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LETTERS

A Novel Isomerization of 6,6-Tetramethylenefulvene to Cyclopent-1-enyl Cyclopentadiene and its Cycloaddition Reactions: Synthesis of Polycyclic Molecular Frameworks

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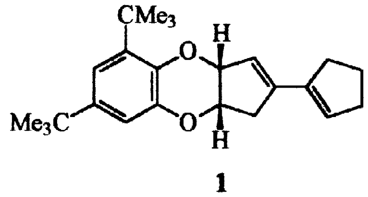
***Abstract*:** The acid catalysed isomerization of 6,6-tetramethylenefulvene to cyclopent-1-enyl cyclopentadiene and the reactions of the latter with various dienophiles leading to novel polycycles are reported.

Ever since the discovery of fulvenes,[1] these compounds have been the subject of extensive investigations both from the standpoints of theory[2] and organic synthesis.[3] FMO considerations have led to the delineation of a well-defined reactivity profile of fulvenes in cycloadditions.[4] The current interest in the use of fulvenes as synthons for substituted cyclopropanes[5] and vinylfulvenes,[6] their electrocyclic closure to dihydropentalenes[7], and the observation of remote substituent effects in the reactivity and stereoselectivity of Diels-Alder reactions involving fulvenes[8] are worthy of note.

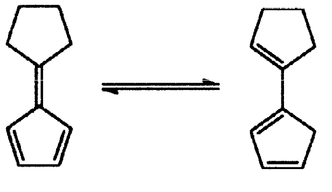
During the course of our investigations on the cycloaddition of *o*-quinones to electron rich dienes,[9] we observed an anomalous product **1** resulting from the reaction of 3,5-di-*tert*-butyl-*o*-benzoquinone and 6,6-tetramethylenefulvene **2**. The structure of **1** was established by X-ray crystallography.

Although we surmised that **1** arises from the hetero Diels-Alder reaction of 3,5-di-*tert*-butyl-*o*-benzoquinone with cyclopent-1-enyl cyclopentadiene **3**, the latter resulting from the isomerization of **2**, no direct proof for this was forthcoming and such an isomerization was without precedent[10]. Subsequently after much fruitless experimentation, we have been able to isolate **3** and investigate its Diels-Alder cycloaddition and our preliminary results are presented here.

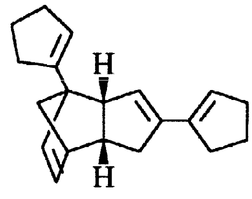


1

6,6-Tetramethylenefulvene **2** obtained by the pyrrolidine catalyzed condensation of cyclopentanone and cyclopentadiene, on treatment with a trace amount of acetic acid under carefully controlled conditions,[11] smoothly rearranged to cyclopent-1-enylcyclopentadiene **3**. It may be noted that semi empirical calculations revealed a difference in the heat of formation between **2** and **3** which is of the order of 4.9 kcal/mol. As expected of an activated cyclopentadiene, **3** readily undergoes dimerization to **4**.



2 **3**



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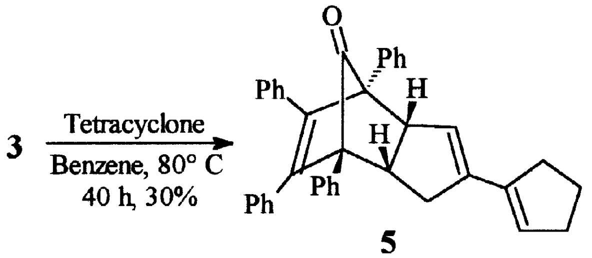
A benzene solution of **3** on heating with tetracyclone afforded an adduct in 30% isolated yield for which structure **5** has been assigned on the basis of spectral and analytical data.[12,13] Final proof for the structure was obtained by single crystal X-ray determination.[14] A considerable amount of the dimer **4** was also isolated.



