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(Hydroxyphenyl)carbenes[1,2]

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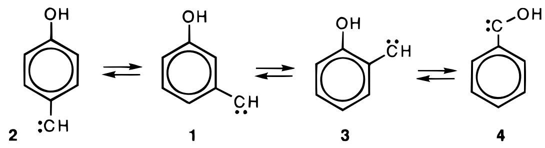
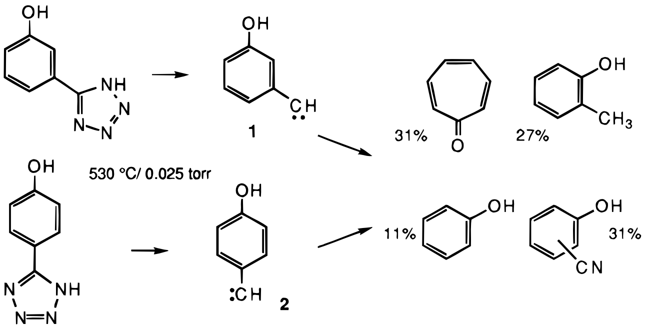
Although the phenylcarbene rearrangement still poses vexing mechanistic questions,[3] it nonetheless provides synthetic opportunities,[4] as the benzene ring can operate to transport divalency from one position on the ring to another. In this way, one might generate carbenes unavailable from conventional syntheses. For example, we hoped that (*m*-hydroxyphenyl)carbene (**1**) and (*p*-hydroxyphenyl)carbene (**2**) would rearrange to their ortho isomer (**3**) and, perhaps, hydroxyphenylcarbene (**4**).

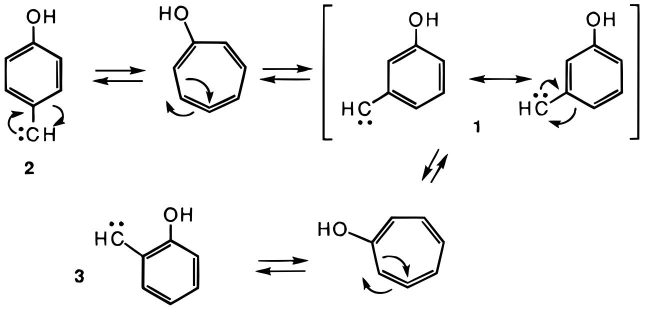


The carbenes were generated through pyrolysis of the corresponding tetrazoles,[5] themselves produced from the commercially available cyano compounds. The tetrazoles were dropped bit by bit from a solids addition funnel onto a hot Pyrex surface and the products collected downstream in a liquid nitrogen cooled trap. Under these conditions at 530 °C/0.025 Torr, both the meta and para isomers gave very similar products in comparable yields of about 50%.

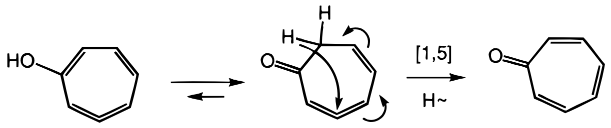


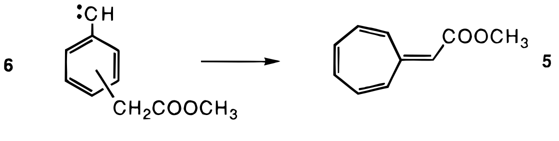
One major product in each case is the cyanophenol from which the starting tetrazole was synthesized. The retro 1,3-dipolar addition is a common reaction of these tetrazoles and merely serves to diminish the useful yield of carbene products; it is of no mechanistic significance. Phenol, formed here in about 11% relative yield, is representative of a minor, if not well-explained, process in many phenylcarbene reactions, net loss of carbon. We suspect that reactions of phenylcarbenes with walls or other molecules, followed by cleavage to give phenyl radicals, is the major source of this compound. It is the other two products, tropone and *o*-cresol, that are of most interest.

The mechanism of the phenylcarbene rearrangement is still a subject of some controversy, but there is general agreement on the intermediacy of seven-membered rings and some evidence that cycloheptatetraenes are the vital ingredients in this process.[3,6] We regard it as not quite certain that cycloheptatrienylidenes are not the productive species in this reaction, but in any event, there is very little difference between the slightly nonplanar cycloheptatetraenes and the planar cycloheptatrienylidenes. The ring-expansion/ring-contraction mechanism shown below for the interconversion of the para, meta, and ortho carbenes uses cycloheptatetraenes.



