Tetrahedron Letters,Vol.25,No.21,pp 2275-2278,1984 0040-4039/84 $3.00 + .00
Printed in Great Britain

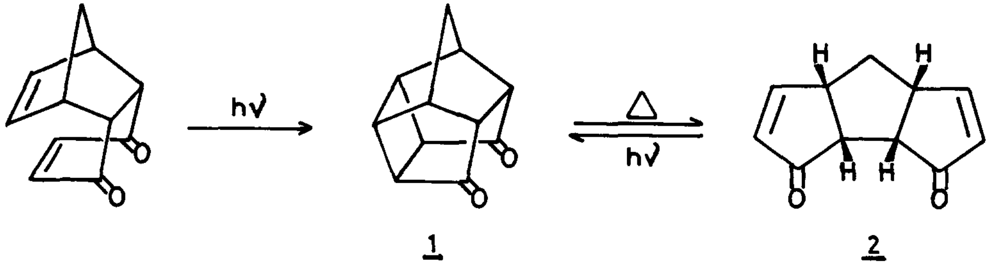
LEWIS ACID CATALYSED [2+2] CYCLOREVERSION OF COOKSON'S CAGE KETONES UNDER AMBIENT CONDITIONS: MODEL SYSTEM FOR LIGHT ENERGY CONVERSION

Goverdhan Mehta*, D. Sivakumar Reddy and A. Veera Reddy
School of Chemistry, University of Hyderabad
Hyderabad 500134, India

Abstract: Design of 'push-pull' Cookson's cage ketones and their quantitative [2+2] cycloreversion to cis, syn, cis-triquinanes at room temp, under Lewis acid catalysis, is reported. This observation has promising ramifications on the utility of 1 ⇄ 2 system for reversible storage of solar energy.

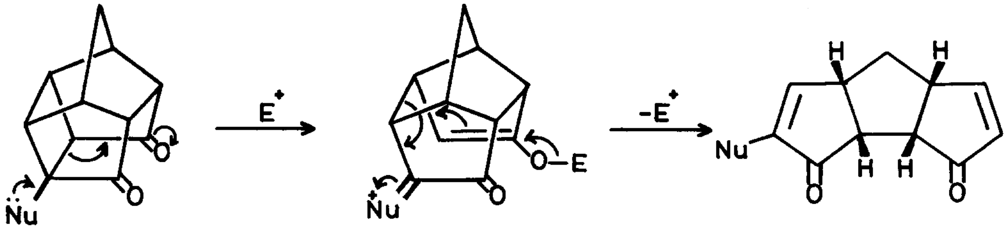
Since the initial discovery[1] of the photo-thermal metathesis sequence depicted in Scheme 1, we have demonstrated the generality[2] and applicability of this theme in the syntheses of naturally occurring triquinanes[3] as well as polyquinane fragments of dodecahedrane.[4] Another facet of Scheme 1, which attracted our attention was the reversible nature of the key 1 ⇄ 2 change with prospects for solar energy storage[5] in the strained pentacyclic molecule 1. In order to 'tap' energy from 1 in a meaningful way, it was necessary to chemically manipulate it in such a manner that 1 → 2 conversion could be accomplished catalytically and at room temp. instead of the 150-560° temp. regimen previously employed by us.[2,6] This required development of a conceptually new strategy for effecting the 1 → 2 change and is depicted in Scheme 2. In this letter, we delineate an efficient realisation of Scheme 2 which significantly amplifies the synthetic utility of 1 → 2 change and renders it amenable for exploitation as a light energy storage system.

Scheme 1

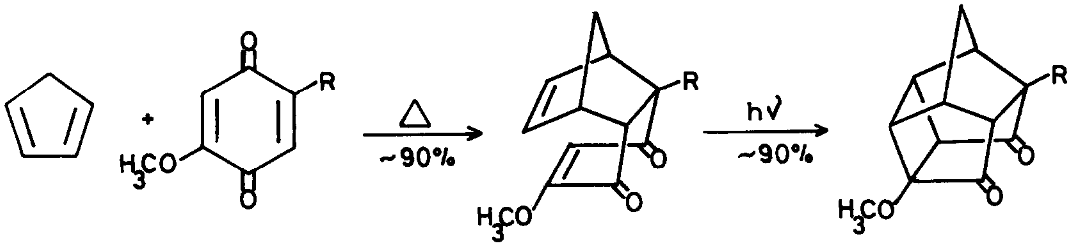


The 'push-pull' substituted pentacyclic diones 3 and 4 were efficiently synthesised in a straightforward manner as indicated.[10] Exposure of a dichlorometnane or benzene solution of either 3 or 4 to catalytic amounts of BF_3-etherate at ambient temp. (25-30°) led to instant conversion to cis, syn, cis-bis-enones 5 and 6, respectively, in quantitative yield.[10] The cycloreversion of 3 and 4 could

