

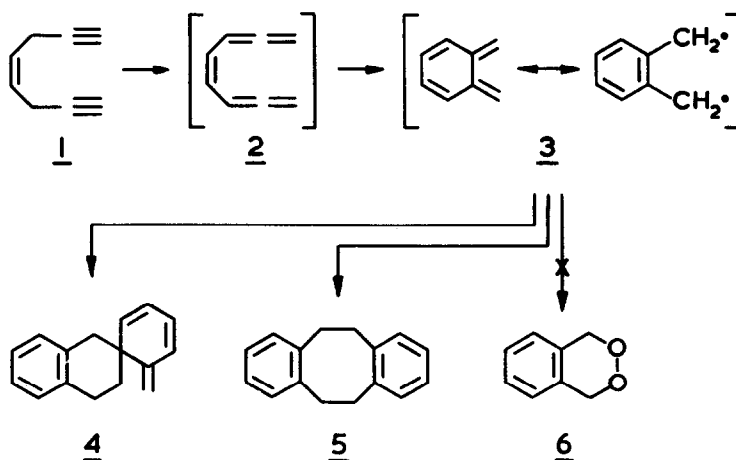
o-DIPROPADIENYL BENZENE AND 2,3-DIPROPADIENYL NAPHTHALENE. THE OXIDATION
OF DIALLENGES TO CYCLIC PEROXIDES WITH TRIPLET OXYGEN ¹

C.M. Bowes, D.F. Montecalvo and F. Sondheimer ²

Chemistry Department, University College, Gordon Street, London WC1H 0AJ

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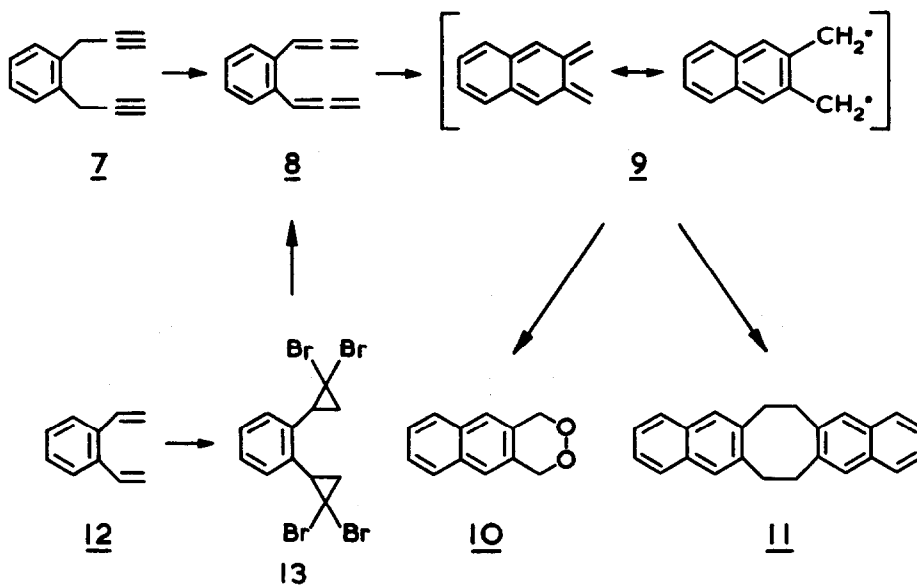
Several years ago it was reported by our group ³ that treatment of cis-4-octene-1,7-diyne (1) with KOBu^t led to the dimers 4 (25%) and 5 (2%), presumably via the diallene 2



and o-quinodimethane (3). We have now found that the analogous reactions of o-dipropargylbenzene (7) and 2,3-dipropargylnaphthalene (14) rather surprisingly give rise to the cyclic peroxides 10 and 17, respectively, in addition to more usual products. These transformations have been shown to involve the diallenes 8 and 15 as intermediates, which are oxidized with triplet oxygen to 10 and 17, presumably via 2,3-naphthoquinodimethane (9) and 2,3-anthraquinodimethane (16).

o-Dipropargylbenzene (7) (mp 38-38.5°) ⁴ was obtained in 35% yield by the reaction of α,α' -diiodo-o-xylene with an excess of ethynylmagnesium bromide in THF in the presence of CuCl and NaI. Treatment of 7 in THF with KOBu^t in HOBu^t at -78°, followed by warming to -10°, ⁵ shaking for 30 seconds, isolation with ether, and chromatography on SiO₂, gave the following new naphthalene derivatives: ⁶ (a) the peroxide 10 (25%), mp 156-167°; m/e 186; λ_{max} (EtOH) 225 nm (ϵ 104,000), 253sh (2100), 261 (3200), 270 (4500), 280 (4800), 291 (3100), 305 (370), 319 (190); NMR (CDCl₃): τ 2.1 - 2.7 (6H, m, aromatic), 4.60 (4H, s, CH₂); (b) the dimer 11 (8%), mp 296-297°; (c) an isomeric mixture of naphthalenic "complex dimers" (47%). The structure of 10 was confirmed by reduction with LiAlH₄ to 2,3-bis-

