cf. Figure 1), we expect the hydrogen bond strength to be decreased in comparison with 1. The quantitative SOJT theory[3] is also in agreement with the idea of a slightly weakened hydrogen bond in 3 ($\lambda = 0.992$) in comparision to 1 ($\lambda = 0.989$). The above chemical shifts of the hydroxylic protons support this picture.

In the case of 2-substitution (2) the qualitative SOJT theory predicts a very small effect ($\delta\Delta E = 0.004\beta$), and apparently other factors play a dominant role in this compound.

Experimental Section

α-Methyl-1-cinnamoyl-2-methoxynaphthalene (4). A solution of α-methylcinnamic acid (40.6 g, 0.25 mol) and 2-methoxynaphthalene (39.6 g, 0.25 mol) in 1,2-dichloroethane was treated with phosphorus pentachloride (52.0 g, 0.25 mol) and the solution was refluxed with stirring for 5 min. The solution was cooled in an ice bath, and aluminum chloride (33.9 g, 0.25 mol) was slowly added after which the mixture was refluxed for 10 min. The reaction mixture was cooled and quenched with iced hydrochloric acid, and the organic layer was separated. The aqueous layer was extracted with methylene chloride, and then the organic layers were combined and washed with sodium carbonate solution and water. After drying over magnesium sulfate, the solvent was removed to give a viscous green oil (43.7 g, 58% yield). Crystallization from hexane (charcoal) gave yellow needles, 76.2–77.7 °C. Anal. Calcd for $C_{21}H_{18}O_2$: C, 83.42; H, 5.99. Found: C, 83.57; H, 6.13. IR (CsI) 3040 (w, sh), 3010 (w), 2980 (w), 2940 (w), 2840 (w), 1950 (vw), 1617 (vs), 1592 (s, sh), 1574 (m, sh), 1505 (s), 1464 (m, sh), 1444 (s), 1431 (s, sh), 1387 (w), 1337 (w), 1271 (m), 1250 (s), 1230 (s), 1210 (m), 1180 (m), 1163 (w), 1148 (m), 1079 (m), 1059 (s), 1018 (w), 990 (s), 951 (vw), 924 (w), 902 (m), 886 (m), 859 (m), 801 (vs), 763 (m), 748 (m), 727 (vw), 713 (vvw), 690 (m), 633 (m), 610 (m), 580 (m), 546 (m), 517 (s), 448 cm^{-1} (m); UV (hexane) λ_{max} 226 nm (ϵ 69 350), 278 (23 800), 293 (18 300, sh), 320 (4100), 335 (3900); ^{1}H NMR ($CDCl_3$, Me_4Si) δ 1.83 (d, $J = 1.5$ Hz, 3 H), 3.95 (s, 3 H), 6.8–8.3 (m, 12 H); mass spectrum (relative intensity), *m/e* 145 (20), 185 (100), 302 (62).

