The Preparation and Some Reactions of 3-Oxidopyrylium

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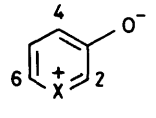
Routes to 3-oxidopyrylium and its derivatives are described. These reactive species can be trapped with a wide range of unsaturated materials including olefins, which react across the 2,6-positions, whilst dienes can be observed to react across the 2,4-positions.

Whilst Katritzky and his team have made extensive studies on 3-oxidopyridinium ylides (1),[1] work on the corresponding oxygen analogue, 3-oxidopyrylium (2), has been largely ignored. Recently, however, Hendrickson and Farina illustrated that this intermediate could be readily prepared from the corresponding pyranulose acetate (3) by the action of heat.[2] Furthermore, since the pyranulose acetate (3) is itself readily prepared from simple furan derivatives,[3] a route is now possible to a wide range of substituted 3-oxidopyrylium compounds. Herein we describe, (*a*) some further intermolecular trapping reactions with the parent system that extend the range of reactions observed by Hendrickson and Farina,[2] and (*b*) trapping experiments on the reactive intermediates under mild, room temperature conditions.

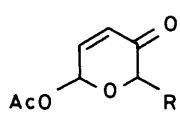
In their work [2] Hendrickson and Farina noted that 3-oxidopyrylium only reacted sluggishly with electron-deficient dipolarophiles giving reasonable yields of adducts with only the most reactive of these, such as acrolein. Both experimental studies [4] and theoretical interpretations [5] have shown, however, that 1,3-dipoles can behave as ambident species, reacting faster with either electron-deficient or electron-rich olefins than neutral, unsubstituted ones. Huisgen,[4] for example, obtained U-shaped curves when plotting reaction rates of a given dipole with different dipolarophiles against the ionisation potential of the latter. We have therefore studied the behaviour of 3-oxidopyrylium species with electron-rich and strained olefins.

Heating the pyranulose acetate (3) with ethyl vinyl ether (1.5 equiv.) in acetonitrile solution in a sealed tube at 150 °C for 17 h gave, after work-up, one major product, identified as the cycloadduct (5), isolated in 47% yield. The assigned regio- and stereo-chemistry of the adduct (5) followed from its ^{1}H n.m.r. spectrum (see also discussion below) which showed a coupling constant of 7 Hz across the 5,6-positions, reflecting *endo*-addition † of the vinyl ether across the oxidopyrylium intermediate; this stereochemical course is opposite to that of, for example, acrolein which gives, predominantly, the *exo*-adduct.[2] Presumably secondary orbital interactions influence the respective modes of addition. The regioselectivity of addition follows from standard F.M.O. arguments.[5,6]

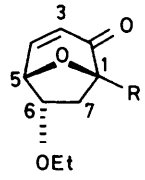
In order to avoid the need for heating, an attempt was made to generate the ylide (2) with base in the presence of an excess of ethyl vinyl ether as trapping agent. Hendrickson and Farina found that, with triethylamine as base, the ylide species could be generated, but dimerised before reaction with electron-deficient dipolarophiles.[7] Using a 1 : 6 ratio of the acetate (3) to the vinylic ether and triethylamine as base the cycloadduct (5) was produced in 56% yield; when the molar excess of the vinyl ether was reduced, some formation of the dimer (7) was observed. The rate of generation of the ylide (2) appears to depend on the strength of the tertiary base used. For example,



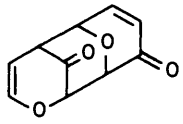
(1) X = RN
(2) X = O



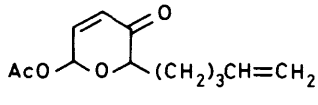
(3) R = H
(4) R = Me



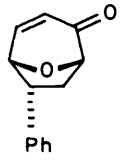
(5) R = H
(6) R = Me



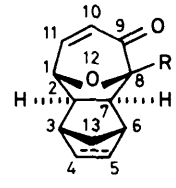
(7)



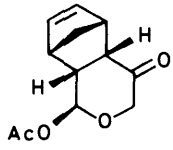
(8)



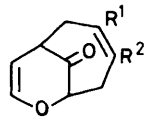
(9)



(10) 4,5-double bond, R = H
(11) 4,5-single bond, R = H
(12) 4,5-single bond, R = Me
(N.m.r. numbering scheme)



(13)



(14) $R^1 = R^2 = Me$
(15) R^1 = H or Me,
R^2 = Me or H, respectively

it has been shown that the substituted pyranulose acetate (8) undergoes intramolecular addition faster when using 1,5-diazabicyclo[4.3.0]non-5-ene (DBN) as base than with triethylamine.[8] However, for the intermolecular reaction between the acetate (3) and ethyl vinyl ether, DBN proved too strong and only small quantities of the desired adduct (5) could be

† The *endo*-isomer is assigned as that in which the olefinic substituent ends up *anti* to the oxido bridge; the *exo*-isomer is that in which the substituent is *syn* to the oxido bridge.

detected. Probably the higher concentration of the ylide produced with DBN lends itself to the formation of dimer, which is unstable to this base.

