3,3-dimethylglutarate and 200.0 g (1.52 mol) of 2-methylphenylacetonitrile. The reaction mixture was stirred and refluxed under N_2 with slow removal of the ethanol until 80% of the ethanol had been removed. The mixture was cooled to 25 °C, poured into ice water, and extracted with ether (3 × 300 mL). The basic aqueous solution was acidified with cold 6 N HCl and the resulting oil extracted into ether. The combined ether extracts of the acidified aqueous layer were washed with water, dried ($MgSO_4$), and filtered and the ether removed to leave 309.1 g (67%) of a light yellow viscous oil. Spectral data indicate this to be ethyl 6-(2′-methylphenyl)-6-cyano-5-keto-3,3-dimethylhexanoate: IR (neat) 3.17–3.66 (enolic OH), 4.54 (CN), 5.68 (ester C=O), 5.95 (ketone C=O), 6.10, 6.21 μm (enolic C=C); NMR ($CDCl_3$) δ 0.75–1.43 (m, $CO_2CH_2C\mathbf{H}_3$), 1.22 (s, 3,3-CH_3), 2.32 (s, 2′-CH_3), 2.36 (s, $C\mathbf{H}_2CO_2Et$), 2.73 (s, $C\mathbf{H}_2CO$), 4.23 (q, $CO_2C\mathbf{H}_2CH_3$), 4.93 and 12.3 (s, C**H**CN and enolic OH), 7.23 (m, aromatic).

A solution of 296.1 g (0.982 mol) of ethyl 6-(2′-methylphenyl)-6-cyano-5-keto-3,3-dimethylhexanoate, 880 mL of glacial acetic acid, 310 mL of water, and 310 mL of concentrated sulfuric acid was refluxed for 48 h. The mixture was cooled to room temperature, and 600 mL of water and 300 mL of isopropyl ether were added. The mixture was stirred and cooled in an ice bath and filtered and the white solid washed several times with water and several times with isopropyl ether. This solid was dried overnight in a vacuum oven to give a white powder, mp 179.5–180.5 °C.

The mixed melting point of this material and the product obtained from the photolysis of 2-diazo-5,5-dimethyl-1,3-cyclohexanedione in toluene is 179–180 °C. The IR, NMR, and TLC of **11** prepared by photolysis and **11** prepared by the above method are identical.

Acknowledgment. The author would like to express his appreciation to Dr. John A. Durden for valuable suggestions made during the course of this work.

Registry No. 5, 1460-08-8; **6**, 56964-05-7; **7**, 68427-45-2; **8**, 71871-65-3; **9**, 1807-68-7; **10**, 71885-47-7; **11**, 724-40-3; **12**, 71871-66-4; **13**, 71871-67-5; **14**, 68427-50-9; **15**, 68427-46-3; **16**, 68427-47-4; **17**, 71871-68-6; **18**, 71871-69-7; **19**, 71871-70-0; **20**, 71871-71-1; **21**, 71871-72-2; **22**, 71871-73-3; **23**, 71871-74-4; **24**, 71871-75-5; **25**, 71871-76-6; **26**, 7230-19-5; **27**, 71871-77-7; **28**, 71871-78-8; **29**, 68427-48-5; **30**, 68427-49-6; **31**, 68427-51-0; **32**, 68427-52-1; benzene, 71-43-2; mesitylene, 108-67-8; toluene, 108-88-3; ethylbenzene, 100-41-4; cumene, 98-82-8; 3,5-dimethyl-*tert*-butylbenzene, 98-19-1; *m*-xylene, 108-38-3; *m*-chlorotoluene, 108-41-8; *m*-methylanisole, 100-84-5; 3,5-dimethylanisole, 874-63-5; *m*-tolunitrile, 620-22-4; ethyl 3,3-dimethylglutarate, 71885-49-9; 2,4-dimethylphenylacetonitrile, 68429-53-8; ethyl 6-(2′,4′-dimethylphenyl)-6-cyano-5-keto-3,3-dimethylhexanoate, 68427-53-2; 5-phenyl-1,3-cyclohexanedione, 493-72-1; tosyl azide, 941-55-9; decalin-1,3-dione, 68429-52-7; diethyl 3,3-dimethylglutarate, 17804-59-0; 2-methylphenylacetonitrile, 22364-68-7; ethyl 6-(2-methylphenyl)-6-cyano-5-keto-3,3-dimethylhexanoate, 71871-79-9.

Photoisomerizations of Protonated Phenols. Extension of the Photochemistry of Cyclohexa-2,5-dienones

