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4-NITROBENZENEDIAZONIUM SALT AND CYCLOPENTADIENE

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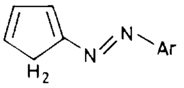
Summary *The title reaction, carried out without solvent at -50°C raised to room temperature, produces the hydrazonic 1:2 adduct* 6 *and the 1:3 adducts* 9a *and* 9b *whereas in methanol at -10°C the intermediate cyclopentadienone-4-nitrophenylhydrazone* (5) *adds a solvent molecule; the azo coupling does not require the cyclopentadienide anion, as demonstrated by the behavior of spiro[2.4]heptadiene* (12).

In 1900 Thiele[1] obtained "intensiv gefärbte Körper, die indessen, wie die meisten Cyclopentadienderivate, sehr leicht verharzen" from benzenediazonium chloride and cyclopentadiene. Eibner and Laue[2] regarded a small amount of brown crystals, mp 130°C, as phenylazocyclopentadiene. These findings became part of K.H. Meyer's general concept of azo coupling.[3] Terentjew and Gomberg[4] explained the binding of cyclopentadiene by diazotized 4-nitroaniline with the formation of 1 or 2.



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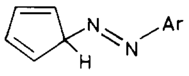

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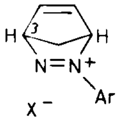

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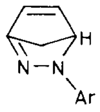

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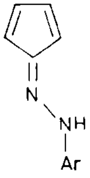
The alleged azo coupling reactions of 1,3-dienes were recognized by Carlson, Sheppard, and Webster[5] to be Diels-Alder reactions of the arenediazonium nitrogens. Does this revision include the reaction with cyclopentadiene ? Deprotonation of the bicyclic adduct 3 at the 3-position to furnish 4 as well as dehydrogenation of 3 yielding a bridged pyridazinium ion would violate Bredt's rule. The possibility of an endothermic and reversible cycloaddition of dienes to arenediazonium ions[6] could give competing pathways a chance. Indeed we established the azo coupling of cyclopentadiene, although only secondary products were isolated.

The suspension of 4-nitrobenzenediazonium chloride in 10 equiv. of cyclopentadiene was stirred for 30 min at -50°C, slowly warmed to room temperature and



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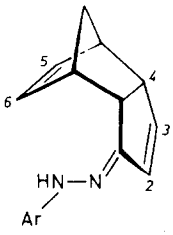

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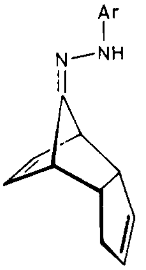

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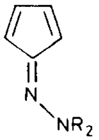


8 R = CH_3,H

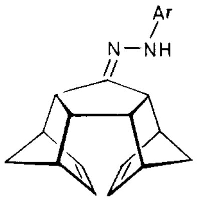
Ar = (4)-$NO_2C_6H_4$

kept for 15 min at 20°C. Removal of the hydrocarbon in vacuo, work-up with dichloromethane/water and thick-layer chromatography on silica gel furnished 31% of the yellow 1:3 adduct 9 (mp 182-183°C) and 35% of the orange 1:2 adduct 6 (mp 164-165°C).[7] When the reaction mixture above was stirred further 16 hr at room temperature, 60% of the 1:3 adduct 9 was isolated. It was shown that 6 was converted to 9 by renewed treatment with cyclopentadiene.

In the ^{1}H-NMR spectrum ($CDCl_3$) of 6 the NH absorbs at δ 7.78 between the two branches of the AA'XX' of $C_6H_4NO_2$. The olefinic region displays a broad singlet at 5.82 (5-H and 6-H) and the AB part of an ABX spectrum at 6.11 and 6.33 for 2-H and 3-H with $J_{2,3}$ = 5.8, $J_{2,4}$ = 0.8 and $J_{3,4}$ = 2.5 Hz. The conjugation with C=N shifts the 2-H and 3-H signals downfield and causes $\Delta\delta$ 0.22 ppm; this pattern is consistent with 6 but not with 7. The light absorption of 6, λ(max) 399 nm and log ε 4.46 (dichloromethane), corresponds to that of an α,β-unsaturated 4-nitrophenylhydrazone, not compatible with 7.

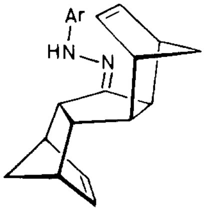
The primary product 1 of azo coupling is expected to tautomerize to the nitrophenylhydrazone 5 of cyclopentadienone. In the Diels-Alder reaction with a second molecule of cyclopentadiene, 5 could assume the role of a dienophile or a diene affording 6 and 7, respectively. According to Hafner and Goliasch,[8] cyclopentadienone cannot be captured by dienophiles but combines with cyclopentadiene. The analogy gives 6 a preference over 7. Hafner et al.[9] prepared the hydrazones 8 which are lacking the dimerization tendency of cyclopentadienone.

