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PYROLYSIS OF 8-DIAZO-7,9-DIPHENYLCYCLOPENT(A)ACENAPHTHYLENE

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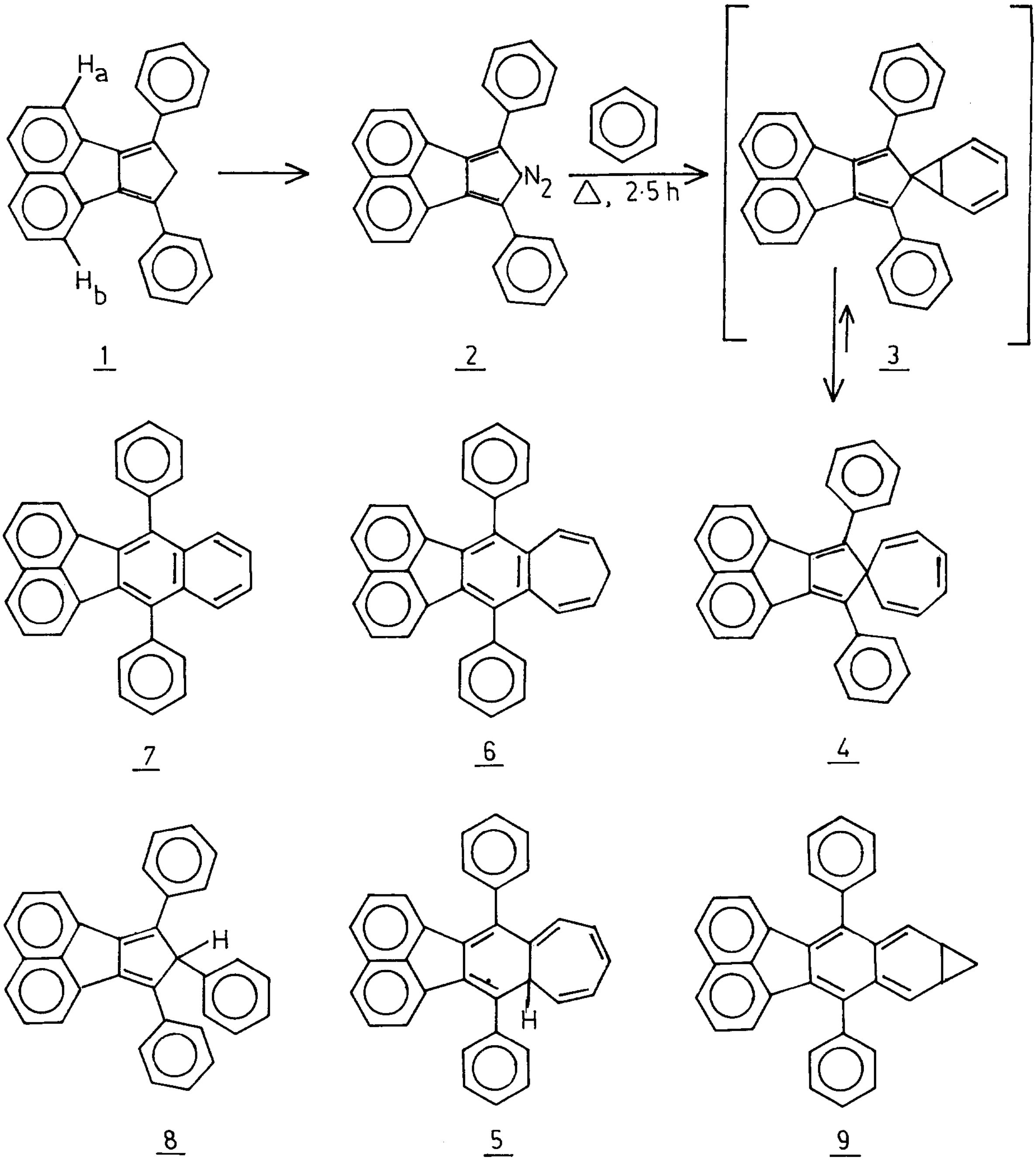
Abstract: Pyrolysis of the title compound in benzene is described.