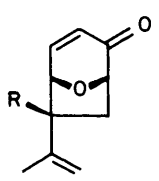
Although other vinyl ethers have also been shown to react with the ylide (2), attempted reaction with vinyl acetate failed, as did intermolecular reactions with simple olefins. On the other hand, olefins bearing aromatic substituents, such as styrene, reacted smoothly to give the cycloadduct (9) in 65% yield. Again, ^{1}H n.m.r. studies showed this to be the *endo*-adduct depicted.

Strained olefins also participate in reactions with the ylide (2). Thus, either norbornadiene or norbornene will react with the acetate (3) in the presence of triethylamine to produce cycloadducts. With norbornadiene one major adduct (10) was observed, formed in 50% yield, m.p. 110 °C. The assigned stereochemistry of this cycloadduct again follows from its ^{1}H n.m.r. spectrum, in which the coupling constants across positions 1,2 and 7,8 [see (10)] are both less than 2 Hz, attributable to a dihedral angle approaching 90°, as expected for the *exo*-adduct. The methylene bridge of the norbornadiene molecule usually favours the *syn*-configuration * in intermolecular cycloadditions,[9] as a result of steric constraints, and the assignment is substantiated here by the shielding influence observed on one of the protons at position 13 by the oxygen bridge; these methylene protons resonate at δ 1.35 and 2.21 in deuteriochloroform solution.

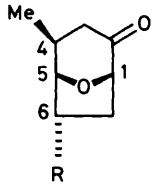
That both norbornene and norbornadiene react to form the '*exo-syn*' isomers depicted reflects both steric and electronic factors; *endo*-approach of these olefins to oxidopyrylium is disfavoured by the bicyclic nature of the reacting olefins. Intramolecular cycloaddition of isolated olefinic bonds to the dipolar system also favours the *exo*-approach.[8] The *syn*-orientation of addition to the olefinic bond of norbornene and norbornadiene has been explained by hyperconjugative effects resulting in a deformation of the olefinic protons towards the *endo*-face of the bicyclo[2.2.1]heptene system, creating both steric accessibility to and a greater electronic density at the *exo*-face.[9]

Ylides of the type (2) are also expected to undergo pericyclic additions across other centres depending on electronic demands. Thus 4π-electron systems, such as dienes, might be expected to add across the 2,4-positions, as observed with certain 3-oxidopyridinium derivatives.[10] With cyclopentadiene, cycloaddition across the enone moiety of (3) occurred faster than formation of, and reaction with, the ylide (2), to give the product (13). This reaction is related to the observed cycloadditions of dienes to the 4,5-pyranulose double bond under Lewis-acid catalysed conditions.[11] With less reactive dienes, observation of reaction across the 2,4-positions of the ylide (2) was possible. Thus 2,3-dimethylbutadiene reacted with (3) in the presence of triethylamine to give, as principal product, the adduct (14) (44%) as well as a small quantity of the 2,6-adduct (16), tentatively assigned as the *endo*-isomer. No dimer formation was detected in this reaction. In the presence of isoprene, two major components were isolated from the reaction products. Trapping across the 2,4-positions of the ylide gave a mixture of regioisomers (15), ratio 3 : 2, in a yield of 30%. Also formed was a single 2,6-adduct assigned structure (17) (26%); the *endo*-configuration followed from its n.m.r. parameters, the coupling constant between positions 5,6 being 7 Hz.

The reactions of some simple pyranulose acetate derivatives have also been explored. The methyl derivative (4) is readily prepared from furyl methyl carbinol. With ethyl vinyl ether, in the presence of triethylamine, cycloaddition again proceeds but at a much slower rate than for the unsubstituted system (3); reaction required up to seven days to produce 50% of the adduct (6). Pyrolysis conditions could be used with (4) but only in the presence of thermally stable dipolarophiles. Thus, norbornene reacted with the methylated pyranulose (4) at 145 °C to produce, after 16 h, the adduct (12) (67%).



