

Typical Rearrangement.—To a constricted tube with a small magnetic stirrer was added 0.26 g (0.001 mol) of 1 followed by 5 ml of dry hexane and 1.3 ml of 1.6 *N* (0.002 mol) *n*-butyllithium-hexane. The tube was purged with nitrogen, sealed and placed in a bath at $75 \pm 2^\circ$ with stirring for 48 hr. Water (3 ml) was added to the reaction mixture, and the organic layer was separated and extracted with 3 *N* HCl. The remaining nonbasic phase was retained for further analysis. The acid extracts were made basic with 50% sodium hydroxide and the basic products extracted with pentane. Careful distillation to concentrate the product resulted in 0.1–0.2 ml of a products-pentane solution which was analyzed by gas chromatography.

In one run as above, 0.2 ml of TMEDA was added and the reaction time reduced to 1 hr. Controls were also run on solvent plus salt 1 or solvent plus base and analyzed as above.

Registry No.—1, 26154-20-1; 4, 15673-04-8; 4 HCl, 26153-93-5; 5, 26153-85-5; 5 MeI, 26153-94-6; 6, 4474-61-7; 6 MeI, 26153-95-7; 7, 10076-31-0; 11, 26153-88-8; 12, 1071-81-4; *N,N*-dimethyl-*tert*-butylacetamide, 26153-90-2; *N*-methylneopentylamine, 26153-91-3; 3,3,*N,N*-tetramethyl-2-butylamine, 3850-30-4.

o-Quinone Methides. II. Trapping with Production of Chromans

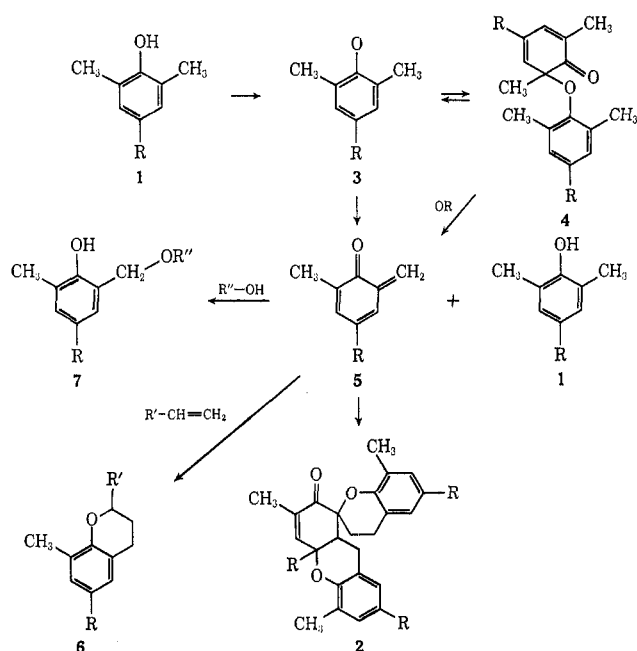
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The first paper¹ demonstrated that phenoxy radicals are a precursor to the formation of the trimer 2. They must pass through an *o*-quinone methide which could not be observed. This work demonstrates that the *o*-quinone methide can be trapped by reactive dienophiles and nucleophilic agents. A convenient synthesis of a variety of chromans results from this reaction. Only one isomer is obtained which suggests the similarity to usual diene reactions.

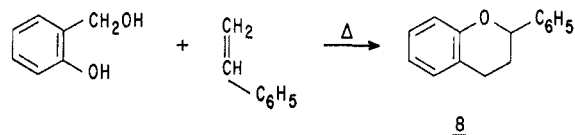
The first paper in this series¹ showed that the oxidation of 2,6-dimethylphenols (1) with metal oxides or basic potassium ferricyanide gave as a product a trimer. The trimer was shown to have the rather complex struc-



ture 2. An examination of the structure suggests that it results from a diene-dienophile addition of three *o*-quinone methides 5. However, spectroscopic evidence demonstrated that both the phenoxy radical 3 and its dimeric *o*-quinol ether dimer 4 were present and were part of the sequence of reactions that resulted in the formation of the trimer. Direct evidence of the existence of the *o*-quinone methide was lacking. It was felt that it should be possible to demonstrate the existence of an *o*-quinone methide by intercepting it with a dienophile more reactive than itself.