Although tetraphenyldiazocyclopentadiene and other related diazo compounds undergo various photochemical changes,[1] it is reported to be recovered unchanged when refluxed in benzene.[2,3] On heating with high boiling solvents like mesitylene, tetraphenyldiazocyclopentadiene gives tetraphenylcyclopentene and nuclear CH insertion products.[2,3] In contrast, we find 8-diazo-7,9-diphenylcyclopent(a)acenaphthylene 2 undergoes ready thermal decomposition in benzene to give products involving the intermediacy of the corresponding carbene. The increased reactivity of the diazo compound 2 can probably be attributed to the better delocalization characteristics in the resulting carbene through annelation by the acenaphthylene system.[4]

Acecyclone was converted to the diene 1 in 80% yield by a modified procedure.[5] The title compound was prepared by the reaction of the diene with p-toluenesulphonylazide in 94% yield.[6] When the diazo compound 2 was refluxed in benzene for 2.5 h, the starting material disappeared and the crude reaction mixture was chromatographed over silica gel. Elution with petrol furnished 5% of 7, 12-diphenylbenzo(k)fluoranthene 7. m.p. 279° (Reported 268°)[7].
λ_{max}(EtOH): 245nm(ϵ 58,870), 299nm(ϵ 40,480), 312nm(ϵ 68,060), 331nm (ϵ 12,870), 346nm(ϵ 10,120), 368nm(ϵ 8,277), 386nm(ϵ 17,480), 410nm(ϵ 18,400); ν_{max} cm^{-1}(KBr): 3030, 1595, 1510, 1490, 1440,1430,1380, 1360, 1070, 1035, 830, 770, 765, 730, 700; δ ($CDCl_3$): 6.67(2H, d, 8Hz), 7.24-7.77(18H, m). The identity of this compound was confirmed by comparision with known sample,


Ha
Hb
1
N2
Δ, 2·5 h
2
3
7
6
4
H
8
H
5
9

prepared by addition of benzyne to acecyclone.[7]

Further elution with petrol, followed by purification using preparative TLC furnished yellow crystals of annelated benzocycloheptatriene. (6, 6%)[8]; m.p. 213°; $\lambda_{max}(CHCl_3)$: 256nm(ϵ 24,780), 286nm(ϵ 19,090), 401nm(ϵ 14,730); $\nu_{max}^{cm^{-1}}(CHCl_3)$: 2930, 2870, 2820, 1640, 1600, 1440, 1360, 1280, 1240, 1200, 1110, 1080, 1040, 955, 865; δ $(CDCl_3)$: 2.47(t, 2H, 7Hz), 5.73-6.06(d.t, 2H, 7Hz; 10Hz), 6.46(d, 2H, 10Hz), 6.56(d, 2H, 8Hz), 7.23-7.79(m, 14H); m/e 418.

Continued elution with benzene, petrol (1:9) gave an yellow compound (4, 21%); m.p. 141-142°; λ_{max}(EtOH): 249nm(ϵ 44,750), 292nm(ϵ 25,000), 402nm (ϵ 20,920); $\nu_{max}^{cm^{-1}}$(KBr): 3020, 1645, 1600, 1575, 1500, 1445, 1360, 840, 800, 790, 780, 755, 705, 665; δ $(CDCl_3)$: 4.95-5.09(d, 2H, 12Hz), 5.60-5.83(m, 4H), 7.08-8.00(m, 16H); m/e 418(100%), 341(33%).

One more yellow product 7,8,9-triphenylcyclopent(a)acenaphthylene(8, 34%) was obtained on elution with benzene, petrol (4:6). m.p. 208°; λ_{max}(EtOH): 251nm(ϵ 41,150), 290nm(ϵ 28,600), 398nm(ϵ 23,710); $\nu_{max}^{cm^{-1}}$(KBr): 3060, 3020, 1580, 1480, 1430, 1345, 1060, 1020, 900, 815, 765, 745, 675; δ $(CDCl_3)$: 5.58(s, 1H), 6.91-7.97(m, 21H); m/e 418(100%), 341(57%). On the basis of spectral data the compound was assigned the structure 8.

Compound 6 can arise by thermally allowed 1,5 hydrogen shift from 5. Efforts are underway to determine whether the conversion of 4 to 5 involves a concerted or radical pathway. The conversion of 6 to 7 involves pyrolytic loss of CH_2 probably from the corresponding norcaradiene 9.[9] When a solution of 6 in chloroform is heated, characteristics peaks due to the structure 6 disappears in UV and the spectrum now displays peaks normally seen for 7.

The NMR spectra of the compounds 6 and 7 show a high field peak integrating for two protons around δ 6.60. It is noted that the upfield shift occurs only when the acenaphthylene portion is fused to six membered ring.[10] This signal probably can be attributed to H_a, H_b protons in the acenaphthylene shielded by two phenyl rings. When acenaphthylene portion is fused to five membered ring as in the case of acecyclone, diene 1, diazo 2, spiro compound 4, and 8 this upfield shift is not seen. Models show that in these cases, phenyls are pushed further away.

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