(16) R = Me
(17) R = H



(18) R = OEt
(19) R = Ph

The described cycloadditions greatly extend the synthetic utility of the intermediate oxidopyrylium ylides. The adducts produced are highly functionalised and readily allow further transformations. Furthermore, the oxygen bridge across the seven-membered carbocyclic ring of adducts such as (5) imparts conformational rigidity on this otherwise flexible system. As a consequence the stereochemistry of chemical transformations can be controlled. An example is the addition of lithium dimethylcuprate, which adds across the enone group of compounds (5) and (9) in a stereospecific manner, the methyl group entering *syn* to the bridging oxygen atom, to give the adducts (18) and (19), respectively. Since the oxygen bridge can be subsequently removed, stereoselective formation of substituted cycloheptanes is possible.

The stereochemical assignments for the cycloadducts follow from detailed n.m.r. studies, including the appropriate decoupling experiments (see Table). Of significance is the coupling constants observed to the bridgehead protons. For *endo*-adducts of the type (5), $J_{5,6}$ is in the range 5—7 Hz, whereas the corresponding protons in the *exo*-adducts, such as (10), show coupling constants in the range 0—2 Hz.[2,6,7] A W-coupling between 1-H and 3-H of 1.5—2.0 Hz was also observed in the adduct enones.

Experimental

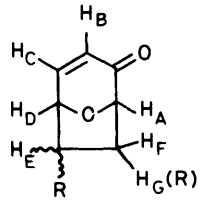
M.p.s were determined on a Kofler hot-stage apparatus. I.r. spectra were recorded with a Perkin-Elmer 297 spectrophotometer either on films or, for solids, as Nujol mulls. Unless otherwise stated, ^{1}H n.m.r. spectra were recorded on either a Perkin-Elmer R32 (90 MHz) instrument or a Jeol FX90Q (90 MHz) spectrometer for solutions in deuteriochloroform (tetramethylsilane as internal reference). Mass spectra were recorded on a Kratos MS25 instrument with accurate mass measurements carried out on an A.E.I.-Kratos MS 9/50 machine.

Thin-layer chromatography (t.l.c.) and short-column chromatography were carried out on Kieselgel GF_{254} (Merck). Solvents were generally distilled and dried before use; light petroleum refers to the fraction of boiling range 40—60 °C and ether refers to diethyl ether throughout. Solvent ratios are described as ratios of volumes before mixing. Thermal cycloaddition reactions were performed in glass tubes, sealed under vacuum (1 mmHg) and not more than one-third filled.

6-*Acetoxy*-2H-*pyran*-3(6H)-*one* (3).—This was prepared from furfuryl alcohol according to literature methods.[3] The product was obtained as a colourless oil, δ 2.1 (3 H, s), 4.1

* Herein the terms *exo* and *endo* are used as defined earlier; the term *syn* refers to the norbornene portion in which the generated bonds are *syn* to the methylene bridge, *i.e.* *exo*-addition with respect to the norbornyl unit.

Table. ^{1}H N.m.r. data of cycloadducts [a]



Compound	A	B	C	D	E	F	G
(5)	4.45 (2, 2, 9)	6.15 (2, 11)	7.20 (4, 11)	4.80 (4, 8)	4.40 (4, 8, 9)	1.60 (2, 4, 14)	2.7 (9, 9, 14)
(6)		6.10 (10)	7.1 (5, 10)	4.75 (5, 7)	4.45 (5, 7, 9)	1.75 (5, 14)	2.3 (9, 14)
(9)	4.65 (1.5, 2, 8)	6.05 (1.5, 10)	6.75 (5.5, 10)	4.85 (5.5, 7)	3.80 (7, 8, 9.5)	1.95 (2, 8, 14)	2.70 (8, 9.5, 14)
(17) [b]	4.58 (1.5, 2, 8)	6.08 (1.5, 11)	7.05 (5, 11)	4.86 (5, 7)	3.15 (7, 7, 10)	1.72 (2, 7, 14)	2.50 (8, 10, 14)
(10) [b]	4.29 (1.3, 1.5)	5.86 (1.5, 10)	7.3 (4.2, 10)	4.49 (1.3, 4.2)	2.24 (1.3, 2, 7)	2.11 (1.3, 2, 7)	
(11) [c]	4.30 (br s)	5.85 (1.5, 10)	7.25 (5, 10)	4.45 (5)	*d*	*d*	

[a] Spectra recorded at 90 MHz except where otherwise stated; $CDCl_3$ as solvent; δ values (*J* in Hz). [b] Carried out at 400 MHz. [c] Carried out at 60 MHz. [d] Hidden under methylene envelope.