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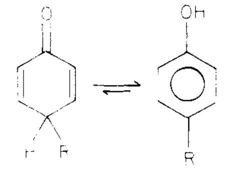
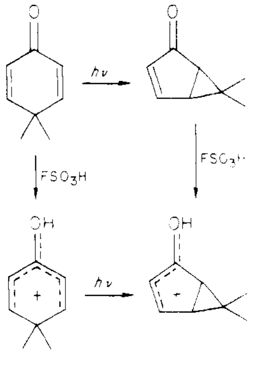
Protonated methyl-substituted phenols have been found to undergo a variety of photoisomerizations when irradiated at a low temperature in FSO_3H. The products obtained depend upon the wavelength of the light used. The general sequence of reactions was shown to be the photochemical transformation of the para-protonated form of a phenol ($\lambda_{max} \sim 310$ nm) to the corresponding protonated bicyclo[3.1.0]hex-3-en-2-one, a reaction which is directly comparable to the photoisomerization observed with cross-conjugated cyclohexadienones. Several bicyclo[3.1.0]hex-3-en-2-ones were recovered by neutralization of the acid solutions. The second step in the overall photoisomerization sequence involved the transformation of the protonated bicyclohexenones ($\lambda_{max} \sim 330$ nm) to protonated phenols. The extent of the photoreaction of the starting protonated phenol was governed by the wavelength of the light used for the irradiation; light of wavelength 300 nm drove only the first step of the sequence, while with broad band irradiation ($\lambda > 320$ nm) both steps occurred. One exception to this general behavior was found with protonated 2,4,6-trimethylphenol. In this case a meta-protonated isomer ($\lambda_{max} \sim 373$ nm) was converted to protonated 1,3,5-trimethylbicyclohex-3-en-2-one on irradiation with light of wavelength greater than 360 nm. With shorter wavelength light, photoisomerizations of the para-protonated form of 2,4,6-trimethylphenol were also observed.

While the photochemical reactions of a large variety of cross-conjugated cyclohexadienones have been examined,[1] these studies have not been extended to molecules having less than two substituents at C_4. The reason for this apparent neglect is not hard to find. Such compounds are difficult to prepare and readily revert to their more stable phenolic tautomers, eq 1. The photochemical behavior of phenols is quite different from that of the cross-conjugated cyclohexadienones with remarkably few isomerization reactions being reported.[2,3]



(1)

Scheme I



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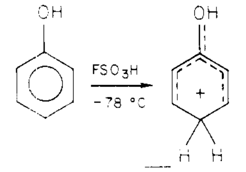
(1) For reviews see: D. I. Schuster, *Acc. Chem. Res.*, 11, 65 (1978); P. J. Kropp, *Org. Photochem.*, 1, 1 (1967); K. Schaffner, *Adv. Photochem.*, 4, 81 (1966); H. E. Zimmerman, *ibid.*, 1, 183 (1963).

Oxygen-protonated cyclohexa-2,5-dienones have been found to undergo very similar photorearrangements to those described for the parent ketones.[4,5] This is illustrated in Scheme I for the dimethyl-substituted system.[4a,6]

Unlike the situation with the cyclohexadienones, it is easy to obtain protonated cyclohexadienones with a single or even no substituent at C_4. This can be achieved by the dissolution of a phenol in an acid such as FSO_3H when protonation occurs on one of the ring carbons, eq 2.[7] With phenols unsubstituted at C_4, the thermodynamically preferred site of proton attachment is the para position, thus giving a protonated cross-conjugated cyclohexadienone. When the phenol is substituted at C_4, protonation also occurs at other sites; however, once more the protonated cross-conjugated dienone is one of the major forms present.



(2)

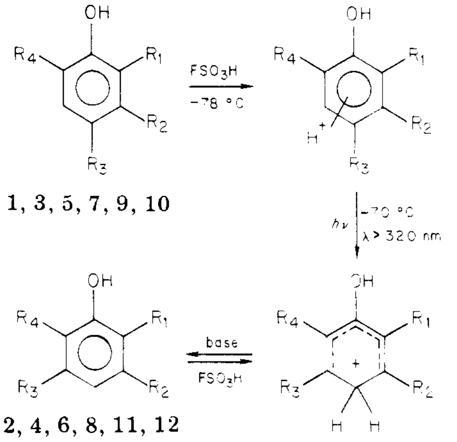
In principle therefore, it should be possible by using FSO_3H as a solvent to extend the range of cyclohexadienone photoisomerizations to include the less substituted systems. Some indication that protonated phenols are photochemically reactive came from an earlier observation we made of the photoisomerization of protonated 3,4-dimethylphenol to protonated 3,5-dimethylphenol.[4a] In this paper, we extend this finding and show that protonated phenols are generally photoreactive, undergoing isomerizations which are directly comparable to those of the protonated dienones.

Results

Fluorosulfuric acid solutions of various protonated phenols were used throughout this work. These solutions were prepared by dissolution of the phenol in the acid at −78 °C. In order to avoid sulfonation reactions, the solutions were kept at low temperatures.

Irradiations with Light of Wavelength Greater than 320 nm. Using a superpressure mercury light source and a window glass filter with a cut off at 320 nm, we observed a general photorearrangement of protonated 4-methylphenols. As is shown in Scheme II, this photoreaction involves the overall migration of the 4-methyl substituent to either the C_3 or C_5 positions of the protonated phenol.

Scheme II



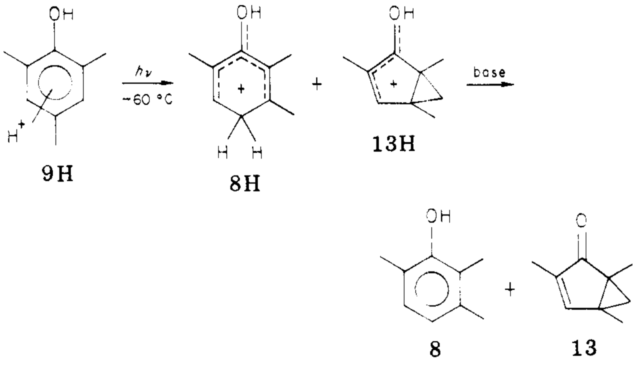
1, 3, 5, 7, 9, 10

2, 4, 6, 8, 11, 12

1, 2, $R_1 = R_4 = H; R_2 = R_3 = CH_3$
3, 4, $R_2 = R_4 = H; R_1 = R_3 = CH_3$
5, 6, $R_4 = H; R_1 = R_2 = R_3 = CH_3$
7, $R_1 = H; R_2 = R_3 = R_4 = CH_3$
8, 9, $R_2 = H; R_1 = R_3 = R_4 = CH_3$
10, 11, $R_1 = R_2 = R_3 = R_4 = CH_3$
12, $R_1 = R_2 = CH_3; R_3 = R_4 = H$

