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THE CONDENSATION OF 2,2'-BINAPHTHYL WITH MALEIC ANHYDRIDE

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Abstract—The condensation of 2,2'-binaphthyl with maleic anhydride gave the 3,4-benzotetraphene derivatives **5**, **6** and **8**.

Naphthalene reacts with maleic anhydride to form an endocyclic adduct in very low yield.[1] With 2,2'-binaphthyl (**1**) one would rather expect a diene synthesis to take place in 1,1'-position, using the potential double bonds between the 1,2-positions, to form the picene derivative **2**. This is not the case.

If 2,2'-binaphthyl was refluxed with excess maleic anhydride and a small amount of iodine, several condensation products were obtained among which the dihydro compound **6** was the main constituent. This could be easily isolated by its sparingly soluble Na salt. Somewhat more soluble is the Na salt of the compound **8**. Its constitution became obvious when heated to 300° in vacuum. The endocyclic maleic anhydride complex "M" was split

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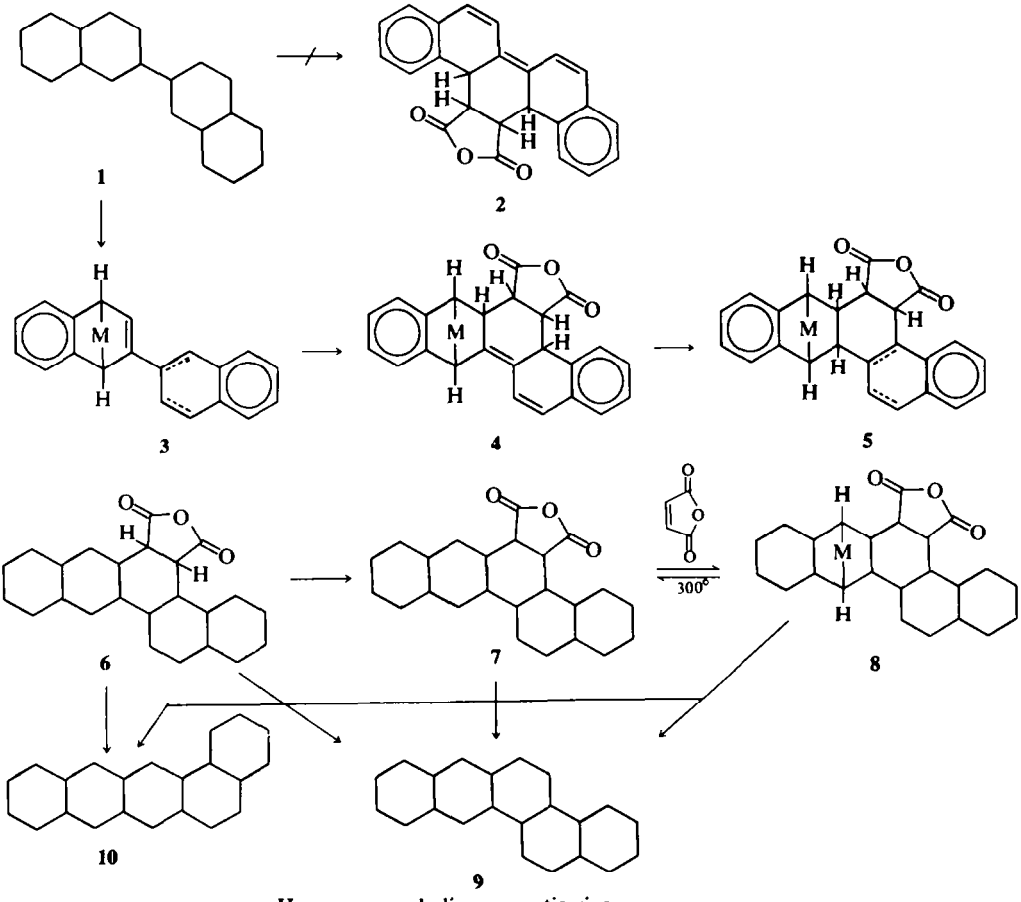

Hexagons symbolize aromatic ring.
"M" = maleic anhydride complex.
H atoms in hydroaromatic rings are marked "H".

out and the red anhydride **7** was formed. Heating this with maleic anhydride formed again **8**. Decarboxylation of **7** gave 3,4-benzotetraphene (**9**).

The red anhydride **7** was also formed from the dihydro compound **6** by dehydrogenation with chloranil. The mother liquor of the Na salts of the compounds **6** and **8** contained another tetracarboxylic acid which is a tetrahydro derivative and contains a naphthalene complex as shown by the UV spectrum. Since it could be dehydrogenated to **7** with chloranil it must have the structure **5**. It was formed from the primary reaction product **4** by the migration of one H atom.

The primary adduct **4** could not be isolated. The UV spectra of the other compounds were all compatible with the assumed structures. The Na salt of the compound **6** showed a spectrum related to 2,2'-binaphthyl (**1**). The Na salt of **7** gave a spectrum very similar to 3,4-benzotetraphene (**9**) and the Na salt of **8** gave a phenanthrene type spectrum. It appears that the reaction must have taken place via the endocyclic adduct **3**.

Pure 3,4-benzotetraphene was only obtained by decarboxylation of the anhydride **7**. This confirms the assumption of a 3,4-benzotetraphene skeleton for the preceding compounds **4**, **5** and **6**.

