Photochemical Transformations of Protonated Phenols. A One-Step Synthesis of Umbellulone from Thymol

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UV irradiation of thymol (**7**) at 254 or 300 nm in trifluoromethanesulfonic acid affords ten products, eight of which have been isolated and characterized. Four competitive processes are suggested to be operating in the formation of the photoproducts: (i) regioselective type A rearrangement leading to umbellulone (**8**, about 10%), (ii) formal C2 → C3 migration by type A rearrangement and ring opening which affords the principal product, 3-isopropyl-5-methylphenol (**12**, 17%), (iii) intermolecular transalkylation leading to diisopropylphenols **13–15** (17%), and (iv) formation of piperitenone (**10**, 5%) initiated by hydrogen abstraction. A mechanism for the formation of **10** is proposed. Both para- and ortho-protonated **7** are suggested to be involved in product formation.

The intramolecular photorearrangements of cyclohexa-2,5-dienones (**1**) leading to bicyclo[3.1.0]hex-3-en-2-ones (**3**) represent one of the most intensively studied photochemical reactions (Scheme I, the type A photorearrangement). It is now generally accepted that these transformations[1,2] take place *via* 3,5-bonding in the excited state to form, depending on reaction conditions, either a zwitterionic or a radical-like intermediate **2** which can undergo a rearrangement to give the lumiketone **3**. Several reviews[3-5] and recent studies[6-8] on this subject have appeared. However, almost all of the cyclohexa-2,5-dienones which have been investigated so far possess two substituents in the 4-position. A similar rearrangement is known to occur with conjugated 2,4-dienones.[9]

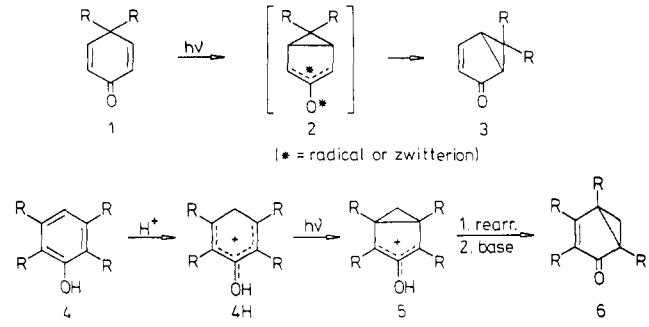
Recently, protonated cyclohexa-2,5-dienones[10] as well as C-protonated phenols[11-13] have been found to undergo photorearrangements very similar to those described for the cyclohexadienones in neutral media. Moreover, by using fluorosulfonic or trifluoromethanesulfonic (triflic) acid as a protonating medium for phenols, it was possible to extend the range of cyclohexa-2,5-dienone photoisomerization even to systems lacking substituents at C4 (Scheme I, **4** → **6**). The preparative utility of this route to bicyclo[3.1.0]hexenones was demonstrated[13] by accomplishing the synthesis of 1,3,4,5-tetramethylbicyclo-[3.1.0]hexenone (**6**, R = CH_3) and of the parent compound (**6**, R = H). No byproducts were reported in these reactions.

We report the results on the photochemical behavior of protonated 2-isopropyl-5-methylphenol (**7**, thymol). The investigation was stimulated by the prospect of effecting a simple synthesis of the terpenoid ketone 4-methyl-1-isopropylbicyclo[3.1.0]hex-3-en-2-one (**8**, umbellulone) from the readily available precursor. Umbellulone (**8**) is the main constituent of *Umbellularia californica* Nutt.[14] and to our knowledge three independent syntheses of this ketone have been reported,[15-17] each of them employing rather complicated multistep procedures.

Results and Discussion

The UV spectrum of thymol (**7**) in triflic acid shows three distinct absorption maxima at 262, 310, and 352 nm, respectively. Irradiation of the protonated thymol in a Rayonet reactor at 350 nm did not result in any detectable photoreaction. However, relatively complicated mixtures of products were produced when wavelengths of 254 or 300 nm were used and the ratio of products was found to be independent of the two wavelengths. These results contrast to earlier reports,[12,18] in which similar systems afforded varying ratios of products on photoexcitation with light at different wavelengths.