At any point in this mechanism, ketonization of one of the seven-membered rings, followed by a hydrogen shift, leads to tropone. We seem to have intercepted the intermediate in the phenylcarbene rearrangement by providing an energetically attractive intramolecular rearrangement. Only once before has a simple seven-membered intermediate been diverted in such a fashion; Tomioka and Taketsuji found 8-(methoxycarbonyl)heptafulvene (**5**) on generation of carbene **6** by flash vacuum pyrolysis.[7] There is an earlier report by Wentrup and Becker of isolation of seven-membered-ring-containing compounds in a more complicated multi-ring system,[8] and Dunkin and his group have exploited a nitrene version of this process in a matrix synthesis of azepin-4-ones.[9]





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[1] Portions of this work are taken from the A.B. Thesis of Adam H. Golden, Princeton University, 1986. We thank the National Science Foundation for support through grants CHE 83-18345 and CHE9322579.

[2] Very similar results have been obtained in the laboratories of Harold Shechter at The Ohio State University. We thank professor Shechter for stimulating conversations, for sharing his data, and for agreeing to simultaneous publication.

[3] Gaspar, P. P.; Hsu, J.-P.; Chari, S.; Jones, M., Jr. *Tetrahedron* **1985**, *41*, 1479 and references therein.

[4] For two examples of the phenylcarbene rearrangement used as a "divalency transport system", see: Chambers, G. R.; Jones, M., Jr. *Tetrahedron Lett.* **1978,** 5193. Boxberger, M.; Volbracht, L.; Jones, M., Jr. *Tetrahedron Lett.* **1980**, 3669.

[5] Gleiter, R.; Rettig, W.; Wentrup, C. *Helv. Chim. Acta* **1974**, *57*, 2111. Decomposition of the *o*-tetrazole leads only to the corresponding nitrile. Apparently the proximate OH catalyzed the reverse cycloaddition. At any rate, no sign of carbene chemistry appears.

[6] Wentrup, C. In *Methoden der Organische Chemie (Houben-Weyl)*; Regitz, M., Ed.; G. Thieme Verlag: Stuttgart, 1989; Vol. E19b, pp 824−976. Platz, M. S.; Maloney, V. M. In *Kinetics and Spectroscopy of Carbenes and Biradicals*; Platz, M. S., Ed.; Plenum Press: New York, 1990; Chapter 8.

[7] Tomioka, H.; Taketsuji, K. *J. Org. Chem.* **1993**, *58*, 4196.

[8] Wentrup, C.; Becker, J. *J. Am. Chem. Soc.* **1984**, *106*, 3705.

[9] Dunkin, I. R.; El Ayeb, A.; Lynch, M. A. *J. Chem. Soc., Chem. Commun.* **1994**, 1695.

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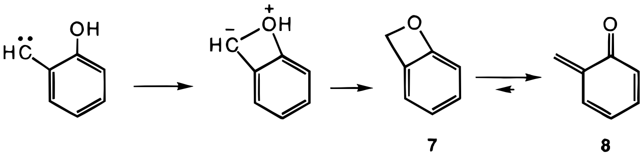
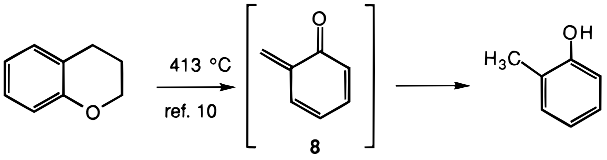
The formation of *o*-cresol is also informative. First of all, the meta and para isomers are not formed (<5% of the ortho isomer). Why only the ortho isomer? We suggest that we are seeing the product of a cascade of intermediates beginning with (*o*-hydroxyphenyl)carbene. Ylide formation followed by hydrogen migration (or direct O-H insertion) leads to the unknown benzooxetene **7**. Opening to *o*-benzoquinone methide (**8**) would surely follow.



We speculated that in the gas phase **8** would abstract hydrogen to give *o*-cresol and were gratified to find that Paul and Gajewski, who generated **8** through pyrolysis of chroman under conditions comparable to ours, did find *o*-cresol as the major product.[10] The source of hydrogen in our reaction remains unknown.