The photoisomerizations were followed by low-temperature ^1H NMR spectroscopy directly on the irradiated acid solutions. Products were identified by independent protonations of the authentic phenols.[7] In the case of the photoisomerization of **3H**, protonated 2,3-dimethylphenol, **12H** was considered as a possible product, but no evidence for its formation could be found. Minor amounts of what appeared to be intermediate compounds were seen during the course of certain of these photoisomerizations, the structures of which will become evident later.

In the case of protonated 2,4,6-trimethylphenol **9H**, a further major photoproduct was observed in addition to **8H**. The presence of this additional product was particularly evident in the ^1H NMR spectra of the irradiated solutions where three methyl group resonances were observed at considerably higher field than those of either **8H** or **9H**. Neutralization of the irradiated acid solution yielded 8 and a further compound identified as the ketone **13**.



9H 8H 13H

8 13

The structural assignment of **13** rests largely on its spectroscopic properties. Mass spectral examination of **13** showed that it was isomeric with **8** and **9**. The presence of an unsaturated carbonyl group was clearly indicated by the presence of a strong absorption at 1690 cm^{-1} in the infrared spectra of **13**, a position typical of bicyclo[3.1.0]hexenones.[8] The ^1H NMR spectrum of **13** (Table I) exhibited three resonances at high field attributable to the methyl groups. One of these was a doublet ($J = 1.3$ Hz) coupled to the vinyl proton resonance at δ 6.95. The cyclopropyl methylene proton resonances appeared as an AB doublet. The positions of these resonances are very similar to those previously reported for bicyclo[3.1.0]hexenones[9,4b] and to the several further examples of these ketones described later in this paper.

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(2) H. D. Becker, "Chemistry of the Hydroxyl Group", S. Patai, Ed., Wiley, New York, 1971, 835; D. Bryce-Smith and A. Gilbert, *Tetrahedron*, **32**, 1309 (1976).

(3) T. Matsuura, Y. Hiromoto, A. Okada, and K. Ogura, *Tetrahedron*, **29**, 2981 (1973); *Tetrahedron Lett.*, 3727 (1970).

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(5) For a review of the photoreactions of protonated ketones, see: R. F. Childs, "Reviews of Chemical Intermediates", in press.

(6) J. S. Swenton, E. Saurborn, R. Srinivasan, and F. I. Sonntag, *J. Am. Chem. Soc.*, **90**, 2990 (1968).

(7) R. F. Childs and B. D. Parrington, *Can. J. Chem.*, **52**, 3303 (1974); S. M. Blackstock, K. E. Richards, and G. J. Wright, *ibid.*, **52**, 3313 (1974); J. W. Larsen and M. Eckert-Maksic, *Croat. Chem. Acta*, **45**, 503 (1973); *J. Am. Chem. Soc.*, **96**, 4311 (1974); G. A. Olah and Y. K. Mo, *J. Org. Chem.*, **38**, 353 (1973).

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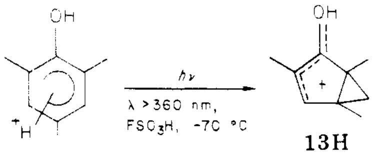
Table I. ^1H NMR Chemical Shifts of Bicyclo[3.1.0]hexenones^a

compd no.	chemical shift, ppm^c						coupling constant, Hz
	H_1	H_3	H_4	H_5	H_6		
13	(1.35)^b	(1.56 d)	6.95 q	(1.24)^b	0.85 d	1.31 d	$J_{CH_3,H_4} = 1.3$; $J_{CH_2} = 3$
13H	(1.71)^b	(1.82 d)	8.25 q	(1.68)^b	2.19 d	3.25 d	$J_{CH_4,H_4} = 1.0$; $J_{CH_2} = 4$
16	2.18 m	(1.62 d)	7.09 q	(1.40)	(1.11 d)	1.64 m	$J_{CH_3,H_4} = 1.5$; $J_{CH_3,H_6} = 5.5$
16H	3.13	(1.93)	8.25	(1.77)	(1.50 d)	3.33 dq	$J_{CH_3,H_6} = 6$; $J_{1,6} = 3$
17	(1.35)	5.31 q	(2.12 d)	1.78	(1.13 d)	1.42 m	$J_{CH_3,H_2} = 1.2$; $J_{CH_3,H_6} = 5.8$
17H	(1.67)	6.12	(2.67)	3.34	(1.44 d)	2.90 m	$J_{CH_3,H_6} = 7$
18	2.18 m	(1.70 d)	6.84 q	(1.46)	(1.05 d)	1.87 m	$J_{CH_3,H_6} = 5.7$; $J_{CH_3,H_4} = 1.5$
18H	3.34	(2.02)	8.02	(1.80)	(1.45 d)	^{d}	$J_{CH_3,H_6} = 5.5$
19	(1.38)	(1.67 d)	7.08 m	1.83t	(1.13 d)	^{d}	$J_{CH_3,H_4} = 1.5$; $J_{CH_3,H_6} = 6$
19H	(1.73)	(1.92)	8.31 m	3.43	(1.43 d)	3.10	$J_{CH_3,H_6} = 7$
20	2.23^b m	(1.55)	(2.06)	2.11^b m	1.17 m	1.43 m	
20H	3.32^b m	(1.87)	(2.55)	3.60^b m	2.43 m	2.69 m	
21	(1.40)	(1.65 d)	7.26 q	2.16 m	1.22	1.30	$J_{CH_3,H_4} = 2$
21H	(1.76)	(1.93)	8.40	3.62 m	2.42 m	3.07 m	