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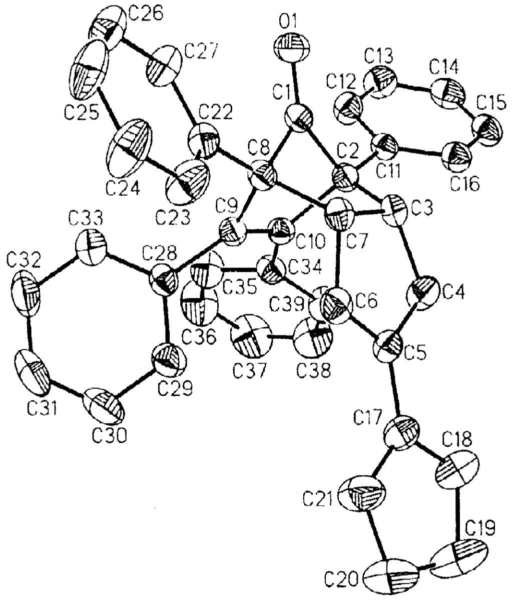
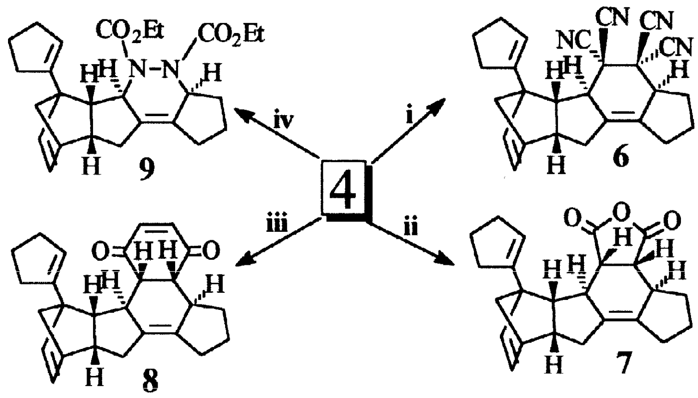


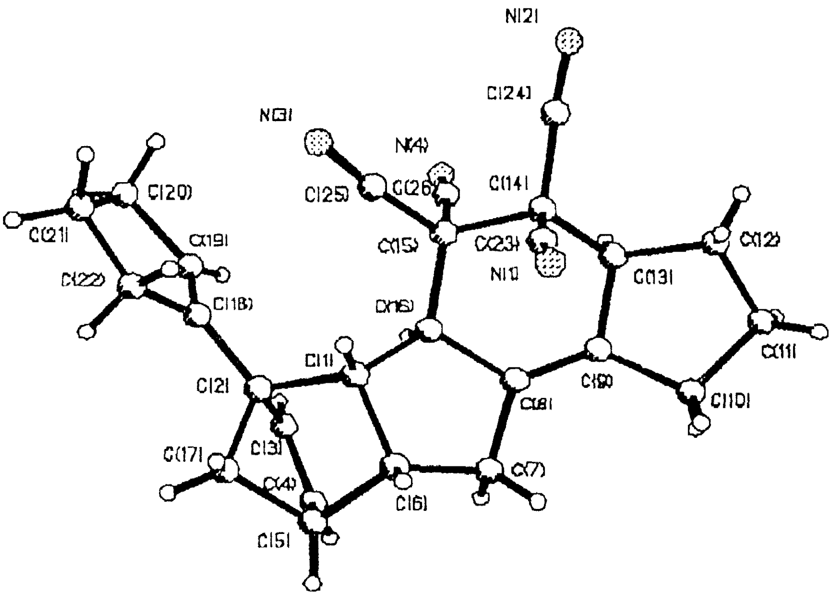
X-Ray Crystal structure of 5

Subsequently, the cycloadditions of **3** with maleic anhydride, TCNE,[15,16] DEAD and *p*-benzoquinone were investigated. In these cases **3** undergoes rapid dimerization by the Diels-Alder route; the dimer then participates in a subsequent Diels-Alder reaction with the added dienophile (Scheme 1).