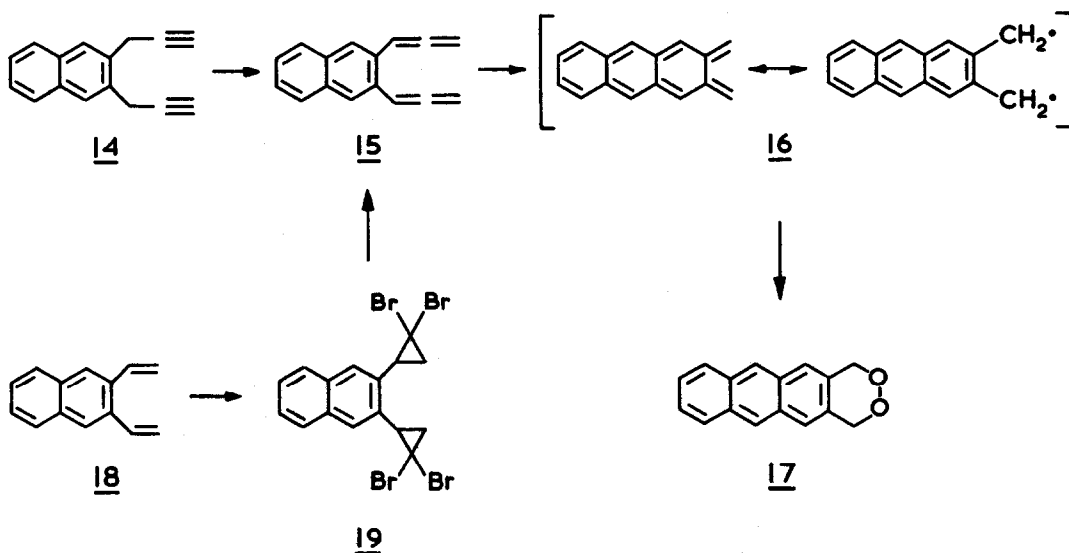
(hydroxymethyl)naphthalene, mp 159-160°, identical with an authentic sample.⁷ The structure of 11 was confirmed through an independent synthesis (in ca 1% yield) from 2,3-bis(bromomethyl)naphthalene⁷ and zinc in DMF at room temperature.⁸



The formation of 10, 11 and the "complex dimers" (total yield, 80%) from 7 was presumed to involve 8 and 9 as intermediates. Proof that *o*-dipropadienylnaphthalene (8) is indeed an intermediate in the reaction of 7 with KO^tBu was provided by rapid ether extraction, evaporation ($\leq 20^\circ$), and layer chromatography on SiO_2 . This led to 8 ($> 80\%$ pure) as an unstable oil; m/e 154 (40° , 40 eV); λ_{max} (MeOH) 264 nm; IR (neat): 1930 (s) cm^{-1} ; NMR (CCl_4): τ 2.4 - 3.0 (4H, m, aromatic), 3.61 (2H, t, $J = 7\text{Hz}$, $-\text{CH}=\text{}$), 4.96 (4H, d, $J = 7\text{Hz}$, $\text{CH}_2=\text{}$). The diallene 8 was converted fairly rapidly into the above described naphthalenes on standing in solution, and this transformation could be followed readily from the typical UV spectral change ($t_{1/2} = 16$ min, in MeOH at 30°). The diallene 8, showing identical properties, could also be prepared from *o*-divinylbenzene (12) by reaction with an excess of dibromocyclopropane (generated from CHBr_3 , 50% aqueous NaOH, and triethylbenzylammonium chloride),¹⁰ followed by treatment of diastereomeric diadducts 13 [mp 152-153° (18%);^{10,11} mp 73-75° (9%)] with LiMe in ether at -35° .

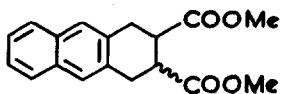
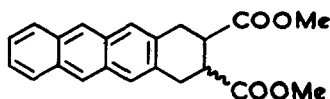
That atmospheric triplet oxygen was responsible for the oxidation of the diallene 8 to the peroxide 10¹² was shown by the facts that the yield of 10 was decreased from 25% to 10% when attempts were made to exclude oxygen in the reaction of 7 with KO^tBu , was increased to 42% when oxygen was bubbled through the mixture, and these yields were essentially unchanged when the reactions were carried out in the dark. When crude 8 (from 7) was extracted with oxygen saturated ether, and oxygen was then bubbled into the dilute ether solution for 3 hours, the peroxide 10 was obtained in 78% yield (based on 7).