Scheme 2

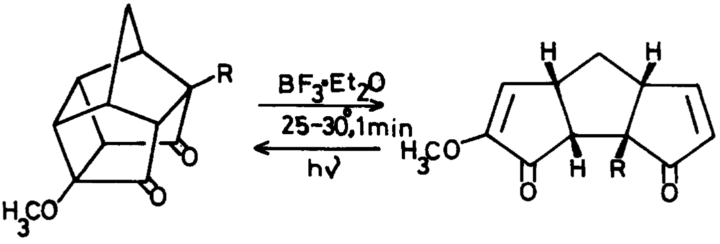


also be brought about by a variety of other Lewis acids like SnCl$_4$, TiCl$_4$ and AlCl$_3$ with comparable outcome but protic acids like p-TSA, TFA and Nafion-H proved inefficient. Several, more adorned



3 R=H
4 R=CH_3

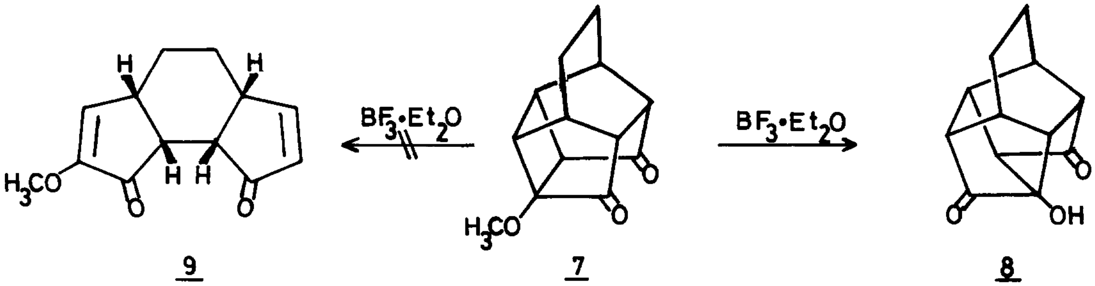
derivatives of 3 and 4 responded in an analogous manner to Lewis acid catalysis and established the generality of the reaction. Finally, the triquinane bis-enones 5 and 6 on either exposure to Sunlight (pyrex, EtOAc) or irradiation through a 450 W UV lamp (pyrex, EtOAc) cage cyclised back to 3 and 4, in high yield.



3 R=H
4 R=CH_3

5 R=H
6 R=CH_3

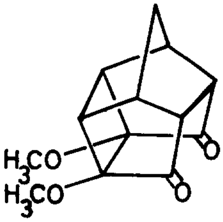
The pentacyclo [5.4.0.0^{2,6}.0^{3,10}.0^{5,9}] undecan-8,11-dione ring system present in 3 and 4 seems to be endowed with optimal stereo-electronic requirement for the facile [2+2] cycloreversion. The higher homologue 7[10,11] of 3 on treatment with BF$_3$-etherate furnished only the pentacyclic hydroxy-dione 8 and no expected[12] cycloreversion product 9 was encountered.



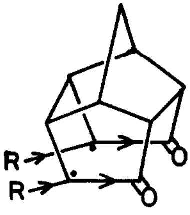
Acknowledgements: We thank SERC, Department of Science and Technology and CSIR, Govt. of India for financial support of this work.

References and Notes:

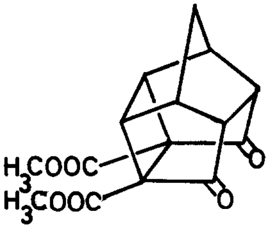
1. G. Mehta, A.V. Reddy and A. Srikrishna, Tetrahedron Letts., 1979, 4863; G. Mehta, J. Chem. Educ., 1982, 57, 313.
2. (a) G. Mehta, A. Srikrishna, A.V. Reddy and M.S. Nair, Tetrahedron, 1981, 37 4543; (b) A.V. Reddy, Ph.D. Thesis, University of Hyderabad, May, 1982.
3. G. Mehta and A.V. Reddy, J. Chem. Soc., Chem. Commun., 1981, 756; G. Mehta, A.V. Reddy, A.N. Murthy and D.S. Reddy, ibid, 1982, 540; G. Mehta, D.S. Reddy and A.N. Murthy, ibid, 1983, 824.
4. G. Mehta and M.S. Nair, ibid, 1983, 439.
5. H.D. Scharf, J. Fleischauer, H. Leissmann, I. Ressler, W. Schleker and R. Weitz, Angew. Chem. Intl. Ed., 1979, 18, 652 and references cited therein.
6. We have shown[2a,b] that electron donating substituents (i) at C_1 and C_7 on the pentacyclic dione 1 significantly mellow and accelerate the thermal [2+2] cycloreversion to 2 and attributed[2b,7] this pronounced effect to the capto-dative stabilisation[8] of the intermediate diradical species (ii). In keeping with this explanation, we also observed that electron withdrawing groups (iii) at C_1 and C_7 disfavoured the cycloreversion.[2b] These findings have recently been further extended by Okamoto et.al.[9] However, the dramatic results described in this communication raise the question, howmuch 'radical like' are the thermal cycloreversions of 'push-pull' substituted caged diketones, e.g., 3 and 4? We are currently evaluating this aspect and will be reporting our findings in the near future.