The ^{1}H-NMR spectrum ($CDCl_3$) of the 1:3 adduct 9 revealed that the sharp melting crystal consists of a 1:1 mixture of isomers. Two NH signals occur at δ 7.65 and 7.80; whereas the low-field parts of the aromatic AA'XX' spectra of the two isomers coincide, the high-field parts do not. HPLC (du Pont 830, Zorbax Sil, benzene) allowed the separation: mp 188-189°C and 202-203°C. The light absorption, λ(max) 391 nm, is shifted to shorter waves compared with 6. In the mass spectrum of 9, one observes the parent peak m/e 347 (15%), 281 (M^+ - cyclopentadiene, 74%), and 215 (M^+ - 2 cyclopentadiene, 100%). The presence of two norbornene-type double bonds in 9 was demonstrated by the 1,3-dipolar cycloaddition of 2 equiv. of phenyl

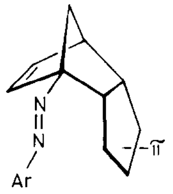


9a

Ar = (4)-$NO_2C_6H_4$



9b



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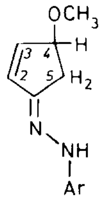
azide at 20°C furnishing a crystalline bisadduct (dec.p. $\sim$203°C).[7]

It was tacitly assumed that the formation of 6 from 5 + cyclopentadiene follows the *endo* principle. The *tentative* structures 9a and 9b are both endo adducts with respect to the second cyclopentadiene unit. The rigid stereochemistry of the hydrazone group thwarts the C_S and C_2 symmetry of the carbon skeleton. The ^{13}C-NMR spectra indicate nonequivalent saturated and olefinic carbon atoms in both adducts.

Ranganathan et al.[10] recently described the formation of 96% of a 1:2 adduct 10 (mp 175-178°C) from 4-nitrobenzenediazonium fluoborate and excess cyclopentadiene *in refluxing methanol;* structure 10 was allegedly supported by all spectra. We found it difficult to understand why the primary azo compound 1 did not tautomerize to the hydrazone and why 1 acted in the role of the diene in the subsequent addition of cyclopentadiene. Our attempt at reproducing the result furnished 20% of our 1:3 adduct 9. The reported ^{1}H-NMR data [10] - the splitting of the XX' branch of $C_6H_4NO_2$ was ascribed to π isomers - suggested that the Indian authors had isolated the 1:1 crystal of 9a + 9b.



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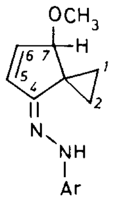

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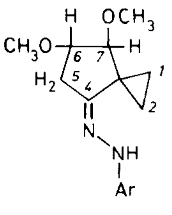

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Ar = (4)-$NO_2C_6H_4$

The reaction of 4-nitrobenzenediazonium fluoborate with 1 equiv. of cyclopentadiene *in methanol at -10°C* produced 57% orange crystals of 11 (mp. 171-173°C), the methanol adduct of intermediate 5, besides 12% 6. The vinylic AB part of ABX at δ 6.46 and 6.63 with $J_{2,3}$ = 5.5 Hz and the AB spectrum of 5-H_2 with $J_{5,5}$ = 16.4 Hz, further split by 4-H, establish structure 11.

The azo coupling of cyclopentadiene does not involve anion formation. In order to make this evident, 4-nitrobenzenediazonium fluoborate was reacted with 1 equiv. of the spirodiene 12 in methanol. Thick-layer chromatography on SiO_2 provided 15% of the methanol adduct 13 (mp 146-148°C) and 13% of the bis-adduct 14 (mp 140-141°C); λ(max) 399 and 392 nm are in accordance with the unsaturated and saturated ketone 4-nitrophenylhydrazone. The ^{1}H-NMR spectra indicate four non-equivalent protons at the 3-membered ring of 13 and 14. The exchangeable NH occurs at δ 7.90 in 13 and 7.48 in 14. The 5-H_2 in 14 appears as an AB pattern at δ 2.48 and 2.82 with J_{gem} = 17.9 Hz, further coupled to 6-H with 4.0 and 6.0 Hz.

The results point out that Meyer's azo coupling reaction of aliphatic 1,3-dienes is the competing pathway if the favored Diels-Alder reaction does not lead to a stable product.

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