

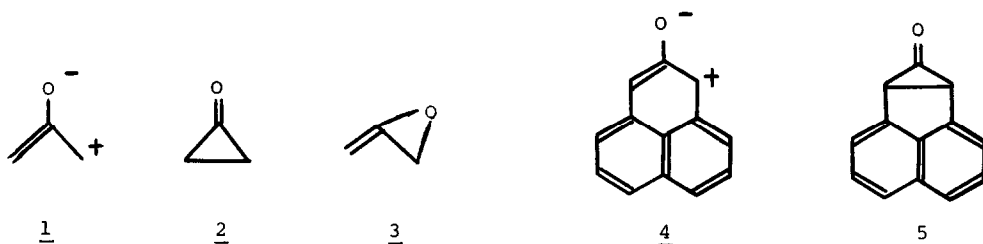
2,3-DIHYDROPHENALEN-2-ONE AND THE STRUCTURE OF "BLUE 342"

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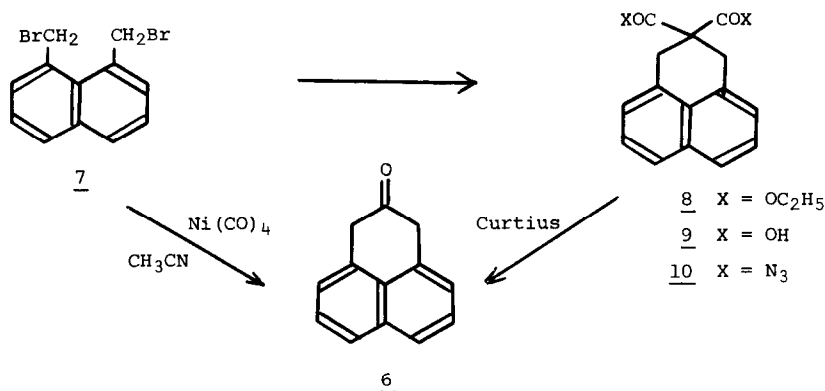
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ABSTRACT: Syntheses of the labile ketone 6 are described. Bromine rapidly converts 6 to a deep blue substance, C₂₆H₂₀O, for which the heptacyclic structure 15 is uniquely established.

Both experimental and theoretical considerations have led to the suggestion that the 2-oxyallyl zwitterion 1 may be involved in the nonstereospecific Favorskii rearrangement of α -haloketones,¹ in the racemization of (+)-2,3-trans-di-t-butylcyclopropanone² and in certain cycloadditions of substituted cyclopropanones.³ To date, however, no simple intermediates corresponding to zwitterion 1 have been directly observed,⁴ nor is there calculational agreement⁵ as to the stability of species 1 relative to its cyclopropanone (2) or allene oxide (3) tautomer.



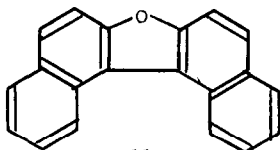
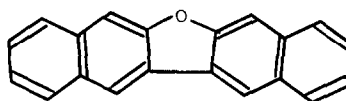
As a favorable test case we have explored the synthesis of the tricyclic oxyallyl zwitterion 4, in which phenalenium cation resonance would stabilize the open form 4 relative to its cyclopropanone counterpart 5. To prepare system 4 we required convenient access to 2,3-dihydrophenalen-2-one, 6, a ketone which had not been described in the literature. Ketone 6, an unexpectedly labile and air-sensitive substance, has now been synthesized in our laboratories by two independent routes. The first of these proceeds from 1,8-bis(bromomethyl)naphthalene 7 by way of the known malonate 8.⁶ Hydrolysis to the diacid 9 followed by a double Curtius rearrangement⁷ of the diazide 10 (C₂H₅OH, reflux, 60 min, then steam distilled with 2% H₂SO₄ under N₂) gave ca. 30% yield of pale green needles of ketone 6. Sublimation at 90° (0.1 mm) followed by two rapid recrystallizations from ether gave nearly pure 6 as an off-white solid, mp 110-111°;⁸ ir (CHCl₃), 1700 cm⁻¹; nmr (CHCl₃), δ 7.7-7.0 (m, 6H), 3.86 (s, 4H); ms, $\frac{m}{e}$ 182 (M, 100%), 154 (M-CO, 49%), 153 (84%), 152 (45%); uv (CH₃OH), 227 nm (ϵ = 65,000), 267 sh, 277 (5500), 287 (6500), 296 (5000). A more direct route to ketone 6 was provided by direct carbonylation of dibromide 7 with Ni(CO)₄ [CAUTION!] in CH₃CN at 50-60°, which after 3 hrs led to 6 as the only isolable organic product in yields ranging from 20 to 40%.