(2 H, ABq, *J* 18 Hz), 6.0 (1 H, d, *J* 11 Hz), 6.3 (1 H, d, *J* 4.5 Hz), and 6.9 (1 H, dd, *J* 4.5, 11 Hz).

*6-Acetoxy-2-methyl-*2H*-pyran-*3(6H)*-one* (4).—This was prepared from 2-(1-hydroxyethyl)furan, using the literature method described for the unmethylated derivative (3).[3] The product, a mixture of epimers, was isolated as a colourless oil (80% from the furan), δ 1.2—1.4 (3 H, CH_3), 2.10 (3 H, s, CH_3CO_2), 4.3—4.5 (1 H, 2-H), 6.4 (1 H, 6-H), and 6.85 (1 H, 5-H) (Found: M^+ 170.05794; Calc. for $C_9H_{10}O_4$: *M* 170.05790).

Cycloadditions with the Pyranulose Acetate (3).—(*a*) *With ethyl vinyl ether.* The acetate (0.11 g) and ethyl vinyl ether (0.09 g, 1.81 equiv.) in acetonitrile (0.5 ml) were heated in a sealed tube at 150 °C for 17.5 h. The solvent was then removed under reduced pressure, the residue filtered through a pad of silica gel (1 : 1 ether–$CHCl_3$) and then chromatographed through silica gel with the same solvent mixture as eluant, to give one major fraction (0.075 g, 40%) as a pale yellow oil, identified as 6-endo-6-*ethoxy*-8-*oxabicyclo*[3.2.1]*oct*-3-*en*-2-*one* (5), $\nu_{max.}$ 1 690 cm^{-1}; δ 1.15 (3 H, t, *J* 8 Hz, Me), 1.6 (1 H, m, *J* 2,4, 14 Hz, 7-H), 2.7 (1 H, m, *J* 9, 9, 14 Hz, 7-H), 3.5 (2 H, q, *J* 8 Hz), 4.4 (1 H, ddd, *J* 4, 8, 9 Hz, 6-H), 4.45 (1 H, ddd, *J* 2, 2, 9 Hz, 1-H), 4.8 (1 H, dd, *J* 4, 8 Hz, 5-H), 6.15 (1 H, dd, *J* 2, 11 Hz, 3-H), and 7.20 (1 H, dd, *J* 4, 11 Hz, 4-H) (Found: C, 64.4; H, 7.35%; M^+ 168.07816. $C_9H_{12}O_3$ requires C, 64.3; H, 7.1%; M^+ 168.078 64).

The reaction was repeated under base-catalysed conditions. The acetate (0.156 g), in dichloromethane (2.5 ml) was stirred at room temperature with ethyl vinyl ether (0.43 g, 6 equiv.) and triethylamine (0.12 g, 1.2 equiv.) in a stoppered flask under N_2 for 15 h. The solvent was removed under reduced pressure, the residue dissolved in ether and filtered through silica gel before being chromatographed through a short column of silica gel (10 g), eluting with 1 : 1 ether–$CHCl_3$. The only product identified was the adduct (5) (94 mg, 56%). When the base-catalysed reaction was repeated, using only 2 equiv. of the vinylic ether, the adduct (5) (40%) was accompanied by quantities of the dimer (7) (35 mg), m.p. 144 °C (lit.,[7] m.p. 143—147 °C).

(*b*) *With styrene.* The acetate (3) (1.0 g) in dichloromethane (3 ml) containing freshly distilled styrene (4.0 g, 6 equiv.) was cooled to 0 °C before triethylamine (0.97 g, 1.5 equiv.) was added and the mixture then stirred at room temperature for 16 h. The solvent was removed under reduced pressure and the crude product chromatographed through silica gel (100 g; 1 : 2 ether–chloroform) to afford 6-endo-6-*phenyl*-8-*oxabicyclo*[3.2.1]*oct*-3-*en*-2-*one* (9) as a low-melting solid (0.84 g, 65%), m.p. 42 °C, $\nu_{max.}$ 1 695 cm^{-1}; δ 1.95 (1 H, m, J 2, 8, 14 Hz, 7-H), 2.70 (1 H, m, *J* 8, 9.5, 14 Hz, 7-H), 3.80 (1 H, m, *J* 7, 8, 9.5 Hz, 6-H), 4.65 (1 H, m, *J* 1.5, 2, 8 Hz, 1-H), 4.85 (1 H, dd, *J* 5.5, 7 Hz, 5-H), 6.05 (1 H, dd, *J* 1.5, 10 Hz, 3-H), 6.75 (1 H, dd, *J* 5.5, 10 Hz, 4-H), and 7.2 (5 H, s, aromatic H) (Found: C, 77.5; H, 6.1. $C_{13}H_{12}O_2$ requires C, 78.0; H, 6.1%).

