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[2+2] CYCLOADDITION OF BENZYNE TO *CIS,TRANS*- AND *CIS,CIS*-1,5-CYCLOOCTADIENE

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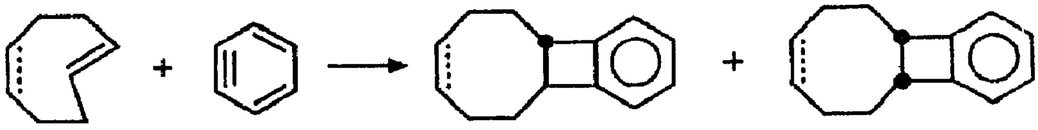
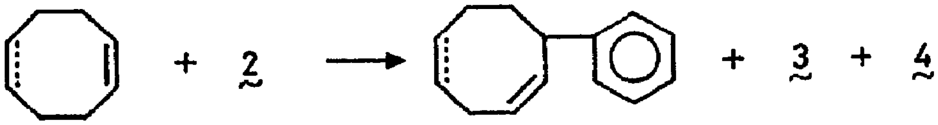
Abstract: The relative rates of formation of *cis* and *trans* [2+2]cycloadducts of benzyne to *cis*, *trans*- and *cis*, *cis*-1,5-cyclooctadiene, *trans*- and *cis*-cyclooctene are discussed and properties of the adducts (e.g., their unusual hydrogenation) are described.

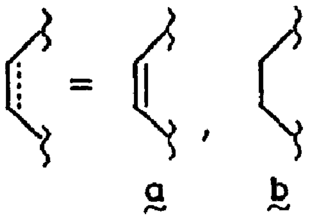
Benzyne, **2**, (generated in situ by heating benzenediazonium-2-carboxylate suspended in an aprotic solution to ca. 50 °C) has been found by Gassman and Benecke[1)] to add to *trans*-cyclooctene (**1b**) to give [2+2]-cycloadducts **3b** and **4b** in a ratio of 3.5 : 1.



1 **2** **3** **4**



5 **6**



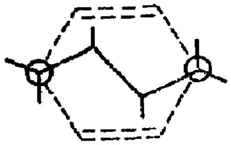
	3a : **4a**		**3b** : **4b**
From **1a**	13 : 1	From **1b**[1)]	3.5 : 1
From **5a**	1 : 6.4	From **5b**	1 : 40

Table: [2+2]cycloadduct ratios obtained from **1**(**a**, **b**) and **5**(**a**, **b**).

These authors also found that *cis*-cyclooctene (**5b**) under the same conditions gave mainly the ene type product **6b** and some **4b**.

We find that *cis*, *trans*-1,5-cyclooctadiene (**1a**) under the same conditions gives the analogous [2+2]cycloadducts **3a** and **4a** in a ratio of 13 : 1 and that *cis*, *cis*-1,5-cyclooctadiene (**5a**), in analogy to **5b**, gives a mixture which consists mainly of **6a** and which, besides considerable amounts of biphenylene, also contains small amounts of 3a and 4a in a ratio of 1 : 6.4. We have also determined the very small amounts of 3b formed from 5b in addition to 6b and 4b. The ratios 3 : 4 are summarised in the Table.

3a and 4a, obtained from the reaction of 1a, were isolated by preparative g.l.c.. Both compounds were liquids which analysed for $C_{14}H_{16}$ (required: C 91.25, H 8.75, mol. wt. 184; found: 3a, C 90.30, H 8.95, mol. wt. (MS) 184; 4a, C 90.81, H 9.35, mol. wt. (MS) 184) and had UV absorptions characteristic of the benzocyclobutene moiety[1,2] (λ_{max}(log ε) : 3a, 273 (3.31), 266 (3.33), 260 (3.14), 215 nm (3.75); 4a, 273 (3.30), 266 (3.31), 260 (3.15), 213 nm (3.80)). The 100 MHz ^{1}H-NMR spectra of both compounds display twofold molecular symmetry. 3a (in CCl_4) shows multiplets centered at δ = 1.5 (2H), 2.0 (2H), and 2.2 (4H), an approximately symmetric signal, 20.5 Hz wide, at 3.18 (2 benzylic CH), the A_2 part of an $A_2X_2Y_2$ system with $J_{AA'}$ = 11.1, J_{AX} = J_{AY} = 8.3, $J_{AX'}$ = $J_{AY'}$ = −0.6, $J_{XY'}$ = −0.1, $J_{XX'}$ = $J_{YY'}$ = 0 cps, and J_{XY} undetermined (values obtained by LAOCOON analysis), at 5.64 (-CH=CH-), and an A_2B_2 system at 6.89 and 6.98 (4 arom. H). 4a (in CCl_4) shows a multiplet between δ = 1.75 and 2.5 (8H), an unsymmetric signal, 26 Hz wide, at 3.64 (2 benzylic CH), the A_2 part of an $A_2X_2Y_2$ system at 5.66 (-CH=CH-), and an A_2B_2 system at 6.82 and 6.97 (4 arom. H). The olefinic A_2 parts of 3a and 4a differ strongly; that of 3a is superimposable with that of 1,8-<u>trans</u>-bicyclo[6.2.0]deca-4,9-diene (which contains an eight ring structure identical to that in 3a) and that of 4a is very similar to that of the corresponding <u>cis</u> compound[3]. The <u>cis</u> configurations of the double bonds in 3a and 4a follow both from the unreactivity of both compounds towards cyclopentadiene (1b at room temp. gives the Diels-Alder adduct immediately) and from the J_{HH} value of 11.1 cps (ca. 16 cps are found for various <u>trans</u>-cyclooctenes[4]). Treatment with KOtbu in dimethyl sulfoxide at 150 °C converted 4a to 3a[5] which confirms that both compounds are epimers about the benzylic methine groups. On cooling below 0 °C, the olefinic and benzylic portions in the 100 MHz spectrum of 3a broaden and below −50 °C the olefinic portion forms a complex multiplet 50 Hz wide and the benzylic portion splits into two signals of equal intensity at ca. 3.07 and 3.29 ppm. Warming to room temp. restores the original spectrum. This change corresponds to a freezing of the ring flip process between two equivalent conformations of the <u>trans</u>-fused cyclooctene ring as shown in the Figure. The spectrum of 4a, on the other hand, remains unchanged on cooling to −70 °C; this reflects the fact that the <u>cis</u> fused cyclooctene ring has only a single preferred conformation.