[a] Ketones in $CDCl_3$; protonated ketones in FSO_3H at −50 °C; d = doublet, q = quartet, m = multiplet. [b] Assignments may be reversed. [c] Numbers in parentheses refer to chemical shifts of methyl resonances. [d] Position uncertain.

Protonation of **13** in FSO_3H gave **13H**. The ^1H NMR spectrum of **13H** was completely consistent with the assigned structure. In particular the methylene proton resonances of **13** are shifted downfield on protonation and occupy positions typical of similar bicyclo[3.1.0]hexenyl cations.[10,11]

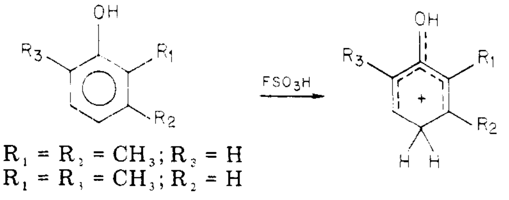
The relative amounts of photoproducts **8H** and **13H** obtained from **9H** were found to be very dependent on the wavelength of the light used in the irradiations. Using the window glass filter (cut off 320 nm) and a super-pressure mercury light source, we found the ratio of **8H** to **13H** to be 3:1. With a filter with a cut off at 360 nm, **13H** was the only product observed. Under these longer wavelength conditions, it was not possible to drive the reaction to completion, and a photostationary state was reached consisting of equal amounts of **9H** and **13H**. The same photostationary state was also reached by irradiation of a FSO_3H solution of **13H**.



9H

13H

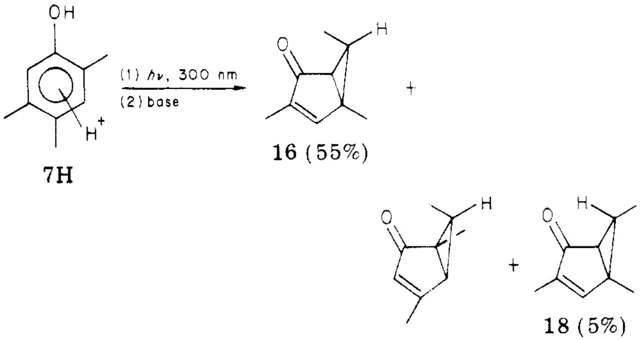
In contrast to the isomerizations seen with the protonated 4-methyl substituted phenols, no rearrangements could be detected on irradiation of **2H**, **4H**, **14H**, or **15H**, with light of wavelength greater than 325 nm.



14, $R_1 = R_2 = CH_3$; $R_3 = H$
15, $R_1 = R_3 = CH_3$; $R_2 = H$

Irradiations at 300 nm. When the irradiations were carried out using a light source giving a comparatively narrow band of light centered at 300 nm, the major products formed were protonated bicyclo[3.1.0]hexenones. Under these conditions, phenols both with and without a methyl group at C_4 were found to be photoactive. Four protonated phenols were investigated in detail.

Protonated 2,4,5-trimethylphenol (**7H**) underwent photoisomerization on irradiation to give a series of cations. Neutralization of the acid gave a mixture which was shown by GLC to consist of two major and two minor products. The two major products were obtained in pure form and assigned to structures **16** and **17**. A sufficient amount of one of the minor components was obtained for spectroscopic examination, and it appeared to have the structure indicated by **18**.



7H

16 (55%)

17 (38%)

18 (5%)

Compounds assigned structures **16**, **17**, and **18** displayed strong carbonyl absorptions at ca. 1690 cm^{-1}, typical of α,β-unsaturated ketones. In each case, the presence of a doublet ($J \sim 6$ Hz) of relative intensity three in the ^1H NMR spectra (Table I) was indicative of the presence of a methyl group at C_6. The assignment of the stereochemistry at C_6 was made by comparison of the chemical shifts of the C_6 methyl resonances with other bicyclo[3.1.0]hexenones in which it has been generally noted that resonances of the C_6 endo substituents are shielded in comparison with the C_6 exo substituent resonances.[4b,8]

Further confirmation of these structural assignments was made by protonation of **16**, **17**, and **18** in FSO_3H. The chemical shifts of the proton resonances of the cations so obtained (Table I) are fully consistent with their structures. Cation **16H** was found to be thermally unstable and rearrange quantitatively to **17H** at +10 °C with a first-order rate constant of $3.7 \times 10^{-3}\ s^{-1}$. No other product could be detected as a result of this thermal isomerization. Irradiation of **17H** at low temperatures, using a 350-nm light source, caused it to isomerize quantitatively to **6H**.