2,3-Dipropargylnaphthalene (14) (mp 90.5 - 91.5°) was obtained in 30% yield from 2,3-bis(iodomethyl)naphthalene [from 2,3-bis(bromomethyl)naphthalene ⁷ and NaI in acetone], as described for 7. Treatment of 14 with KOBu^t in HOBU^t at -78°, followed by warming to -15°, shaking for 30 seconds, and isolation as described for 8, gave 48% of 15 as needles, mp 75-77°; m/e 204 (35°, 70 eV); λ_{max} (MeOH) 257 nm (ϵ ca 60,000); IR (KBr): 1930(s) cm^{-1} ; NMR (CDCl₃): τ 2.1 - 2.8 (6H, m, aromatic), 3.44 (2H, t, $J = 7$ Hz, -CH=), 4.83 (4H, d, $J = 7$ Hz, CH₂=). The diallene 15 was transformed to anthracenic products on standing, a change which could again be monitored simply by UV spectroscopy ($t_{1/2} = 100$ min, in MeOH at 30°). The same diallene 15 was obtained in ca 10% yield from 2,3-divinylnaphthalene (18) via the bis(dibromocarbene) adducts 19 [mp 226-228° (12%); mp 143-145° (1%)], as described for the synthesis of 8 from 12.



Leaving a solution of 15 in oxygen saturated MeOH for 3 days at room temperature (with or without exclusion of light) resulted in 97% of the peroxide 17 ¹³ as yellow plates, mp 228-231°; m/e 236; λ_{max} (MeOH) 250sh nm (ϵ 82,000), 256 (162,000), 327 (2300), 344 (4300), 362 (5100), 382 (4300); NMR (CDCl₃, 65°): τ 1.65 - 2.7 (8H, m, aromatic), 4.58 (4H, s, CH₂). The structure was confirmed by reduction with LiAlH₄ to 2,3-bis(hydroxymethyl)-anthracene, mp 267-269°, identical with an authentic sample. The peroxide 17 was originally obtained directly from 14 by treatment with KCBu^t, preferably by bubbling in oxygen (51% yield). It is of interest that all attempts similarly to prepare the peroxide 6 from 1 were unsuccessful.

Corroborative evidence for the intermediates 9 and 16 was provided by trapping experiments. The diallene 8 (from 7) in ether with dimethyl fumarate and dimethyl maleate at room temperature gave 20 (72% based on 7; mp 123-124°) and 21 (43% based on 7; mp 116-118°),

20, trans21, cis22, trans23, cis

respectively. Similarly 15 (from 14) with these esters yielded 22 (68% based on 14; mp 218-220°) and 23 (35% based on 14; mp 183-185°), respectively. Each of these reactions was at least 95% stereospecific. Further experiments are in progress to investigate the nature of 9 and 16,¹⁴ a subject which we propose to discuss subsequently.

REFERENCES AND NOTES

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- To whom inquiries should be addressed.
- D.A. Ben-Efraim and F. Sondheimer, *Tetrahedron Letters* 313 (1963).
- UV, IR, NMR and mass spectra, compatible with the assigned structures, were obtained for all new compounds.
- Above -10°, appreciable quantities of *o*-propadienylpropynylbenzene and *o*-dipropynylbenzene were obtained.
- Related conversions of *o*-dipropargylbenzene derivatives to naphthalene derivatives (naphtho[b]cyclobutenes) via diallenes have been described [M.P. Cava, B. Hwang and J.P. van Meter, *J. Amer. Chem. Soc.* 85, 4031 (1963); H.A. Staab and B. Draeger, *Chem. Ber.* 105, 2320 (1972)], although the presumed diallene intermediates were not isolated.
- W. Ried and H. Bodem, *Chem. Ber.* 89, 708 (1956), and references quoted there.
- See K. Alder and M. Fremery, *Tetrahedron*, 14, 190 (1961).
- 2,3-Naphthoquinodimethane (9) has been postulated as an intermediate in the formation and pyrolysis of naphtho[b]cyclobutene [M.P. Cava and R.L. Shirley, *J. Amer. Chem. Soc.* 82, 654 (1960); M.P. Cava, R.L. Shirley and B.W. Erickson, *J. Org. Chem.* 27, 755 (1962)].
- See L. Skattebøl, G.A. Abskharoun and T. Greibrokk, *Tetrahedron Letters* 1367 (1973), and references quoted there.
- L. Skattebøl, *J. Org. Chem.* 29, 2951 (1964).
- For other examples of peroxide formation with triplet oxygen, see R. Criegee, *Angew. Chem.* 74, 703 (1962); D.H.R. Barton, G. Leclerc, P.D. Magnus and I.D. Menzies, *J. Chem. Soc. Chem. Comm.* 447 (1972).
- When attempts were made to exclude oxygen, insoluble anthracenic dimers, in addition to 17, were obtained.
- For recent SCF molecular orbital calculations of 9 and 16, see G.J. Gleicher, D.D. Newkirk and J.C. Arnold, *J. Amer. Chem. Soc.* 95, 2526 (1973).