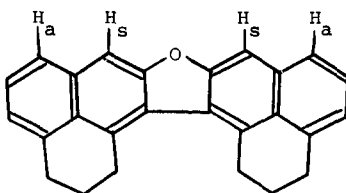
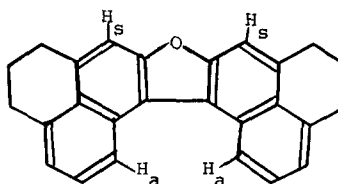
Halogenation of ketone 6, directed toward the α -haloketone precursor of zwitterion 4, led to remarkable results! When 6 was treated with Br₂ in CCl₄, C₆H₆, CHCl₃ or HOAc, or with SO₂Cl₂ in CCl₄ under a variety of conditions a deep ink-blue color immediately developed, often accompanied by a paramagnetic black precipitate. When the halogenation was carried out slowly by adding 66 mg Br₂ in 6 ml C₆H₆ to a solution of 75 mg ketone 6 in 3 ml heptane at 0° over 2.5 hrs, a deep blue solution resulted which on filtration and evaporation gave 67 mg of a blue solid. On purification by tlc (Si gel, C₆H₆), this blue product could be precipitated from C₆H₆-hexane as a granular blue-black solid which gave a single nonpolar spot on tlc. The blue unknown showed a single strong peak at m/e = 342 in the mass spectrum, with negligible fragmentation. Although this was consistent with the molecular formula C₂₆H₁₄O, our unknown ("Blue 342") invariably contained 1-3% bromine by analysis and gave combustion analyses which were correspondingly 1-3% low in carbon.

"Blue 342" obtained as described showed neither OH nor C=O absorption in the infrared. The electronic spectrum of "Blue 342" in CH₃CN was 614 nm ($\epsilon = 20,500$), 568 (10,300), 520 sh, 424 (1100), 398 (1200), 340 (3200), 308 (9200), 295 (6500), 252 (4600). In heptane, the 614 nm peak moved to 625 nm. "Blue 342" exhibited a powerful blue-red fluorescence in heptane solution when excited in the range 280-360 nm, with strong emission maxima at 604 and 642 nm having relative intensities 1:9; in CH₃CN only weak emission was observed. The material gave no nmr signal and exhibited a distinct esr signal appearing as a series of peaks at $g = 2.0026$, with total linewidth ca. 30 gauss. It is now known that rigorously purified "Blue 342" is not paramagnetic (*vide infra*) and the above esr spectrum is that of a trace impurity which however served to complicate our initial structural studies.

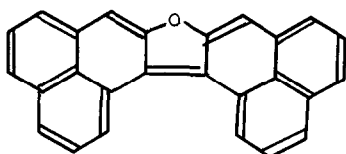
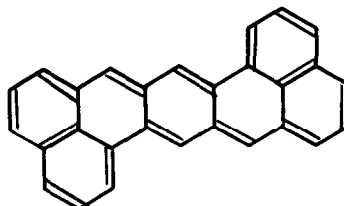
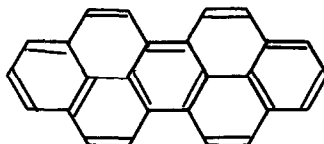
"Blue 342" was inert to OH⁻, Ac₂O/NaOAc, NaBH₄, PhSH or diluted HCl, and its electronic spectrum was pH independent. It reversibly formed unstable black salts with BF₃ or HBr. In the absence of nmr data, characterization was sought through chemical transformations. This was ultimately achieved by thorough hydrogenation of "Blue 342" (Pd/C/EtOAc, 1 atm, 8 hrs); incomplete hydrogenation led to reappearance of the "Blue 342" chromophore. From hydrogenation there was obtained a colorless crystalline hexahydro derivative (m/e = 348, C₂₆H₂₀O, 100%) having a highly structured uv (C₆H₆) at 369 nm ($\epsilon = 7770$), 352 (5890), 338 (2520) and 305 (2400) which resembled that of several known dinaphthofurans including compounds 11⁹ and 12.¹⁰

1112

The 220 MHz spectrum of hexahydro blue indicated the twofold symmetry of this molecule. The aliphatic region consisted of a 4H quintet at δ 1.97 and an 8H quintet at δ 3.06, in precise accord with the aliphatic AA'B₂B₂' pattern of 2,3-dihydrophenalene reported by Prinzbach.¹¹ The aromatic region consisted of a 2H doublet at δ 7.28 ($J = 8$ Hz) and another 2H doublet at δ 8.94 ($J = 8$ Hz) each coupled to a 2H triplet centered at δ 7.52 ($J = 8$ Hz). A 2H singlet at δ 7.50 was superimposed on the above triplet. These data indicated two identical aromatic subunits containing three adjacent protons, plus two identical isolated protons. Of all possible C₂₆H₂₀O structures derivable from two phenalene units, containing a dinaphthofuran chromophore and the requisite twofold symmetry, only two structures, 13 and 14, met the nmr multiplicity requirements. However, the downfield doublet at δ 8.94 in the nmr spectrum of hexahydro blue was incompatible with structure 13, where the most downfield o-coupled proton, H_a, would be expected to come around δ 7.5-7.9.¹² In contrast, the structure 14 for hexahydro blue nicely rationalized all features of the nmr, with the downfield, H_a and the singlet H_s both predicted¹⁴ to appear near the observed chemical shifts δ 8.94 and 7.50, respectively.

