Anal. Calcd for $C_{15}H_{13}O_2Br$: C, 59.03; H, 4.29. Found: C, 62.11, 62.24; H, 4.59, 4.59.

These figures are in agreement with those for a mixture of acid IV (96%) and acid II (4%). Further recrystallization from ligroin (bp 80–100°) raised the melting point to 155–156°. However this sample is still not pure since the melting point for pure acid IV prepared in another manner[8] is reported to be 164°.

Thin layer chromatography using silica gel and butanol saturated with aqueous ammonia (C_4H_9OH–concentrated ammonia–H_2O 8:15:5) readily separated acid II (R_f 0.96) and acid IV (R_f 0.58). Crude acid IV directly from the Friedel–Crafts reaction, part B, had an additional spot (R_f 0.45) which was found to be the starting acid I.

Methylation of acid IV (1.34 g, mp 146–148°) with an ether solution of diazomethane furnished the methyl ester. Evaporation of the ether left a residue which was recrystallized first from petroleum ether and then from isopropyl alcohol, mp 99–101°.

Anal. Calcd for $C_{16}H_{15}O_2Br$: C, 60.20; H, 4.74. Found: C, 60.13; H, 4.80.

3-Phenylcinnamic Acid (V).—The methyl ester of acid IV (0.37 g) and a solution of potassium hydroxide in anhydrous methanol (4 ml, 50%) were refluxed for 3 hr in a water bath. The reaction mixture was cooled, diluted with distilled water, and acidified to yield white needles, mp 140–156°. Recrystallization raised the melting point to 157–158°. The melting point of a mixture of this sample with an authentic sample[9] was also 157–158°. Also the infrared spectra of the two samples were identical.

Decarboxylation of 2,3,3-Triphenylpropionic Acid.—Acid II (1 g) was mixed with finely powdered soda lime (4 g) and about 1 g of copper powder[10] and heated with a free flame in a small distilling flask. The heating was continued was until no more material distilled. The crystalline part of the distillate was filtered to remove the major part of the accompanying oil and recrystallized from methanol, mp 123–124°. This substance was identified as stilbene by its characteristic nmr spectrum[11] and by observing the melting point of a mixture with authentic *trans*-stilbene.

Registry No.—I, 6286-30-2; IV, 19811-27-9; IV methyl ester, 24689-50-7.

(8) E. P. Kohler and G. L. Heritage, *Amer. Chem. J.*, **33**, 34 (1900).

(9) Prepared by the Reformatsky reaction of benzophenone with ethyl bromoacetate, followed by saponification and dehydration.

(10) The copper was used to more nearly duplicate the conditions used by Earl and Wilson who carried out the decarboxylation in a copper flask.

(11) Determined using the Varian A-60A spectrometer. See spectrum no. 306, Varian catalog of nmr spectra.

Stereochemistry of Dicoordinated Oxygen. II. Reinvestigation of the Purported 1,8-Monooxynaphthalene

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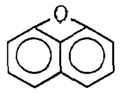
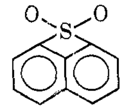
In connection with studies of unusual ether structures,[1] an old report of the preparation of a "*peri*-monoxynaphthalene" (1) was of great interest.[2] It was claimed that heterogeneous oxidation of α-naphthol with aqueous $FeCl_3$, or dehydration at 300° in a CO_2 atmosphere of 1,8-dihydroxynaphthalene gave good yields of 1, whose structure was assigned from combustion analysis, cryoscopic molecular weight, and chemical behavior.[2] Such a claim might ordinarily be discarded out-of-hand;[3] however, the recent isolation of a stable *peri* sulfone 2,[4] the evidence for 1,8-naphthyne,[4,5] and the existence of other highly strained aromatic systems, particularly benzocyclopropene,[6] warranted a reexamination of this highly unusual system.

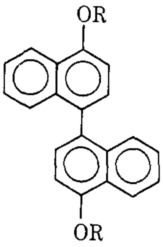


1

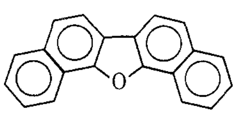


2

Following the published procedures in detail[2] and with some modifications, no trace of a substance corresponding to 1 or to the properties given for 1 could be detected. Rather, the only nonresinous, isolable products were starting material (α-naphthol) and 4,4′-dihydroxy-1,1′-dinaphthyl (**3a**)[7,8] purified as its diacetate **3b**. Although **3a** has the same melting point (300–302°) assigned to 1,[2] it is difficult to reconcile the cited properties[2] with those of a naphthol. There is some evidence[8] that with hot acid (HI) or at very high temperature (>300°) **3a** undergoes a rearrangement and dehydration to dinaphthofuran (4) (mp 183°). Neither of these conditions is applicable to the $FeCl_3$ reactions (see Experimental Section) and no product resembling **4** was detected. It is concluded that the reported synthesis of 1 is erroneous, and that $FeCl_3$ oxidation does occur to form the expected coupling product.[7,8]



3a, R = H
b, R = Ac



4

Experimental Section[9]

Oxidation of α-Naphthol.—In a typical experiment, a 750-ml aqueous mixture of α-naphthol [Eastman, distilled, mp 95.5–96.0° (lit.[10] mp 94°)] (30 g, 0.21 mol) and $FeCl_3$ (100 g, 0.6 mol) was refluxed for 60 min, giving a heterogeneous, purplish mixture. Filtration gave 5.5 g of dark blue powder and 27.4

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(1) Paper I: A. J. Gordon and J. P. Gallagher, *Tetrahedron Lett.*, 2541 (1970).

