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PROPELLANES. XXXV. ATTEMPTED PREPARATION OF A [5]PRISMANE DERIVATIVE FROM DIELS-ALDER ADDUCTS OF TETRAENIC PROPELLANES[1]

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Thermolysis of a suitable azopropellane did not give a prismane derivative.

One of our motives in conducting Diels-Alder reactions with *cis*oid-azo-dienophiles was to convert the rings thus incorporated in the propellanes into azo groups which could then be subjected to thermal and/or photochemical conditions in order to eject nitrogen. We have reported on azopropellanes obtained from the tetraenic ether 11 *via* its *mono*- and *bis*-adducts with 4-phenyl-1,2,4-triazoline-3,5-dione.[2] We have prepared similar adducts of the tetraenic methylimide 1[3] and although the same method[2] may be used to convert the ureide ring into an azo group we also prepared the adduct of 1 with dibenzyl azodicarboxylate. The latter adduct 4 would be expected to yield the *bis*-hydrazo compound 7 by hydrogenolysis and spontaneous decarboxylation of the carbamic acid groups thus obtained.

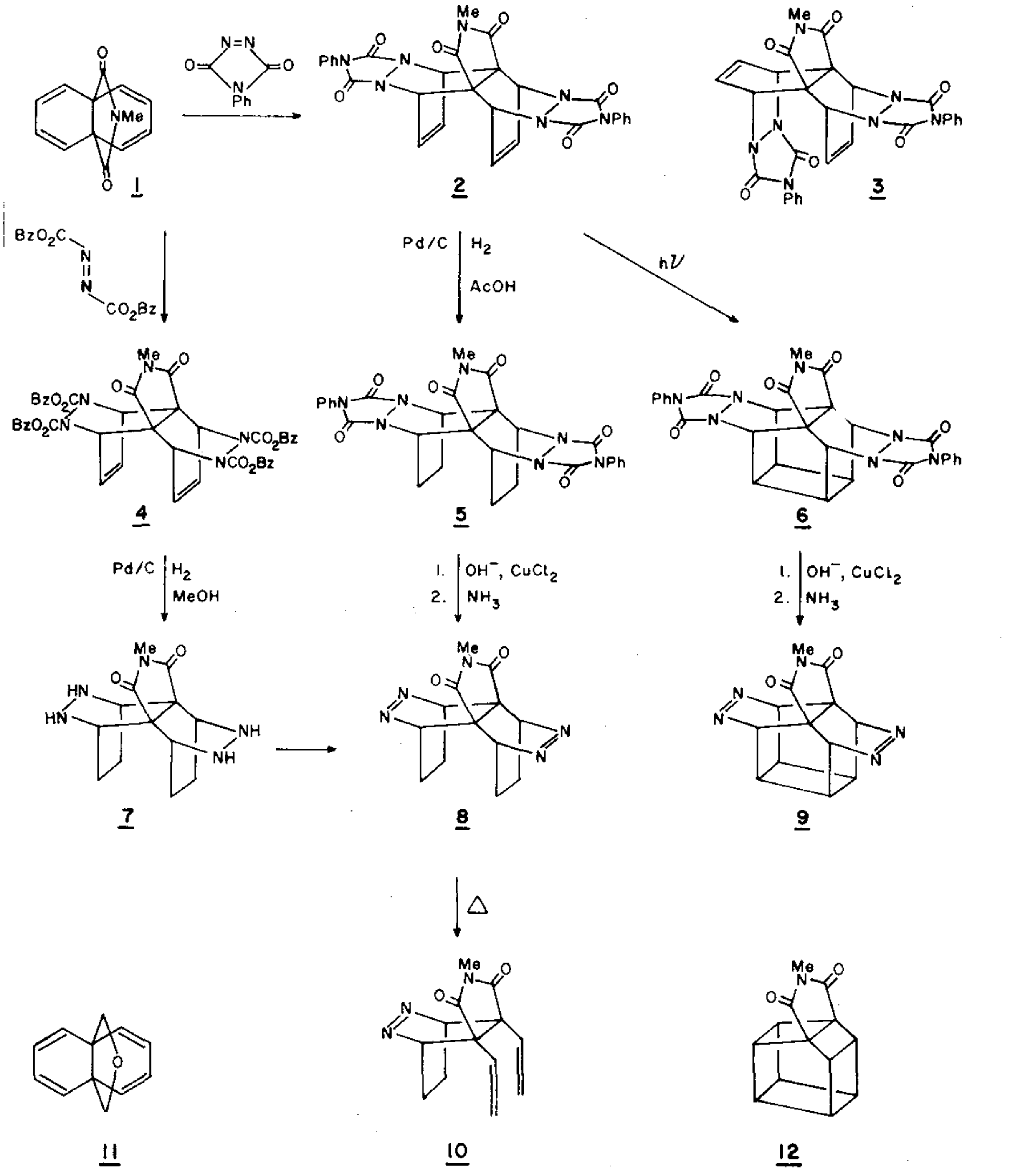
We have reported[3] the sole formation of one *bis*-adduct 2 from 1 and the *cis*oid azo-dienophile shown in the reaction scheme. We have now found when working in larger scale that as much as 25% yield of the unsymmetrical *bis*-adduct 3 accompanies 2. Using the same reaction conditions[3] but crystallizing the crude product gave 2, m.p. 277° (acetonitrile) (*ca* 3 parts) and concentration of the mother liquor gave 3, (1 part), m.p. 308° (acetonitrile).[4]

