

AN EXTREMELY UNUSUAL REACTION OF 2,3,4-TRIPHENYL-3-AZABICYCLO[3.2.0]HEPTA-1,4-DIENE WITH DIMETHYL ACETYLENEDICARBOXYLATE

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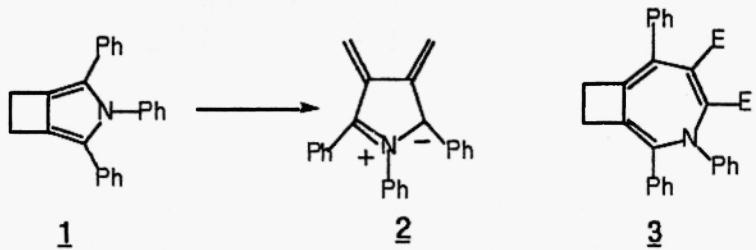
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Abstract : 2, 3, 4-Triphenyl-3-azabicyclo[3.2.0]hepta-1,4-diene underwent, in a sealed tube, an extremely novel reaction with dimethyl acetylenedicarboxylate to give 6-phenyl-2-[(Z)-1,2-bis(methoxycarbonyl)-vinyl]-4-methylene-1,5-diphenyl-6-azabicyclo[3.1.0]hex-2-ene 8, in addition to the azepine 3. The structure was established by an X-ray analysis.

Benzocyclobutene and related compounds including heteroanalogues represent a unique compromise between the thermodynamic stability associated with an aromatic system and the kinetic reactivity of a strained cyclobutene.¹ Although the parent 3-thiabicyclo[3.2.0]hepta-1,4-diene and its derivatives are relatively well known,^{2,3} the only one example of the corresponding aza-analog has been reported by Garratt et al. who have synthesized 6,7-di-tert-butyl-3-thiabicyclo[3.2.0]hepta-1,4-diene and its pyrrole and furan analogues by the base-catalyzed rearrangement of the corresponding 4-heterohepta-1,6-dienes.⁴

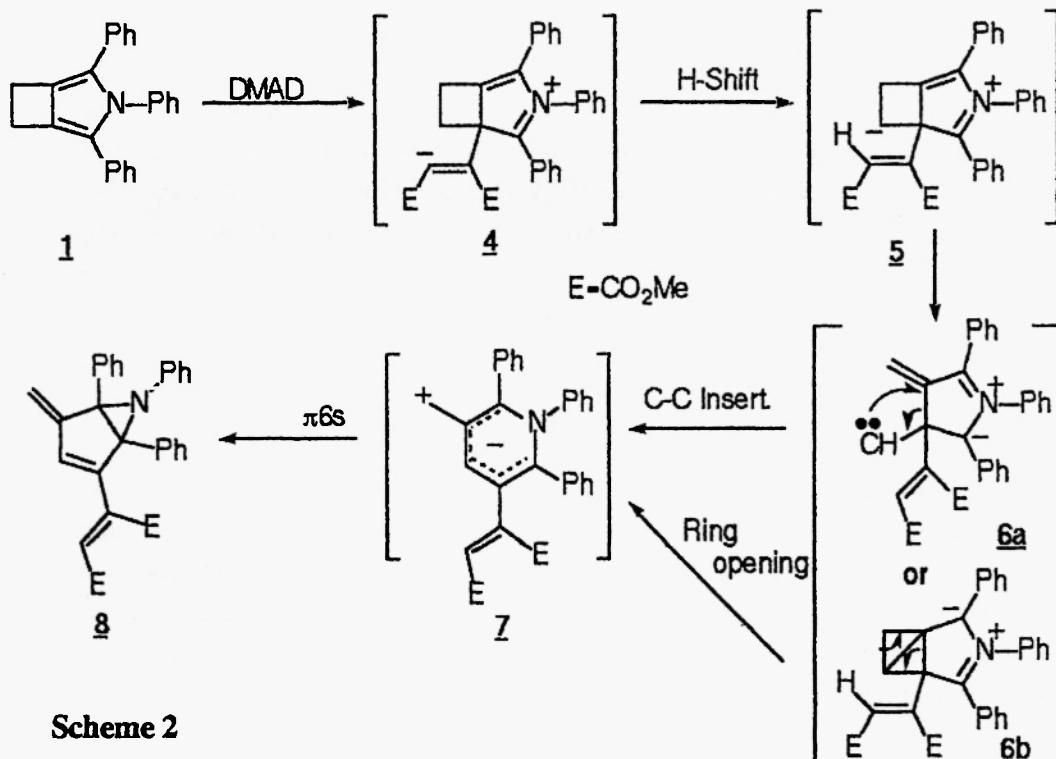
Previously, we have shortly reported synthesis of 2,3,4-triphenyl-3-azabicyclo[3.2.0]hepta-1,4-diene 1 and its novel reaction with dimethyl acetylenedicarboxylate (DMAD) under refluxing toluene giving the azepine 3.⁵ In connection with several synthetic projects employing high pressure technique, we envisaged to perform the title reaction under high pressure as well as in sealed tube conditions, since we hoped the compound 1 serves either as a diene or an azomethine ylide or both of them as shown in Scheme 1. In contrast to the previous result,⁵ when the reaction was performed in a sealed tube, the other product 8 was obtained albeit in low yield, along with the same azepine 3 described before. This is the subject of the present communication.