(i)



(ii)



(iii)

7. See, the detailed footnote 26 and Table 2 in ref. 2a.

8. H.G. Viehe, R. Merenyi, L. Stella and Z. Janousek, Angew. Chem., Intl. Ed., 1979, 18, 917.

9. Y. Okamoto, K. Kanematsu, T. Fujiyoshi and E. Osawa, Tetrahedron Letts., 1983, 5645.

10. All new compounds reported here were fully characterised on the basis of their spectral data. Selected spectral data for some compounds is summarised here. 3, mp. 85°, ^{1}H nmr (100 MHz, $CDCl_3$): δ 3.43(3H,s), 3.0-3.3(2H,brs), 2.7-3.0(3H,m), 2.6(2H,brs), 2.0(2H,brs); ^{13}C nmr (25 MHz, $CDCl_3$): δ 210.7(s), 209.8(s), 82.1(s), 54.7(q), 53.2(d), 50.7(d), 48.5(d), 43.9(2C,d), 43.0(d), 41.9(t), 36.3(d). 4, mp 78°, ^{1}H nmr(100 MHz, $CDCl_3$): δ 3.4(3H,s), 1.84-3.24(8H,m), 1.08(3H,s); ^{13}C nmr (25 MHz, $CDCl_3$): δ 211.5(s), 210.6(s), 81.7(s), 58.5(s), 58.1(d), 53.0(q), 49.2(d), 47.5(d), 44.0(d), 41.9(d), 40.3(t), 34.7(d), 16.4(q). 5, mp 107°, ^{1}H nmr(100 MHz, $CDCl_3$): δ 7.49(1H,dd,J_1=6Hz,J_2=3Hz), 6.13 (1H,d,J=3Hz), 5.9(1H,dd,J_1=6Hz,J_2=3Hz), 3.63(3H,s), 3.48(2H,m), 3.3(2H,brs), 2.3(1H,td,J_1=14Hz, J_2=9Hz), 1.85(1H,d,J=14Hz); ^{13}C nmr(25 MHz, $CDCl_3$): δ 207.1, 200.0, 166.5, 156.1, 132.8, 128.8, 57.1, 53.5, 52.1, 50.5, 43.9, 32.7. 6, mp 102-3°, ^{1}H nmr(100 MHz, $CDCl_3$): δ 7.42(1H,dd,J_1=6Hz, J_2=3Hz), 6.28(1H,d,J=3Hz), 5.86(1H,dd,J_1=6Hz,J_2=3Hz), 3.68(3H,s), 1.8-3.6(5H,m), 1.42(3H,s); ^{13}C nmr (25 MHz, $CDCl_3$): δ 208(s), 199.9(s), 164.0(d), 155.2(d), 131.0(d), 129.4(d), 59.4(s), 59.0(d), 57.1(q), 56.7(d), 42.7(d), 31.4(t), 21.1(q). 7, mp 105°, ^{1}H nmr(100 MHz, $CDCl_3$): δ 3.43(3H,s), 3.06(3H,br), 2.48(2H,br), 2.2(2H,br), 1.8(4H,m); ^{13}C nmr(25 MHz, $CDCl_3$): δ 209.7, 208.6, 84.6, 52.8, 52.5, 47.8, 44.6, 39.0, 32.3, 30.9, 30.3, 16.5, 16.2. 8, mp 204°, ir(KBr): 3310, 1770 cm^{-1}; ^{13}C nmr(25 MHz, $CDCl_3$): δ 209.3, 208.9, 79.3, 49.9, 41.6(2c), 38.9, 33.2, 32.2, 30.3, 18.0, 17.3.

11. Compound 7 was assembled in two steps from 1,3-cyclohexadiene and methoxy-p-benzoquinone via Diels-Alder reaction and photochemical [2+2] cycloaddition.

12. G. Mehta, A.V. Reddy and A. Srikrishna, Ind. J. Chem., 1981, 20B, 698.

(Received in UK 20 March 1984)