1,3-Bridged Aromatic Systems. XIII. Reactions of Hindered Grignard Reagents with Oxygen[1]

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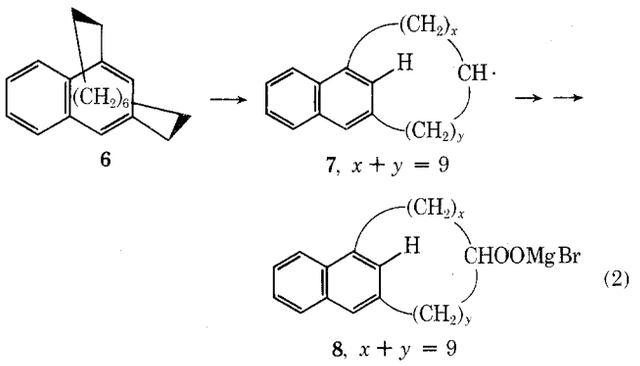
While there has been some controversy[2-4] as to whether the initiation step in the reactions of Grignard reagents with oxygen is ionic or involves radical intermediates, the reaction is now considered[5-9] to occur as shown in eq 1. The

$$\begin{aligned} RMgX + O_2 &\longrightarrow R\cdot + \cdot OOMgX \\ R\cdot + O_2 &\longrightarrow ROO\cdot \\ RMgX + ROO\cdot &\longrightarrow R\cdot + ROOMgX \end{aligned} \qquad (1)$$

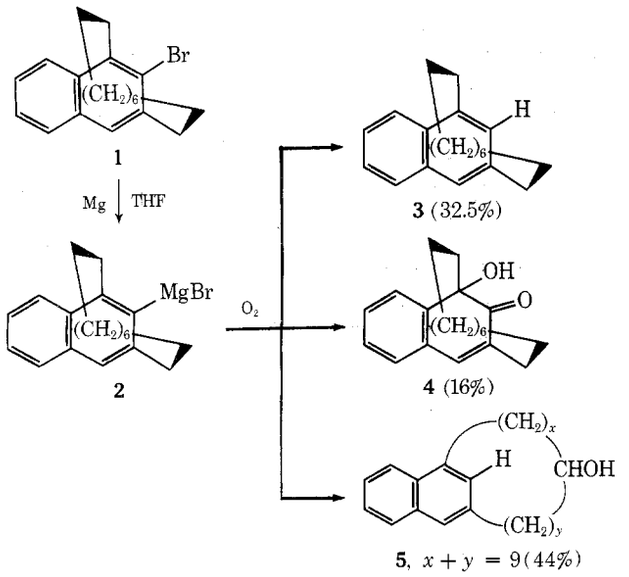
previous report[10] that the reaction of **2** with oxygen (Scheme I) gives the transannular alcohols **5** is consistent with rapid radical transfer[12,13] as shown in eq 2; however,



6 → **7**, $x + y = 9$ → **8**, $x + y = 9$ (2)

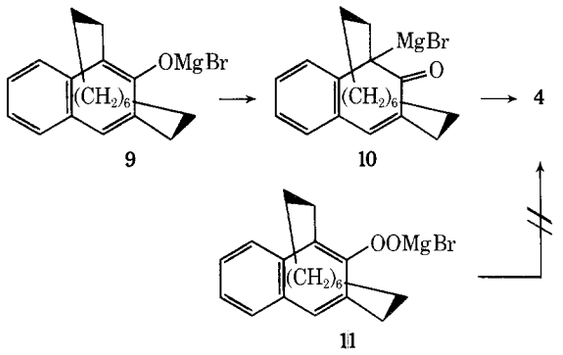
the reaction sequence leading to **3** and **4** has not been established. We have reinvestigated the process outlined in Scheme I with the following observations.

Scheme I[11]



(1) The expected[9] phenol **9** is not detected in the products of the reaction, but is the probable precursor to the keto alcohol **4** as shown in Scheme II; we had originally considered that **4** may be derived from the hydroperoxide **11**.

Scheme II

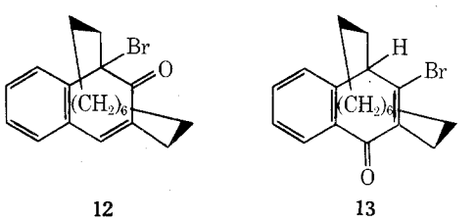


Reaction of **2** with the bromomagnesium salt of *tert*-butyl hydroperoxide, a process that should give **9** by an ionic process,[8] gave **4** in high yield. These results were obtained in the presence of excess **2**; consequently, the intermediate **9** is oxidized more rapidly by hydroperoxide salt to **4** than is the Grignard reagent **2** to **9**. That the phenolate ion **9** would rearrange to **10** is reasonable since such rehybridization within the aryl ring would reduce strain in the cyclophane system;[14] tertiary C–MgX bonds are known[3,15] to react with hydroperoxide to give alcohols.

(2) Reduced cyclophane **3** is not derived to any appreciable extent from unreacted Grignard reagent **2** since decomposition of the reaction product with D_2O gave **3** which contained only 7.3% of the d_1 species (mass spectrum).