Although no evidence of carbene **4** was found under these conditions, there are examples in which an ortho trap prevents further reaction. For example, from the work of Sekiguchi and Ando,[11] Crow and McNab,[12] and ourselves,[1] it was found that acetophenone was not a product of reactions of the (methoxyphenyl)carbenes in the gas phase. However, under other pyrolysis conditions a few percent of benzaldehyde can be isolated,[2] and this probably reflects further conversion to **4**.

To summarize: we have used the phenylcarbene rearrangement to generate (hydroxyphenyl)carbenes that reveal themselves through rearrangement to seven-membered intermediates that undergo hydrogen shifts to give tropone. (*o*-Hydroxyphenyl)carbene (**2**) can be intercepted through formation of an *o*-benzoquinone methide that goes on to produce *o*-cresol.

Experimental Section

General. ^{1}H NMR spectra were obtained on a General Electric QE-300 spectrometer on samples dissolved in $CDCl_3$ or DMSO-d_6. Melting points were determined on a Thomas-Hoover capillary melting point apparatus and are uncorrected. Infrared spectra were obtained on a Perkin-Elmer 283B Infrared spectrometer. Mass spectra were taken on a Hewlett-Packard 5992B Gas chromatograph−mass spectrometer. Analytical gas chromatography was done on a Hewlett-Packard 5890 analytical gas chromatograph and preparative work on a Varian Aerograph A90P machine.

(*m*-Hydroxyphenyl)tetrazole. To a solution of 4.66 g (0.11 mol) of LiCl, 5.88 g (0.11 mol) of ammonium chloride, and 7.15 g (0.11 mol) of sodium azide in 100 mL of DMF was added 5.95 g (0.05 mol) of *m*-cyanophenol (Aldrich). The solution was heated under a reflux condenser to 125 °C for 10−12 h. Higher temperatures caused sublimation of ammonium azide, and lower temperatures reduced yields. The solution was cooled to room temperature, and the solvents were removed with a rotary evaporator at 0.2 Torr to leave a thick red-brown slurry. This was dissolved in 100 mL of distilled water and acidified to pH 2 with concd HCl. A light brown precipitate appeared. The mixture was cooled to 5 °C, and the resulting solids were isolated by suction filtration. The solids were washed repeatedly with distilled water and dried. The residual solid was ground into a fine powder in preparation for flash vacuum pyrolysis. Yield: 4.0 g (61%). A melting point was not determined because the high temperature required induced decomposition. ^{1}H NMR (δ, DMSO-d_6): 6.94−6.97 (dd, $J = 2,3$ Hz, 1H), 7.35−7.45 (m, 3H), 9.91 (s, 1H).

(*p*-Hydroxyphenyl)tetrazole. In a manner exactly parallel to the synthesis of the *meta* compound, the *para* tetrazole was synthesized in 50% yield. ^{1}H NMR (δ, DMSO-d_6): 6.95 (d, $J = 12$ Hz, 2H), 7.83 (d, $J = 12$ Hz, 2H), 10.2 (br s, 1H).

Flash Vacuum Pyrolysis. The finely ground tetrazoles were slowly dropped from a solids-addition funnel onto a hot (530 °C) quartz surface (quartz three-necked flask). One neck of the flask was connected to a trap cooled by liquid nitrogen. Products collected in the trap were rinsed down with Spectrophotometric Grade acetone and analyzed immediately by analytical and preparative gas-chromatography. Analytical GC: 2 m × 1/8 in. 3% SP-2250 column, programmed from 80 to 200 °C over 40 min with a 25 mL/min flow rate of He. Prep. GC: 4 ft × 1/4 in. 10% OV-17 column operated at 110 °C with a flow rate of 200 mL/min He. The products were identified by comparison of retention times and spectra (^{1}H NMR, IR) with those of commercial samples. The absence (<1%) of *m*-cresol and *p*-cresol was verified by the use of commercial samples.

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(10) Paul, G. C.; Gajewski, J. J. *J. Org. Chem.* **1993**, *58*, 5060.
(11) Sekiguchi, A.; Ando, W. *Bull, Chem. Soc. Jpn.* **1977**, *50*, 3067.
(12) Crow, W. D.; McNab, H. *Aust. J. Chem.* **1979**, *32*, 99.