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CHEMISTRY OF p,p'-DIBENZENES

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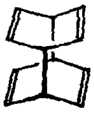
Summary: The 3,4-tetramethylene derivative 6 of p,p'-dibenzene 1 has been synthesized for the first time. As in the case of its benzo-analog 5, its principal thermal reaction is its rearrangement to the corresponding cis-syn-o,o'-isomers.

There is substantial theoretical interest[1] in the benzene 4n cyclodimer subset of the $(CH)_{12}$ series of isomers. Among the three members of this subset, 1-3, only p,p'-dibenzene 1 has not been reported.[2,3] We have synthesized in our laboratory the pentacyclic precursor of 1, 4,[4] as well as the 3,4-dibenzo derivative 5.[5] Since both compounds were synthesized inefficiently in poor yield, 4 was precluded as the practical synthetic precursor for 1. The difficulty in the synthesis of 4 lies in the poor yield (1.5%) of the photocycloaddition of a 1,3-cyclohexadiene to benzene while that of 5 lies in the lead tetraacetate induced bis-decarboxylation of the 1,2-diacid. An important aspect on the research of theoretically interesting molecules is a convenient synthesis in practical overall yield. Based on the knowledge gained in our laboratory on the syntheses of related compounds,[6-8] we wish to report the first synthesis of a derivative of 1, 3,4-tetramethylene-p,p'-dibenzene 6, as well as an efficient synthesis of 5, and a study of their thermal reactions.



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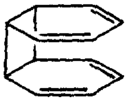

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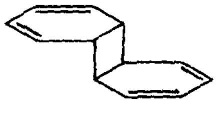

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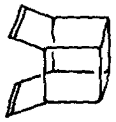

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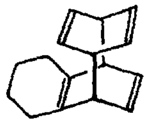

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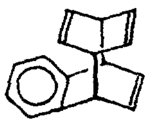

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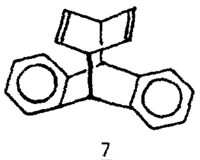

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Compound 5 may be synthesized from naphthalene readily in two steps, while 6 was synthesized in 9 steps with an overall yield of 6.6% (Scheme). Therefore, up to a gram of these compounds may be made available in a relatively short period of time. During our syntheses, we noted that both 5 and 6 are thermally labile; they rearrange in solution at an observable rate at room temperature or below to the corresponding cis,syn-o,o'-isomers via the Cope Rearrangement. However, if we carry out our synthetic operation in temperature-controlled rooms ranging from -30 to 4°C, 5 may be synthesized in >98% purity and 6 in ≈85% purity. Nevertheless, 6 thus prepared is sufficiently pure for our kinetic investigation, pmr $\delta(CHCl_3)$: 1.57(m, 4, CH_2), 1.97(q, 4, allylic CH_2), 2.67(quintet, 2, H-1,4), 3.04 (heptet, 2, H-5,8), 6.28(m, 2, H-9,10), 6.30 and 6.39 ppm(m, 4, H-6,7 and 11,12). However, the Cope rearrangement products may be removed from 6 as their Diels-Alder adducts with 4-methyl-1,2,4-triazoline-3,5-dione at -20°C leaving tetralin as the only detectable impurity by pmr spectroscopy.

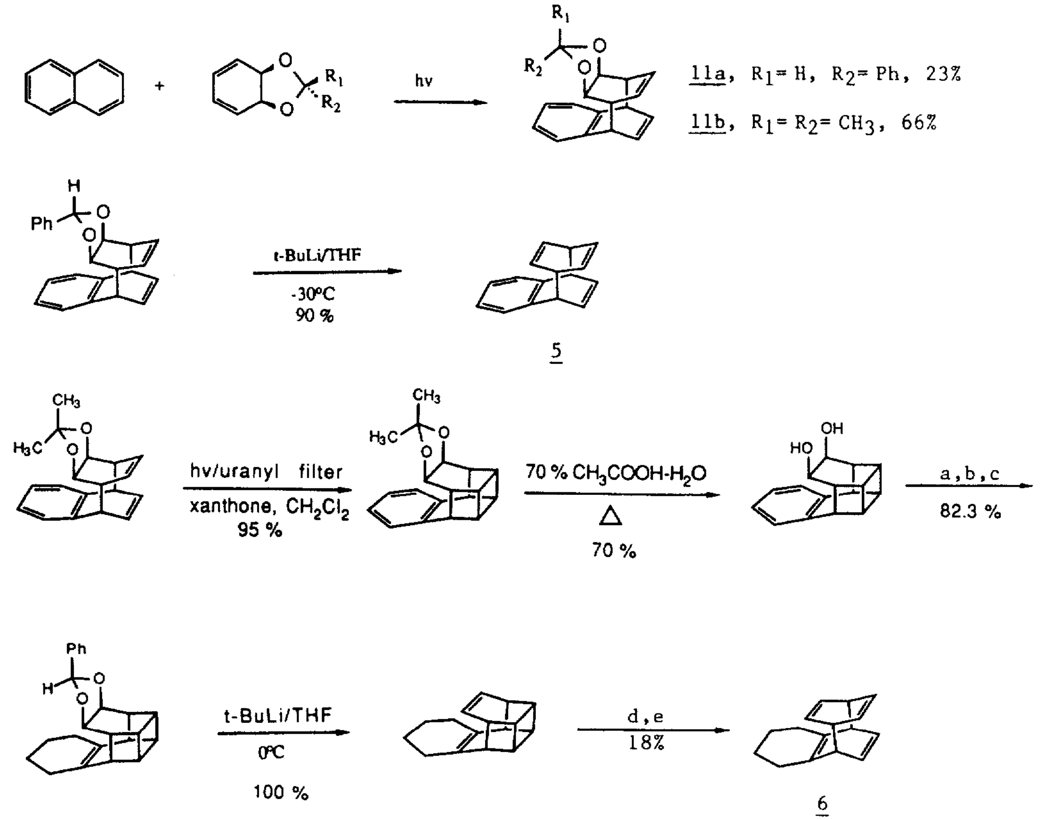
The thermal conversion of 5 to 8 is achieved in quantitative yield at 21°C, but the thermal rearrangement of 6 yields a mixture of two isomers of cis,syn-o,o'-dibenzenes 9 and 10 in approximately equal amount together with some products of thermolysis, benzene and tetralene (reactions 1 and 2). All attempts to separate these two isomers by chromatographic techniques have been unsuccessful. The relative amounts of these products do not vary within experimental error at the temperature ranging from -5 to 25°C.