(*c*) *Norbornadiene.* The acetate (3) (0.30 g) and norbornadiene (1.0 g, 5.7 equiv.) in dichloromethane (1.5 ml) were stirred with triethylamine (0.29 g, 1.5 equiv.) at room temperature for 16 h. The solvent was removed under reduced pressure and the residue chromatographed through silica gel (25 g), eluting with 1 : 1 ether–light petroleum to afford the *cycloadduct* (5) as a white solid (0.18 g, 50%), m.p. 110 °C; $\nu_{max.}$ 2 940 and 1 690 cm^{-1}; δ (400 MHz, $CDCl_3$) 1.35 (1 H, m, *J* 1.3, 1.3 9 Hz, 13-H), 2.11 (1 H, m, *J* 1.3, 2, 7 Hz, 7-H), 2.21 (1 H, m, *J* 1, 1.5, 9 Hz, 13-H), 2.24 (1 H, m, *J* 1.3, 2, 7 Hz, 2-H), 2.81 (1 H, m, *J* 1, 1.5, 1.5, 2 Hz, 3-H), 2.89 (1 H, m, *J* 1, 1.5, 1.5, 2 Hz 6-H), 4.29 (1 H, br, s, *J* 1.3, 1.5 Hz, 8-H), 4.49 (1 H, dd, *J* 1.3, 4.25 Hz, 1-H), 5.86 (1 H, dd, *J* 1.5, 10 Hz, 10-H), 6.24 (2 H, m, 4-H and 5-H), and 7.3 (1 H, dd, *J* 4.25, 10 Hz, 11-H) (Found: C, 76.4; H, 6.4%; M^+ 188.084 00. $C_{12}H_{12}O_2$ requires C, 76.6; H, 6.4%; M^+ 188.083 72).

(*d*) *Norbornene.* In a manner similar to that used with norbornadiene, the acetate (3) (2.5 g) was treated with norbornene (9 g, 6 equiv.) in the presence of triethylamine. Work-up afforded the 1,2,3,4,4a,5,9,9a-*octahydro*-5,9-*epoxy*-1,4-*methanobenzocycloheptene*-6-*one* (11) * (1.9 g, 63%) as a white solid, m.p. 82 °C; $\nu_{max.}$ 1 690 cm^{-1}; δ($CDCl_3$) 0.8—2.5 (10 H, m, CH and CH_2 groups), 4.30 (1 H, br, s, 8-H), 4.45 (1 H, d, *J* 5 Hz, 1-H), 5.85 (1 H, dd, *J* 1.5, 10 Hz, 10-H), and 7.25 (1 H, dd, *J* 5, 10 Hz, 11-H) (Found: C, 75.8; H, 7.8. $C_{12}H_{14}O_2$ requires C, 75.8; H, 7.4%).

(*e*) *Cyclopentadiene.* The acetate (3) (0.35 g) in dichloromethane (2 ml) was stirred with cyclopentadiene (0.50 g, 3.4 equiv.) at room temperature for 15 h. The crude product was chromatographed through silica gel (20 g), eluting with 1 : 1 ether–chloroform to afford the 1-*acetoxy*-4a,5,8,8a-*tetrahydro*-5,8-*methanobenzo*[c]*pyran*-4(1H,3H)-*one* (13) as a

* The numbering used in the n.m.r. assignments is shown in formulae (10), (11), (12), and is not the same as that used in the systematic names.

colourless oil (0.40 g, 80%); $\nu_{max.}$ 3 000 and 1 740 cm^{-1}; δ 1.45 (2 H, m, *J* 1.5, 3, 12 Hz, bridgehead H_2), 2.1 (3 H, s, acetate), 2.95 (1 H, m, C*H*·CH·OAc), 2.9 (1 H, m, C*H*·CH=CH), 3.05 (1 H, m, C*H*·CH=CH), 3.35 (1 H, m, CHCO), 3.9 (2 H, ABq, *J* 18 Hz, OCH_2), 5.65 (1 H, d, *J* 5 Hz, C*H*OAc), and 6.2 (2 H, m, vinylic H) (Found: C, 64.55; H, 6.2%; M^+ 222.089 22. $C_{12}H_{14}O_4$ requires C, 64.85; H, 6.35%; M^+ 222.089 202).

