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REARRANGEMENT OF 10-OXABENZO-SYN-SESQUINORBORNENE BY LIGHT AND BY ACIDS

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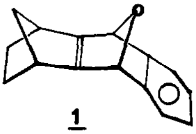
Abstract - 10-Oxabenzo-syn-sesquinorbornene (1)is rearranged by either UV irradiation or strong acid to 2,3-norborneno-1-naphthol (5), whose methyl ether is formed by the acid rearrangement in the presence of methanol. The mechanism of the acid rearrangement is discussed. With strong acid, cyclopentadiene reacts with 1-naphthol to yield 2- and 4-cyclopentenyl-1-naphthols.

The title compound, 1, has been observed to isomerize on irradiation in hydrocarbon solvents [1], but the structure of the product was not established.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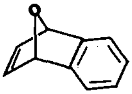
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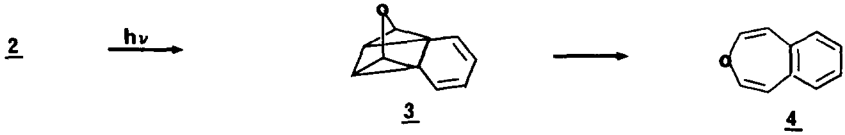
In the case of the related compound 2 (1,4-dihydronaphthalene-1,4-endoxide) irradiation leads to the benz(f)oxepin 4, with the quadricyclane 3 being proposed as an intermediate [2].



Any rearrangement of 1 in the manner of the prototype 2 would involve a double violation of Bredt's rule; it was therefore of interest to establish the structure of the stable product in the present case. This product, now obtained in good yield both photochemically and by the action of strong acids, proves to be 2,3-norborneno-1-naphthol 5.

The same product 5 (identical NMR and IR spectra) was obtained from both photochemical and acid-catalyzed rearrangements, the isolation being easier by the latter procedure. 3 ml of concentrated hydrochloric acid was added to a solution of 150 mg of 1 in 10 ml of carbon tetrachloride, and the mixture was heated under nitrogen for 24 hours. After washing and drying the organic layer, 120 mg (80%) of 5 was obtained. Similar yields of 5 were obtained using the strongly acidic ion exchange resin Amberlyst XN-1010 .

^{13}C NMR: 148.2(s), 142.8(s), 133.9(s), 130.2(s), 127.4(d), 127.2(s), 125.1(d), 123.9(d), 121.3(d), 111.2(d), 48.1(t), 43.9(d), 38.9(d), 27.7(t), 27.1(t) .

^{1}H NMR ($CDCl_3$): δ8.35-8.05(m, 1H), 7.90-7.65 (m, 1H), 7.55-7.33 (m, 2H), 7.30 (s, 1H), 5.30 (br s, 1H), 3.62 (m, 1H), 3.48 (m, 1H), 1.10-1.81 (m, 6H) .

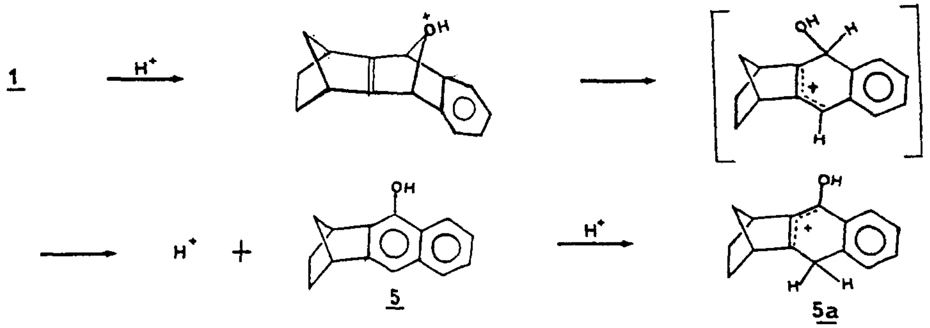
IR: 3600-3100 (br), 2900, 1700, 1580, 1240, 900 cm^{-1} .

M.S.: m/e calcd for $C_{15}H_{14}O$, 210.1045 obsd 210.1049 .

The acid-catalyzed formation of 1-naphthol from 1,4-endoxydihydronaphthalene (2) was observed many years ago [3] , and is consistently formulated as a cationic sequence beginning with protonation of the oxygen bridge.

Scheme 1 shows the application of this mechanism to the rearrangement of 1 . The C-O cleavage opening the bridge, if not actually concerted with the departure of the proton from the bridgehead, must be immediately followed by this proton removal.

Scheme 1



The rearrangement of 1 was observed under stable-cation conditions at -30°by slowly mixing 1 with fluorosulfonic acid in nitrogen-saturated CD_2Cl_2 in an NMR tube.

^{13}C NMR: 204.3(s), 181.5(s), 147.5(s), 138.1(s), 137.5(d), 129.9(d), 129.7(s), 128.5(d), 125.6(d), 51.5(d), 48.3(t), 39.8(d), 36.4(t), 26.0(t), 25.0(t) .

By comparing ^{13}C NMR chemical shifts of allylic carbocations derived from isodicyclopentadienes[4] and substituted naphthalenium ions [5,6] , it can be concluded that in this case the observed carbocation was 5a, derived from direct protonation of 5 .

The total rate of the photo-rearrangement of 1 was unaffected by the presence of triethylamine. Thus the photochemical process involves no protonation, but a benzylic-allylic cleavage of a bridge O-C bond in the excited state, unassisted by the phenolic product.