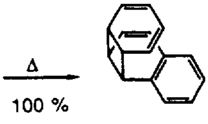
At 0°C, $\tau_{1/2}$ of 6 is 4.2 hr, while that of 5 may be extrapolated to be 102 hr. The activation parameters for the rearrangement of 5 and for the rearrangement and the dissociation of 6 were calculated by studying their thermal decompositions at seven different temperatures ranging from 23.7-44.7°C for 5 and -4.8-19.0°C for 6. The results are given below:

Compound	ΔE_a(kcal·m^{-1})	$\Delta H^\dagger$(kcal·m^{-1})	$\Delta S^\dagger$(e.u.)	$\Delta G^\dagger_{25°}$ (kcal·m^{-1})
5	23.4±0.4	22.8±0.4	-1.4±1.3	23.2±0.8
6				
rearrangement	22.4±1.1	21.8±1.1	0.9±3.9	21.5±2.3
thermolysis	23.0±1.3	22.4±1.2	1.7±4.2	21.9±2.5
total	22.8±1.1	22.2±1.1	3.0±4.0	21.3±2.3

Grimme has pointed out that there is a linear dependence between the difference of heats of activation, $\Delta\Delta H^\dagger$, and the resonance energy gained, ΔRE, in the thermolysis of two series of adducts of aromatic hydrocarbons, $4\pi_s+2\pi_s$ adducts of aromatic hydrocarbons and benzene as well as adducts of aromatic hydrocarbons and 1,3-cyclopentadiene, with a slope of -0.43.[9] It is also interesting to note that the $\Delta\Delta H^\dagger$ values of thermolyses between analogs of these two series are within experimental error of each other. Since the $\Delta\Delta H^\dagger$ between the $4\pi_s+4\pi_s$ benzene:anthracene dimer 7 and 6 is 10.3 kcal·m^{-1} which is the same within experimental error of the two systems of analogus compounds studied by Grimme, 10.2 and 10.6 kcal·m^{-1}, the $\Delta H^\dagger$ of thermolysis of 5 may thus be extrapolated from the linear relationship between $\Delta\Delta H^\dagger$ and ΔRE of the $4\pi_s+4\pi_s$ adducts to be 27.2 kcal·m^{-1}, much

Scheme



5 

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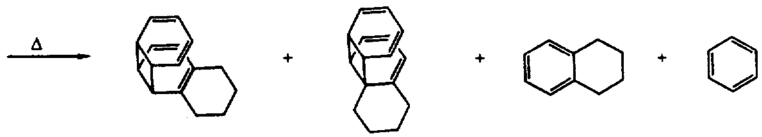
6 

9, 33% 10, 34% 33% (2)

a. $Na/NH_3/C_2H_5OH$; b. H_2/PtO_2; c. $PhCH(OCH_3)_2$, TsOH; d. (Bicyclo[2.2.1]hepta-2,5-diene)RhC dimer; e. KCN.

higher than that of the Cope Rearrangement. It is, therefore, not surprising that the Cope Rearrangement is the only detectable thermal process of 5.

On the basis of our experimental observations, 1, p,p'-dibenzene or tricyclo-$[4.2.2.0^{5,8}]$dodeca-2,6,9,11-tetraene, if synthesized, will also undergo the Cope Rearrangement rapidly under ordinary laboratory conditions which will limit the range of exploration of its chemistry. However, since related compounds are known to undergo novel electrophilic additions,[9] attempts will be made to explore the participation of multiple π-systems in the electrophilic addition of 5, 6 and related compounds.

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