5060 *J. Org. Chem.* **1993,** *58,* 5060-5062

o-Benzoquinone Methide: An Intermediate in the Gas-Phase Pyrolysis of Chroman

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Received February 22, 1993[•]

Gas-phase pyrolysis of chroman gives *o*-cresol, benzofuran, and styrene in a 4:2:1 ratio at 413 °C. In the presence of 2-butene, a moderately stereospecific 4 + 2 reaction occurs with the likely intermediate, *o*-benzoquinone methide, 1. The addition of 2-butene increased the amount of reaction and decreased the extent of formation of benzofuran and styrene. Addition of hydrogen gas increased the amount of hydrodealkoxylation product, styrene, and gave more of its reduction product, ethylbenzene, at the expense of benzofuran. Only a slight increase in the amount of *o*-cresol was observed upon addition of hydrogen gas. No dehydrochroman was observed in the reactions, and pyrolysis of 4*H*- and 2*H*-benzopyran gave no *o*-cresol, but instead gave styrene, benzofuran, 1-indanone, and some chroman.

o-Benzoquinone methide, 1, is a reactive intermediate which has potential synthetic utility.[1] Direct observation of it was reported using low-temperature infrared[2] and UV[4] as well as photoelectron spectroscopy.[3] *o*-Benzoquinone methide has also been trapped by electron-rich dienophiles in the liquid phase to give Diels–Alder adducts of chroman derivatives.[2,5,6] However, no stereochemistry has been reported for the reaction, nor have attempts to trap 1 in the gas phase succeeded.[7] Reported here is the successful trapping of 1 by 4 + 2 *syn* addition of simple olefins in the gas phase. These efforts came as a result of a mechanistic investigation of the mechanism of the gas-phase pyrolysis of chroman, 2, a reaction first reported by Maccoll.[8] The major products at 500–650 °C are *o*-cresol, 3, benzofuran, 5, and styrene, 6, in a roughly 4:3:1 ratio, respectively.[8]

Results and Discussion

Chroman Pyrolysis. In our well-conditioned, gas-phase, static reactor system at 413 °C, low pressures (1–1.5 Torr) of chroman give 3, 5, and 6 in a 55:26:13 ratio initially along with ca. 5% of other material in a first-order decay process (Table I). It makes little difference whether the reaction is done in the presence or absence of added nitrogen gas.

The major product, 3, would appear to be the result of a retro 4 + 2 reaction to give ethylene and 1, and the latter might react with hydrogen gas or hydrogen atoms, *vide infra*, to give *o*-cresol (Scheme I).

The mechanistic origin of benzofuran and styrene can reasonably be attributed to radical chain reactions. Benzofuran could be formed through hydrogen abstraction by some radical followed by a ring-contracting neophyl rearrangement and hydrogen addition to a methyldihydrobenzofuran, 7, which may be the 5% other product. Radical-induced loss of methane from this material would parallel the pyrolytic conversion of tetralin to indene.[9] The styrene can be formed by hydrodealkoxylation, namely, addition of hydrogen atom to the oxygen-bearing aromatic carbon followed by β scission of the C–O bond and then a second β scission to give formaldehyde and 2-phenylethyl radical which undergoes loss of hydrogen atom (Scheme II, note that the question of rate-determining step is not addressed).

Diels–Alder Reaction of *o*-Benzoquinone Methide. In order to test the retro Diels–Alder hypothesis, excess (100–300 equiv) *cis*- and *trans*-2-butene were added to the reaction mixture in separate experiments, and the 4 + 2 products, **4c** and **4t**, were formed with substantial stereospecificity and almost to the exclusion of all other products, with a ca. 50% greater rate (Table I). Though previously unknown, the stereochemistry of **4c** and **4t** could be assigned by the 0.3–0.5 ppm upfield shift of the methine hydrogens in **4t** relative to **4c**.[10] While the dependence of the rate on the concentration of 2-butene was not specifically examined, it is difficult to believe that it is inducing the reaction; rather, it is simply trapping 1. The greater rate of reaction with 2-butene present suggests then that ethylene is adding back to 1 in the absence of 2-butene (Scheme I). Remarkably, the 2-butene also reduces the percentages of the radical chain products possibly because it is functioning as a radical inhibitor. It is also possible that 1 is itself abstracting hydrogen atoms from chroman to initiate short radical chains, and removal of 1 by high concentration of olefins reduces the rate of formation of the radical products.

The source of hydrogen to give *o*-cresol in the pyrolysis of chroman is of concern. From the data of Table I, insufficient hydrogen is generated by the two radical chain products even allowing formaldehyde to give hydrogen atoms or gas and CO. The ethylene produced would appear to be the only source of hydrogen. It is also possible, but demonstrably unlikely, that chroman undergoes a radical-

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[•] Abstract published in *Advance ACS Abstracts*, August 15, 1993.

