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INVESTIGATIONS IN THE CYCLOBUTANE SERIES. XXVI (1). ATTEMPTED SYNTHESIS OF 1-*TERT*.-BUTYL-BENZOCYCLOBUTADIENE AND 1.2-DI-*TERT*.-BUTYL-BENZOCYCLOBUTADIENE

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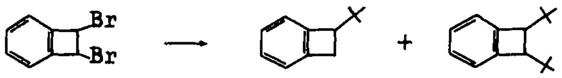
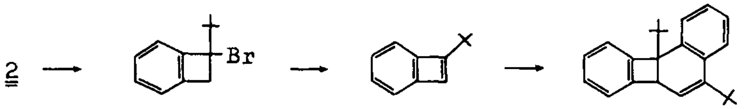
Recently we have tried to synthesize cyclobutadienes stabilized by steric hindrance due to bulky substituents (2,3). In this paper we report our attempts to obtain benzocyclobutadienes bearing one or two *tert*.-butyl groups grafted on the four-membered ring.

By treatment of *trans*-1.2-dibromo-benzocyclobutene (**1**) with *tert*.-butyl-magnesium chloride, 1-*tert*.-butyl-benzocyclobutene (**2**) (4), b.p. 60°/2 mm (28%), together with *trans*-1.2-di-*tert*.-butyl-benzocyclobutene (**3**), b.p. 90°/2 mm (6.5%) were obtained. The structures of **2** and **3** were proved by ozonolysis to the corresponding succinic acids and by means of NMR spectra. In the NMR spectrum of **2**, the three protons of the cyclobutene ring form a multiplet of AB_2 type between δ 2.79-3.30 ppm, the *tert*.-butyl group gives a singlet at δ 0.93 ppm while the aromatic protons give two signals at δ 6.98 and 7.01 ppm. The NMR spectrum of **3** presents three singlets at δ 7.02 ppm (four aromatic protons) , at δ 0.95 ppm (18 H from *tert*.-butyl groups) and at δ 3.00 ppm (two benzylic protons of the cyclobutene ring).



1 2 3

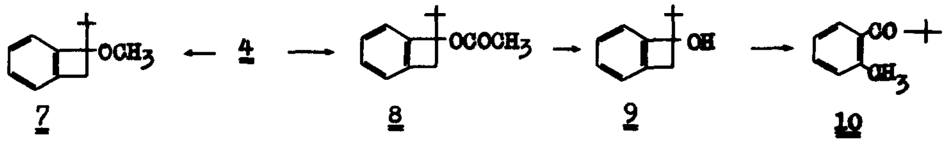
By treating 2 with N-bromosuccinimide, 1-bromo-1-*tert*.-butyl-benzocyclobutene (4), b.p. 110°/5 mm, was obtained with 70% yield. The NMR spectrum of 4 presents a quartet centered at δ 3.60 ppm (J = 14.5 Hz), corresponding to a geminal coupling in the cyclobutene ring.



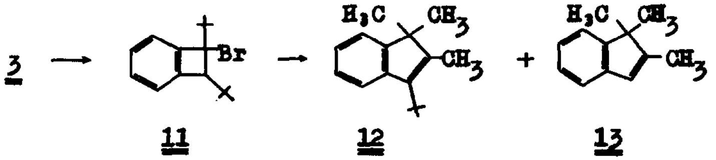
4 5 6

In order to obtain *tert*.-butyl-benzocyclobutadiene (5) the dehydrobromination of 4 with bases was attempted. With potassium *tert*.-butoxide in dimethylformamide, *tert*.-butanol or dimethylsulfoxide, in the absence of air, a dimer with the probable structure of 5.10b-di-*tert*.-butyl-6a.10b-dihydro-benzo[a]biphenylene (6), m.p. 100°, was obtained with 44% yield, analogous to the dimer of unsubstituted benzocyclobutadiene, obtained by Cava and Napier (5). Support in favour of structure 6 was provided by the coupling (J = 7.0 Hz) between the olefinic proton (δ 6.01, 6.13 ppm) and the vicinal saturated proton (δ 4.20, 4.32 ppm).

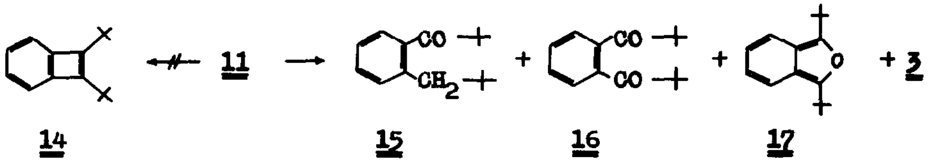
With sodium methoxide in methanol or potassium acetate in acetic acid, substitution reactions of 4 occurred. The ether 7, b.p. 86°/6 mm (82%) and the acetoxy-derivative 8 (68%) were obtained respectively; the latter gave on hydrolysis the alcohol 9, b.p. 90°/5 mm, ν_{OH} 3628 cm^{-1}. The alcohol 9, in presence of potassium tert.-butoxide, underwent a ring opening leading to 1-methyl-2-pivaloyl-benzene (10), b.p. 100°/5 mm (70%), ν_{CO} 1700 cm^{-1}.



On bromination with NBS, the di-tert.-butyl-benzocyclobutene (3) yielded 1-bromo-1.2-di-tert.-butyl-benzocyclobutene (11), b.p. 125°/2 mm (36%). On heating at 140-150° (on a gas-chromatography column), 11 was converted to 1.1.2-trimethyl-3-tert.-butyl-indene (12) and 1.1.2-trimethyl-indene (13) (in the ratio 4:1). The formation of 12 and 13 from 11 can be rationalized by the ionization of bromine from 11 followed by a neopentylic rearrangement; the resulted carbonium ion loses either a proton or a tert.-butyl cation, yielding 12 resp. 13.



Attempts to obtain di-tert.-butyl-benzocyclobutadiene (14) by treatment of 11 with potassium tert.-butoxide in dimethylformamide or dimethylsulfoxide led to a mixture of oxygen containing compounds, the ratio of which varied with the solvent and the reaction conditions.



The following compounds were isolated and identified : the initial hydrocarbon 3 ; 1-pivaloyl-2-neopentyl-benzene (15), ν_{CO} 1700 cm^{-1}, NMR spectrum : δ 0.90 (9H), 1.18 (9H), 2.41 (2H), 7.16 ppm (4H) ; 1.2-dipivaloyl-benzene (16), m.p. 145°, NMR spectrum ($CDCl_3$) : δ 1.27 (18H), 7.35 and 7.39 ppm (4H). In some experiments 2.5-di-tert.-butyl-3.4-benzofuran (17) could also be evidenced, NMR spectrum: δ 1.16 (18H) and 5.60-6.11 ppm (4H). On standing in the presence of air this compound was converted to the diketone 16.

From the above experiments it results that the presence of a single tert.-butyl group do not prevent dimerisation of the benzocyclobutadiene ring. When two tert.-butyl substituents are present in the cyclobutadiene ring the dimerisation is no more possible, nevertheless the molecule keeps enough reactivity towards water and oxygen so as to give open-chain oxygenated compounds.

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