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INTRAMOLECULAR OLEFIN METATHESIS OF TRICYCLIC BRIDGED DIENONES. REGIOSPECIFIC AND REVERSIBLE CYCLOREVERSION OF TRISHOMOCUBANONES TO CIS,SYN,CIS-TRICYCLOPENTANOIDS

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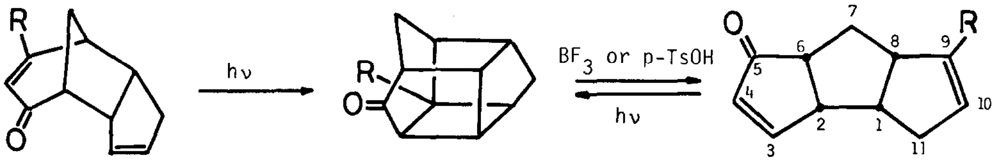
Summary: Trishomocubanones derived via photochemical [2+2] cycloaddition from 10-substituted tricyclo[5.3.1.0^{2,6}]undeca-4,9-dien-8-ones were converted to cis,syn,cis-tricyclo[6.3.0.0^{2,6}] undecane derivatives by regiospecific acid catalyzed cycloreversion. The products easily underwent cyclization back to the trishomocubanes on exposure to sunlight.

In a previous paper, we reported intramolecular photoreactions of tricyclic bridged dienones such as the compounds **1** giving trishomocubane derivatives **2** as the major products.[1] In connection with this, we wish here to report a regiospecific acid catalyzed cycloreversion of the photoadducts **2** to cis,syn,cis-tricyclo[6.3.0.0^{2,6}]undecane (triquinane) derivatives **3**, which easily cyclize back to **2** on exposure to sunlight. This reaction provides an alternative way to the preparation of tricyclopentanoid system[2] and a novel preliminary model for light energy storage. During the course of our study, Mehta and co-workers described the photochemical formation of the trishomocubanes from cis,syn,cis-triquinane bis-enones and acid-induced cycloreversion of these cage compounds to their precursor bis-enones.[3]



1 **2** **3**

a: R=Ph, b: R=Me, c: R=H

Treatment of cage compound **2a**[1] with BF$_3$ etherate in benzene at room temperature for 30 min led to nearly quantitative formation of **3a**. The cycloreversion reaction was also accomplished by refluxing in toluene for 24 hours. The structure of **3a** was revealed by its spectral characteristics: IR (CHCl$_3$) 1695 cm^{-1} ; ^{1}H NMR (CDCl$_3$) δ 7.62 (1H, dd, J=5, 3 Hz), 7.26 (5H, br s), 6.00 (1H, dd, J=5, 2 Hz), 5.79 (1H, m) ppm; ^{13}C NMR (50 MHz, $CDCl_3$) δ 212.0 (s), 164.5 (d), 146.7 (s), 136.0 (s), 132.8 (d), 128.4(2C, d), 127.1(d), 126.1(2C, d), 125.0 (d), 54.8(d), 53.1(d), 50.2(d), 45.1 (d), 34.3(t), 31.0 (t); UV (EtOH) λ_{max} 219 (ε=14760), 247 nm (ε=9050); M^+ m/e 236.

The formulation of 3a was supported more clearly by its facile and quantitative cyclization to 2a on irradiation in benzene solution in a Pyrex tube by a 500-W high pressure mercury lamp or by exposure to sunlight.

Similarly, compound 2b and 2c were converted to the tricyclic dienone 3b[4] and 3c[5], respectively, though they required longer reaction time or higher temperature (p-TsOH/Bz, r.t., 6 hr for 2b$\rightarrow$3b; BF_3/Bz, refluxing temp., 6 hr for 2c$\rightarrow$3c). Both compounds also reverted back to the corresponding cage ketones almost quantitatively on irradiation in the same manner.

The effective photocyclization of 3a-3c by sunlight can be accounted for by their n-π^* absorption bands at 310-360 nm (cyclohexane, log ε 1-2). The quantum yields for the formation of 2a-2c at ca 330 nm in cyclohexane were 0.74, 0.54, and 0.53, respectively (potassium ferrioxalate actinometry using a 500 W xenon lamp in Shimadzu spectrofluorophotometer RF-501S).

References

1. T. Ogino and K. Awano, Chem. Lett., 1982, 891.
2. For another example of the formation of cis,syn,cis-tricyclopentanoid derivatives via intramolecular photo-thermal metathetic sequence, see G. Mehta, A.V. Reddy, and A. Srikrishna, Tetrahedron Lett., 1979, 4863; G. Mehta and A.V. Reddy, J. Chem. Soc., Chem. Commun., 1981, 756.
3. G. Mehta and A. Srikrishna, J. Chem. Soc., Chem. Commun., 1982, 218.
4. IR ($CHCl_3$) 1690, 1580 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.64 (1H, dd, J=6, 3 Hz), 5.96 (1H, dd, J=6, 2 Hz), 5.04 (1H, br s), 1.58 (3H, br s) ppm; ^{13}C NMR ($CDCl_3$) δ 213.0 (s), 164.8 (d), 143.1 (s), 132.7 (d), 124.0 (d), 56.5 (d), 52.9 (d), 50.1 (d), 44.7 (d), 33.8 (t), 28.1 (t), 14.4 (q) ppm; UV (EtOH) λ_{max} 220 (ε=9000) nm; M^+ m/e 174.
5. IR ($CHCl_3$) 1695, 1585 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.65 (1H, dd, J=6, 3 Hz), 5.97 (1H, dd, J=6, 2 Hz), 5.49 (2H, br s) ppm; ^{13}C NMR ($CDCl_3$) δ 212.9 (s), 164.5 (d), 135.8 (d), 133.2 (d), 129.8 (d), 54.0 (d), 52.9 (d), 50.0 (d), 44.0 (d), 35.0 (t), 30.5 (t) ppm; UV (EtOH) λ_{max} 213 (ε=13900) nm; M^+ m/e 160.

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