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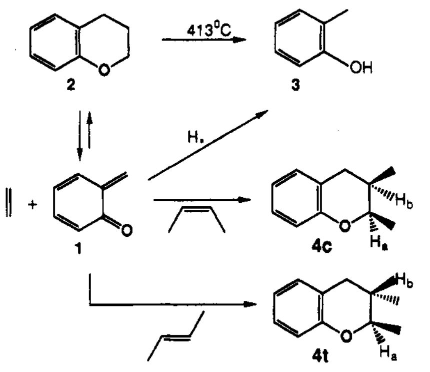
0022-3263/93/1958-5060$04.00/0

Table I. Pyrolysis Products from Chroman, 2, and Added Reagents at 413 °C for 4.5 h

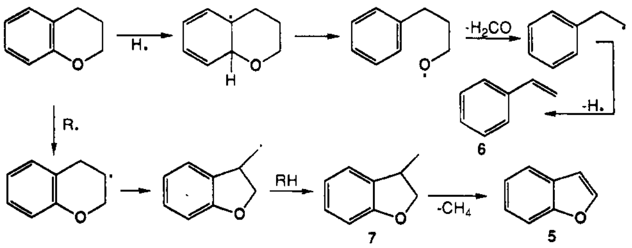
	fraction of products							
% 2 recovered	3	5	6	EtPh	others	4c	4t	added gas
91.0	0.556	0.265	0.132	0.0	0.047			N_2
85.4	0.039	0.028	0.0	0.008	0.03	0.894[a]		*cis*-2-butene ca. 170 Torr
84.1	trace	0.027	0.0	0.009	0.032	0.0	0.930	*trans*-2-butene ca. 135 Torr
90.3	0.611	0.173	0.055	0.161	0.0			H_2 ca. 335 Torr

[a] The ratio of 4c to 4t is 6:1 from *cis*-2-butene having an 8:1 ratio of *cis* to *trans* isomers. These are within experimental error considering the ^{1}H NMR integrations.

Scheme I



Scheme II



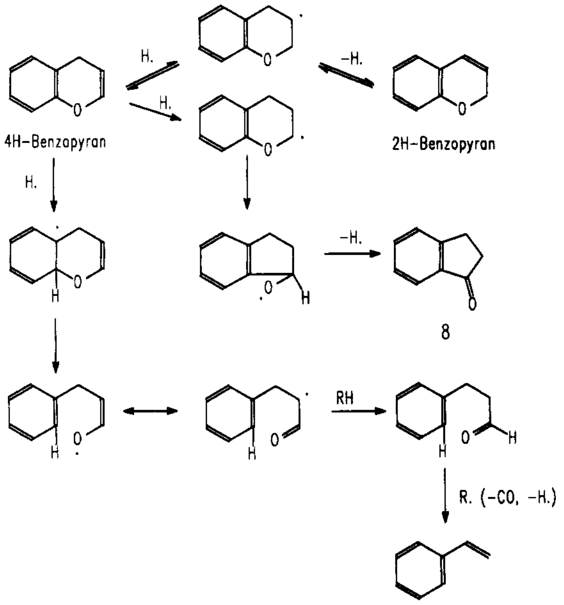
induced dehydrogenation like that of tetralin,[9] and the resulting vinyl ether gives 1 and acetylene and does so faster than 2. Further, there is no NMR evidence for large amounts of dehydrogenation products. In addition, pyrolyses of 4*H*- and 2*H*-benzopyran[11] result in mostly styrene and 1-indanone, 8, and even some chroman (Table II), but no *o*-cresol is formed (see below). Since all reactions except the retro Diels–Alder reaction of chroman appear to be free-radical chain reactions started by unknown initiator(s), a comparison of relative rates is inappropriate since initiator concentrations are unknown. However, the product distributions should be a valid fingerprint of the free-radical reactivity of the starting materials in each case.

In an attempt to characterize the hydrogen which adds to 1, that is, molecular or atomic hydrogen, half an atmosphere of hydrogen gas was added to the reaction flask containing small amounts of chroman (Table I). This provided a small increase in the amount of *o*-cresol and an even greater percent increase in hydrodealkoxylation product all at the expense of benzofuran. The suggestion here is that hydrogen gas itself is not as good a trapping agent of 1 as 2-butene. However, whatever radicals are produced in the system react with dihydrogen to give hydrogen atoms which promote the hydrodealkoxylation and trap 1. This also helps rationalize the diminished conversion to benzofuran in the presence of hydrogen gas.