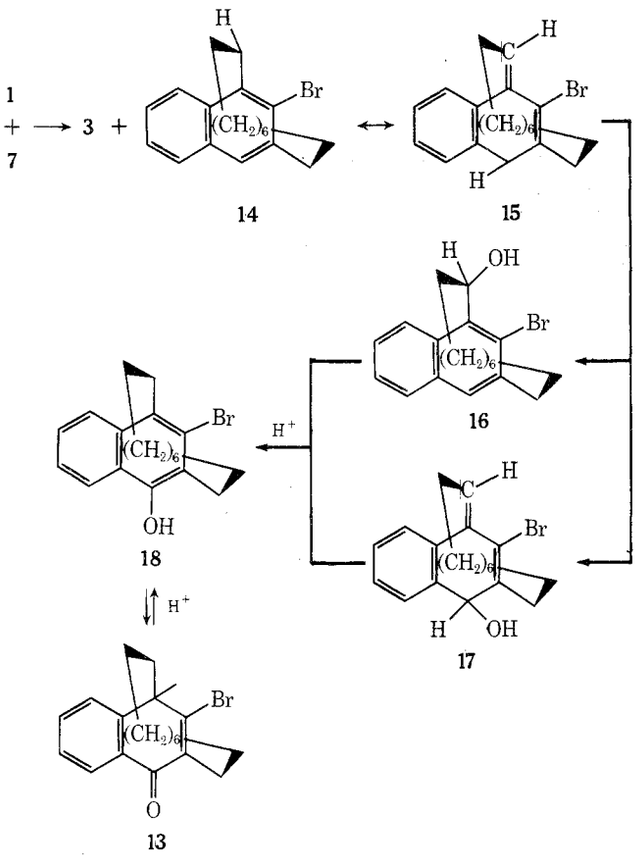
(3) Reduced cyclophane **3** (and the aryl H in **5**) is not derived to any appreciable extent by reaction of either **6** or **7** with solvent. When the reaction of **2** with oxygen was carried out in pure perdeuteriotetrahydrofuran as solvent, the reduced cyclophane **3** contained only 9% of the d_1 species (mass spectrum); the principal ketone[2] obtained by oxidation of **5** showed essentially no (0.4%) d_1 species.

(4) A new, relatively unstable, bromine-containing product was isolated from the reaction mixture (ir shows ν at 1660 cm^{-1}, characteristic[16] of conjugated phenone; pmr shows peri-H at δ 7.7, one benzylic proton at δ 3.0 and two allylic protons at δ 2.6) for which structures **12** and **13** were



considered. Compound **12** could form by elimination of magnesium oxide from **11**. The single benzylic proton at δ 3.0, however, suggests structure **13**. The isolation of **13** suggests that unconverted **1**, which is generally recovered from such reactions, is the source of hydrogen leading to **3**, as shown in Scheme III. The proposed intermediate alco-

Scheme III



hols **16** and/or **17** could be formed[17] by a normal sequence of reactions from **14** or **15**; the conjugated ketone **13** is assumed to result by prototropic rearrangement of **16** and/or **17** upon acid work-up. That **13** would exist in the keto form rather than the phenolic enol form **18** is interesting and is attributed to relief of strain in the cyclophane system.[14]

Experimental Section

Reaction of 2 with Oxygen. The crude product obtained from **1** (0.75 g)[10] was separated into four bands by preparative chromatography as previously described[10] which were removed with 15% methanol in chloroform to give: (1) leading band, mixture of **1** and **3** (0.240 g); pure **3** (0.107 g, mp 39–40° from ethanol[10]) obtained from trailing edge after rechromatography;[18] (2) yellow oil (0.063 g), mostly **13**; (3) nearly pure **4** (0.101 g; 0.086 g by sublimation, mp 140–142°[10]); (4) alcohols **5** (0.248 g). The yields of **3**, **13**, **4**, and **5** based on consumed **1** were 32.5, 9, 16, and 44%, respectively.

Compound **13**: mp 110–112° from diethyl ether, 0.042 g, yellow solid; high-resolution mass spectral parent ion 360.1089 ($C_{20}H_{25}BrO$); ν 1660 cm^{-1}; pmr δ 7.7 (m, aromatic H, 1.0), 7.6–7.1 (m, aromatic H, 3.0), 3.0 (broad m, ArCH, 1.0), 2.6 (broad m, $=CCH_2$, 2.0), 2.3–0.5 (m, CH_2, 17.5).

Anal. Calcd for $C_{20}H_{25}BrO$: C, 66.48; H, 6.97; Br, 22.12. Found: C, 66.36; H, 7.17; Br, 21.72.

