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

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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 cisoid-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 \( \text{I} \) via its mono- and bis-adducts with 4-phenyl-1,2,4-triazoline-
3,5-dione.\(^1\) We have prepared similar adducts of the tetraenic methylimide \( \text{I} \)\(^3\) and
although the same method\(^2\) may be used to convert the ureide ring into an azo
group we also prepared the adduct of \( \text{I} \) with dibenzyl azodicarboxylate. The latter
adduct \( \text{I} \) would be expected to yield the bis-hydrazo compound \( \text{II} \) by hydrogenolysis
and spontaneous decarboxylation of the carbamic acid groups thus obtained.

We have reported\(^3\) the sole formation of one bis-adduct \( \text{II} \) from \( \text{I} \) and the
cisoid 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 \( \text{III} \)
accompanies \( \text{II} \). Using the same reaction conditions\(^3\) but crystallizing the crude
product gave \( \text{II} \), m.p. 277° (acetonitrile) (ca 3 parts) and concentration of the
mother liquor gave \( \text{III} \), (1 part), m.p. 308° (acetonitrile).\(^4\)
The Diels-Alder adduct 4 of 1 with dibenzyl azodicarboxylate [m.p. 45-47°;
Nmr (CDCl₃): τ 2.60 (s, 10H); 4.60 (s, 4H); Ir (KBr): 3040, 3010, 2940, 2880, 1750,
1490, 1450, 1370, 1250 cm⁻¹; Uv (CH₂CN): 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° (CHCl₃-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 ammonia² again afforded 8.

Irradiation of 2 afforded the known 6² which we hoped to employ successfully
under the proper reaction conditions to give via 9 [m.p. > 340°; Nmr (CDCl₃) τ:
3.84 (br s, 4H); 7.17 (s, NCH₃); 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 (CH₂Cl₂): 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
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

4. The compounds described in this paper gave satisfactory analytical results and spectra in keeping with their proposed structures.

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