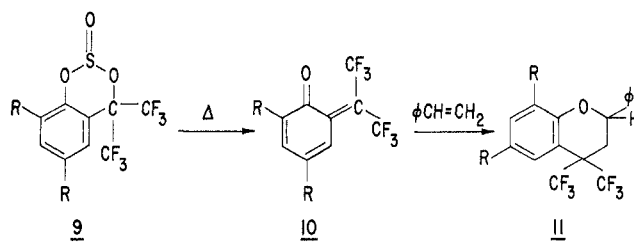
There have been a few examples of the presence of an *o*-quinone methide being demonstrated by its being

trapped. Hultzs² heated saligenin in the presence of styrene to form the chroman 8. Other reactions of



this type have been reported^{3,4} but all involve the application of heat to convert the phenol precursor to the *o*-quinone methide.

Near the end of this work, an *o*-quinone methide which is stabilized by trifluoromethyl groups was reported by Sheppard.⁵ This was prepared by pyrolysis of the sulfite ester 9. The quinone methide 10 was not isolable but reacted with styrene to give the chroman 11.



There is another method of trapping quinone methides. This involves the addition of nucleophiles to the conjugated system. Filar and Winstein⁶ have studied this addition to *p*-quinone methides, but they had no examples of an *o*-quinone methide. Very little work has been done where *o*-quinone methides have been studied in solution.

With this background of previous work, it was decided to concentrate on the generation of the sus-

(1) D. A. Bolon, *J. Org. Chem.*, **35**, 715 (1970).

(2) K. Hultzs, *Chem. Ber.*, **74**, 898 (1941), *J. Prakt. Chem.*, **158** 275 (1941).

(3) G. R. Sprengling, *J. Amer. Chem. Soc.*, **74**, 2937 (1952).

(4) M. Wakselman and M. Vilkas, *C. R. Acad. Sci., Ser. C*, **258**, 1526 (1964).

(5) W. A. Sheppard, *J. Org. Chem.*, **33**, 3297 (1968).

(6) L. J. Filar and S. Winstein, *Tetrahedron Lett.*, **25**, 9 (1960).

pected *o*-quinone methide in solution in the presence of various trapping agents.

***o*-Quinone Methides.**—The bulk of the work in this paper was done with the readily available 4-*tert*-butyl-2,6-dimethylphenol (1, R = *tert*-butyl). Other phenols such as 4-methoxy-2,6-dimethylphenol and 4-phenyl-2,6-dimethylphenol were used on occasion to convince us that the reaction was general but the bulk of the work was done on 1 (R = *tert*-butyl).

The first step in the metal oxide oxidation of the phenol 1 is the removal of the phenolic hydrogen to yield a phenoxy radical 3. These radicals dimerize to yield an *o*-quinol ether 4, which exists in equilibrium with the radical.¹ This system disproportionates to yield an *o*-quinone methide 5 and the phenol 1. In an inert solvent the fate of the *o*-quinone methide is normally trimerization to 2.

It was believed that 5 should have an appreciable lifetime. Previously attempts had been made to observe the group by spectroscopic means but its lifetime was too short for the methods used.

The oxidation of 1 in the presence of a variety of electron-rich dienophiles was then carried out. In Table I are shown the chromans obtained by this

This is demonstrated also in the case where 4-methoxy-2,6-dimethylphenol was oxidized in ethyl vinyl ether. The chief product in this reaction is the trimer 2 (R = CH₃O).