Scheme I



Analysis of the photolysate by GLC after 41 h of irradiation showed, apart from starting material (37%), three major and seven minor products. The surprisingly difficult separation of umbellulone (**8**) from thymol (**7**)[19] was ac-

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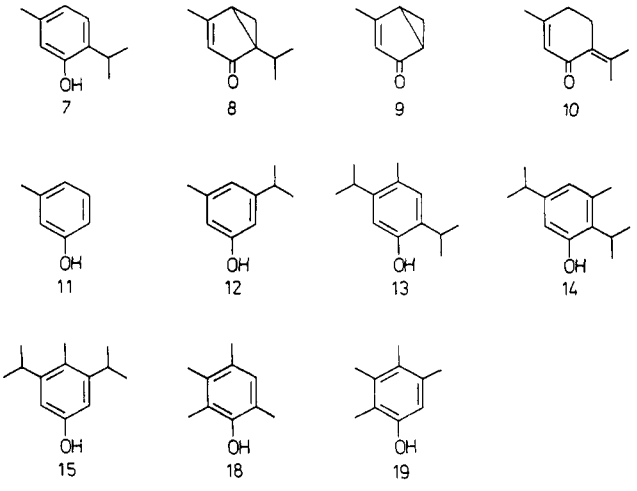
Table I. ^1H and ^{13}C NMR Data (ppm) of the Compounds 8, 9, and 10. Multiplicities are Given within Parentheses and Coupling Constants in Hz

	^1H NMR[a]			^{13}C NMR		
	8	9[b]	10	8	9	10[c]
1				208.1 (s)	206.9 (s)	191.7
2	5.32 (pent), J = 1.4, 1.4	5.32 (sept), J = 1.5	5.89 (q), J = 1.4	124.1 (d)	123.2 (d)	129.0
3				177.7 (s)	178.1 (s)	159.6
4	2.08 (ddd),[d] J = 1.4, 3.3, 6.9	2.16 (d pent),[d] J = 1.3, 3.5, 4.7, 8.4	2.29 (br t), J = 0.9, 6.2	29.1 (d)	25.6 (d)[e]	31.9
5	(a) 1.37 (dd), J = 3.6, 6.9 (b) 1.23 (t), J = 3.4, 3.4	(a) 1.44 (ddd), J = 3.6, 8.4, 6.8 (b) 1.26 (dt), J = 3.6, 3.5, 3.5	2.67 (br t), J = 1.3, 6.2	38.1 (t)	34.1 (t)	28.0
6		2.32 (br pent), J = 3.5, 4.7, 6.8		40.7 (s)	25.7 (d)[e]	128.8
7	2.12 (d), J = 1.4	2.15 (d), J = 1.5	1.94 (dt), J = 0.9, 1.4	18.7 (q)	18.8 (q)	23.8
8	2.15 (hept),[d] J = 6.9, 6.9			26.4 (d)		142.5
9	0.97 (d), J = 6.9		2.10 (t), J = 1.3	20.2 (q)		22.5
10	1.04 (d), J = 6.9		1.86 (s)	19.4 (q)		22.9

[a] The coupling constants have been determined with the help of resolution enhancement and homodecoupling. [b] Connectivity was determined from a homonuclear correlated 2-D NMR experiment. [c] For assignment see: Bohlmann, F.; Zeisberg, R.; Klein, E. *Org. Magn. Reson.* **1975**, *7*, 426. [d] Partly hidden. [e] Exchangeable.

