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FORMATION OF METHYL-SUBSTITUTED 2-INDANONES AND 1,2-DIHYDROBENZOCYCLOBUTENES BY THE PYROLYSIS OF o-, m-, and p-TOLYL PROPARGYL ETHERS

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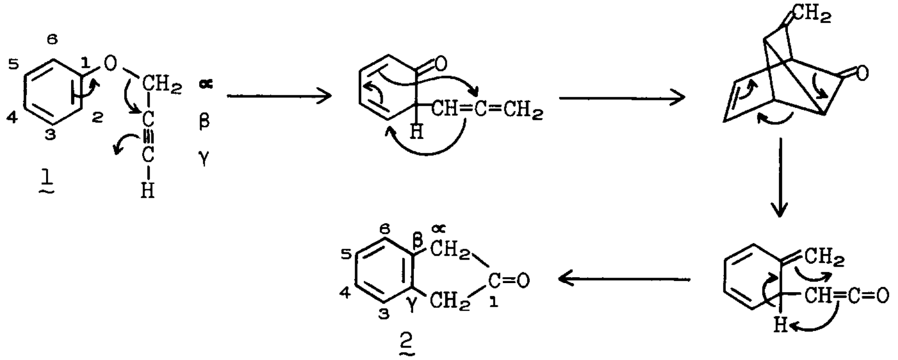
A few years ago we reported that the flash vacuum pyrolysis (FVP) of phenyl propargyl ether (1) gives substantial yields of 2-indanone (2, 26%) and 1,2-dihydrobenzocyclobutene (3, 31%).[1] The mechanism shown in the Scheme was proposed to account for the formation of 2. No mechanism for the formation of 3 was proposed but it was shown that 3 did not arise from the decarbonylation of 2. Moreover, a puzzling result which was not accounted for was that no 1,2-dihydrobenzocyclobutenes were obtained from the methyl substituted phenyl propargyl ethers studied. In order to gain further support for the mechanism for the formation of 2-indanones shown in the Scheme and to define better the scope and mechanism for the formation of 1,2-dihydrocyclobutenes, a study of the 3 isomeric tolyl propargyl ethers was undertaken. In this communication we report the results of this study.

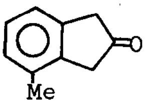
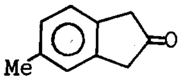
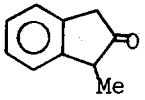
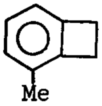
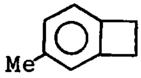
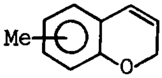
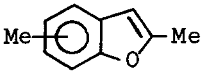
Scheme



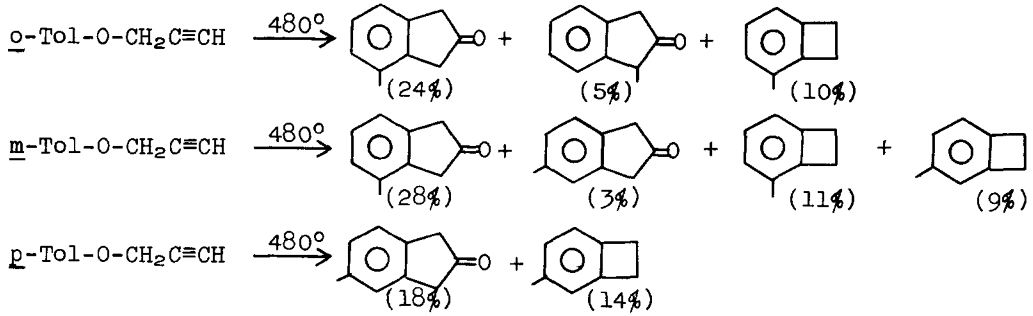
In the Table are presented the yields of the products from the pyrolysis of these three ethers.[2,4,6] In all three cases a significant amount of starting material was recovered when the pyrolysis was carried out at 400° and thus 480° appears to be a better temperature for these pyrolyses.

The yields of the 2-indanones and 1,2-dihydrobenzocyclobutenes obtained from each isomeric ether are summarized in the following equations.

