Tetrahedron Letters Vol. 21, pp 3513 - 3516
© Pergamon Press Ltd. 1980. Printed in Great Britain

0040-4039/80/0901-3513$02.00/0

INTRAMOLECULAR DE MAYO REACTIONS LEADING TO ZIZAANE AND RELATED TERPENCID RING SYSTEMS

Andrew J. Barker and Gerald Pattenden*

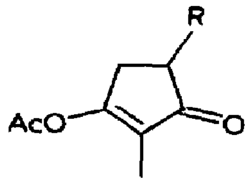
Department of Chemistry, The University,
Nottingham, NG7 2RD

Summary Further aspects of the regioselectivity of intramolecular photocycloadditions amongst enolised cyclopentane-1,3-diones are defined; elaboration of the cycloadduct (15) derived from (14) provides an expeditious route to the zizaane ring system (17).

THE synthesis of bicyclo[3.2.1]octenones from cyclopentane-1,3-dione enol acetates, based on intramolecular photocycloaddition and Grob fragmentation of the resulting cycloadducts[1], shows considerable promise as a flexible route to this important ring system, found in several groups of natural terpenoids, e.g. zizaane, cedrane, gibberellane. In this paper, we describe some new features of the regioselectivity of the intramolecular photocycloadditions, and application of the sequence in elaborating the zizaane ring system (viz. 17) present in several sesquiterpenoids isolated from vetiver oil.[2]

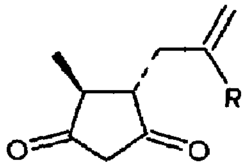
Analysis of ^{1}H and ^{13}C magnetic resonance data of a number of enol acetates derived from 2,4-disubstituted cyclopentane-1,3- diones (Ac_2O - NaOAc, 25°), shows that these compounds exist in the single isomeric form shown in (1). By contrast, cyclopentane-1,3-diones which lack a C-2 methyl substituent give rise to mixtures of enol acetates (viz. 2 and 3).

Irradiation of a 1 : 1 mixture of enol acetates derived from cyclopentanedione (4a) was previously shown to lead to the crystalline cycloadduct (5a; 62%), whose syn-stereochemistry followed from X-ray measurements.[1] The minor product (16%) from this irradiation has now been confirmed as the anti-epimeric structure (6a) by conversion to the same mixture of epimers of the bicyclo-octanedione (7a) produced from (5a), after saponification - retro aldolisation (5% KOH-EtOH, 0-5°, 2 h). In a similar manner, irradiation of the 3 : 2 mixture of enol acetates obtained from dione (4b) led to a 5 : 4 mixture of syn- and anti-epimers, (5b) and (6b), of the corresponding tricyclic adduct (72%), which after conversion to the acetate-mesylate (8) ($NaBH_4$-MeOH, 0°; then CH_3SO_2Cl-Et_3N), followed by saponification and fragmentation, gave (40%) the angular methyl substituted bicyclo-octenone (9), ν_{max} (film) 1735 cm^{-1},

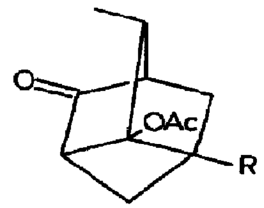


(1)

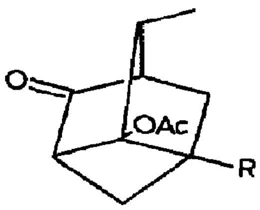
(2) (3)



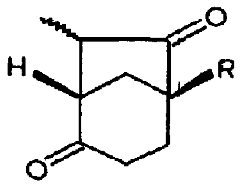
(4)



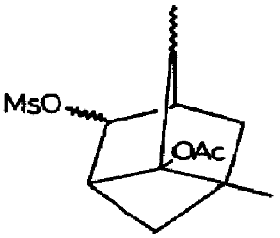
(5)



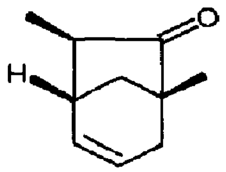
(6)