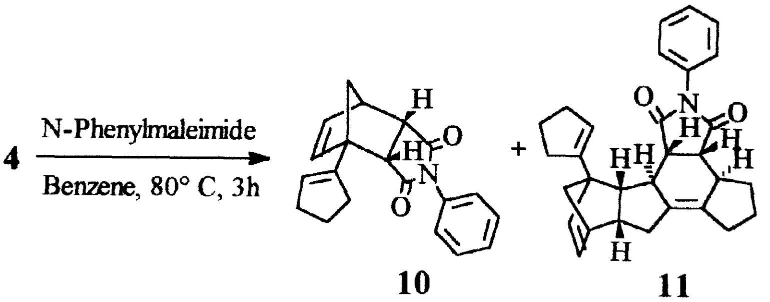
Scheme 1

i) TCNE, Benzene, RT, 45 min., 52%; ii) Maleic anhydride, Benzene, 80° C, 66%; iii) *p*-benzoquinone, RT, 24h, 44%; iv) DEAD, Benzene, RT, 1h, 46%



X-Ray crystal structure of 6

Interestingly the reaction of **3** with N-phenylmaleimide gave two products, **10** resulting from **3** and the other one **11** arising from the dimer **4** in 18% and 30 % yields respectively.[17]



In conclusion, we have uncovered a novel isomerization of 6,6-tetramethylenefulvene to cyclopent-1-enylcyclopentadiene. The dimerization of **3** followed by the cycloaddition of the dimer to dienophiles offers a convenient route to complex polycyclic arrays; the latter are potentially amenable to further transformations to a variety of interesting structures including polyquinanes. The MNDO calculations indicate that these reactions are HOMO diene controlled.