2-Methyl-9-hydroxyphenalenone (2). Instead of quenching the above reaction, more aluminum chloride (33.9 g, 0.25 mol) was added and refluxing was continued overnight. The reaction mixture was decomposed with iced hydrochloric acid, and the organic layer was washed with water and dried over magnesium sulfate. Removal of the solvent gave a red oil (ca. 50 g) which was suitable for use in the Scholl reaction. The oil was intimately mixed with aluminum chloride (100 g) and the container immersed in an oil bath which had been preheated to 180 °C. The reaction mixture was held at this temperature for 1 h with stirring and then poured into iced hydrochloric acid. Extraction was carried out with methylene chloride, and the organic layer was washed with water and dried over magnesium sulfate. The solvent was removed to give a black oil (30 g), which was distilled (sublimation vessel), recrystallized from ethanol (charcoal), sublimed, and recrystallized from ethanol to give yellow needles (5.9 g, 11% yield), 127.8–129.1 °C. Anal. Calcd for $C_{14}H_{10}O_2$: C, 79.97; H, 4.80. Found: C, 80.12; H, 4.90. IR (CsI) 3060 (vvw), 2950 (vvw), 2920 (vvw), 1632 (vs), 1585 (vs), 1480 (w, br), 1363 (m), 1322 (vw), 1260 (m), 1215 (m), 1180 (vw), 1160 (w), 1130 (vw), 1040 (w), 1005 (w), 940 (w), 920 (w, sh), 900 (m), 835 (s), 767 (m), 730 (m), 692 (m), 605 (vw), 563 (w), 536 (w), 464 (m), 428 (w), 402 cm^{-1} (w); UV (hexane) λ_{max} 235 nm (ϵ 21 300), 258 (8200), 267 (8400), 305 (2400, sh), 317 (4200, sh), 335 (9300), 350 (17 600), 374 (2500, sh), 393 (4800, sh), 406 (6000, sh), 414 (8000), 429 (5700, sh), 439 (8400); ^{1}H NMR ($CDCl_3$, Me_4Si) pattern, δ 2.40 (3 H), δ_X 7.86 (1 H, ($J_{AX} = 1.0$ Hz), AB pattern, δ_A 7.16, δ_B 8.04 ($J_{AB} = 9.6$ Hz, 2 H), AB_2 pattern, δ_A 7.51, δ_B 7.9 ($J_{AB} = 8$ Hz, 3 H), 16.27 (s, 1 H); mass spectrum (relative intensity) *m/e* 152 (13), 153 (7), 181 (26), 182 (9), 210 (100).

5-Methyl-9-hydroxyphenalenone (3). 6-Methyl-2-methoxynaphthalene[16] (9.0 g, 0.052 mol) and cinnamoyl chloride (8.0 mL, 0.052 mol) were dissolved in 100 mL of 1,2-dichloroethane. After the reaction flask was cooled in an ice bath, aluminum chloride (7.0 g, 0.052 mol) was slowly added to the flask, while the solution was mechanically stirred. After about 1 h when the reaction had come to room temperature, a further 7.3 g of aluminum chloride was added to the solution and the reaction mixture taken to reflux. After 3 h the reaction mixture was quenched with iced hydrochloric acid and filtered. The filtrate was extracted with methylene chloride. The solid was repeatedly boiled with hot methylene chloride and filtered until the filtrate became colorless. All the organic extracts were combined, dried over anhydrous sodium sulfate, and taken down on a rotary evaporator to give a yellow solid (10 g). The compound was purified by two sublimations followed by a recrystallization from ethanol (charcoal) to yield yellow needles (4.21 g, 38%) 198.4–198.5 °C. Anal. Calcd for $C_{14}H_{10}O_2$: C, 79.97; H, 4.80. Found: C, 80.18; H, 4.85. IR (CsI) 3030 (vw), 2920 (vw), 1631 (vs), 1598 (vs), 1356 (m), 1280 (w), 1238 (m), 1160 (m), 950 (b), 865 (s), 835 (w), 782 (w), 748 (w), 688 (m), 545 (w), 535 (w), 500 cm^{-1} (w); UV (hexane) λ_{max} 239 nm (ϵ 26 400), 259 (10 600) 268 (sh 9900), 318 (sh, 5100), 332 (12 000), 348 (25 200), 378 (2400), 400 (4800), 422 (7900), 442 (7800), 448 (7900); ^{1}H NMR ($CDCl_3$, Me_4Si) δ 2.61 (s, 3 H), AB pattern, δ_A 7.13, δ_B 7.99 ($J_{AB} = 9.4$ Hz, 4 H), 7.80 (s, 2 H), 15.83 (s, 1 H); mass spectrum (relative intensity), *m/e* 153 (26), 181 (54), 182 (43), 210 (100).