(2) E. Ayers, British Patent 394,511 (June 29, 1933).

(3) Particularly in view of the reported melting point (>300°); this work has been cited with criticism more recently [V. Balasubramaniyan, *Chem. Rev.*, **66**, 593 (1966)].

(4) R. W. Hoffmann and W. Sieber, *Justus Liebigs Ann. Chem.*, **703**, 96 (1967); *Angew. Chem.*, **77**, 810 (1965).

(5) C. Rees and R. Storr, *J. Chem. Soc. C*, 760, 765 (1969); R. W. Hoffmann, G. Guhn, M. Preiss, and B. Dittrich, *ibid.*, 769 (1969).

(6) For example, in *o*-di-*tert*-butylbenzene the high strain is relieved by bending of the bonds to the alkyl groups out of the aromatic plane [E. M. Arnett, J. C. Sanda, J. M. Bollinger, and M. Barber, *J. Amer. Chem. Soc.*, **89**, 5389 (1967)]; a classic example is the 2,2-paracyclophanes [for recent studies on spectroscopic properties, see O. Weigang, Jr., and M. Nugent, *ibid.*, **91**, 4555, 4556 (1969)]. Benzocyclopropene: *e.g.*, R. Anet and F. A. L. Anet, *ibid.*, **86**, 525 (1964).

(7) Originally prepared by a similar oxidation of α-naphthol: R. Willstätter and L. Schuler, *Chem. Ber.*, **61**, 362 (1928).

(8) G. Clemo, J. Cockburn, and R. Spence, *J. Chem. Soc.*, 1265 (1931).

(9) All melting points are uncorrected. Ir spectra were recorded on a Beckman IR-8; mass spectra were determined on Varian-Mat CH-5. Combustion analyses were obtained from MHW Laboratories, Garden City, Mich.

(10) E. Heilbron, "Dictionary of Organic Compounds," Oxford University Press, New York, N. Y., 1965.

g of mechanically separable, large chunks. Sublimation of the powder (100° *in vacuo*) followed by hot benzene extraction of the sublimate residue gave a total of 2.5 g (8.5%) of α-naphthol (melting point, mixture melting point, ir); only purple-brown tarry material remained, from which no other compounds in workable amounts could be separated by sublimation, extraction, or column chromatography. Hot benzene digestion of the large chunks yielded 6.1 g of gray-white powder, mp 285–295°, which was suspected to be **3a** (yield 10%). Heating for 30 min with excess Ac_2O and a few drops of pyridine gave an oil which solidified. Recrystallization from benzene–petroleum ether (30–60°) gave white solid **3b**: mp 217–218° (lit.[11] mp 217°); ir (KBr) 1760 (s), 1370 (m), 1200 (s), 1150 (m), 760 (m); mass spectrum *m/e* 370 (parent). *Anal.* Calcd for $C_{24}H_{18}O_4$: C, 77.82; H, 4.90; O, 17.28. Found: C, 78.10; H, 4.93. Evaporation of the benzene supernatant (from the chunks) gave a dark, tarry residue (19 g); chromatography on alumina, using various benzene, petroleum ether (30–60°), chloroform eluent mixtures gave several fractions, all of which were fluffy, high melting (dec), dark powders, whose ir spectra (Nujol) exhibited broad OH (3400), carbonyl (1650), and other strong peaks at 1580 and 760 (*inter alia*). These powders are probably condensation products of the quinone and quinol type.

Dehydration of 1,8-Dihydroxynaphthalene.—The solid diol [K and K, recrystallized from H_2O, mp 140.5–141.0° (lit.[10] mp 140°)] (5 g) was heated at 300° in a CO_2 atmosphere; some evolution of H_2O was observed. After 15 min, the dark, glassy residue was cooled and subjected to standard work-up (extraction, sublimation, chromatography, etc.). Only starting material (~100 mg) could be identified from the otherwise intractable mixture.

Acknowledgment.—The generous support of the National Science Foundation (NSF GP-7325) is greatly appreciated.

(11) Z. Rappaport, Ed., "Handbook of Tables for Organic Compound Identification," 3rd ed, Chemical Rubber Publishing Co., Cleveland, Ohio, 1967, p 127.