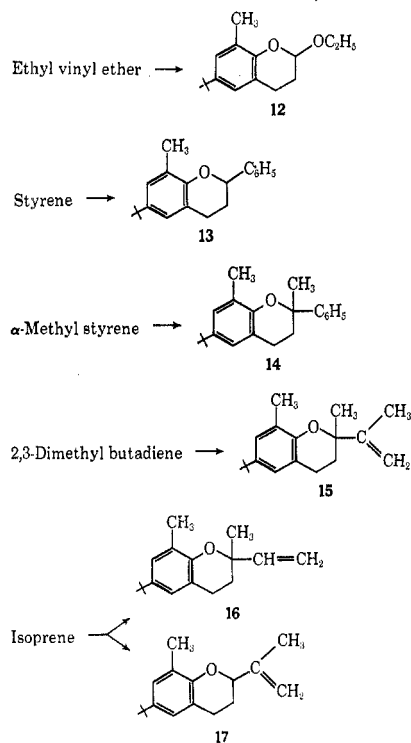
Another class of dienophile that was tried was the styrenes. Both styrene and α -methylstyrene were successful in trapping the *o*-quinone methide and gave chromans like 13 and 14. These reagents were not so successful as the vinyl ethers and consequently the chromans had to be distilled from the trimer as well as some thermally polymerized styrene. The yields were low.

A third set of dienophiles were used and these were the dienes. One of the bonds in a conjugated diene acts as a dienophile and traps the *o*-quinone methide giving a vinylchroman like 15. The presence of the vinyl group was demonstrated by ir and nmr spectral data and by catalytic reduction of the vinyl group in 15.

In the case of an unsymmetrical diene like isoprene, two chromans are formed. Both result from an addition to the two different bonds of the isoprene rather than from a difference in orientation of one of the olefinic bonds. The isomer which results from the more stable intermediate 16 is favored over the one that yields 17 by a 2:1 ratio.

In Table II are listed some of the dienophiles that

TABLE I
CHROMANS FROM 4-*tert*-BUTYL-2,6-DIMETHYLPHENOL



method. This confirmed our belief that *o*-quinone methides were present. The reaction with ethyl vinyl ether was run using the ether as a solvent and in a 1:1 mol ratio with the phenol and using benzene as a solvent. In both cases the chief product was the chroman 12. This reaction is a competition as the yield of the chroman is substantially lower where a 1:1 ratio of inert solvent to dienophile is used than when the dienophile is used as the solvent. When the yield of the chroman is reduced by diluting the dienophile, the other product that is obtained is the trimer corresponding to 2.

TABLE II
DIENOPHILES THAT YIELD CHROMANS UPON REACTION WITH *o*-QUINONE METHIDES

Dienophile	Amount, ml	Chroman, %
None ^a
Isoprene	5	30 ^b
2,3-Dimethylbutadiene	5	24
Butadiene	5	10 ^c
Cyclohexadiene-1,3	5	8
Ethyl vinyl ether	5	100
Isobutyl vinyl ether	5	65 ^c
α -Methylstyrene	5	13
Diethyl ketene acetal	5	20 ^c
<i>n</i> -Propyl methacrylate	5	6 ^c
Isoprene	1	12
Isoprene	5	30
Isoprene	10	85

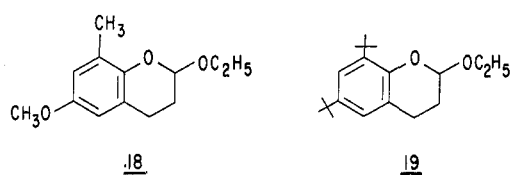
^a The blank run showed 10% recovery of phenol indicating the silver oxide is only 90% effective or that some of the silver oxide is oxidizing something other than the phenol. ^b 20% of 10, 10% of 11. ^c These materials were trapped off the vpc and identified by mass spectrometry.

successfully trap the *o*-quinone methide. These were run in a standard fashion where equimolar amounts of 4-*tert*-butylxylenol and silver oxide were reacted in benzene. The dienophile was added in the amount indicated and the products then analyzed by gas chromatography. The per cent composition given under the chroman then is a measure of the trapping efficiency of the dienophile. It is evident that the most effective are the dienes. The three isoprene samples show the large effect that the concentration of the trapping agent has upon the rate of trapping. This is a measure of the competition of the *o*-quinone methide with itself.