9-Hydroxyphenalenone (1). When the above procedure (synthesis of 3) was followed for the preparation of 9-hydroxyphenalenone (starting from cinnamoyl chloride and 2-methoxynaphthalene on a 0.5-mol scale), 85 g (86% yield) of crude product was obtained, 193–202 °C (lit. mp 202.4 °C);[8–12,17] IR (CsI) 3050 (br, vvw), 1632 (vs), 1585 (vs), 1483 (m), 1420 (vw), 1360 (m), 1305 (vw), 1239 (vs), 1185 (w), 1143 (w), 961 (vw), 922 (br, w), 845 (s), 807 (vw), 760 (w), 730 (w), 690 (m), 610 (br, w), 552 (vw), 528 (w), 491 (w), 470 (w), 429 cm^{-1} (m); UV (hexane) λ_{max} 234 nm (ϵ 22 600), 256 (9400), 264 (9100), 315 (sh, 4300), 329 (10 400), 344 (21 000), 390 (4800), 411 (8100), 436 (8300); ^{1}H NMR ($CDCl_3$, Me_4Si) AB pattern, δ_A 7.15, δ_B 8.05 ($J_{AB} = 9$ Hz, 4 H); AB_2 pattern δ_A 7.58, δ_B 8.0 ($J_{AB} = 8$ Hz, 3 H), δ 16.02 (s, 1 H); mass spectrum (relative intensity), *m/e* 141 (15), 169 (53), 170 (48), 198 (100).

Registry No. 1, 7465-58-9; 2, 78229-05-7; 3, 78837-89-5; 4, 78837-90-8; α-methylcinnamic acid, 1199-77-5; 2-methoxynaphthalene, 93-04-9; 6-methyl-2-methoxynaphthalene, 26386-94-7; cinnamoyl chloride, 102-92-1.

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On the Formation of 2*H*-Cyclohepta[*b*]furan-2-ones by the Pyrolysis of Aryl Propiolates and Phenyl Tetrolate

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In recent years equilibration of acetylenes with methylenecarbenes ($RC{\equiv}CR' \rightleftharpoons RR'C{=}C{:}$) above 500 °C has been established for aryl- and alkyl-substituted acetylenes[1,2] and for acetylene itself[3] and the methylenecarbenes have been trapped in intramolecular insertion reactions. Acyl acetylenes undergo this rearrangement, and flash

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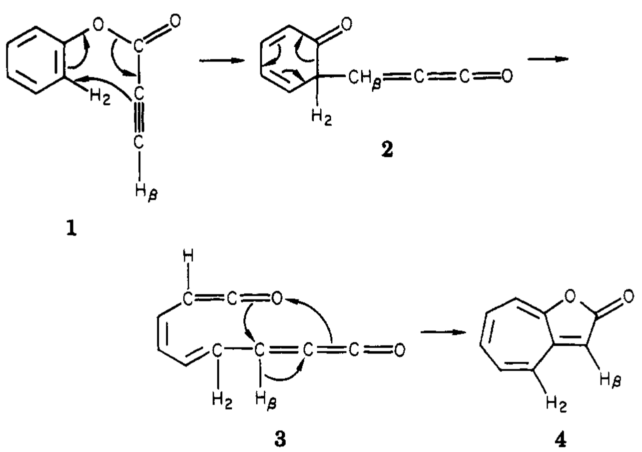
Scheme I