On irradiation with 300-nm light, **9H** was found to give products in addition to those seen before. Recovery of the neutral compounds by quenching the acid solution gave **13** and two other compounds in a ratio of 26:59:15. These

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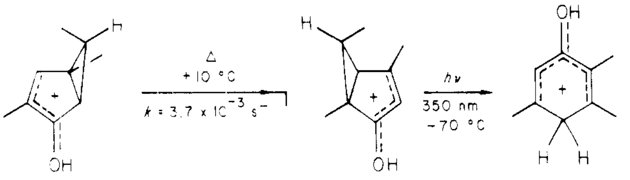
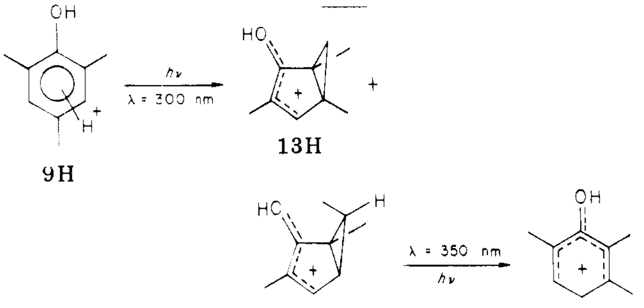
(10) (a) R. F. Childs, M. Sakai, B. D. Parrington, and S. Winstein, *J. Am. Chem. Soc.*, **96**, 6403 (1974); R. F. Childs and S. Winstein, *ibid.*, **96**, 6409 (1974).

(11) P. Vogel, M. Saunders, N. M. Hasty, Jr., and J. A. Berson, *J. Am. Chem. Soc.*, **93**, 1551 (1971).



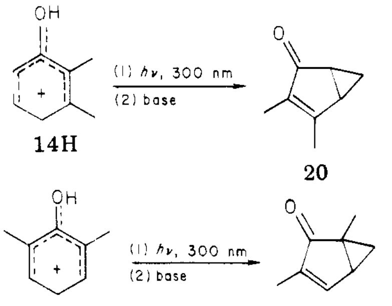
16H **17H** **6H**

additional products proved to be very difficult to separate; however, the major component appeared to be **19**. Dissolution of **19** in FSO_3H gave **19H** (Table I). **19H** was cleanly converted to **8H** on irradiation with light of wavelength 350 nm.



9H **13H** **19H** **8H**

Irradiation of FSO_3H solutions of **14H** and **15H** at 300 nm again led to the formation of new cationic species. Quenching of the acid solutions gave in each case a single photoproduct, and these were identified as **20** and **21**, respectively. Two bicyclohexenones could possibly be formed from **14H**; however, only a single product was observed. Further confirmation of these structures was obtained on protonation of these ketones.



14H **20** **15H** **21**

Irradiation of protonated 2,4,6-trimethyl- and 2,6-dimethylanisole, phenol, cresol, and 2,5-dimethylphenol did not lead to the formation of any detectable products.

The ultraviolet spectra of some protonated phenols and bicyclo[3.1.0]hexenones are shown in Table II, and a summary of the photoisomerization observed is given in Table III.

Discussion

The ease with which these phenols succumb to photorearrangements when dissolved in FSO_3H contrasts markedly with the singular lack of comparable reactions when they are irradiated in more conventional media.[2,3] This fact together with the well-established ready protonation of phenols in strong acids such as FSO_3H indicates that protonated phenols are the photoreactive species.

Table II. UV Spectra of Cations

compd no.	λ_{max}, nm	log ε
20H[a]	325	3.01
21H[a]	328	3.45
19H[a]	336	3.03
16H[a]	323	2.11
14H[b]	334	3.26
9H[b]	314, 373	4.46, 3.88
7H[b]	314	4.48

[a] In H_2SO_4 at 0 °C. [b] In FSO_3H at −75 °C.

Table III. Summary of Photoisomerizations[a]

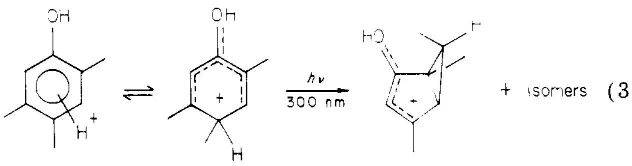
starting cation	lamp[b] system	wavelength of light, nm	products (%)[c]
1H	A	>320	2H (>90)
3H	A	>320	4H (>90)
5H	A	>320	6H (>90)
7H	A	>320	6H (>90)
7H	B	300	16H (55), 17H (38), 18H (5), other (2)
9H	A	>320	8H (75), 13H (25)
9H	A	>360	13H (>90)
9H	B	300	13H (28), 19H (58), other (14)
10H	A	>320	11H (>90)
14H	B	300	20H (>90)
15H	B	300	21H (>90)
17H	C	350	6H (>90)
19H	C	350	8H (>90)

[a] All reactions in FSO_3H at −70 °C. [b] A, Phillips super pressure; B, RPR-3000 Å; C, RPR-3500 Å; see Experimental Section for details. [c] Percentages expressed of products only.

The protonation of phenols in FSO_3H and related acids has been extensively studied, and the major features of these reactions are well understood. Proton attachment can take place on oxygen, or on the ortho, meta, or para ring carbons of a phenol, depending very much on the nature of any of the other substituents. A thermodynamic distribution of products is observed in acids such as FSO_3H. Frequently, as for example is the case with phenols unsubstituted at C_4, only one of the possible isomers of the protonated phenols is seen by ^1H NMR spectroscopy. However, this does not rule out the intervention of a minor component being the photoreactive species.