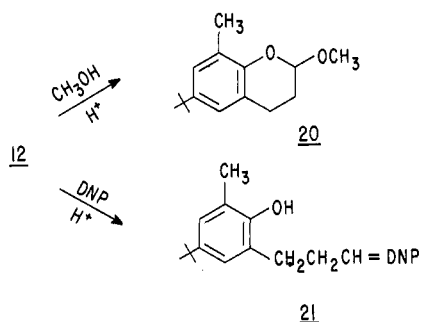
Some of these chromans were not preparatively made but were collected from the vpc and identified by ir and by mass spectra.

There also were some olefins that would not compete for the *o*-quinone methide. Some of these are 3,3-dimethylbutene-1, isoquinoline, cyclooctadiene-1,3, vinylbenzoate, norbornene, acrylonitrile, *N*-vinylpyrrolidone, and 1-pyrrolidinocyclohexene. Isolated double bonds and those substituted with deactivating groups are not reactive enough to interfere with the trimerization. Cyclooctadiene is puzzling because it should be active enough and it may even be expected to react in view of the success of cyclohexadiene. It is possible that the flexibility of the eight-member ring offers some sort of steric hindrance.

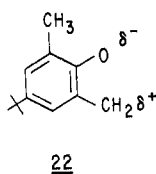
Several other phenols were used in place of the 4-*tert*-butyl-2,6-xyleneol in a similar reaction. When ethyl vinyl ether was used as a solvent both 4-methoxy-2,6-dimethylphenol and 2-methyl-4,6-di-*tert*-butylphenol yielded the corresponding chromans **18** and **19**.



Several reactions were performed on the chroman **12**. The acetal linkage was thought to be susceptible to hydrolysis. However, prolonged refluxing in acidified aqueous ethanol resulted in recovery of the chroman. When the solvent was switched to methanol, the recovered material was the chroman **20** demonstrating the stability of the chroman ring even after an acid-catalyzed cleavage. When the same reaction was carried out in the presence of an aldehyde trap such as 2,4-dinitrophenylhydrazine (DNP), the β -phenol propionaldehyde derivative **21** was obtained demonstrating the ring opening equilibrium.



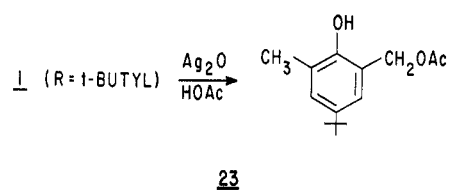
The trapping reaction is obviously a cycloaddition of a diene (the *o*-quinone methide) to a dienophile. These experiments do not distinguish between a two-step or a concerted process. The very specific orientation as obtained here suggests some sort of prior complexation of the reactants allowing polar effects to direct the addition. All of the products can be accounted for by assigning the polarized form **22** to the *o*-quinone methide and then using this to predict the orientation.



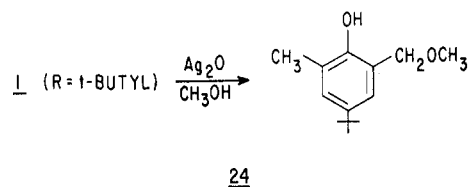
Any dienophile that has some stabilizing effect on the developing benzylic carbonium ion should preferentially add in a single orientation. In addition, other agents should add to this developing charge separated species.

***o*-Quinone Methides and Nucleophiles.**—Several nucleophiles were also found to be capable of intercepting the *o*-quinone methide. When 4-*tert*-butyl-2,6-xyleneol is oxidized in the presence of acetic acid, the chief product formed is the 2-(α -acetoxyethyl)-6-methyl-4-*tert*-butylphenol **23**. This material could not be isolated directly because upon heating it split out acetic acid and regenerated the *o*-quinone methide which trimerized.

The phenol **23** was isolated by converting it to the trimethylsilyl ether by use of bis(trimethylsilyl)acetamide.⁷ This ether could be distilled and the free phenol then reisolated by hydrolysis of the trimethylsilyl ether.