Figure

Remarkably, the benzene rings in compounds 3 and 4 were rapidly hydrogenated under mild conditions (10% Pd on charcoal (FLUKA), ethanol, 1 at H_2, room temp.) which normally would not attack benzene rings and which are even used to prepare unsubstituted benzocyclobutene from its halogenated derivatives[2,6]. Thus, 3a took up 4 mol H_2 to give a liquid $C_{14}H_{24}$ product (required: C 87.42, H 12.58, mol. wt. 192; found: C 87.55, H 12.47, mol. wt. (MS) 192) showing only a broad band at $\delta = 0.9-2.2$ in its ^{1}H-NMR spectrum, and 4b took up 3 mol H_2 to give a different liquid $C_{14}H_{24}$ product (found: C 87.52, H 12.47, mol. wt. (MS) 192), ^{1}H-NMR: $\delta = 1.0-1.9$ (20 H), 2.2-2.5 (4H). This hydrogenation occurred so readily that, e.g., 3b could not be prepared by partial hydrogenation of 3a.

Pure 4b was isolated from the crude $C_{14}H_{18}$ fraction (1 g), obtained from 6 g 5b and 1.7 g benzenediazonium-2-carboxylate, by shaking over night with a solution of 7.5 g $NaIO_4$ and 1 g $KMnO_4$ in 300 ml H_2O and 30 ml acetone, extracting the mixture with 20 ml cyclohexane, shaking the cyclohexane solution with several portions conc. H_2SO_4 (the last portion remained colorless), and Kugelrohr distillation (100 °C, 0.05 Torr) to give 0.1 g of a mixture of 4b and 3b from which 4b readily crystallised; it had the reported m.p. (58 °C) and spectral data[1]. 6a was not isolated pure; its constitution however is evident from the ^{1}H-NMR spectrum of the crude $C_{14}H_{16}$ fraction obtained from 5a which according to g.l.c. contained one main product: δ (in CCl_4) = 1.4-3.0 (ca. 6H), 4.0 (ca. 1H), 5.2-6.0 (ca. 4H), 7.1 (ca. 5H).

The 3:4 ratios in the raw reaction mixtures, as given in the Table, were determined by capillary g.l.c. using the pure compounds as references. All products 3 and 4 are completely stable under the reaction and g.l.c. conditions.

Discussion: The partial loss of steric configuration during the cycloaddition reaction, as evidenced by the formation as by-products of adducts 4 from 1 and of adducts 3 from 5 (see Table), is consistent with a diradical mechanism for this cycloaddition[1,7,8]. Systems a and b, while showing retention indices[8] of the same order of magnitude (a: 13 x 6.4 = 83; b: 3.5 x 40 = 140) differ in that, both with 1 and with 5, a has a stronger tendency to form trans fused rings ($[trans/cis]_{average} = (13/6.4)^{1/2} = 1.43$) than b ($[trans/cis]_{average} = (3.5/40)^{1/2} = 0.3$). This tendency parallels the relative thermodynamic stabilities of compounds 3 and 4 in systems a vs. b as evidenced by equilibration experiments[5], even though 3 and 4 under the reaction conditions do not interconvert. This indicates that the greater stability of the trans conformer of the C_8 ring as compared to the cis conformer in system a, but not so in system b, is not only a property of the adducts 3 and 4[5] but also of the intermediate diradicals.

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