The failure of the protonated 2,4,6-trimethyl- and 2,6-dimethylanisole to undergo photoisomerization would seemingly rule out oxygen-protonated systems from consideration. These anisoles are essentially completely oxygen protonated in FSO_3H, and it is unlikely that the presence of a methyl group on the oxygen as compared to an O-protonated phenol would dramatically alter the ability of such systems to photorearrange. Rather, it would appear that C-protonated phenols are involved in these photoreactions.

With protonated 4-methyl-substituted phenols, the initial photoproduct is a protonated bicyclo[3.1.0]hexenone in which the original C_4 substituent ends up at C_6. This type of rearrangement is exactly analogous to the photoisomerizations of protonated cyclohex-2,5-dienones[2] and would suggest that it is the para-protonated phenol which is undergoing the photoisomerization, eq 3.

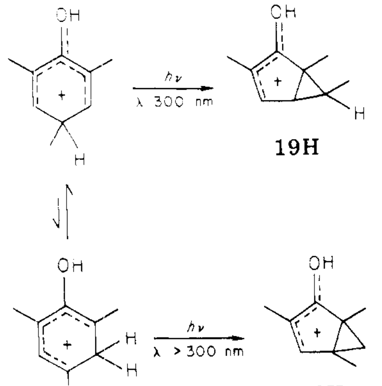


Evidence to support this comes from the wavelength of the light required to achieve the reaction. A para-protonated phenol would be expected to have a maximum in its UV spectrum at ca. 300–330 nm.[12] The protonated phenol **14H**, for example, which is essentially completely protonated in the para position, has a maximum at 334 nm, Table II. Protonated cyclohexa-2,5-dienones exhibit maxima in this same region.[13]

Ortho- and meta-protonated phenols would be expected to have much longer wavelength absorption spectra than their para-protonated isomers. Protonated cyclohex-2,4-dienones typically show absorption maxima in the range 360–400 nm[4a,13] whereas, as will be shown later in this paper, meta-protonated species can reasonably be expected to have maxima at ca. 370 nm. Irradiation of FSO_3H solutions of these phenols with light of wavelength greater than 360 nm did not, with the notable exception of protonated 2,4,6-trimethylphenol, lead to the formation of any products.

Protonated 2,4,6-trimethylphenol represents a unique case among the phenols examined in this work in that two different types of bicyclo[3.1.0]hexenones are formed in the photoisomerization. One of these, **19H**, bearing a methyl group at the C_6 carbon is closely related to the other isomerizations discussed above and likely involves the para-protonated phenol as a starting point. The other product, **13H**, has no methyl substituents at C_6. As **13H**, unlike **19H**, was produced on irradiation of **9H** with light of wavelength greater than 360 nm, it would appear clear that a cation other than the para-protonated phenol is involved in the reaction.

2,4,6-Trimethylphenol is different from the rest of the phenols in that in FSO_3H/SbF_5 media the major product formed is the meta-protonated isomer.[7] There is no evidence for meta protonation in the ^1H NMR spectrum of **9** in FSO_3H solutions; however, the UV spectrum of **9** in this acid shows a band at 373 nm (Table II). This absorption is similar to that of protonated mesitylene[14] (λ_{max} 355 nm) and protonated chloromesitylene (λ_{max} 381 nm). The latter compound is known to protonate in the meta position in FSO_3H.[15] It would thus seem likely that it is the meta-protonated form of **9H**, in equilibrium with the other protonated forms, which undergoes photoisomerization to give **13H**. This type of photorearrangement is directly analogous to that observed with the benzenonium ions.[10]



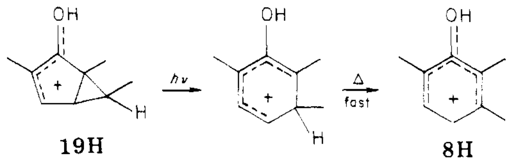
19H

13H

The conversion of the protonated phenols **14H** and **15H** to **20H** and **21H**, respectively, could be considered to take place either by a dienone type photorearrangement of the para-protonated phenols or through a meta-protonated form as suggested above for **9H**. The former route would however seem to be operative with **14H** and **15H**. In the first place, the isomerizations of these phenols take place only with the shorter wavelength light (λ = 300 nm). Second, if the intervention of meta-protonated species were common, then they should also be encountered with protonated phenols such as **7H**. Rather, it would appear that the involvement of meta-protonated phenols in these photoisomerizations is restricted to the 2,4,6-trimethyl system where the three methyl groups are so placed as to exert maximum stabilization of the meta-protonated form.

The thermal isomerization of **16H** to **17H** has its counterpart in the degenerate rearrangements of protonated hexamethylbicyclo[3.1.0]hexenones first described by Hart[16] (cf. ref 10). In the case of the rearrangement of **16H** to **17H**, the driving force is presumably the greater thermodynamic stability of **17H** which results from the positioning of the methyl groups. The activation energy for this cyclopropyl walk reaction (**16H** → **17H**; $\Delta G^{\ddagger} = 19.6$ kcal/mol) is some 2.2 kcal/mol greater than that reported for the analogous rearrangement of the hexamethyl analogue.[10] This difference is comparable to that found for the effect of the C_6 methyl group on the cyclopropyl merry-go-round reactions of the bicyclo[3.1.0]hexenyl cations themselves.[10] As would be expected, the overall stereochemistry at C_6 appears to be retained during the rearrangement of **16H** to **17H**.[10,16,17]

As can be seen from the results in Table II, the protonated bicyclohexenones exhibit absorption maxima in their UV spectra at ca. 330 nm. Thus under the conditions where broad spectrum light is used in the photoisomerizations, the reaction products would also absorb strongly. As it was shown that protonated bicyclohexenones undergo a photoinduced ring opening to give back a protonated phenol, it is not unexpected that only low concentrations of these bicyclic intermediates were detected with the broad spectrum light source. The photoinduced ring opening of the protonated bicyclohexenones is known to occur to give the equivalent of a protonated phenol which undergoes a subsequent thermal rearrangement to the more stable protonated form. Hydride shifts occur more easily than methyl shifts in cations of this type, and thus a protonated 6-methyl-substituted bicyclohexenone would be converted to a protonated phenol with the methyl group in the meta position, eq 4.