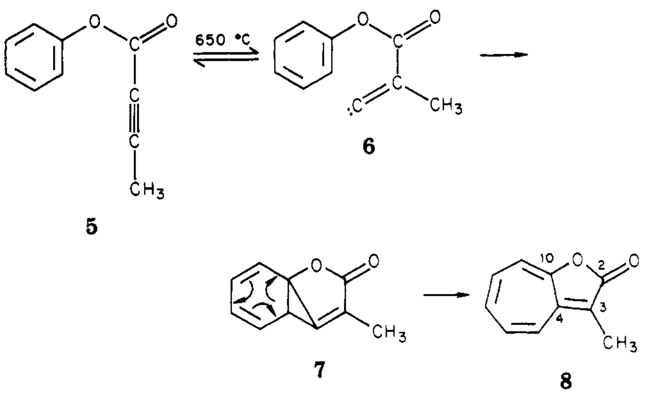


vacuum pyrolysis (FVP) of the ketone $RCOC{\equiv}CCH_3$ (R = 1-methylcyclopentenyl) at 650 °C gives a bicyclic enone by intramolecular insertion in the intermediate $RCO(CH_3)C{=}C$:.[4] Alkoxycarbonyl acetylenes also rearrange, and FVP of diphenylmethyl propiolate at 640 °C produces diphenyl-2-(3*H*/5*H*)-furanones by an intramolecular insertion reaction of the methylenecarbene $Ph_2CHO_2CCH{=}C$:.[5] The reverse process is also known, and methyl phenylpropiolate has been synthesized by rearrangement of $CH_3O_2C(Ph)C{=}C$: generated by FVP.[6] There is thus ample precedent for the generation under the conditions of FVP of methylenecarbenes from propiolates. Tetrolates would be expected to equilibrate similarly although this pathway may constitute only a minor route in the overall reaction.

Trahanovsky et al. proposed in 1976 that the flash vacuum pyrolysis of phenyl propiolate 1 at 650 °C gave 30–45% of 2*H*-cyclohepta[*b*]furan-2-one (4) by an initial Claisen-type rearrangement to 2, ring opening to 3, and final rearrangement of 3 to the lactone 4 (Scheme I).[7] Similar reactions were demonstrated for 2,4,6-trimethylphenyl and 1,2-dihydroinden-5-yl propiolates. We have outlined the pathway of Scheme I in two reviews,[8,9] but we are not convinced by it. In particular the concerted cyclization with migration of H_β implied by structure 3 and associated arrows seems unlikely.

We have found that FVP of phenyl tetrolate (5) at 650 °C (0.05 torr) through a packed silica tube similarly gave the 3-methyl lactone 8, albeit in poor yield (4–5%). As expected, the reaction is not clean; much carbon is deposited on the silica packing, and the less polar fraction of the product contains at least nine components (GLC), including starting material 5 and styrene. The formation of 8 is in accord with Scheme I, but would require migration of a methyl group in place of H_β, and we consider its formation is more in accord with Scheme II. The pathways of formation of 4 from the propiolate and of 8 from the tetrolate may be different, but it is proposed that both reactions proceed by the mechanistic pathway shown in Scheme II.

Scheme II



It does not appear possible to distinguish between these two pathways by labeling experiments. We predict that ^{13}C labeling of one acetylenic carbon of 5 should lead to scrambling of the label between α and β acetylenic carbons in starting material recovered from FVP and to similar scrambling between C3 and C4 in the product 8. Such scrambling, however, is to be expected in FVP of all acetylenes of this type and should be observed even if 8 were formed according to the pathway of Scheme I.

The styrene formed in the pyrolysis may be a bisdecarbonylation product of the 3-methyl lactone. We speculate that the first decarbonylation of 8 leads to methyl(tropon-2-yl)carbene and then 2-vinyltropone; a second decarbonylation forms styrene. Bisdecarbonylation is prominent in the mass spectrum of 8.

Experimental Section

Phenyl Tetrolate (5). Tetrolic acid (2.52 g, 30 mmol), phenol (4.23 g, 45 mmol), dicyclohexylcarbodiimide (6.28 g, 30.6 mmol), and 4-(dimethylamino)pyridine (70 mg) were dissolved in dichloromethane (65 mL), and the solution was refluxed for 9 h. The solvent was removed (Büchi) and the residue was stirred with hexane (60 mL) overnight. The insoluble material was washed with further hexane (60 mL), and the combined hexane extracts were filtered through silica gel (3 g), washed successively with 1% NaOH (5 × 20 mL), 1% H_2SO_4, and $NaHCO_3$ solutions, dried (Na_2SO_4), and evaporated to an oil. Distillation at 110 °C (bath) (0.2 torr) gave a colorless oil (3.92 g, 81%): IR (film) 2290, 2245, 1730 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.02 (s, 3 H), 7.0–7.7 (m, 5 H). Anal. Calcd for $C_{10}H_8O_2$: C, 74.99; H, 5.03. Found: C, 75.13; H, 4.95.

