Hydroxypentacyclo*[6.2.1.1^{3,6}.0^{2,7}.0^{4,10}]*dodecan*-5-*one Internal Hemiacetal* (5; R = H).—An n.m.r. tube containing a solution of (4; R = Na) (0.028 g) in [$^2H_6$]DMSO (0.6 ml) which had been heated at 90 °C for 90 h was opened, the contents poured into water, and extracted into ether. After drying (Na_2SO_4), the ethereal solution was examined by g.l.c., revealing the presence of two components in a ratio of 35 : 65. The minor component co-injected with an authentic sample of (4; R = H). Evaporation of solvent yielded a waxy solid (0.022 g) and preparative t.l.c. (eluting with ether) gave (4) and (5) (R = H) which was recrystallized from light petroleum to give crystals, m.p. 180—182 °C (sublimes), $\nu_{max.}$ (CCl_4) 3 600, 3 390, 2 990, 2 880, 1 460, 1 330, 1 280, 1 240, 1 230, 1 115, 1 070, 1 035, 905, and 875 cm^{-1}, δ_H ($CHCl_3$) 1.50—2.05 (4 H, complex m), 2.10—3.1 (8 H, unresolved), 3.25 (1 H, s, removed on addition of D_2O), 4.45 (1 H, dd, J 7.2 and 3.6 Hz), δ_C ($CDCl_3$) 36.6(d), 37.7(t), 39.7(t), 42.1(composite, d), 44.6(d), 45.8(d), 47.7(d), 53.0(d), 54.9(d), 84.0(d), and 113.8(s), m/e 190(100%), 124(83), 125(64), 79(31), 145(30), and 118(28) (Found: C, 75.5; H, 7.4; M^+, 190.0989. $C_{12}H_{14}O_2$ requires C, 75.8; H, 7.4%; M^+, 190.0994).

N.m.r. Sample Preparation and Variable-temperature Investigation.—Solutions of (4; R = Na) in [$^2H_6$]DMSO were prepared by previously described methods.[1] The mixed-solvent samples were prepared by addition from a microsyringe of [$^2H_6$]dimsyl sodium in [$^2H_6$]DMSO (0.116 ml of 0.86M solution) to a solution of (4; R = H)(0.019 g) in [$^2H_5$]-pyridine (0.30 ml) under nitrogen. The resulting clear solution was transferred to an n.m.r. tube by flex-needle and sealed under nitrogen. ^{13}C N.m.r. spectra for the kinetic experiments were recorded on a Brüker WP 80 FT spectrometer fitted with a Brüker B VT temperature unit. Aquisition parameters were those used in our previous work.[1]

Preparation of (4; R = Ac) *and* (4; R = p-$NO_2C_6H_4CO$).—

Compound (4; R = H) was acetylated with acetic anhydride in pyridine. Standard aqueous work-up and ethereal extraction gave the acetate (4; R = Ac) as a clear viscous oil (see Table 1 for spectral data). Compound (4; R = p-$NO_2C_6H_4CO$) was prepared by reaction of (4; R = H) with p-nitrobenzoyl chloride in pyridine. Standard aqueous work-up, ethereal extraction, and recrystallization from anhydrous ethanol gave crystals, m.p. 183—184 °C, suitable for X-ray crystallography.

Structure Determination of (4; R = p-$NO_2C_6H_4CO$).—*Crystal data.* $C_{19}H_{17}NO_5$, $M = 339$, monoclinic, $a = 7.321(2)$, $b = 17.942(4)$, $c = 11.866(5)$ Å, $\beta = 96.07(2)°$, $U = 1550.0$ Å^3, $Z = 4$, $D_c = 1.46$ g cm^{-3}, μ(Mo-K_α) = 1.27 cm^{-1}, space group $P2_1/c$ (No. 14), 1 303 unique reflexions with $F > 3\sigma(F)$, $R = 4.8\%$.