Decarboxylation of the compounds **6** and **8** yielded a mixture of 3,4-benzotetraphene (**9**) and 1,2-benzotetracene (**10**). In the latter cases an interesting rearrangement must have taken place during the decarboxylation. This is obviously dependent on the dihydro structure of the compounds **6** and **8**.

EXPERIMENTAL

The condensation. Maleic anhydride (200 g) and 2,2'-binaphthyl (50 g) were refluxed and all traces of water removed. Iodine (0·5 g) was added and the mixture refluxed for 1½ hr. The excess maleic anhydride was mainly removed by vacuum distillation and the viscous residue poured into water (300 ml). On heating to 60° and pressing, the melt changed into whitish crumbs. These were filtered off and washed with little water. The solid product was treated with warm Na OH (5%) soln. The Na salt suspension was allowed to cool and filtered off as Filtrate "A".

5,6-Dihydro-3,4-benzotetraphene-5,6-dicarboxylic anhydride (**6**). The above Na salt was washed with cold water (filtrate "B") and then dissolved in several portions of hot water and fitered off from the unreacted binaphthyl (7 g). Acidification of the aqueous soln gave a ppt of the dihydro-compound (13 g). Recrystallisation from Ac_2O and then from xylene gave pale yellow needles, m.p. 296°, which did not dissolve in conc H_2SO_4. The anhydride tends to oxidize slowly in soln to form the red anhydride **7**. UV spectrum of the di-Na salt in water: p, 3260, 3140; β, 2645, 2200 Å. (Found: C, 82·4; H, 4·2. $C_{24}H_{14}O_3$ requires: C, 82·3; H, 4·0%).

Maleic anhydride adduct of 3,4-benzotetraphene-5,6-dicarboxylic anhydride (**8**). The above filtrate "B" was heated to boiling and acidified with HCl. The pale yellow ppt was filtered off (9·5 g).

It was converted into the dianhydride **8** by boiling with Ac_2O. It can be recrystallized from the same solvent in which it is sparingly soluble. It forms pale greenish yellow prisms, m.p. 312° dec, which do not dissolve in conc H_2SO_4. On warming a red soln is formed. UV spectrum (phenanthrene type) of the tetra-Na salt in water: α, 3600, 3425; p, 3110; β, 2690, β', 2220 Å. (Found: C, 74·9; H, 3·3. $C_{28}H_{14}O_6$ requires: C, 75·3; H, 3·2%).

3,4-Benzotetraphene-5,6-dicarboxylic anhydride (**7**). The above dianhydride was melted in vacuum over 300°. The maleic anhydride distilled off and the red melt solidified in long needles. Recrystallisation from xylene gave long red needles, m.p. 283°, which do not dissolve in conc H_2SO_4. UV spectrum (3,4-benzotetraphene type) of the di-Na salt in water: α, 3860; p, 3700, 3520; β, 3070; β', 2480; 2180 Å. (Found: C, 83·1; H, 3·8. $C_{24}H_{12}O_3$ requires: C, 82·8; H, 3·5%).

From **6**. The dihydro-compound (**6**, 15 g) was refluxed with Ac_2O (300 ml) and chloranil (12 g) added. The dehydrogenated anhydride (**7**) crystallized already from the hot soln. After 1 hr refluxing the suspension was allowed to cool and the red needles filtered off. Longer standing causes chloranil derivatives to crystallize out. Recrystallisation from xylene gave the pure anhydride as above.

It can also be obtained by dehydrogenation of the compound **5** (see below) by refluxing it (1 g) with chloranil (2 g) in Ac_2O (70 ml) for 7 hr. On cooling mixed crystals (1·5 g) came out. These were heated in vacuum in order to sublime the chloranil derivatives off. The anhydride remained as a molten red residue which crystallized on cooling. Purification as above.

If the anhydride **7** was refluxed with excess maleic anhydride the dianhydride **8** crystallized out as pale yellow prisms.

Tetrahydro-derivatives **5**. The mother liquor "A" was heated and acidified with HCl. The ppt formed a lump, which when treated with warm AcOH changed into crystals which were filtered off and washed with AcOH, yield 8 g. This product still containd some of the dihydro-compound **6**. When boiled with Ac_2O colourless crystals began to separate from the hot soln. These were sparingly soluble in Ac_2O and formed prisms or needles, m.p. 338°, which did not dissolve in conc H_2SO_4. UV spectrum (naphthalene type) of the tetra-Na salt in water: α, 3220; p, 2830, 2750; β, 2325 Å. (Found: C, 74·2; H, 4·0. $C_{28}H_{18}O_6$ requires: C, 74·7; H, 4·0%).

3,4-Benzotetraphene (**9**). Two pellets of KOH were melted in a test tube. The red anhydride (**7**) was added and the melt heated until the formation of the pale yellow salt was completed. The hydrocarbon was sublimed off in vacuum and recrystallized from xylene. It had m.p. 391° and dissolved in conc H_2SO_4 to give a red soln which changed to violet and finally to blue-green on standing. These properties and the UV spectrum were in agreement with the lit.[2]

Mixture of 3,4-benzotetraphene (**9**) *and 1,2-benzotetracene* (**10**). If the compounds **6** or **8** were submitted to the same decarboxylation a mixture of the above two hydrocarbons was obtained which had absorption bands in cyclohexane at: 4450, 4170; 3920, 3800, 3630, 3450; 3280, 3130, 3070; 2870; 2500 Å.[2] They were formed in about equal amounts. They can be separated by chromatography.

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