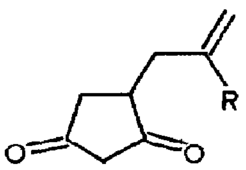
(7)



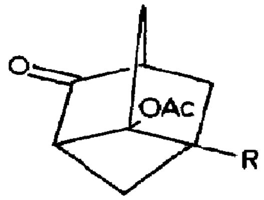
(8)



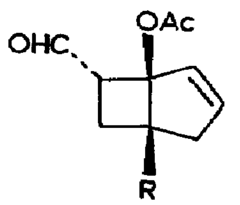
(9)



(10)



(11)



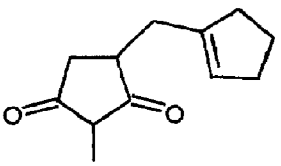
(12)

a R = H; b R = Me

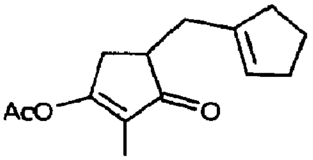
τ4.07 m (:CH), 4.43 dt (J 9 and 3, $:CHCH_2$), 7.1 - 7.6 m (2H), 7.85 - 8.2 m (4H), 8.83(Me), 8.92 d (J 7, CHMe). Irradiation of mixtures of enol acetates derived from the less substituted cyclopentanediones (10a) and (10b)[3] gave rise to single cycloadducts corresponding to (11a, 80%) and (11b, 40%) respectively; these adducts were found to be more photo-labile than (5/6), and rapidly underwent fragmentation to bicyclo[3.2.0]heptenes (12).

In the examples cited above and elsewhere[1], the intramolecular de Mayo reactions thus show considerable regioselectivity, irrespective of the compositions of the cyclopentanedione enol acetates. This feature suggests that equilibration between the enol acetates (2) and (3) must be rapid during the irradiations.

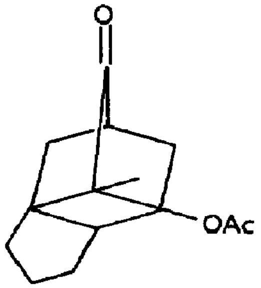
Acetylation of the 2,4-disubstituted cyclopentane-1,3-dione (13)[3], m.p. 107 - 110° gave rise to a single enol acetate, assigned constitution (14), ν_{max} 1765, 1700, 1660 cm^{-1}, τ8.37 t (J 1.5, :CMe). Irradiation of (14) in hexane in the usual manner led to one major photoproduct (82%), an oil showing spectral data, ν_{max} 1760, 1730 cm^{-1}, τ 7.97(OAc), 8.93(Me), consonant with structure (15), resulting from the *alternative mode* of intramolecular cycloaddition in (14). Reduction with NaBH$_4$ led to the corresponding carbinol which was converted into the mesylate (16), τ5.31 m (CHO), 7.25 - 8.9 m (12H), 7.91, 7.93(OAc), 8.85, 8.99 (Me). Saponification and fragmentation then led (33%) to the alkene (17), an oil ν_{max} 1705, 1660 cm^{-1}, τ4.41(:CH), 7.29(CH•CO), 7.4 - 8.8 m (9H), 8.33(:CMe) containing the zizaane ring system.[4]



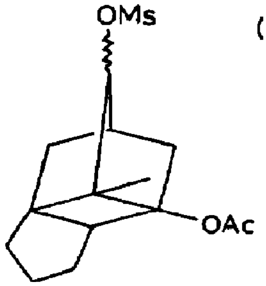
(13)



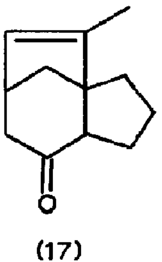
(14)