The crystals were air-stable, transparent needles in general and precession photographs revealed the unambiguous space group. Intensity data were obtained from a crystal of roughly hexagonal cross-section with dimensions 0.24 × 0.26 × 0.45 mm and collected on an Enraf Nonius CAD-4 computer controlled Kappa axis single-crystal diffractometer with measurements made out to $\theta = 25°$ with an ω–2θ scan. No absorption correction was applied. The structure was solved by direct methods with the MULTAN-76 suite of programs. The first cycle revealed only the atoms of the p-nitrobenzoate fragment, but this information, together with the use of the tangent-formula recycle procedure, led to all the non-hydrogen atoms being found at the next step. Least-squares refinement then proceeded smoothly; at R 13% anisotropic refinement of the temperature factors of the non-hydrogen atoms was introduced. The temperature factors of the hydrogen atoms were restrained to a B value of 5 Å^2; the refinement of their positional parameters was well behaved. A parabolic weighting scheme $w^{-1} = 1.917 - 0.116F_o + 0.00242F_o^2$ gave a reasonably uniform fit to $\Sigma w\Delta F^2$ against $\sin^2\theta/\lambda^2$ and also F_o^2. At the final stage (R 4.8%), a difference Fourier synthesis contained no peak exceeding 0.3 e.

TABLE 3

Atomic co-ordinates for structure of (4; p-$NO_2C_6H_4$-CO) *

Atom	x/a	y/b	z/c
O(1)	−0.314 3(4)	0.524 5(2)	0.283 7(3)
O(2)	−0.267 8(5)	0.605 7(2)	0.157 5(3)
O(3)	0.535 6(4)	0.413 8(2)	0.081 9(3)
O(4)	0.361 7(3)	0.312 0(1)	0.092 5(2)
O(5)	0.898 6(4)	0.218 1(2)	0.222 7(3)
N(1)	−0.230 2(5)	0.548 8(2)	0.208 5(3)
C(1)	−0.068 9(5)	0.505 9(2)	0.179 3(3)
C(2)	0.069 2(5)	0.543 3(2)	0.133 6(3)
C(3)	0.220 5(5)	0.502 7(2)	0.108 8(3)
C(4)	0.226 8(5)	0.426 6(2)	0.126 0(3)
C(5)	0.082 5(5)	0.390 6(2)	0.169 4(3)
C(6)	−0.066 9(5)	0.430 7(2)	0.198 4(3)
C(7)	0.392 5(5)	0.384 9(2)	0.097 1(3)
C(8)	0.519 0(5)	0.264 6(2)	0.075 3(4)
C(9)	0.548 3(6)	0.257 6(2)	−0.049 6(4)
C(10)	0.363 1(7)	0.219 5(3)	−0.092 4(4)
C(11)	0.395 5(6)	0.153 0(2)	−0.013 4(4)
C(12)	0.466 5(6)	0.185 0(2)	0.102 4(4)
C(13)	0.646 3(6)	0.138 3(2)	0.145 0(4)
C(14)	0.680 4(7)	0.083 8(3)	0.050 7(4)
C(15)	0.573 1(6)	0.121 7(3)	−0.050 5(4)
C(16)	0.688 3(6)	0.193 8(3)	−0.063 3(4)
C(17)	0.859 0(6)	0.183 7(3)	0.023 0(4)
C(18)	0.810 9(5)	0.189 3(2)	0.142 9(4)
C(19)	0.877 7(6)	0.098 4(3)	0.025 6(4)
H(2)	0.068 7(56)	0.595 6(23)	0.120 7(35)
H(3)	0.324 0(56)	0.524 9(23)	0.077 6(36)
H(5)	0.082 4(57)	0.338 9(23)	0.179 5(35)
H(6)	−0.167 0(58)	0.410 3(25)	0.227 3(37)
H(8)	0.622 3(56)	0.283 8(24)	0.124 6(35)
H(9)	0.581 1(55)	0.303 9(23)	−0.075 4(36)
H(101)	0.251 4(55)	0.247 9(24)	−0.083 0(36)
H(102)	0.357 1(55)	0.204 6(25)	−0.177 8(36)
H(11)	0.284 0(55)	0.116 8(24)	−0.014 4(37)
H(12)	0.375 1(55)	0.181 7(24)	0.157 5(35)
H(13)	0.641 5(55)	0.115 7(24	0.225 3(35)
H(14)	0.645 0(58)	0.026 3(23)	0.065 0(36)
H(15)	0.553 3(55)	0.092 4(23)	−0.116 4(35)
H(16)	0.737 8(56)	0.194 2(24)	−0.128 9(36)
H(17)	0.962 3(55)	0.215 4(24)	0.012 2(35)
H(191)	0.969 4(58)	0.078 6(22)	0.082 8(37)
H(192)	0.901 2(56)	0.078 0(24)	−0.045 4(36)

* Numbering of atoms is that given in Figure 2.