Perdeuteriotetrahydrofuran (98.5% d, E. Merck, Darmstadt) was distilled from $LiAlD_4$ prior to use. Calculations of protio to d_1 species were calculated from mass spectral data as described by Biemann.[19]

Reaction of 2 with *tert*-Butyl Hydroperoxide. A solution of *tert*-butyl hydroperoxide[20] (0.13 g, 1.45 mmol, 99.2% solution[21,22]) in dry (from $LiAlH_4$) tetrahydrofuran (5 ml) was added slowly to a solution of **2** (from **1**,[10] 1.00 g, 2.90 mmol) in dry tetrahydrofuran (15 ml) packed in ice,[15] and the resulting solution was stirred, under nitrogen, for 16 hr while warming to room temperature. The mixture was cooled and 50 ml of 5% aqueous hydrochloric acid was added; the organic material was extracted with ether which was subsequently dried ($MgSO_4$) and concentrated. Chromatography of the oil (0.513 g) obtained from the ether as described above [petroleum ether (bp 60–90°) followed by petroleum ether (bp 30–60°)–5% ether] gave: (1) **3** (1.93 mmol), mp 40–41°,[10] and (2) crude **4** (0.213 g, 98.4% yield; 0.119 g from acetone, 55% yield, mp 138–140°[10]).

Registry No.—**1**, 25097-45-4; **3**, 25097-46-5; **4**, 25097-53-5; **5**, 52358-29-9; **13**, 52358-30-2; *tert*-butyl hydroperoxide, 75-91-2.

References and Notes

(1) Supported by the National Science Foundation GP-35429.
(2) C. W. Porter and C. S. Steele, *J. Amer. Chem. Soc.*, **42**, 2650 (1920).
(3) C. Walling and S. A. Buckler, *J. Amer. Chem. Soc.*, **77**, 6032 (1955).
(4) C. Walling, "Free Radicals in Solution," Wiley, New York, N.Y., 1957.
(5) G. A. Russell, *J. Amer. Chem. Soc.*, **76**, 1595 (1954).
(6) M. E. H. Howden, H. Maercker, J. Burdon, and J. D. Roberts, *J. Amer. Chem. Soc.*, **88**, 1732 (1966).
(7) R. C. Lamb, P. W. Ayers, M. K. Tooney, and J. F. Garst, *J. Amer. Chem. Soc.*, **88**, 4261 (1966).
(8) C. Walling and A. Cioffari, *J. Amer. Chem. Soc.*, **92**, 6609 (1970).
(9) J. F. Garst, C. D. Smith, and A. C. Farrar, *J. Amer. Chem. Soc.*, **94**, 7707 (1972).
(10) W. E. Parham, R. W. Davenport, and J. K. Rinehart, *J. Org. Chem.*, **35**, 2662 (1970).
(11) The yields of products are based on **1** consumed.
(12) G. A. Russell and R. F. Bridger, *J. Amer. Chem. Soc.*, **85**, 3765 (1963).
(13) While aryl radicals react with oxygen 10^3 faster than hydrogen abstraction,[11] models show that four bridge hydrogen atoms are in close proximity to the radical site in **6**, and thus are in high concentration relative to molecular oxygen.
(14) W. E. Parham, D. C. Egberg, and W. C. Montgomery, *J. Org. Chem.*, **38**, 1207 (1973).
(15) S. O. Lawesson and N. C. Yang, *J. Amer. Chem. Soc.*, **81**, 4230 (1959).
(16) N. B. Colthup, L. H. Daly, and S. E. Wiberly, "Introduction to Infrared and Raman Spectroscopy," Academic Press, New York, N.Y., 1964, p 244.
(17) Product **13** could form by related reactions involving abstraction of hydrogen from the other benzylic methylene group.
(18) Leading edge contained 52% of **1** and 48% of **2**; liquid chromatographic analysis [8 ft × ⅛ in. Porasil A, petroleum ether (bp 30–60°); 1 ml/min, six recycles].
(19) K. Biemann, "Mass Spectrometry: Organic Chemical Applications," McGraw-Hill, New York, N.Y., 1962, Chapter 5.
(20) Kindly supplied as 90% solution by Lucidol Chemical Division, Pennwalt Corp.
(21) Concentrated by azeotropic distillation: *cf.* P. D. Bartlett and H. Minato, *J. Amer. Chem. Soc.*, **85**, 1858 (1963).
(22) P. D. Bartlett, E. P. Benzing, and R. E. Pincock, *J. Amer. Chem. Soc.*, **82**, 1762 (1960).

Reactions of *N*-Sulfinylamides with Sulfoxides Bearing Electronegative Substituents

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It has been reported that *N*-sulfinylsulfonamides react with sulfoxides to give sulfimides.[1a,b] In an attempt to get various types of sulfimides for investigation of reactivities, we used sulfoxides containing electron-withdrawing groups on the α carbon. The reaction did not afford the expected substituted sulfimides **7** but led to the rearranged derivatives **3** and their thermal decomposition products **4**.

Reaction of *N*-sulfinyl-*p*-toluenesulfonamide (**1a**) with 2-(methylsulfinyl)acetophenone (**2a**) in refluxing benzene gave 2-(methylthio)-2-(*p*-toluenesulfonamido)acetophenone (**3a**), 2,2-bis(*p*-toluenesulfonamido)acetophenone (**4a**), and 2-methylthioacetophenone (**5a**) in 5, 71, and 11% yields, respectively. The reaction in refluxing ether, however, necessitated prolonged heating and resulted in the formation of **3a** (61%) and **4a** (15%). The structure of **3a**