complished by using column chromatography on basic aluminum oxide deactivated with 1% tartaric acid by which a crude separation of ketones from phenols was obtained. Silica gel columns were used for further separations. Of the ten products formed eight have been isolated in pure form and assigned the structures **8–15**. Three



of these, **8** (9.5%), **10** (5%), and **12** (17.3%), are isomeric with the starting material and arise by different types of rearrangements. Compounds **9** (2%) and **11** (6%) lack the isopropyl group due to dealkylation while compounds **13** (3%), **14** (4%), and **15** (10%) can be derived from isopropylated starting material. The structures of the products follow from their MS and ^1H and ^{13}C NMR spectra. The spectroscopic data of the ketones **8–10** are given in Table I (*cf.* ref 20–23). The shift reagent $Eu(fod)_3$ was used to distinguish between the isomeric phenols **13–15**. The lanthanide-induced shifts (LIS) together with measurements of the nuclear Overhauser effect (NOE) proved to be valuable tools for determining the substitution pattern in the diisopropylmethylphenols (see the Experimental Section). The extensive long-range ^1H–^1H couplings observed in the NMR spectra of **13** and **14** are noteworthy. The coupling constants of **14** are reported in the Experimental Section, whereas those of **13** were unresolved.

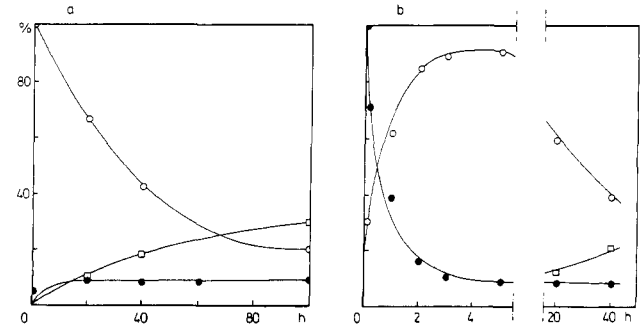


Figure 1. Irradiation of **7** (a) and **8** (b) in triflic acid at 300 nm: thymol (**7**, ○), umbellulone (**8**, ●) and 3-methyl-5-isopropylphenol (**12**, □).

The protonated thymol (**7**) was studied by NMR. The spectrum was found to be fully consistent with a species protonated in the *para* position, thus giving a protonated cyclohexa-2,5-dienone (see the Experimental Section). In a control experiment thymol (**7**) was found to be essentially stable with respect to acid-catalyzed dealkylation when stored at room temperature in the dark in triflic acid. However, after 96 h at 40 °C in the dark 10% of *m*-cresol was formed but no isopropylated phenols. In a third control experiment, three parallel tests were performed for 2 h at <5 °C (see the Experimental Section). Thymol in triflic acid gave no *m*-cresol by a thermal reaction and addition of propene under similar conditions gave no isopropylated products. Finally, an irradiated sample only gave a trace of *m*-cresol, while isopropylated phenols were present in substantial amounts (*vide infra*).

Formation of umbellulone (**8**) *via* the type A photorearrangement of cross-conjugated dienones was anticipated (*vide supra*). The isomer 3-isopropyl-5-methylbicyclo-[3.1.0]hex-3-en-2-one was not detected in any run. Thus the type A rearrangement only occurred in one direction locating the C3 methyl group in the β-position of the α,β-unsaturated ketone rather than on the cyclopropane ring (path *a*, Scheme II). Related regiospecificity has been reported previously for the photorearrangment of 3-methyl-substituted 2,5-hexadienones in neutral media.[24,25]

The experiment, in which the principal products were measured as a function of time (Figure 1, part a), showed that the percentage of umbellulone (**8**) rapidly leveled off to a nearly constant value of approximately 10% of the reaction mixture, while 3-isopropyl-5-methylphenol (**12**)

