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DI- AND TETRAMETHYLBENZOBICYCLO[2.2.0]HEXA-2,5,-DIENE

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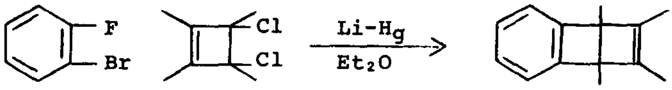
We have been able to generate 5,6-benzo-1,2,3,4-tetramethylbicyclo[2.2.0]hexa-2,5-diene[1] (3) in a simple one-step procedure involving the treatment of an ether solution of o-bromofluorobenzene (1) and 3,4-dichloro-1,2,3,4-tetramethylcyclobutene (2)[2] with lithium amalgam.**



1 2 3

Adduct (3) was formed in 13% yield and could be isolated by a combination of crystallization and thin-layer chromatography techniques. Its nmr spectrum[3] consisted of three singlets at τ2.87, 8.43 and 8.61, whose respective integral ratios were 2:3:3. The ultraviolet spectrum of 3 (n-hexane) exhibited maxima at 264 (ε605), 270 (ε850) and 277 (ε765) mμ.

On heating in tetrachloroethylene solution at 70°, adduct (3) rearranges ($t_{\frac{1}{2}}$ = 1.5 hrs) to 1,2,3,4-tetramethylnapthalene (4) as evidenced by the disappearance of the nmr spectrum of 3 and the concomitant apperance of new signals (broad multiplet centered at τ2.33, singlet τ7.40 and singlet τ7.60 in the respective integral ratios of 2:3:3.[4] The product of the rearrangement, m.p. 106° (lit m.p. for 4 106.5 - 107.5°)[5], formed a picrate whose

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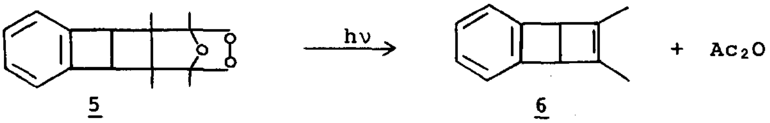
** The reaction may be viewed formally as a Diels-Alder reaction between benzyne and tetramethylcyclobutadiene.

melting point, 179-180°, was in agreement with that reported for the corresponding derivative of 1,2,3,4-tetramethylnapthalene.[5]

A second example of a benzobicyclo[2.2.0]hexa-2,5-diene, with the interesting feature of having no substitution on bridgehead positions 1 and 4, was synthesized using a photolytic method[6] for introduction of the olefinic double bond. Photolysis of ozonide (5) in dichloromethane at -20°, using a high-pressure mercury lamp and a Pyrex filter, produced a mixture of 5,6-benzo-2,3-dimethylbicyclo[2.2.0]hexa-2,5-diene (6) and its valence bond isomer, 2,3-dimethylnapthalene (7).*



After irradiation of the sample for six hours, the intensity of the nmr signals for 5 was less than 10% of its original value and four new signals had appeared in the methyl region of the spectrum at τ7.58, 7.83, 7.95 and 8.35. The most intense peak was at τ7.83 and was ascribed to acetic anhydride. This signal as well as that at τ7.95 could be removed by extraction of the sample with aqueous sodium carbonate. The remaining two high-field signals were present in the relative ratio 3.2:1 corresponding to the methyl groups of 6 (τ8.35) and 7 (τ7.58) respectively.

Heating a carbontetrachloride solution of the mixture of 6 and 7 at 80° for two hours caused the signal at τ8.35 to decrease in intensity. Prior to heating, the solution also exhibited signals at τ2.91 and 5.17 which disappeared concomitantly with the signal at τ8.35. Dilution of the final solution with authentic 2,3-dimethylnapthalene produced no new signals in the nmr spectrum.

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* The irradiation was carried out in a sealed nmr tube.

Ozonide (5) was produced in quantitative yield by treating a pentane solution of 6,7-benzo-1,2,3,4-tetramethyltricyclo[4.2.0.0^{5,8}]octa-2,6-diene (8) with ozone at -20°. Careful crystallization from EtOH-H_2O gave needles, m.p. 80-81°. Ultraviolet (cyclohexane) 265 (ε995), 271 (ε1070), 277 (ε1570) mμ and nmr (CCl_4) τ2.91, 6.62, 8.73, 8.77 (2:1:3:3) spectra were consistent, as was elemental analysis,* with the assigned structure.

Olefin (8) was generated in 70% yield** through the action of lithium amalgam on a diethyl ether solution of benzocyclobutene dibromide[7] (9) and 3,4-dibromo-1,2,3,4-tetramethylcyclobutene (10).[8] Preparative thin-layer chromatography on silica-gel with hexane followed by crystallization from acetone gave needles, m.p. 59-60°. The spectral properties; nmr (CCl_4) τ2.92 (2), 6.70 (1), 8.85 (3), 8.92 (3), UV max. (cyclohexane) 265 (ε765) 271 (ε1190) 277 (ε1290) mμ were consistent with the assigned structure.

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* All new compounds, with the exception of 6, which was not analyzed, gave elemental analysis consistent with the assigned structure.

** Utilization of dichloro rather than dibromocyclobutene (10) resulted in a lower (35%) yield of 8.

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REFERENCES

[1] The unsubstituted member (5,6-benzobicyclo[2.2.0]hexa-2,5-diene) was reported by R. N. McDonald and D. G. Frickey, J. Am. Chem. Soc., **90**, 5315 (1968)

[2] R. Criegee and A. Moschel, Chem. Ber., **92**, 2181 (1959)

[3] Carbontetrachloride with internal tetramethylsilane

[4] This is in close agreement with the values for 4 reported by F. F. Yew, R. J. Kurland and B. J. Mair, Anal. Chem., **36**, 843 (1964).

[5] C. L. Hewett, J. Chem. Soc., 302 (1940).

[6] a. R. Criegee, Chimia, **22**, 392 (1968)
b. P. R. Story, M. W. Herbert III, T. K. Hall, J. C. Farine and C. E. Bishop, Tetrahedron Lett., 3291 (1968)

[7] M. A. Cava and D. R. Napier, J. Am. Chem. Soc., **79**, 1705 (1957)

[8] R. Criegee and K. Noll, Ann. Chem., **627**, 1 (1959)