The above reaction, when repeated in the presence of triethylamine, also gave the cycloadduct (13) as the major product (75%).

(*f*) 2,3-*Dimethylbutadiene*. The acetate (3) (0.30 g) and 2,3-dimethylbuta-1,3-diene (0.70 g, 4.5 equiv.) in dichloromethane (2 ml) was cooled to 0 °C and triethylamine (0.3 g, 2 equiv.) added before the mixture was stirred at room temperature for 16 h. The solvent was removed under reduced pressure and the crude product chromatographed through silica gel (15 g) using 1 : 1 ether–light petroleum as eluant. Two fractions were collected. The less polar, major product, isolated as a colourless oil, was the 3,4-*dimethyl*-7-*oxabicyclo*[4.3.1]*deca*-3,8-*dien*-10-*one* (14) (0.14 g, 49%), $\nu_{max.}$ 2 940, 1 725, and 1 650 cm^{-1}; δ 1.75 (3 H, s, Me), 1.9 (3 H, s, Me), 2.25 (1 H, dd, *J* 4, 14 Hz, methylene H), 2.35 (2 H, m, methylene H), 2.75 (1 H, dd, *J* 8, 12 Hz, methylene H), 3.05 (1 H, m, *J* 1.8, 4, 9, 10 Hz, CH·CO), 4.45 (1 H, m, *J* 1.8, 4, 9 Hz, CHO), 4.5 (1 H, dd, *J* 6, 10 Hz, C*H*=CH–O), and 6.35 (1 H, d, *J* 6 Hz, O–C*H*=CH) (Found: C, 74.0; H, 7.95%; M^+ 178.0994. $C_{11}H_{14}O_2$ requires C, 74.15; H, 7.9%; M^+ 178.0994).

The more polar, minor component (22 mg, 8%), isolated as a colourless oil, was identified as the 6-*isopropenyl*-6-*methyl*-8-*oxabicyclo*[3.2.1]*oct*-3-*en*-2-*one* (16), $\nu_{max.}$ 2 980, 1 695, and 1 650 cm^{-1}; δ 1.0 (3 H, s, CH_3), 1.60 (1 H, dd, *J* 2.5, 14 Hz, 7-H), 1.7 (3 H, br s, CH_3), 2.2 (1 H, m, *J* 8, 14 Hz, 7-H), 4.6 (1 H, m, *J* 1.5, 2.5, 8 Hz, 1-H), 4.78 (1 H, m, vinyl H), 4.8 (1 H, d, *J* 4 Hz, 4-H), 4.9 (1 H, m, vinyl H), 5.95 (1 H, dd, *J* 1, 5, 11 Hz, 3-H), and 7.2 (1 H, dd, *J* 4, 11 Hz, 4-H) (Found: M^+ 178.098 82. $C_{11}H_{14}O_2$ requires M^+ 178.099 373).

(*g*) *Isoprene*. The acetate (3) (0.30 g) and 2-methylbuta-1,3-diene (0.80 g, 6 equiv.) in dichloromethane (1.5 ml) were stirred with triethylamine (0.34 g, 1.8 equiv.) at room temperature for 16 h before work-up in the normal manner. Chromatography through silica gel (20 g) using 1 : 1 ether–light petroleum as eluant afforded two fractions. The less polar oil was identified as the 2,4-cycloadducts (15) (0.11 g, 33%), which were not readily separable. The mixture showed $\nu_{max.}$ 2 940, 1 730, and 1 660 cm^{-1}. The ^1H n.m.r. spectrum showed the presence of a major and a minor isomer, ratio 3 : 2; the mixture has signals at δ 1.76 (3 H, s, Me, major isomer), 1.88 (3 H, s, Me, minor isomer), 2.05—2.75 (4 H, m, 2 × CH_2), 3.05 (1 H, m, HC=CH·C*H*·CO), 4.45 (1 H, m, –CH–O), 4.5 (1 H, m, OCH=C*H*), 5.53—5.55 (1 H, m, C*H*=CMe), and 6.36 and 6.37 (1 H, m, OC*H*=CH) (Found: C, 73.05; H, 7.4. $C_{10}H_{12}O_2$ requires C, 73.2; H, 7.3%).