Thermal Migrations of Allyl Groups in Linearly Conjugated Cyclohexadienones[1]

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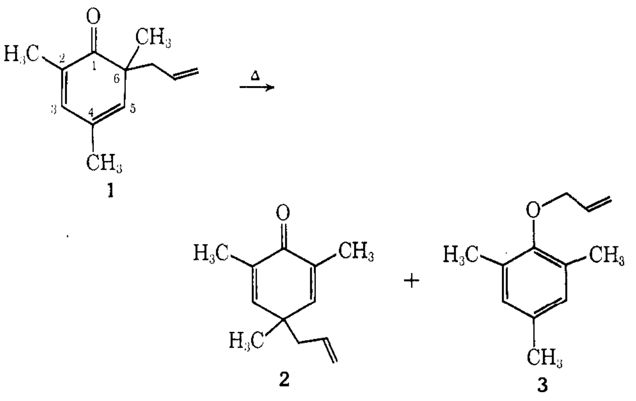
Received May 19, 1970

Allyl groups at the quaternary carbons of linearly conjugated cyclohexadienones undergo facile thermal [3,3] sigmatropic shifts to C-4 (Cope migrations) or to the carbonyl oxygen (reverse-Claisen migrations).[2]



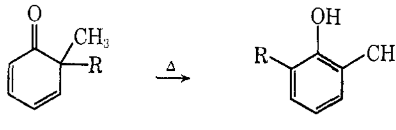
1

2

3

Migration of allyl or 2-butenyl groups to C-4 is the major reaction when C-4 is unsubstituted,[3] or when C-4 bears a methyl group and an unsubstituted allyl group migrates.[4] Thus, rearrangement of **1** gives **2** as the major product, presumably accompanied by smaller amounts of **3**.[4] This process is a useful synthetic method for the preparation of cross-conjugated cyclohexadienones, which are often difficult to prepare in other ways.

Other work in this laboratory has shown that migrating groups which cannot undergo [3,3] shifts (*e.g.*, benzyl and cyclopropylmethyl groups) will undergo [1,5] sigmatropic shifts from C-6 to C-2 of the dienone (eq 1).[5] We have also shown that substituted allyl groups undergo acid-catalyzed [1,5] shifts to C-2 when the "normal" acid-catalyzed Cope migrations to C-4 are inhibited by the presence of bulky substituents at C-4 or at the terminus of the migrating allyl chain.[6]

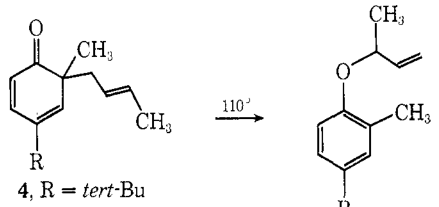


(1)

No previous work reports whether allyl groups can similarly undergo thermal [1,5] shifts in addition to, or in preference to, the normal [3,3] shifts. It seemed of interest to determine whether such shifts can occur.

In order to maximize the possibility of observing [1,5] shifts, it was desirable to inhibit, insofar as possible, the competing [3,3] shifts. It seemed difficult to design a molecule in which the possibility of reverse-Claisen migration to oxygen would be severely inhibited. It was found, however, that the normally more important Cope migration to C-4 could be inhibited quite easily by steric interference between appropriate substituents at C-4 and at the end of the migrating allyl chain.

Dienone **4** was chosen as a molecule in which migration to C-4 should be quite difficult. Thermal rearrangement of **4** at 110° was found to give a quantitative yield of the reverse-Claisen rearrangement product, **5**. Vpc analysis showed that less than 0.5% of any [1,5] migration to give 2-butenyl-4-*tert*-butyl-6-methylphenol could have occurred.



4, R = *tert*-Bu
6, R = CH_3

5, R = *tert*-Bu
7, R = CH_3

Thermal rearrangement of dienone **6** similarly gave a quantitative yield of ether **7**. This not only demonstrates that [1,5] migration cannot compete with the reverse-Claisen migration, but shows that the normal

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(1) Reactions of Cyclohexadienones, XXVI. Part XXV: *J. Amer. Chem. Soc.*, **92**, 6252 (1970).

(2) B. Miller in "Mechanisms of Molecular Migrations," Vol. I, B. S. Thyagarajan, Ed., Interscience, New York, N. Y., 1968.

(3) (a) F. Kalberer, K. Schmid, and H. Schmid, *Helv. Chim. Acta*, **39**, 555 (1956); (b) D. Y. Curtin and R. J. Crawford, *J. Amer. Chem. Soc.*, **79**, 3156 (1957).

(4) B. Miller, *ibid.*, **87**, 5115 (1965).

(5) B. Miller and K.-H. Lai, unpublished work.

(6) (a) B. Miller, *Chem. Commun.*, 1435 (1968); (b) B. Miller, *J. Amer. Chem. Soc.*, **91**, 2170 (1969).