19H **8H** (4)

It is clear from the results presented above that the photorearrangement of protonated cyclohexa-2,5-dienones can be extended to encompass a wide range of protonated phenols. Indeed the photoreactions of these protonated phenols can be regarded as a direct extension of the photochemistry of cross-conjugated cyclohexadienones. In

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[12] There has been controversy over the UV spectra of protonated phenols due at least in part to reactions of the phenols with the acid medium. A. J. Kresge, Y. Chiang, and L. E. Hakka, *J. Am. Chem. Soc.*, **93**, 6167 (1971); O. V. Arapov, A. M. Kutrievich, and M. Ya Zarubin, *Zh. Org. Khim.*, 12, 2384 (1976); D. M. Brouwer, E. L. Mackor, and C. MacLean, "Carbonium Ions", Vol. 2, G. A. Olah and P. v. R. Schleyer, Eds., Wiley-Interscience, New York, 1970, p 837.

[13] E. C. Friedrich, *J. Org. Chem.*, **33**, 413 (1968); V. P. Vitullo, *ibid.*, **34**, 224 (1969); A. J. Waring, *J. Chem. Soc., Perkin Trans. 2*, 84 (1973).

[14] G. Dallinga, E. L. Mackor, and A. A. Verrijn Stuart, *Mol. Phys.*, **1**, 123 (1958).

[15] D. M. Brouwer, *Recl. Trav. Chim. Pays-Bas.*, **87**, 335, 342 (1968).

[16] D. W. Swatton and H. Hart, *J. Am. Chem. Soc.*, **89**, 5075 (1967); H. Hart, T. R. Rodgers, and J. Griffiths, *ibid.*, **91**, 754 (1969).

[17] The case of the cyclopropyl migration converting **16H** to **17H** raises the question as to whether the regiochemistry observed by Pavlik in the photoisomerization of protonated cyclohexadienones is governed by the thermodynamic stability of the products or is a function of competing photochemical pathways.[4c]

this regard, it is interesting that the degree of substitution at C_4 does not appear to be important in determining whether a given system will undergo photoisomerization. Examples of cations with a dimethyl grouping, a single methyl group, or even no substituent at C_4 have all been found. Some limitation is found to the generality of these photoisomerizations; for example, protonated phenol itself does not appear to photoisomerize. However, the type of transformation reported here does permit the convenient synthesis of a wide range of methyl-substituted bicyclohexenones.

Experimental Section

General. ^{1}H NMR spectra were obtained on Varian A-60 and EM-390 instruments, both of which were fitted with variable temperature probes. The probe temperature was measured with a methanol sample, and all spectra of protonated phenols were recorded at −50 °C. Chemical shifts of the resonances of cations dissolved in FSO_3H were referenced to internal tetramethylammonium tetrafluoroborate taken as δ 3.10. Cary 14 and Perkin-Elmer 283 instruments were used to obtain the UV and IR spectra, respectively. Analytical gas chromatography was carried out using a Varian 3700 gas chromatograph and a column packed with carbowax 20M (15%) on Chromosorb W (column A). Preparative gas chromatography was performed on a Varian Aerograph A-90-P3 instrument fitted with a OV-101 (1.5%) on Chromosorb W column (column B).

Protonations were carried out by adding cooled FSO_3H to the phenol or ketone in an NMR tube kept at −78 °C. Dissolution of the organic base was achieved by stirring the acid with a thin glass rod.

Photochemical Procedures. Two types of equipment were used. The first involving a Phillips SP 500-W super-pressure mercury lamp has been previously described.[10a] The filters used were window glass with a cut off at 320 nm or a Corning filter No. 3060 with a cut off at 360 nm.

A second type of photochemical apparatus consisted of a partially silvered quartz Dewar which was surrounded by ten lamps. The lamps used were Southern New England Ultraviolet Co. RPR-3000 Å or RPR-3500 Å depending on the wavelength desired. The Dewar was filled with methanol and held at −70 °C with a FTS Systems Flexicool Unit, FS-2084P1. The cooling probe of this refrigeration unit was inserted directly into the center of the quartz Dewar.

For both systems, the samples were contained in 5-mm, clear, thin-walled NMR tubes. The samples were not degassed, and the tubes were sealed with the usual plastic caps. The photoisomerizations were monitored by low-temperature ^{1}H NMR spectroscopy directly on the acid solutions, products being identified in the case of the protonated phenols by comparison of the spectra of authentic samples.[7] The observed isomerizations are summarized in Table III.