Another nucleophile that would trap the *o*-quinone methide was methanol. If the oxidation of 4-*tert*-butyl-2,6-xyleneol is run in methanol with an excess of the phenol over the oxidizing agent, the primary product formed is 4-*tert*-butyl-2-methoxymethyl-6-methylphenol **24**.



The methoxy group is not deactivating enough and if a higher oxidant:phenol ratio than 1 is used the primary product **24** is itself oxidized and adds another molecule of methanol. This has been shown in the work of Orlando⁸ where the second methoxy attaches to the same methyl as the first methoxy. The phenol with two methoxy groups was not isolated but was identified by mass spectrum. Because of this spectrum of possible products, this particular reaction is not a good preparative method.

These trapping reactions demonstrate that an *o*-quinone methide is present in the oxidation of 4-*tert*-butyl-2,6-xyleneol and that it is susceptible to trapping. A variety of 2-methyl substituted phenols yield the *o*-quinone methide with the only proviso being that there be no α hydrogen on the 4 position. In addition, a variety of dienes and nucleophilic reagents can intercept the *o*-quinone methide on its way to self-trimerization. This offers a new route to a variety of substituted chromans. The specific orientation observed in these reactions is expected of diene reactions and offers little suggestion as to whether the reaction is concerted or two step.

(7) J. F. Klebe, H. Finkbeiner, and D. M. White, *J. Amer. Chem. Soc.*, **88**, 3390 (1966).

(8) C. M. Orlando, *J. Org. Chem.*, in press.

Experimental Section

4-*tert*-Butyl-2,6-Xylenol.—This material was prepared by alkylation of 2,6-dimethylphenol with isobutylene.

Measurement of the Efficiency of Quinone Methide Trapping.—A standard solution was prepared in benzene containing 1 mol of 4-*tert*-butyl-2,6-xylenol and 0.1 mol of *m*-terphenyl as an internal standard per 25 ml of solution. In individual runs, the appropriate trapping dienophile was mixed with 25 ml of the standard solution and oxidized with 0.232 g (1 mol) of silver oxide.

After 1 hr, a sample of the solution was silylated with bis(trimethylsilyl)acetamide⁷ and analyzed on a vpc using a 2-ft silicon rubber column with a 60 ml/min flow of helium and 100–300° at 10°/min programming. The various peaks were integrated and compared with the standard. Duplicate runs agreed with each other $\pm 5\%$.

In those cases where the prepared chroman was not one of the materials in Table III, the material was collected from the vpc and identified by ir, nmr, and mass spectrometry. The results of this experiment are given in Table II.

2-Ethoxy-6-*tert*-butyl-8-methylchroman 12.—This is a general reaction for the preparation of chromans. It is written for the specific preparation of 12, but can be used for all of the chromans listed in Table III.

In a magnetically stirred, water-cooled flask were placed 4-*tert*-butyl-2,6-dimethylphenol (8.9 g, 0.05 mol), ethyl vinyl ether (10 ml), and silver oxide (15 g, 0.06 mol). The mixture was stirred until the dark color of the silver oxide turned to the light grey of reduced silver in about 0.5 hr.

The slurry was filtered and the filtrate distilled. After a forerun of ethyl vinyl ether, the chroman 12 was obtained as a pale yellow oil, bp 103–110° (0.65 mm), 9.9 g (80% yield). Redistillation gave pure chroman [bp 106–107° (0.6 mm.)].

Anal. Calcd for C₁₆H₂₄O₂: C, 77.4; H, 9.7; mol wt, 248. Found: C, 77.2; H, 9.8; mol wt, 241.

2,8-Dimethyl-2-isopropyl-6-*tert*-butylchroman.—Absolute ethanol (100 ml), 2,8-dimethyl-2-isopropenyl-6-*tert*-butylchroman 15 (1.92 g, 0.0074 mol) and platinum oxide (0.1 g) were shaken in a hydrogenation apparatus. Hydrogen uptake was very rapid until 1 equiv was absorbed. The reaction was stopped and the solvent evaporated after filtration of the catalyst. The oil that was left was distilled and virtually all of the material distilled at 113° (0.4 mm): ir (CCl₄) C=C at 1646 cm⁻¹ is not present.