The minor, more polar product from the column was the 6-*isopropenyl*-8-*oxabicyclo*[3.2.1]*oct*-3-*en*-2-*one* (17) (0.09 g, 29%) which showed $\nu_{max.}$ 2 980, 1 700, and 1 650 cm^{-1}; δ (400 MHz) 1.72 (1 H, m, *J* 2, 7, 14 Hz, 7-H), 1.80 (3 H, m, *J* 1, 3 Hz, Me), 2.50 (1 H, m, *J* 8, 10, 14 Hz, 7-H), 3.15 (1 H, m, *J* 1.5, 7, 7, 10 Hz, 6-H), 4.58 (1 H, m, *J* 1.5, 2, 8 Hz, 1-H), 4.74 (1 H, m, *J* 1.5, 3, 5 Hz, vinylic H), 4.86 (1 H, dd, *J* 5, 7 Hz, 5-H), 4.89 (1 H, m, *J* 1.5, 3, 5 Hz, vinylic H), 6.08 (1 H, dd, *J* 1.5, 11 Hz, 3-H), and 7.05 (1 H, dd, *J* 5, 11 Hz, 4-H) (Found: C, 72.85; H, 7.7%; M^+ 164.083 75. $C_{10}H_{12}O_2$ requires C, 73.1; H, 7.4%; M^+ 164.0837).

Cycloadditions with Methylated Pyranulose Acetate (4).—(*a*) *With ethyl vinyl ether*. 6-Acetoxy-2-methyl-2*H*-pyran-3(6*H*)-one (4) (2.0 g) and ethyl vinyl ether (7 g, 8 equiv.) in dichloromethane (4 ml) were stirred with triethylamine (3.5 g, 3 equiv.) at room temperature for 7 days. The solvents were removed under reduced pressure and the residue chromatographed on silica gel (150 g), using 1.5 : 1 ether–light petroleum as eluant, to afford 6-endo-6-*ethoxy*-1-*methyl*-8-*oxabicyclo*[3.2.1]*oct*-3-*en*-2-*one* (6) (0.90 g, 42%) as a pale yellow oil, $\nu_{max.}$ 1 695 cm^{-1}; δ 1.2 (3 H, t, *J* 7 Hz, CH_3CH_2), 1.5 (3 H, s, Me), 1.75 (1 H, dd, *J* 5, 14 Hz, C-7), 2.3 (1 H, dd, *J* 9, 14 Hz, 7-H), 3.5 (2 H, q, *J* 7 Hz, CH_3CH_2), 4.45 (1 H, m, *J* 5, 7, 9 Hz, 6-H), 4.75 (1 H, dd, *J* 5, 7 Hz, 5-H), 6.10 (1 H, d, *J* 10 Hz, 3-H), and 7.1 (1 H, dd, *J* 5, 10 Hz, 4-H) (Found: M^+ 182.094 288. $C_{10}H_{14}O_3$ requires M^+ 182.094 33).

(*b*) *Norbornene*. The acetate (6) (2.0 g) and norbornene (4.0 g, 3.6 equiv.) in acetonitrile (5 ml) were sealed in a thick-walled glass tube under vacuum (1 Torr) and heated at 145 °C for 16 h. The acetonitrile and excess of norbornene were removed under reduced pressure and the product chromatographed through silica gel (150 g), using 1 : 1 ether–light petroleum as eluant, to afford the 5-*methyl adduct* (12) (1.6 g, 67%) as a pale yellow oil, $\nu_{max.}$ 1 690 cm^{-1}; δ 0.8—2.4 (10 H, m), 1.35 (3 H, s, Me), 4.4 (1 H, d, *J* 5.5 Hz, 1-H), 5.85 (1 H, d, *J* 10 Hz, 10-H), and 7.3 (1 H, dd, *J* 5.5, 10 Hz, 11-H) (Found: C, 76.3; H, 8.2. $C_{13}H_{16}O_2$ requires C, 76.5; H, 7.85%).