TABLE Products from the Pyrolysis of o-, m-, and p-Tolyl Propargyl Ethers

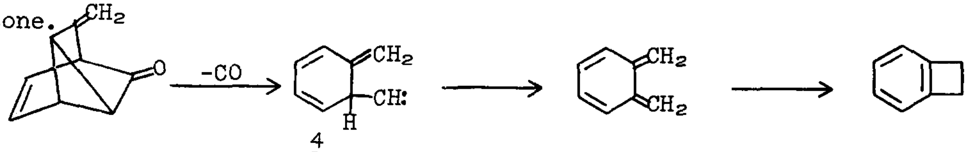
Compound	Yield, %[a]					
	ortho		meta		para	
	400°	480°	400°	480°	400°	480°
Tol-O-$CH_2C\equiv CH$	23	-	36	-	31	-
 [b]	15	24	16	28	-	-
 [c]	-	-	1.4	3	9	18
 [d]	8	5	-	-	-	-
 [e]	5	10	5	11	-	-
 [f]	-	-	4	9	8	14
Tol-OH	29	28	13	17	31	39
Tol-CH=CH_2	4	11	1	3	2	3
	5	-	5	-	5	-
	-	3[g]	-	3[h]	-	6[i]
TOTAL	89	81	81	74	86	80

a) Yields based on 2 or more determinations. b) Mp 54-55°C; IR ($CDCl_3$) 1760, 1400, 1143 cm^{-1}; NMR ($CDCl_3$) δ7.08 (s, 3, aryl), 3.51 (s, 2, CH_2), 3.39 (s, 2, CH_2), 2.23 (s, 3, CH_3). c) Mp 55-56°C (lit.[7] 55°C); IR ($CDCl_3$) 1761, 1627, 1502, 1400, 1195, 1172, 1161 cm^{-1}; NMR ($CDCl_3$) δ7.10 (broad s, 3, aryl), 3.50 (s, 4, CH_2), 2.36 (s, 3, CH_3). d) IR ($CDCl_3$) 1753, 1745, 1475, 1450, 1185, 1152 (lit.[8] (CCl_4) 1773, 1748); NMR ($CDCl_3$) 7.23 (s, 4, aryl), 3.52 (s, 2, CH_2), 3.48 (q, J=8.40 Hz, 1, CH), 1.40 (d, J=8.40 Hz, 3, CH_3). e) NMR ($CDCl_3$) δ7.18-6.65 (m, 3, aryl), 3.09 (s, 4, CH_2), 2.16 (s, 3, CH_3). f) NMR ($CDCl_3$) δ6.92 (broad s, 2, aryl), 6.85 (broad s, 1, aryl), 3.11 (s, 4, CH_2), 2.31 (s, 3, CH_3); reported ref. 9. g) Probably 2,7-isomer; NMR ($CDCl_3$) δ7.25 (m, 1, aryl), 7.00 (m, 2, aryl), 6.31 (finely split s, 1, H_3), 2.49 (s, 3, CH_3), 2.44 (finely split s, 3, CH_3). h) Probably a mixture of the 2,4- and 2,6-isomers; no spectral data were obtained for this mixture. i) Probably 2,5-isomer; NMR ($CDCl_3$) δ7.21 (m, 2, aryl), 7.06 (d, J=2.7 Hz, 1, aryl), 6.26 (m, 1, H_3), 2.39 (finely split s, 6, CH_3); no exact mass determination was obtained.



The 2-indanones obtained from each ether are those in accord with the mechanism in the Scheme. For both the ortho and meta ethers the initial Claisen rearrangement can occur in two different directions and in each case the 2-indanones from both pathways were obtained, although not in equal amounts.

From these data it is also seen that the methyl 1,2-dihydrobenzocyclobutenes obtained correspond to the methyl 2-indanones produced except that no 1-methyl isomer is formed from the ortho ether. The production of only a single isomer from the para ether rules out a mechanism which allows scrambling of the ring positions.[10] A mechanism which accounts for these results is the formation of carbene **4** from the decarbonylation of the intermediate tricyclic ketone.