The Diels-Alder adduct 4 of 1 with dibenzyl azodicarboxylate [m.p. 45-47°; Nmr ($CDCl_3$): τ 2.60 (s, 10H); 4.60 (s, 4H); Ir (KBr): 3040, 3010, 2940, 2880, 1750, 1490, 1450, 1370, 1250 cm^{-1}; Uv (CH_3CN): 406nm (91)] was prepared by heating the components in toluene under reflux for 24 hr followed by standing at room temp for 24 hr (42%), m.p. 226.5-227°; anal. sample, m.p. 230.5-231.5° ($CHCl_3$-hexane). Irradiation of 4 under different conditions did not afford isolable material. It appears that the benzyl ester groups themselves are not inert.[6]

Catalytic reduction of 4 in methanol using 10% Pd/C afforded the unstable hydrazo compound 7 which is very readily oxidized even by air during recrystallization, m.p. 199° (MeOH). Heating 7 under reflux in methanol and more efficiently by using oxygen in methanolic solution in the presence of 10% Pd/C, gives the *bis*-azo compound 8, m.p. 210-211° (methanol or sublimation). During sublimation it is possible to obtain a less polar fraction which was also isolated from mother liquors of 8; this is 10, m.p. 202° (sint. 191°).

Catalytic reduction of 2 in glacial acetic acid using 10% Pd/C afforded the tetrahydro-derivative 5 (92.5%), m.p. > 340° (acetonitrile). The isomeric tetrahydro-derivative of 3 was analogously obtained (100%), m.p. > 340° (acetonitrile). Alkaline hydrolysis of 5 followed by treatment with cupric chloride and treatment of the complex thus obtained with ammonia[2] again afforded 8.

Irradiation of 2 afforded the known 6[2] which we hoped to employ successfully under the proper reaction conditions to give *via* 9 [m.p. > 340°; Nmr ($CDCl_3$) τ: 3.84 (br s, 4H); 7.17 (s, NCH_3); 7.32 (br s, 4H). Ir (KBr): 2990, 2980, 2940, 2870, 2840, 1785, 1720, 1700, 1510, 1430, 1375, 1305, 1270, 1255, 1230, 1150, 1135, 1025, 825 cm^{-1}. Uv (CH_2Cl_2): 393(129), 386(79), 365(296) nm] the [5]prismane derivative 12, bearing a methylimide ring as a handle, expected to raise the m.p. of such a product. However, 9 was extremely stable thermally; it could be recovered unchanged after heating in a sealed ampoule in *o*-dichlorobenzene at 270°C for 23 hr or even


1
NMe
2
3
Pd/C H2 AcOH
hν
4
5
6
Pd/C H2 MeOH
1. OH⁻, CuCl2
2. NH3
7
8
9
Δ
11
10
12
PhN
NPh
BzO2CN
NCO2Bz
Me

at 290° for 4 hr. At higher reaction times and/or temp, N-methylphthalimide was isolated and identified but no 12. A flow system permitted operation over the temp-range 300-500°. At 500° it was possible to obtain a methylimide product in 17% yield which appeared to contain olefinic bonds (Nmr, Uv) which were unconjugated (no reaction with 4-phenyl-1,2,4-triazoline-3,5-dione) but this is clearly not 12.

Irradiation of 9 has also not given 12. Systematic investigation leads us to believe that 9 indeed undergoes photo-reaction but the mass spectral results show that the product exhibits peaks higher than those expected for the molecular peak of 12. Similar failures are not unknown.[7]

References

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