4-exo-6-endo-6-*Ethoxy*-4-*methyl*-8-*oxabicyclo*[3.2.1]*octan*-2-*one* (18).—To a solution of lithium dimethylcuprate [prepared from cuprous iodide (3.4 g) and methyl-lithium–lithium bromide complex (23.5 ml of a 1.5M-solution in ether) in ether (70 ml)] at −20 °C, was added a solution of the adduct (5) (1.4 g) in ether (10 ml). The reaction mixture was stirred under N_2 at room temperature for 1.5 h, then poured into a saturated solution of NH_4Cl (50 ml) and extracted with ether (3 × 100 ml). The combined ether extract was washed with brine (50 ml) and water (50 ml) and then dried (Na_2SO_4), filtered and the solvent removed by evaporation under reduced pressure. The product was chromatographed through silica gel (100 g), using 1 : 1 ether–chloroform as eluant, to give the *title compound* (18) (1.44 g, 94%), $\nu_{max.}$ 2 960 and 1 730 cm^{-1}; δ 1.0 (3 H, d, *J* 7 Hz, Me), 1.2—2.6 (5 H, m, CH and CH_2), 1.15 (3 H, t, *J* 8 Hz, CH_3CH_2), 3.6 (2 H, q, *J* 8 Hz, CH_2CH_3), 4.2 (1 H, m, 6-H), 4.5 (1 H, dd, *J* 2, 9 Hz, 1-H), and 4.55 (1 H, d, *J* 8 Hz, 5-H) (Found: M^+ 184.109 96. $C_{10}H_{16}O_3$ requires M^+ 184.109 94).

4-exo-6-endo-4-*Methyl*-8-*oxa*-6-*phenylbicyclo*[3.2.1]*octan*-3-*one* (19).—To a solution of lithium dimethylcuprate (20 mmol, prepared as described above) in ether (150 ml) at −20 °C was added the cycloadduct (9) (2.0 g, 10 mmol) in ether (20 ml). The reaction mixture was stirred at room temperature for 1.5 h and then poured into 1M-hydrochloric acid (100 ml), extracted with ether (3 × 150 ml), washed with water (2 × 30 ml) and dried (Na_2SO_4). After filtration the solvent was removed under reduced pressure and the residue chromatographed through silica gel (150 g), using 1 : 1 ether–light petroleum as eluant, to afford the *title compound* (19) (2.1 g, 97%), m.p. 45 °C, $\nu_{max.}$ 1 720 cm^{-1}; δ 1.1 (3 H, d, *J* 7 Hz, Me), 1.15—2.8 (5 H, m), 3.9 (1 H, m, *J* 7, 8, 9.5 Hz, 6-H), 4.4 (1 H, dd, *J* 2, 8 Hz, 1-H), 4.55 (1 H, d, *J* 6.5 Hz, 5-H), and 7.25 (5 H, m, aromatic H) (Found: M^+ 216.114 88. $C_{14}H_{16}O_2$ requires M^+ 216.115 02).

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References

1 N. Dennis, B. Ibrahim, A. R. Katritzky, I. G. Taulov, and Y. Takeuchi, *J. Chem. Soc., Perkin Trans. 1*, 1974, 1883; A. R. Katritzky, J. Banerji, A. Boonyarakvanich, A. T. Cutler, N. Dennis, S. Q. Abbas Rizvi, G. J. Sabongi, and H. Wilde, *J. Chem. Soc., Perkin Trans. 1*, 1979, 399.

2 J. B. Hendrickson and J. S. Farina, *J. Org. Chem.*, 1980, **45**, 3359.

3 O. Achmatowicz, jun., B. Bukowski, B. Szechner, Z. Zwierzchowska, and A. Zamojski, *Tetrahedron*, 1971, **27**, 1973.

4 R. Huisgen, *J. Org. Chem.*, 1968, **33**, 2291; W. Bihlenaier, R. Huisgen, H. V. Reissing, and S. Voss, *Tetrahedron Lett.*, 1979, 261.

5 R. Sustmann, *Tetrahedron Lett.*, 1971, 2721 and 2727; J. M. Lluch and J. Bertran, *Tetrahedron*, 1982, **38**, 1847.

6 M. Hamaguchi, H. Matsuura, and T. Nagai, *J. Chem. Soc., Chem. Commun.*, 1982, 262.

7 J. B. Hendrickson and J. S. Farina, *J. Org. Chem.*, 1980, **45**, 3361.

8 P. G. Sammes and L. J. Street, *J. Chem. Soc., Chem. Commun.*, 1982, 1056.

9 J. Spanget-Larsen and R. Gleiter, *Tetrahedron Lett.*, 1982, 2435.

10 K.-L. Mok and M. J. Nye, *J. Chem. Soc., Chem. Commun.*, 1974, 608.

11 S. A. Sisk and C. R. Hutchinson, *J. Org. Chem.*, 1979, **44**, 3500.

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