Scheme 1

A mixture of 1 (0.16 mmol) and DMAD (0.47 mmol) in dry benzene (1 ml) was heated at 95°C in a sealed tube for 20 h. After evaporation of the solvent, the residue was subjected to chromatography on silica gel, eluting with hexane/ethyl acetate (20/1, 9/1, and 4/1). From the first fraction, the starting material 1 was recovered in 48 % yield. From the second fraction, the orange powder was obtained, which seems to be a mixture of the 1:1 adducts based upon NMR analysis whose integration ratio was 1.3 to 1. Recrystallization of this orange powder from hexane gave orange needles which were proven to be the azepine 3 from the NMR analysis.⁵ The filtrate was concentrated and the residue was recrystallized from methanol, giving colorless prisms. Although the elemental and mass spectral analyses confirmed that the compound had 1:1 composition of 1 and DMAD, its NMR analyses (¹H, ¹³C, and correlation NMR) did not permit us to deduce any reasonable structure. An X-ray crystal structure analysis of the 1:1 adduct established the structure 8,⁶ being consistent with all the NMR data.⁷

The reaction involved seems to be so unusual that mechanistic considerations are still premature. The surprising result can be tentatively interpreted by using the Scheme 2.



Scheme 2

ACKNOWLEDGMENTS

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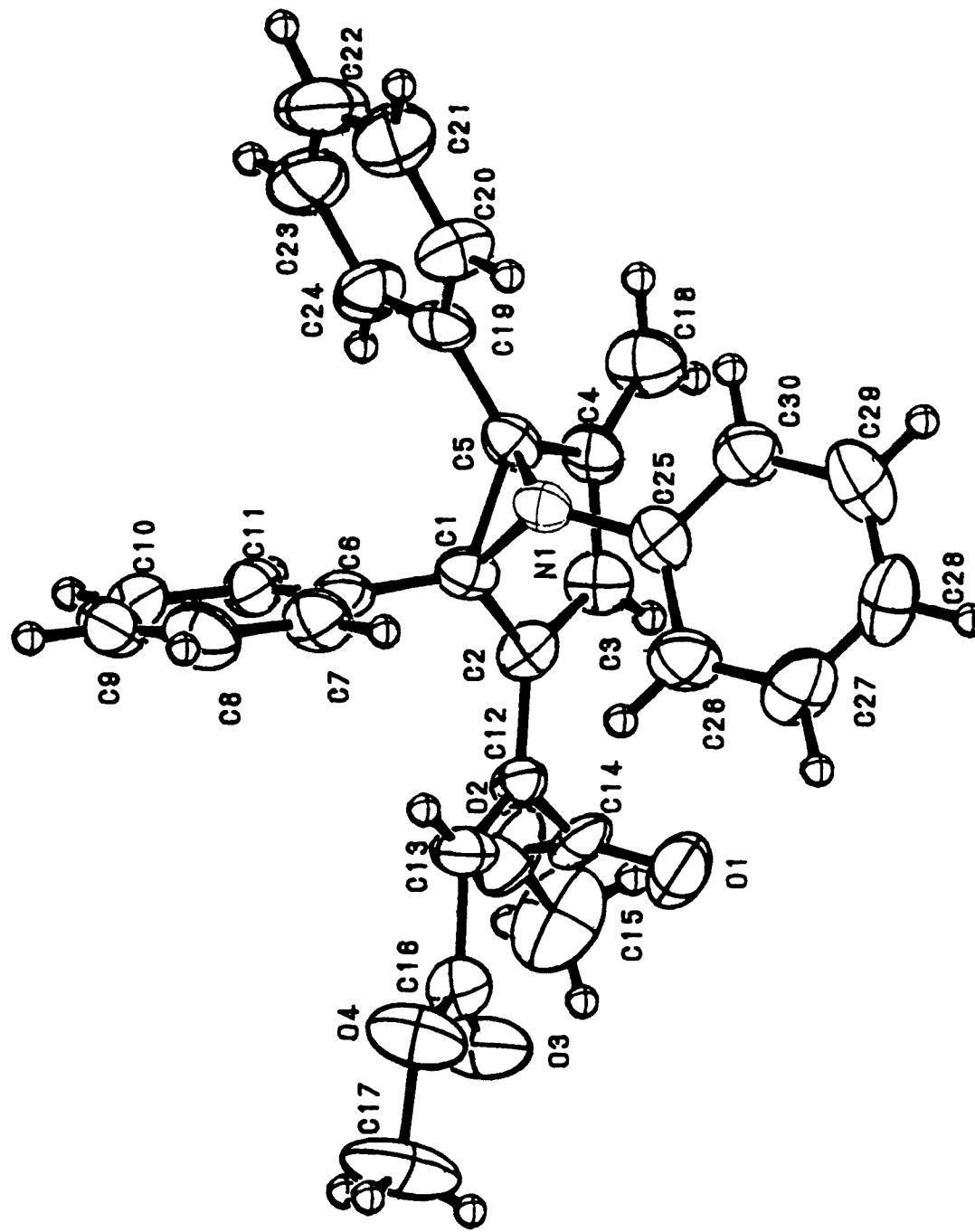