Anal. Calcd for C₁₈H₂₈O: C, 83.1; H, 10.8; mol wt, 260. Found: C, 82.9; H, 10.8; mol wt, 265.

Exchange of the Ethoxy Group on 2-Ethoxy-8-methyl-6-*tert*-butylchroman (12). **Acetal Exchange.**—2-Ethoxy-8-methyl-6-*tert*-butylchroman (0.5 g, 12) was heated to reflux in methanol (20 ml) containing a trace of HCl. After 20 hr the solvent was removed and the residual oil examined by nmr which showed the absence of the ethyl and the presence of a methoxy at 3.37 ppm (TMS). The oil was distilled, bp ~145° (11 mm), M²⁰_D 1.5156 giving a pure sample of 2-methoxy-8-methyl-6-*tert*-butylchroman (20).

Anal. Calcd for C₁₅H₂₂O₂: C, 76.9; H, 9.4; mol wt, 234. Found: C, 77.3; H, 9.9; mol wt, 234.

Hydrolysis of 2-Ethoxy-8-methyl-6-*tert*-butylchroman (12).—Several attempts were made to hydrolyze the ethoxychroman with ethanol-water mixtures but only starting material was recovered. The chroman (2.83 g, 0.012 mol) was dissolved in 95% ethanol (200 ml) containing 2,4-dinitrophenylhydrazine (0.198 g, 0.01 mol) and concentrated sulfuric acid (0.1 ml). The solution was refluxed 3 hr and then water was added to the cloud point, and the reaction cooled. A red oil was obtained which upon further crystallization from ethanol-water yielded yellow crystals (0.8 g, 20% mp 154–156°) of 21.

Anal. Calcd for C₂₀H₂₄N₂O₃: C, 60.0; H, 6.0; N, 14.0; mol wt, 400. Found: C, 60.0; H, 6.1; N, 14.1; mol wt, 398.

2-Methyl-4-*tert*-butyl-6-acetoxymethyl Phenyl Trimethylsilyl Ether.—To a solution of 4-*tert*-butyl-2,6-xylenol (17.8 g, 0.1 mol) in glacial acetic acid (150 ml) powdered potassium permanganate (6.4 g, 0.2 equiv) was added slowly and with stirring. After 2 hr, the permanganate color was gone and the pale yellow solution was poured into water. The organic layer was extracted with ether and the extracts were washed with bicarbonate solution and dried (MgSO₄). The ether was distilled and the residue titrated with bis(trimethylsilyl)acetamide⁷ (22 g, 0.11 mol) to convert the phenol to the trimethylsilyl ether.

TABLE III
PREPARATION OF CHROMANS

No.	Chroman prepared	Phenol	Dienophile	Solvent	Yield, %	Bp° (mm)	Mol wt	Calcd, %		Found, %		Mol wt
								C	H	C	H	
12	2-Ethoxy-6- <i>tert</i> -butyl-8-methylchroman	...	Ethyl vinyl ether	None	80	106–107 (0.6)	248	77.4	9.7	77.2	9.8	241
13	2-Phenyl-6- <i>tert</i> -butyl-8-methylchroman	...	Styrene	None	40	158 (0.5)	280	85.7	8.6	85.5	8.8	297
14	2,8-Dimethyl-2-phenyl-6- <i>tert</i> -butylchroman	...	α -Methylstyrene	CaH ₆ , 75 ml	12 ^b	162–166 (0.5)	294	85.6	8.8	85.9	9.0	297
15	2,8-Dimethyl-2-isopropenyl-6- <i>tert</i> -butylchroman	...	2,3-Dimethylbutadiene	None	26	113 (0.5)	258	83.8	10.1	83.4	10.4	245 ^d
17	2-Isopropenyl-8-methyl-6- <i>tert</i> -butylchroman	...	Isoprene	None	62 ^c	105–110 (0.5)	244	83.7	9.8	83.6	10.0	246 ^d
16	2,8-Dimethyl-6- <i>tert</i> -butyl-2-vinylchroman	...	Isoprene	None	62 ^c	105–110 (0.5)	244	83.7	9.8	83.7	10.0	250 ^f
18	2-Ethoxy-6-methoxy-8-methylchroman	...	Ethyl vinyl ether	None	12 ^e	...	222	70.3	8.1	70.0	8.3	222
19	2-Ethoxy-6,8-di- <i>tert</i> -butylchroman	...	Ethyl vinyl ether	None	80	134 (0.7)	290	78.7	10.4	78.4	10.6	301