The methyl ether 6 was prepared from 5 by methyllithium and dimethyl sulfate and characterized; the same species resulted from quenching of solutions of the cation with methanol.

For 6:

^{13}C NMR: 148.9(s), 147.8(s), 134.0(s), 133.5(s), 127.4(d), 126.9(s), 125.1(d), 124.4(d), 121.9(d), 113.7(d), 61.3(q), 47.9(t), 43.5(d), 40.6(d), 27.6 (double intensity, t) .

^{1}H NMR: δ8.12-8.35(m, 1H), 7.68-7.92(m, 1H), 7.20-7.58(m, 3H), 4.10(s, 3H), 3.75-3.92(br s,1H),3.39-3.53(br s,1H),1.10-2.15(m, 6H) .

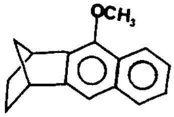
I.R.: 3050, 2950, 1300, 1100, 750 cm^{-1} .

M.S. (70 ev): m/e (relative intensity), 224(100.0), 209(10.4), 196(90.9), 181 (92.8), 165(54.6), 152(71.2), 76(31.4), 63(16.1), 57(12.5) .

The structure of 5 suggested its possible synthesis by a Diels-Alder reaction from cyclopentadiene and the p-tautomer of 1-naphthol. Instead, clean 2- and 4-substitution was observed under catalysis by a strong acid resin.

When a mixture of 1-naphthol and freshly distilled cyclopentadiene was stirred for 2.0 days at room temperature in the presence of Amberlyst XN-1010, 7 and 8 were obtained in a 1:2 ratio together with a small amount of another product, indicated to be the 2,4-dicyclopentadienyl product 9, since its mass spectrum showed a molecular ion with m/e 276. By following the reaction with gas chromatography it was observed that 9 starts to form only when high concentrations of 7 and 8 have accumulated.

When the reaction was carried out at 60°C, 7 was formed in a 4-fold excess over 8, indicating 7 to be the thermodynamically favored product. No significant transformation was observed when 7 and 8 were heated separately without a catalyst. The benzylic proton in 8 (which is also allylic) resonates at δ4.60 and shifts upfield to δ3.72 on hydrogenation to (11) .



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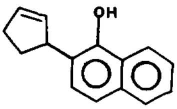

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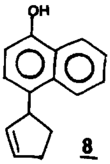

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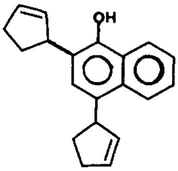

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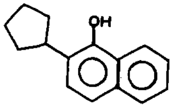

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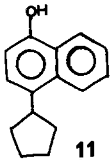

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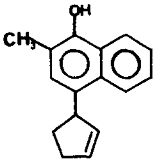
A similar upfield shift was also observed in the case of 7 and its hydrogenated analogue 10. This is in good agreement with the position of the double bond.

Under the same conditions the reaction between 2-methyl-1-naphthol and cyclopentadiene gave 12 as the only product.



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For 7:

^{1}H NMR (CDCl$_3$): δ8.25(m, 1H), 7.80(m, 1H), 7.06-7.62(m, 4H), 6.00(m, 2H), 4.25(m, 1H), 2.10-2.68(m, 4H) .

I.R.: 3490(br),3060, 2850, 1670, 1580, 1400, 1280, 820 cm^{-1} .
mass spectrum, m/e calcd 210.1045, obsd. 210.1039 .

For 8:

^{1}H NMR (CDCl$_3$): δ8.25(m, 2H), 7.55(m, 2H), 7.20(d, J=9.0 Hz, 1H), 6.76(d, J=9.0 Hz, 1H), 6.00(m, 2H), 5.30 (br s, 1H), 4.60(m, 1H), 2.32-2.78(m, 4H) .

I.R.: 3450 (br), 3060, 2950, 1600, 1400, 1290, 820 cm^{-1} .

mass spectrum: m/e calcd 210.1045 obsd 210.1045 .

For 10:

^{1}H NMR (CDCl$_3$): δ7.96-8.45(m, 1H), 7.63-7.90(m, 1H), 7.20-7.60(m, 4H), 5.48 (br s, 1H), 3.00-3.50(m, 1H), 1.25-2.30(m, 8H) .

I.R.: 3500 (br), 3050, 2950, 1580, 1400, 1240, 820 cm^{-1} .

mass spectrum: m/e calcd 212.1201 obsd 212.1206 .

For 11:

^{1}H NMR (CDCl$_3$): δ8.05-8.40(m, 2H), 7.43-7.72(m, 2H), 7.28(d, J=9.0 Hz, 1H), 6.80 (d, J=9.0 Hz, 1H), 5.28 (br s, 1H), 3.48-3.95(m, 1H), 1.00-2.35(m, 8H) .

I.R.: 3400, 1600, 1400, 1280, 1060, 770 cm^{-1} .

mass spectrum: m/e calcd 212.1201, obsd 212.1200 .

For 12:

^{1}H NMR (CDCl$_3$): δ7.98-8.36(m, 2H), 7.32-7.62(m, 2H), 7.10(s, 1H), 5.56-6.18(m, 2H), 5.15(br s, 1H), 4.40-4.72(m, 1H), 2.35(s, 3H), 1.00-2.10(m, 4H) .

^{13}C NMR: 15.7, 32.3, 33.0, 46.3, 115.8, 121.6, 123.8, 124.8, 124.9, 125.1, 126.2, 131.4, 132.1, 133.8, 134.2, 147.1 ppm .

mass spectrum: m/e 224 (M$^+$), 209, 195, 187, 165, 152, 128, 115, 82 .

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