TABLE 4

Bond distances (Å) for (4; R = p-$NO_2C_6H_4CO$) [a] with estimated standard deviations in parentheses

C(8)–C(9)	1.525(6)	C(17)–C(19)	1.537(7)
C(8)–C(12)	1.523(5)	C(18)–O(5)	1.203(5)
C(9)–C(10)	1.555(6)	C(1)–C(2)	1.371(5)
C(9)–C(16)	1.557(6)	C(1)–C(6)	1.367(5)
C(10)–C(11)	1.520(6)	C(2)–C(3)	1.382(5)
C(11)–C(12)	1.530(6)	C(3)–C(4)	1.381(5)
C(11)–C(15)	1.522(6)	C(4)–C(5)	1.383(5)
C(12)–C(13)	1.597(6)	C(5)–C(6)	1.383(5)
C(13)–C(18)	1.516(6)	C(4)–C(7)	1.496(5)
C(13)–C(14)	1.527(6)	C(7)–O(3)	1.200(4)
C(14)–C(15)	1.523(6)	C(7)–O(4)	1.328(5)
C(14)–C(19)	1.528(6)	C(8)–O(4)	1.463(4)
C(15)–C(16)	1.560(6)	C(1)–N(1)	1.482(5)
C(16)–C(17)	1.541(6)	N(1)–O(1)	1.216(4)
C(17)–C(18)	1.504(6)	N(1)–O(2)	1.205(4)

[a] See Figure 2 for numbering system.

TABLE 5

Bond angles (°) for (4; R = p-$NO_2C_6H_4CO$) [a] with estimated standard deviations in parentheses

O(4)–C(8)–C(9)	112.2(3)	C(14)–C(15)–C(16)	102.0(3)
O(4)–C(8)–C(12)	107.2(3)	C(14)–C(13)–C(18)	100.5(4)
C(8)–C(12)–C(13)	110.0(3)	C(15)–C(16)–C(17)	104.3(4)
C(8)–C(12)–C(11)	103.4(3)	C(16)–C(17)–C(19)	101.2(4)
C(8)–C(9)–C(10)	98.4(3)	C(16)–C(17)–C(18)	111.5(3)
C(8)–C(9)–C(16)	108.9(3)	C(17)–C(18)–O(5)	127.9(4)
C(9)–C(10)–C(11)	94.0(3)	O(1)–N(1)–O(2)	124.4(4)
C(9)–C(16)–C(15)	103.3(3)	O(1)–N(1)–C(1)	117.6(4)
C(9)–C(16)–C(17)	120.9(4)	O(2)–N(1)–C(1)	118.0(4)
C(12)–C(13)–C(18)	107.9(3)	N(1)–C(1)–C(2)	118.5(4)
C(12)–C(11)–C(10)	106.0(4)	N(1)–C(1)–C(6)	117.9(4)
C(12)–C(11)–C(15)	100.3(4)	C(2)–C(1)–C(6)	123.6(4)
C(12)–C(13)–C(14)	107.3(4)	C(1)–C(2)–C(3)	117.9(4)
C(13)–C(14)–C(15)	100.5(4)	C(2)–C(3)–C(4)	120.2(4)
C(15)–C(14)–C(19)	105.3(4)	C(3)–C(4)–C(5)	120.3(4)
C(13)–C(18)–C(17)	104.0(4)	C(5)–C(6)–C(1)	117.8(4)
C(13)–C(18)–O(5)	127.2(4)	C(4)–C(5)–C(6)	120.3(4)
C(13)–C(12)–C(11)	106.2(3)	C(3)–C(4)–C(7)	118.4(3)
C(9)–C(8)–C(12)	101.1(3)	C(5)–C(4)–C(7)	121.4(3)
C(10)–C(11)–C(15)	101.2(4)	C(4)–C(7)–O(3)	124.1(4)
C(10)–C(9)–C(16)	101.7(4)	C(4)–C(7)–O(4)	111.4(3)
C(11)–C(15)–C(16)	102.1(3)	O(3)–C(7)–O(4)	124.6(4)
C(11)–C(15)–C(14)	108.8(4)	C(7)–O(4)–C(8)	116.5(3)

[a] See Figure 2 for numbering system.

A list of positional co-ordinates is given in Table 3. A stereoscopic drawing of the molecule is shown in Figure 2. Tables 4 and 5 list bond angles and bond distances in (4; R = p-$NO_2C_6H_4CO$). No unusually close intermolecular contacts were found. Structure factors and thermal parameters are given in Supplementary Publication No. SUP 23220 (15 pp.).*

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* For details of Supplementary Publications see Notice to Authors No. 7, in *J. Chem. Soc., Perkin Trans. 2*, 1981, Index issue.

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