Flash Vacuum Pyrolysis of Phenyl Tetrolate. 3-Methyl-2*H*-cyclohepta[*b*]furan-2-one (8). Pyrolysis of phenyl tetrolate (0.50 g) through a silica tube (30 × 2.5 cm i.d.) packed with silica tubing (5-mm lengths, 5-mm i.d., 7-mm o.d.) at 650 °C (0.05 torr) during 40 min gave a semisolid fraction (0.15 g) in the exit elbow and a more volatile fraction (0.2 g) in the cold trap. Chromatography of the semisolid over silica gel and elution with ethyl acetate–light petroleum (3:7) afforded first a yellow oil followed by an orange crystalline fraction (26 mg, 5%). Recrystallization from hexane gave 8 as orange needles: mp 105–106 °C; IR (CCl_4) 1765, 1610 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 2.02 (s, 3 H), 6.68 (t, *J* = 9.5 Hz, 1 H), 6.76–6.96 (m, 3 H), 7.10 (d, *J* = 11 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 7.87 (CH_3), 108.00 (C3), 111.90, 126.20, 129.52, 131.86, 133.81 (C5–C9), 147.46, 157.60 (C4 and C10), 170.22 (C2); mass spectrum, *m/e* 161 (12), 160 (100, M), 159 (12), 132 (21), 131 (92), 105 (6), 104 (27), 103 (28), 102 (6), 78 (22), 77 (22), 63 (10), 52 (7), 51 (74), 50 (10), 44 (13), 40 (37). Anal. Calcd for $C_{10}H_8O_2$: C, 74.99; H, 5.03. Found: C, 74.82; H, 5.09. The spectral data of this compound are similar to those reported for derivatives of 4. The methyl signal in the ^1H NMR spectrum is sharp and the methyl carbon resonance in the ^{13}C NMR spectrum lacks long-range proton coupling, evidence that is consistent only with the location of the methyl at C3.

The liquid fraction from the cold trap was examined by GLC (6 ft × $^1/_8$ in S.E. 30 column, 130–230 °C), which showed the presence of at least nine components, including starting material

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and sytrene (4.5% yield). FVP of 8 at 650 °C (0.04 torr) gave 8 (93% recovery) and more volatile products, including a trace of styrene. FVP at 750 °C (0.05 torr) gave 8 (50% recovery) and more volatile products, including styrene (2.3% based on total 8 introduced).

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Registry No. 5, 78822-89-6; **8**, 78822-90-9; tetrolic acid, 590-93-2; styrene, 100-42-5.

Regiospecific Base-Catalyzed Hydrogen Exchange of Triarylsulfonium Salts

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Reactions of sulfonium salts with various nucleophilic species are of significant interests from the viewpoints of the fundamental mechanistic understanding as well as of their relevance to the adenosylmethionine-dependent biochemical methylations. In a recent mechanistic study on the reaction of triarylsulfonium salts with a number of the alkoxide nucleophiles, we have shown by the solvent isotope labeling method that the hydrocarbon products, commonly observed in such reactions, are derived via the radical intermediates rather than the corresponding anions.[1] In the course of this mechanistic study, it was necessary to determine the extent and the scope of the base-catalyzed hydrogen exchange of the triarylsulfonium salts with the protic solvent medium, and we report the results of that investigation.

Tri-*p*-tolylsulfonium bromide and triphenylsulfonium bromide were prepared in modest yields from di-*p*-tolyl sulfoxide and *p*-tolylmagnesium bromide, and diphenyl sulfoxide and phenylmagnesium bromide, respectively.[2] The base-catalyzed exchange reactions of the triarylsulfonium salts in the deuterated alcoholic solvents were carried out under argon atmosphere and the conditions given in Table I. The products were extracted with ether, and the unreacted sulfonium salts were recovered by extracting the aqueous phase with dichloromethane. The relative product ratio and the incorporation of the deuterium isotope into the products are summarized in Table I and Table II, respectively.