Table II. Pyrolysis Products from 4*H*- and 2*H*-Benzopyran at 413 °C

time	fraction of products								
(h)	2	3	5	6	EtPh	8	2*H*	4*H*	others
4*H*									
4.6	0.53		0.87	8.66	0.29	1.76	5.6	81.9	0.57
20.5	1.18		4.04	29.85	1.28	8.14	6.88	43.9	4.23
2*H*									
0.0	6.22						84.25	9.53	
4.6	7.47		4.31	7.84		3.14	57.22	17.04	3.0
18.2	7.25		11.4	24.1		7.4	17.73	18.47	11.7

Scheme III



Benzopyran Pyrolyses. The pyrolyses of 4*H*- and 2*H*-benzopyran themselves are interesting in that 1-indanone is a major product besides styrene. Further, the two benzopyrans are interconverted under the reaction conditions at about the same rate as products are formed. The various products suggest free-radical pathways. Hydrogen atom addition and elimination can interconvert the starting isomers, and the free-radical intermediate can give chroman by abstracting a hydrogen. Further, the intermediate derived from 4*H*-benzopyran can give indanone by a ring-contracting neophyl rearrangement to an oxygen-centered radical which undergoes hydrogen atom loss (Scheme III). The origin of styrene would appear to be a hydrodealkoxylation product of the 4*H*-isomer, but a multistep process involving hydrogen atom transfer to give 3-phenylpropionaldehyde which undergoes free-radical-induced decarbonylation would be required (Scheme III).

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Experimental Section[12]

Chroman[13] was purified by fractional distillation. The middle fraction boiling at 80 °C at 6.5 Torr was 99.8% pure by GC. 4*H*- and 2*H*-benzopyran were prepared and purified according to literature procedures.[11] The procedure for 4*H*-benzopyran gives pure material while that for preparation of 2*H*-benzopyran gives ca. 84% pure material with the 4*H*-isomer and chroman being the major contaminants (see Table II).

Pyrolyses. Chroman, 4*H*-benzopyran, and 2*H*-benzopyran (1–1.5 Torr) were pyrolyzed separately in a well-conditioned 2-L Pyrex vessel immersed in a molten salt bath whose temperature was maintained at 412.9 °C for various lengths of time (see Tables I and II). Chroman was also pyrolyzed in the presence of nitrogen, *cis*- and *trans*-2-butene, and dihydrogen (see Table I). In a typical experiment 85–90% recovery of material was obtained as determined from GC analysis of the pyrolysate and comparison to weighed amounts of added external standard, *n*-decane. In the case of the butenes, the excess butene was removed on the vacuum line at −78 °C, and the products were characterized by GC retention times and by ^{1}H NMR and GCMS. The unknowns compounds **4c** and **4t** were characterized by GCMS and ^{1}H NMR of the mixture; the aromatic protons of these materials could be characterized by subtraction of the spectra of the starting material, chroman. ^{1}H NMR **4c**: δ 6.8–7.1 (m, 4H), δ 4.25 (dq, 1H (Ha), J = 2.4, 6.4 Hz), δ 2.95 (broad dd, 1H, J = 5.6, 16.4 Hz), δ 2.50 (broad dd, 1H, J = 5.6, 16.4 Hz), δ 2.09 (m, 1H (Hb)), δ 1.28 (d, 3H, (C2-CH_3), J = 6.4 Hz), δ 0.97 (d, 3H, (C3-CH_3), J = 6.8 Hz). GCMS **4c** (*m/e*); 162 (M^+, 67.5), 147 (26.8), 134 (25.3), 133 (100), 119 (14.2), 107 (73.8), 105 (25.1), 91 (24.7), 78 (25.), 77 (20.6), 51 (12.5). HRGCMS for $C_{11}H_{14}O$: calcd 162.1044, found 162.1042. ^{1}H NMR **4t**: δ 6.8–7.1 (m, 4H), δ 3.78 (dq, 1H (Ha), J = 9.0, 6.4 Hz), δ 2.75 (broad dd, 1H, J = 5.2, 16.4 Hz), δ 2.48 (broad dd, 1H, J = 10.4, 16.4 Hz), δ 1.78 (m, 1H(Hb)), δ 1.39 (d, 3H, (C2-CH_3), J = 6.4 Hz), δ 1.04 (d, 3H, (C3-CH_3), J = 6.8 Hz); GCMS **4t** *m/e*: 162 (M^+, 73.6), 147 (31.0), 133 (60.2), 119 (14.7), 107 (100), 105 (17.2), 91 (22.9), 78 (18.3), 77 (15.5), 51 (7.4). HRGCMS for $C_{11}H_{14}O$: calcd 162.1044, found 162.1047.

Acknowledgment. We thank the Department of Energy for financial support of this work.

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