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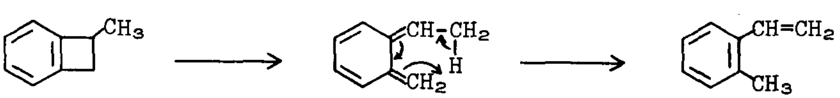
In both this work and our previously reported work[1] no 1,2-dihydrobenzocyclobutenes with methyl groups in the 1-position were obtained. It may be that these compounds are produced but are converted to styrenes by the following sequence of reactions:



This sequence of reactions does account for the higher yield of styrenes from the ortho ether, but does not explain why 2 isomeric styrenes were observed. The small amounts of styrenes from the para and meta (2 isomers) ethers are also not accounted for by this route.

From the data in the Table it is seen that the only other major products are the corresponding phenols which probably arise from phenoxy radicals produced by homolytic cleavage of the ethers. The phenoxy radicals could abstract hydrogen atoms from the polymeric material deposited on the column packing.

The other products, the benzopyrans and benzofurans, are minor and their origins are not certain. Benzopyrans have been obtained from aryl propargyl ethers in the liquid phase.[12]

In summary, the FVP of aryl propargyl ethers provides a convenient route to substituted 2-indanones and the positions of the substituents can be reliably predicted by the mechanism shown in the Scheme. 1,2-Dihydrobenzocyclobutenes with the same substitution patterns as those of the corresponding 2-indanones produced can also be obtained from this reaction if they do not possess a 1-methyl group.

References and Notes:

1. W. S. Trahanovsky and P. W. Mullen, J. Am. Chem. Soc., 94, 5911 (1972).
2. The pyrolysis apparatus and its operating procedure have been described previously.[3] Range of pyrolysis conditions: sample holder, 45°; oven temperature, 400-530°; pressure, 6.1-10.0 x 10^{-4} torr; reaction time, 40-120 min. When the pyrolysis was complete, the trap was opened and the products dissolved in $CDCl_3$. A PMR spectrum was taken of the solution, heptane was added as an internal standard and another PMR spectrum was taken. Total yields of each class of compounds in the product mixture was determined by PMR analysis. The relative yield of each isomer within a class of compounds was determined by GLPC analysis. All products except the benzopyrans were separated and isolated by GLPC. The phenols were extracted from the $CDCl_3$ solutions with base and the resulting basic solutions acidified and extracted with ether. The ether layers were dried, concentrated, and analyzed by GLPC.
3. W. S. Trahanovsky, C. C. Ong, J. G. Pataky, F. L. Weitl, P. W. Mullen, J. C. Clardy, and R. S. Hansen, J. Org. Chem., 36, 3575 (1971).
4. The ethers were prepared by the method of Okajima[5] with the exception that longer reaction times (30-40 hr) were used. Yields ranged from 24 to 40%.
5. Y. Okajima, Yakugaku Zasshi, 80, 318 (1960); Chem.Absts., 54, 18487h (1960).
6. Satisfactory ir, NMR, and mass spectra and exact mass determinations (on P or P-1) were obtained for all new compounds unless indicated otherwise.
7. A. J. Birch, P. Fitton, D. C. C. Smith, D. E. Steere, and A. R. Stelfox, J. Chem. Soc., 2209 (1963).
8. A. T. Blomquist and E. J. Moriconi, J. Org. Chem., 26, 3761 (1961).
9. J. M. Garrett, Tetrahedron Lett., 191 (1969).
10. This result is in marked contrast to that obtained from pyrolysis of the 4-pyridyl propargyl ether[8] which requires a mechanism that scrambles the position which was initially the 4 position.
11. See accompanying communication, J. M. Riemann and W. S. Trahanovsky, Tetrahedron Lett., 0000 (1976).
12. H. Schmid, J. Asindely, and H.-J. Hansen, XXIIIrd International Congress of Pure and Applied Chemistry, Boston, USA, 1971, Vol 1, p. 251.