The multiple deuterium incorporation into the products is clearly a result of the base-catalyzed exchange occurring at the stage of the sulfonium salts, because in the control experiments none of the products, i.e., hydrocarbons, ethers and sulfides underwent the hydrogen exchange under the identical conditions given in Table I. The mass spectral data show that five hydrogens on the *p*-tolyl moiety of the sulfonium salt undergo the exchange with the protic solvent deuterium. The positions of the exchange have been determined to be ortho to the sulfonium substituent and the methyl groups by the following proton NMR analysis. While the authentic tri-*p*-tolylsulfonium bromide shows in the ^1H NMR spectrum the pseudo A_2B_2 pattern centered at δ 7.53 (d, 6 H, ortho H's), 7.40 (d, 6 H, meta H's), and a singlet at 2.314 (9 H, methyl), the partially deuterated tri-*p*-tolylsulfonium bromide recovered from run 1 shows the following ^1H NMR spectral data: δ 7.53 (d, 1.7 H corresponding to 72% D incorporation at ortho positions), 7.40 (a large singlet with satellite doublet, 6 H, meta H's), and three poorly resolved singlets at 2.314, 2.302, 2.292, representing the methyl-d_0, d_1, and d_2, respectively (total 2.3 H corresponding to an overall 74% D incorporation at the methyl positions). Similar ^1H NMR analyses on the di-*p*-tolyl sulfide [pseudo A_2B_2 at 7.23 (ortho H's), 7.09 (meta H's), and singlet at 2.31 (methyl)] obtained from runs 1 and 2 have also corroborated the above determination on the exchange positions. It is of interest to note that the degree of the exchange is quite similar for the ortho (72%) and the methyl (74%) positions in the tri-*p*-tolylsulfonium bromide under the conditions studied.

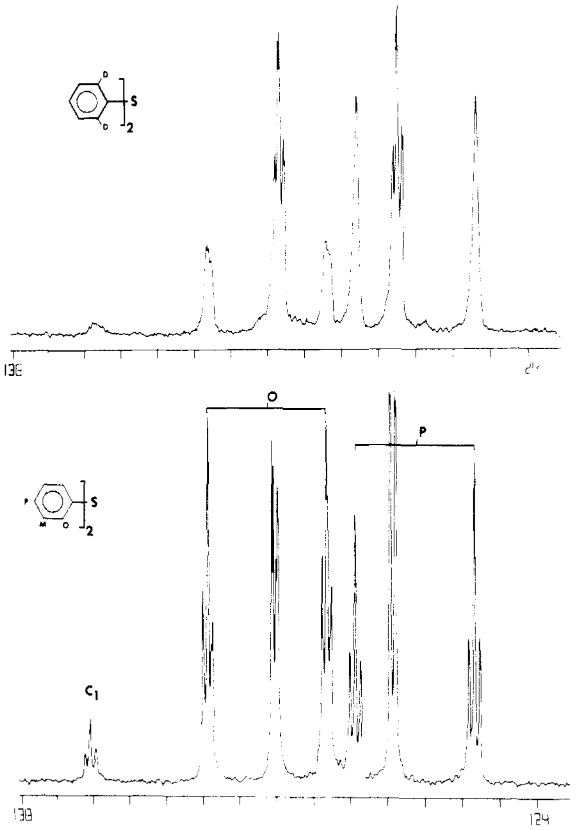

Figure 1. Completely coupled C-13 spectra of authentic (bottom) and partially deuterated (top) diphenyl sulfide.

For the triphenylsulfonium bromide system, the mass spectral data (Table II) show that only two hydrogens of the each phenyl moiety are exchangeable, but the position of the exchange could not be readily determined based on the ^1H NMR analysis because of the nonresolution of the ortho, meta, and para hydrogens either in triphenylsulfonium bromide or in diphenyl sulfide. However, ^{13}C NMR analysis made on the diphenyl sulfide product in run 3 has allowed an unambiguous determination of the exchange positions. The wide-band proton noise-decoupled ^{13}C NMR of authentic diphenyl sulfide shows well-resolved signals at δ 135.797 (C-1), 130.994 (ortho), 129.182 (meta), and 127.000 (para). The assignments of the peaks have been made based on the splitting patterns in the completely coupled spectrum (Figure 1). The completely coupled ^{13}C NMR spectrum of the partially deuterated diphenyl sulfide from run 3 reveals the significantly reduced peak intensities of the ortho carbon due to the deuterium substitution, and modified splitting patterns

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