^a 4-*tert*-Butyl-2,6-dimethylphenol. ^b Chromatographed on alumina. ^c 16 and 17 were obtained as a mixture. They were separated by preparative vpc and gave 20% of 16 and 12% of 17 as isolated yield. ^d 4-Methoxy-2,6-dimethylphenol. ^e A trimer 2 (R = methoxy) of the *o*-quinone methide was obtained in 25% yield. ^f Purified by preparative vpc. ^g 2,4-Di-*tert*-butyl-6-methylphenol. ^h Ir (CCl₄) C=C 1646 cm⁻¹, 12%. ⁱ Ir (CCl₄) C=C 1642 cm⁻¹, 20%.

The material was distilled and after a forerun of silylating by-products the trimethylsilyl ether was obtained [113–114° (0.9 mm), 12.9 g, 42%]. Redistillation gave the pure ether, bp 140° (3.5 mm).

Anal. Calcd for $C_{17}H_{23}O_3Si$: C, 71.2; H, 8.5; mol wt, 236. Found: C, 71.0; H, 8.7; mol wt, 243.

Pyrolysis of 2-Acetoxyethyl-4-*tert*-butyl-6-methylphenol.—A small sample (100 mg) of the title compound was heated at 150° for 18 hr under nitrogen. The deep yellow residue was examined by thin layer chromatography (silica gel–benzene–hexane) and was found to consist of recovered phenol, the trimer **2** ($R = \textit{tert}$ -

butyl) and tars. The trimer was identified by comparison with authentic¹ in R_f values and in ir spectrum.

Registry No.—**12**, 25966-85-2; **13**, 25966-86-3; **14**, 25966-87-4; **15**, 25966-88-5; **16**, 25966-89-6; **17**, 25966-90-9; **18**, 25966-91-0; **19**, 25966-92-1; **20**, 25966-93-2; **21**, 25966-94-3; 2,8-dimethyl-2-isopropyl-6-*tert*-butylchroman, 25966-95-4; 2-methyl-4-*tert*-butyl-6-acetoxyethylphenyl trimethylsilyl ether, 25957-28-2.

Selective Solvation of Hydrophobic Ions in Structured Solvents. Azo-Hydrazone Tautomerism of Azo Dyes in Aqueous Organic Solvents

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The azo-hydrazone tautomerism of a series of 4'-substituted 2- and 4-aryloxy-1-naphtholsulfonates was studied spectrophotometrically in a wide range of protic and aprotic polar solvents with dielectric constants varying from 24.3 (ethanol) to 182.4 (HCONHCH₃). The effect of solvents on the position of the equilibrium between the tautomers does not correlate with bulk solvent properties but depends upon the solvent structure and the microscopic environment of the dye in the solvent matrix. For solvent-sensitive dyes, the hydrazone form is predominant in those neat solvents capable of forming a three dimensional structure, whereas the azo form is favored by neat solvents that form a two dimensional structure or are unstructured. In binary mixtures of water with methanol, ethanol, and *tert*-butyl alcohol, the shift from hydrazone to azo is most pronounced in the predominantly aqueous compositions, *tert*-butyl alcohol having the greatest effect. At alcohol levels associated with reduction of solvent structure, the shift is gradual and nearly independent of the nature of the alcohol. Pronounced shifts from hydrazone to azo also occur in aqueous compositions of DMF- and DMSO-water mixtures. The results are interpreted in terms of selective solvation of the hydrophobic dyes by the organic cosolvent within the water structure. The tautomerism becomes progressively less exothermic as organic solvent is added to the aqueous binaries.