Acknowledgements

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10. The formation of bis cyclopentenyl ferrocene from **2** has been shown to occur *via* sodium (cyclopentylidene)cyclopentadienide. (Reinhart, K. L., Frerichs, A. K., Kittle P. A., Westman, E. F., Gustafson, D. H., Pruett, R. L., and McMahan, J. E., *J. Am. Chem. Soc.* 1960, **82**, 4111). However, to date there are no reports on the isolation and cycloaddition of **3**.
11. To a mixture of 1.951g (23.2 mmol) cyclopentanone and 4.02 g (60.1 mmol) cyclopentadiene, 2.556 g (35.9mmol) pyrrolidine was added dropwise at ice temp. After 1h, it was treated with a slight excess of acetic acid, stirred for 30 min, usual work up gave the crude product which on chromatography on silica gel afforded **3** (2.81g).
12. **General Experimental Procedure**: Cyclopent-1-enylcyclopentadiene and the respective diene or dienophile in dry benzene were treated for the time and temperature specified. Removal of the solvent and chromatography on silica gel with pet..ether ethyl acetate mixture afforded the respective adducts.
13. **Spectral data for 4**. ν_{max} (CCl_4 film) cm^{-1} 3049, 2962, 2929, 2897, 2847, 1613, 1452, 1344, 1249, 1027, 926, 818, 771; δ_H (90 MHz, $CDCl_3$): 6.0 (m, 2H), 5.5 (m, 3H), 3.2 (m, 1H), 2.85 (m, 2H), 2.3 (m, 8H), 1.9 (m, 4H), 1.4 (m, 4H); δ_C (22.4 MHz, $CDCl_3$): 135.95, 135.80, 132.22, 132.10, 131.83, 131.74, 127.92, 126.19, 54.89, 54.71, 50.41, 50.20, 46.30, 45.58, 41.43, 34.87, 34.57, 32.87,32.72,23.08 **Data for 5**: m.p. 184-186 °C; ν_{max} (KBr) cm^{-1}: 2932, 2851, 1770, 1595, 1488, 1434, 1078, 735 and 702; δ_H (300 MHz, $CDCl_3$): 7.513-7.426 (m, 2H), 7.426-7.20(m, 8H), 7.00-6.80 (m, 6H), 6.70-6.534 (m, 4H), 5.90 (s, 1H), 5.60 (s, 1H), 4.353- 4.253 (d, 1H), 3.653- 3.553 (m, 1H), 3.987-2.813 (m, 2H), 2.626-2.274 (m, 4H), 1.966-1.813 (m, 2H); δ_C (50 MHz, $CDCl_3$): 201.538, 145.299, 142.746, 141.016, 139.369, 136.087, 135.822, 135.272, 134.873, 130.439, 130.065, 129.373, 129.624, 128.238, 127.592, 127.427, 127.256, 127.175, 126.753, 126.533, 124.471, 66.816, 65.972, 52.936, 42.291, 36.699, 33.343, 32.932, 23.237. Anal. Calcul. for $C_{39}H_{32}O$: C, 90.66, H, 6.24; Found: C, 91.07, H, 6.22
14. **Crystallographic data for 5**: Triclinic, P1, a = 9.4620 (10) Å, b = 12.6260 (10) Å, c=13.569 (2) Å, α = 63.970 (10)°, β= 84.120 (10)°, γ = 87.070 (10)°, V = 1448.9 (3) $Å^3$, Z = 2, Density = 1.184 Mg/m^3, Temp = 298 K,R1 = 0.0561, wR2 = 0.1247, Formula weight = 516.65, No. of unique reflections = 4738, Radiation source = MoKα (λ = 0.71073Å)
15. **Data for 6** :mp. 204 -206° C; ν_{max} (KBr)/cm^{-1}: 2976, 2902, 2853, 2252, 1469, 1433 and 747; δ_H (300 MHz, $CDCl_3$):6.32-6.30 (m, 2H), 5.72-5.71 (t, 1H), 3.00-2.90 (m, 5H), 2.60-2.27 (m, 8H), 1.96-1.50 (m, 8H); δ_C (22.4 MHz, $CDCl_3$): 142.63, 138.28, 137.08, 136.61, 131.59, 126.37, 111.78, 110.83, 58.59, 56.20, 55.13, 47.82, 47.31, 46.00, 45.76, 44.00, 43.88, 32.69, 31.35, 28.99, 22.67, 22.19. Anal. Calcd. for $C_{26}H_{24}N_4$: C, 79.56; H, 6.16; N, 14.27. Found: C, 79.437; H, 6.159; N, 14.005.
16. **Crystallographic data for 6** : Monoclinic, $P2_{1/n}$, a = 7.850(2)Å, b = 18.988(4)Å, c = 14.065(3)Å, α = 90°, β = 90.45°, γ = 90°, Z = 4, Density = 1.244Mg/m^3, Temp = 293 K, R1 = 0.1404, wR2 = 0.3444, Formula weight = 392.49, No. of unique reflections = 4361, Radiation source = Mo Kα (λ = 0.71073 Å).
17. **Data for 10**: **mp.** 121-123° C. ν_{max} (KBr) cm^{-1}: 2851, 1713, 1598, 1500, 1382, 1186 and 744; δ_H (90 MHz, $CDCl_3$): 7.4-7.1 (m, 5H), 6.35 (s, 2H), 5.9 (m, 1H), 3.5 (m, 3H), 2.5 (m, 4H), 2.0 (m, 2H), 1.8 (d, 2H); δ_C (22.4 MHz, $CDCl_3$): 176.32, 175.60, 141.80, 137.08, 133.98, 131.80, 128.73, 128.22, 126.82, 126.40, 59.36, 56.59, 48.35, 47.55, 45.16, 33.35, 32.51, 23.14. HRMS, Calcd. for $C_{20}H_{19}O_2N$: 305.14157; Found: 305.14092. **Data for 11**: ν_{max} (KBr) cm^{-1}: 2869, 1741, 1601, 1501, 1382, 1181 and 693; δ_H (90 MHz, $CDCl_3$): 7.4-7.1 (m, 5H), 6.2 (m 2H), 5.65 (s, 1H), 3.3 (dd, 1H), 3.25 (m, 2H), 2. 85 (s, 1H), 2.4 (m, 6H), 2.0 (m, 8H), 1.6 (d, 4H); δ_C (22.4 MHz, $CDCl_3$): 177.93, 176.85, 145.91, 140. 36, 137.47, 136.43, 133.35, 131.98, 128.94, 128.25, 126.37, 123.57, 59.18, 56.50, 53.31, 50.02, 47.34, 46.21, 44.62, 43.91, 40.95, 33.29, 32.48, 32.12, 29.38, 28.39, 26.69, 23.35.