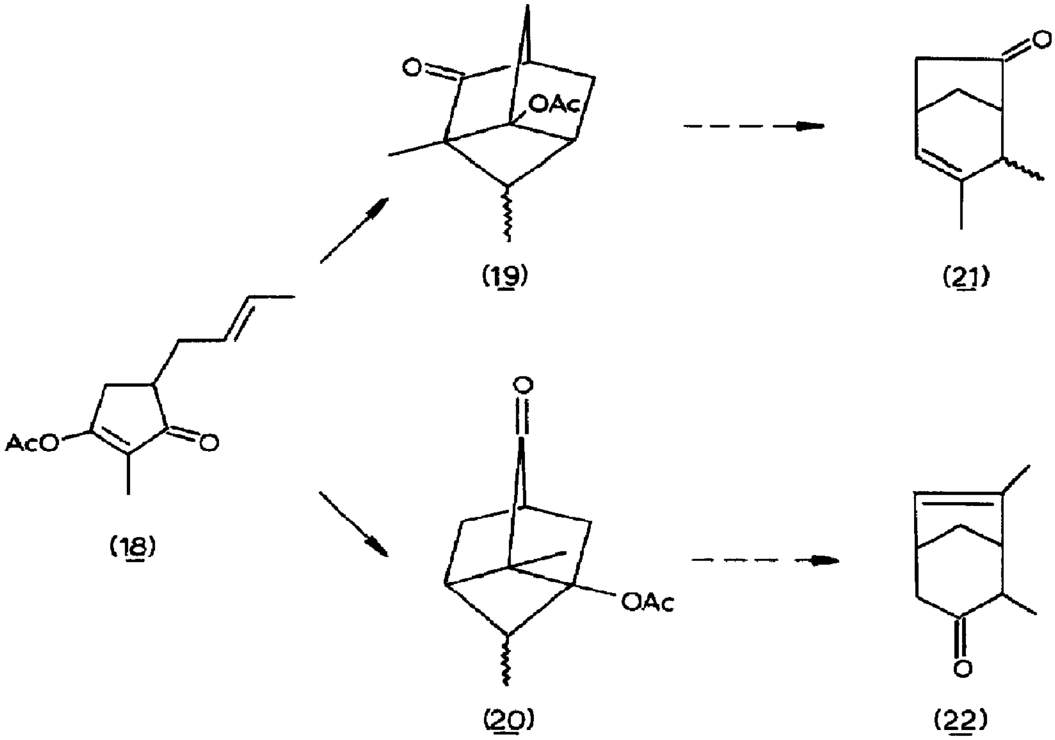
(15)



(16)



(17)



In the case of the enol acetate (18), irradiation produced a favourable 2:3 mixture of the isomeric photoadducts (19), ν_{max} 1740 cm^{-1}, τ7.84 (OAc), 8.95 (Me), 8.76, 9.22 d (*J* 7.5, CHMe), and (20), ν_{max} 1765, 1738 cm^{-1}, τ7.96 OAc), 8.7 d (*J* 7, CHMe), 8.75 (Me), to allow their easy separation and characterisation. The constitutions of the photoadducts were established unambiguously after fragmentation of each to the corresponding bicyclo-octenones (21), ν_{max} 1735, 1650 cm^{-1}, τ 8.42 (:CMe) 8.9, 9.0 d (*J* 7, CHMe), and (22), ν_{max} 1705, 1638 cm^{-1}, τ8.22 (:CMe), 8.92 d (*J* 7, CHMe) respectively, and correlation of their spectral properties.

We thank the S.R.C. for a studentship (to A.J.B.).

References

1. M. Mellor, D.A. Otieno and G. Pattenden, J.C.S. Chem. Comm., 1978, 138.
2. For recent approaches to the zizaane ring system see: E. Piers and J. Banville, J.C.S. Chem. Comm., 1979, 1138 and refs. cited therein.
3. M. Mellor and G. Pattenden, Synth. Comm., 1979, 1.
4. For an approach using a cyclopentanedione enol ether see: W. Oppolzer and S.C. Burford, Helv. Chim. Acta, 1980, 63, 788.

(Received in UK 27 June 1980)