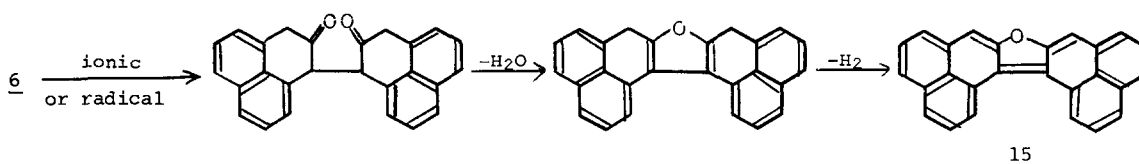
1314

With the structure of hexahydro blue thus defined as 14, the structure of "Blue 342" could be readily formulated as the phenalfulvalene derivative 15. Its spectrum is compatible with its Hückel excitation energy using Streitwieser's correlation ($\Delta E = 0.28\beta$, corresponding to λ_{\max} 635 nm)¹² and resembles the chromophore of the violet substance heptazethrene (16)¹³ which has a similar π -electron system.

1516 (λ 586, 540 nm)17

Our structure 15 fits all of the above data and requires that catalytic hydrogenation of 15 selectively reduces the most accessible external rings. Confirmation of structure 15 was obtained in two ways. Zinc dust pyrolysis of "Blue 342" at 500° gave a 50% yield of peropyrene 17, identified by uv, tlc and ms comparison with an authentic sample. Second, rigorous chromatographic purification of "Blue 342" by multiple tlc over Si gel ultimately gave a sample of 15 (mp 174-175°) free of paramagnetic impurities, which showed a distinct doublet at δ 9.21 (2H, $J = 8$ Hz) for proton H_a , another doublet at δ 7.72 (2H, $J = 8$ Hz) for proton H_b , and the remaining protons at δ 7.2-7.6 as a complex multiplet, in excellent accord with the required structure.¹⁴

"Blue 342", thus established as 15, is obviously a dehydrodimerization product derived by facile coupling of the two precursor units at the benzylic carbons followed by loss of water and H_2 . We have found that the presence of anhydrous MgO during the bromination of ketone 6 delays the appearance of "Blue 342," but that the presence of ca. 0.1 M furan or diethyl fumarate has no effect and yields no adducts. The overall mechanism is likely to be as follows; details of the coupling step are not known but may involve alkylation of an enol by a hydroxyphenalenium ion, or dimerization of two α -keto benzylic radicals. We conclude that the 1-halo derivatives of ketone 6 may not be convenient precursors of the target zwitterion 4; an alternative pathway from ketone 6 is described in the accompanying communication.¹⁵



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References

1. J. G. Aston and J. D. Newkirk, *J. Am. Chem. Soc.*, **73**, 3900 (1951); A. W. Fort, *ibid.*, **84**, 4979 (1962); H. O. House and W. F. Gilmore, *ibid.*, **83**, 3972, 3980 (1961).
2. R. L. Camp and F. D. Greene, *J. Am. Chem. Soc.*, **90**, 7349 (1968).
3. N. J. Turro, et al., *J. Am. Chem. Soc.*, **91**, 2283 (1969).
4. For more complex examples see D. Farnum et al., *Tetrahedron Lett.*, 5003 (1968) and references therein.
5. J. G. Burr and M. J. S. Dewar, *J. Chem. Soc.*, 1201 (1954); R. Hoffmann, *J. Am. Chem. Soc.*, **90**, 1475 (1968); N. Bodor et al., *ibid.*, **92**, 3854 (1974).
6. G. Bergson and A.-L. Pikas, *Acta Chem. Scand.*, **19**, 755 (1965).
7. C. Beard and A. Burger, *J. Org. Chem.*, **26**, 2335 (1961).
8. Found: C, 84.91; H, 6.10.
9. J. N. Chatterjea, V. N. Mehrotra and S. K. Roy, *Chem. Ber.*, **96**, 1167 (1963).
10. J. N. Chatterjea, R. F. Curtis and S. P. Dhoubhadel, *J. Chem. Soc.*, 765 (1961).
11. H. Prinzbach, V. Freudenberg and V. Scheidegger, *Helv. Chim. Acta*, **50**, 1087 (1967).
12. A. Streitwieser, Jr., "MO Theory for Organic Chemists," Wiley, New York (1961), p. 270.
13. E. Clar and I. A. Macpherson, *Tetrahedron*, **18**, 1411 (1962).
14. For relevant nmr models see R. H. Martin, et al., *Tetrahedron*, **20**, 897, 1078 (1964).
15. R. D. Mitchell, J. H. Ellert and N. L. Bauld, *Tetrahedron Lett.*, 0000 (1979). We thank Professor Bauld for advising us of his results prior to publication.