1,3,5-Trimethylbicyclo[3.1.0]hex-3-en-2-one (13). 2,4,6-Trimethylphenol (15 mg) in FSO_3H (0.75 mL) was irradiated at −70 °C in an NMR tube using the Phillips lamp and Corning Glass filter No. 3060 for 1 h (reaction followed by ^{1}H NMR). The acid solution was added to a slurry of sodium carbonate (2 g) in ether (25 mL) kept at −78 °C. The mixture was allowed to warm to 0 °C when water (25 mL) was added. Stirring was continued for a further 10 min and the ether layer separated, washed with sodium hydroxide solution (5%) and water, and dried ($MgSO_4$). Removal of the ether gave an oil (13 mg) which was purified by GLC (column B, 120 °C) to give **13** (retention time 2.3 min) as an oil: IR (film) 1690 cm^{-1} (C=O); MS *m/e* 136.0891 (M^+); calcd for $C_9H_{12}O^+$, 136.0888; ^{1}H NMR spectra of **13** and **13H** are given in Table I.

Anal. Calcd for $C_9H_{12}O$: C, 79.36; H, 8.89. Found: C, 79.3; H, 8.77.

1,3,6-Trimethylbicyclo[3.1.0]hex-3-en-2-one (19). 2,4,6-Trimethylphenol (10 mg) in FSO_3H (0.75 mL) was irradiated for 15 h, using RPR-3000 Å lamps. The FSO_3H was quenched as described for **13** and the resulting oil (8 mg) examined by analytical GLC (column A, 100 °C, 10 min, raised to 150 °C at 5 °C/min). Four peaks were observed: **13** (retention time 5.8 min) (21%); **19** (retention time 22 min) (22%); and two partially separated compounds (retention times 9.95 and 10.95 min) (57%). Collection of the latter two by preparative GLC (column B, 120 °C) gave **19** contaminated with some 10–20% of a further isomer of **19** which appeared to be the corresponding C_6 *exo*-methyl isomer: IR (film) 1695 cm^{-1} (C=O); ^{1}H NMR spectra of **19** and **19H** are given in Table I.

Anal. Calcd for $C_9H_{12}O$: C, 79.36; H, 8.89. Found: C, 79.24; H, 8.78.

1,4,6-Trimethylbicyclo[3.1.0]hex-3-en-2-one (17) and 3,5,6-Trimethylbicyclo[3.1.0]hex-3-en-2-one (16). 2,4,5-Trimethylphenol (10 mg) in FSO_3H (0.75 mL) was irradiated, using the RPR-3000 Å lamps, for 18 h. The products were recovered by quenching the acid solution as described above for **13**. GLC analysis (column A, 115 °C) showed four peaks to be present: retention times 4.2 min (2%), 6.0 min (5%), 6.5 min (55%), 8.5 min (38%). These were separated by preparative GLC (column B, 140 °C). The compound corresponding to the third peak was **16**, isolated as an oil: IR film 1692 cm^{-1} (C=O); ^{1}H NMR of **16** and **16H** given in Table I.

Anal. Calcd for $C_9H_{12}O$: C, 79.36; H, 8.89. Found: C, 79.24; H, 8.78.

The compound corresponding to the fourth peak was **17**, also an oil: IR (film) 1690 cm^{-1} (C=O); ^{1}H NMR spectra of **17** and **17H** are given in Table I.

Anal. Calcd for $C_9H_{12}O$: C, 79.36; H, 8.89. Found: C, 79.10; H, 8.91.

The material corresponding to the second peak which was obtained in sufficient amounts only for spectroscopic examination appeared to be **18**: IR (film) 1694 cm^{-1} (C=O); ^{1}H NMR data, Table I.

3,4-Dimethylbicyclo[3.1.0]hex-3-en-2-one (20). 2,3-Xylenol (10 mg) in FSO_3H (0.75 mL) was irradiated, using the RPR-3000 Å lamps, for 18 h. The crude product (8.5 mg) obtained on quenching the acid solution as described for **13** above was purified by preparative GLC (column B, 125 °C) to give **21** (retention time 3.5 min): IR (film) 1695 cm^{-1} (C=O).

Anal. Calcd for $C_8H_{10}O$: C, 78.64; H, 8.26. Found: C, 78.60; H, 8.20.

1,3-Dimethylbicyclo[3.1.0]hex-2-en-2-one (21). 2,6-Xylenol (10 mg) in FSO_3H (0.75 mL) was treated in exactly the same manner as in the previous experiment. The oil obtained (8 mg) was purified by GLC (column B, 120 °C) to give **21** (retention time 1.8 min): IR (film) 1690 cm^{-1} (C=O).

Anal. Calcd for $C_8H_{10}O$; C, 78.64; H, 8.26. Found: C, 78.82; H, 8.41.

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Registry No. 1H, 53857-65-1; **2H**, 33516-50-6; **3H**, 53857-61-7; **4H**, 53280-71-0; **5H**, 53857-68-4; **6H**, 71929-04-9; **7**, 496-78-6; **7H**, 53857-64-0; **8H**, 71929-03-8; **9**, 527-60-6; **9H**, 53857-72-0; **10H**, 53857-73-1; **11H**, 51205-30-2; **12**, 526-75-0; **13**, 53943-69-4; **13H**, 71929-02-7; **14H**, 71929-01-6; **15H**, 53280-69-6; **16**, 71962-43-1; **16H**, 71963-17-2; **17**, 71913-05-8; **17H**, 71929-09-4; 18, 71913-04-7; **18H**, 71929-08-3; **19**, 71962-42-0; **19**, C_6 *exo*-methyl isomer, 71913-03-6; **19H**, 71929-07-2; **20**, 71913-02-5; **20H**, 71929-06-1; **21**, 71913-01-4; **21H**, 71929-05-0.