Fig. 1 ORTEP Drawing of $\underline{8}$

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- (6) Crystal data for **8**: $C_{30}H_{25}NO_4$, $M=463.53$, dimensions $0.12 \times 0.38 \times 0.56$ mm, monoclinic, space group = $P2_1/c$, $a = 9.33$ (1), $b = 26.026$ (3), $c = 10.959$ (5) Å, $\beta = 108.12$ (5)°, $U = 2529$ (3) Å³, $Z = 4$, $D_c = 1.217$ g/cm⁻³, $\mu = 0.76$ cm⁻¹, $F(000) = 976$. Data were collected on a Rigaku AFC5S diffractometer using graphite-monochromated Mo-Kα radiation ($\lambda = 0.71069$). Of 5152 reflections which were collected, 4803 were unique ($R_{int} = 0.106$). The structure was solved by direct methods and all non-hydrogen atoms were refined anisotropically using full-matrix least squares to give $R = 0.075$, and $Rw = 0.068$ for 1580 independent observed reflections with $I > 2.00\sigma(I)$ and 316 variables for $2\theta_{max} = 55.0$ °.
- (7) mp 174.5-176°C; 13 % yield (crude); ¹H NMR (270 MHz, CDCl₃) 3.64(s, 3H), 3.84(s, 3H), 5.42(s, 1H), 5.56(s, 1H), 5.72(s, 1H), 6.31 (s, 1H), 6.81-7.35 (m, 15H); ¹³C NMR (125.65 MHz, CDCl₃) 51.97(t), 52.69(t), 63.22(s), 65.11(s), 77.47(d), 119.49(d), 120.36(d), 122.28(d), 122.68(d), 127.41(d), 127.53(d), 127.79(d), 127.92(d), 128.19(d), 128.57(d), 129.19(d), 134.55(s), 134.98(s), 139.05(d), 139.22(s), 144.67(s), 145.87(s), 147.88(s), 165.48(s), 167.77(s).

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