A number of spectroscopic methods have established that 4-phenylazo-1-naphthols can exist in solution as hydroxy azo or as quinone hydrazone tautomers.^{1–8} The hydrazone is favored by polar solvents^{2a,5,8} and by electron-withdrawing substituents in the phenyl ring.^{2a,5,9} No systematic studies of the tautomerism have been made in structured solvents or in solvents of high dielectric constants, and no quantitative data are available on the effects of solvent dielectric constant or of specific solvation on the tautomeric equilibrium. We have studied the tautomerism of several water-soluble dyes in a number of neat solvents and in binary aqueous organic solvent mixtures and find that the equilibrium is sensitive to specific solvation and to the hydrogen bonded structure of the solvent.

Results

The neat solvents studied and their dielectric constants at 25° are ethanol (24.3), methanol (32.6), *N,N*-dimethylformamide (DMF, 36.7), acetonitrile

(37.5), dimethyl sulfoxide (DMSO, 46.4), propylene carbonate (65.1), water (78.5), formamide (109.5), and *N*-methylformamide (182.4).

Structure **2** dyes ($X = H, OCH_3, Cl, SO_3^-, \text{ and } CF_3$) give more stable hydrazones than the isomeric structure **1** dyes. Whereas the equilibrium concentrations of all the **1** dyes except **1e** can shift with changes in solvent or solvent composition, the **2** dyes exist predominantly as the hydrazones in all solvents studied. The order of stability of the hydrazones of the **1** dyes in a given solvent is **1e** > **1b** \approx **1c** > **1a** > **1d**. The hydrazone of **1e** was the predominant tautomer in all our solvents and solvent mixtures, whereas the azo form of **1d** was preponderant in all solvents. We estimate that aqueous solutions of **1a** contain equal amounts of both tautomers at 25°, with a shift to the azo form in all other solvents. Dyes **1b** and **1c** exist as greater than 95% hydrazone in water at 25° and as pure azo tautomers in ethanol, *tert*-butyl alcohol, and the aprotic dipolar solvents.

The estimation of the predominant tautomer in the neat solvents was qualitative and was based on the relative preponderance of the two absorption bands. The predominance of one tautomer was so great in a given solvent with **1b** and **1c** that a qualitative approach was sufficient for evaluating solvent properties and for separating solvent types. The only neat solvents in which the hydrazones of **1b** and **1c** were predominant were water and formamide. These dyes were present almost exclusively as the azo tautomers in all the other neat solvents, including *N*-methylformamide.

There is no correlation of the position of the equilibrium with the dielectric constant of the neat solvent,

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(1) H. Zollinger, "Azo and Diazo Chemistry," Interscience, New York, N. Y., 1961, p 322.

(2) (a) A. Burawoy and I. Markowitsch, *Justus Liebigs Ann. Chem.*, **508**, 180 (1932); (b) A. Burawoy, A. G. Salem, and A. R. Thompson, *J. Chem. Soc.*, 4793 (1952).

(3) J. B. Muller, L. Blangey, and H. E. Fierz-David, *Helv. Chim. Acta*, **35**, 2579 (1952).

(4) V. Bekarek, K. Rothschein, P. Vetesnik, and M. Vecera, *Tetrahedron Lett.*, 3711 (1968).

(5) A. H. Berrie, P. Hampson, S. W. Longworth, and A. Mathias, *J. Chem. Soc. B*, 1308 (1968).

(6) K. J. Morgan, *ibid.*, 2151 (1961).

(7) H. Rau, *Ber. Bunsenges. Phys. Chem.*, **72**, 637 (1968).

(8) R. Kuhn and F. Bär, *Justus Liebigs Ann. Chem.*, **516**, 143 (1935).

(9) H. Shingu, *Sci. Pap. Inst. Phys. Chem. Res. (Tokyo)*, **35**, 78 (1938).