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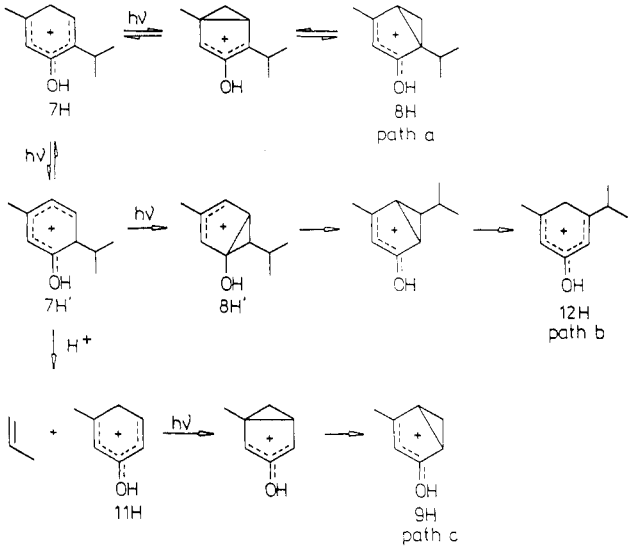
Scheme II



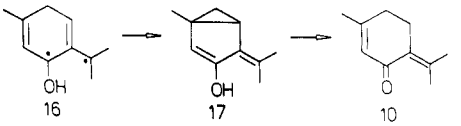
was found to increase with reaction time. At low conversion runs (<10%) GLC analysis of the photolysate showed that compounds **8** (5%), **11** (2%), and **12** (1%) were the only detectable products.

Dissolved in triflic acid umbellulone (**8**) was exposed to irradiation in a separate experiment. As a result a photostationary mixture consisting of **8H** and **7H** in the ratio 1:9 was rapidly formed. GLC analysis, taken during the first 5 h, showed no additonal products. Different mechanisms for the photochemical conversion of bicyclo[3.1.0]hexenones to phenols have been proposed by Wheeler[26] and Chapman,[27] but both found that thymol was the only product formed when umbellulone was irradiated in neutral media at room temperature. However, in our experiment prolonged irradiation gave a reaction mixture of the same composition as when starting with thymol.

Surprisingly, the thymol isomer **12** was found to be the principal product in all high conversion runs. The *para*-protonated species **7H** maintains a photoequilibrium with umbellulone (**8**, Scheme II, path *a*) but further transformations to **12** are difficult to explain along this route. However, the formation of **12** is easily explained by a well-known type of rearrangement which occurs with cyclohexa-2,4-dienones.[9,28] Further, this type of rearrangement has been shown to take place in a variety of solvents including concentrated sulfuric acid.[10] Although the NMR spectrum of thymol (**7**) in triflic acid only showed evidence for *para* protonation in the ground state the insensitivity of NMR as an analytical tool does not exclude the presence of a small amount of the *ortho*-protonated species. On the other hand, a photo-induced equilibrium between **7H** and **7H'** is also possible. A similar equilibrium has been postulated to take place even in *n*-hexane to explain the photochemical behavior of 2,6-di-*tert*-butylphenols.[29] Thus, we have chosen to depict the formation of **12** as in Scheme II, path *b*.

A thermal reaction undoubtedly gives rise to the formation of *m*-cresol when the irradiation is performed in a Rayonet reactor, but the loss of the isopropyl group is not accompanied by thermal alkylation of thymol. Thus, the observed transalkylation is clearly photochemically induced. The nature of this process is not understood (*vide supra*). Under conditions of prolonged irradiation a set of equilibria can occur and the exact sequence of events are difficult to elucidate. However, the formation of the alkylated and rearranged products may tentatively be explained as follows. Compound **14** can arise by *ortho* alkylation of product **12**. Type A rearrangement of *para*-protonated **14** followed by ring cleavage would give **13**. *Ortho* protonation of **13** would give **15** after rearrangement and ring cleavage. The lumiketone 4-methylbicyclo[3.1.0]hex-2-en-3-one (**9**) is formed by a type A rearrangement of *para*-protonated *m*-cresol (**11**), path *c*. The last suggestion was substantiated by separate irradiation of **11**, which afforded **9** among other products.

Scheme III



Piperitenone (**10**) differs from the other products since its formation is not directly related to traditional dienone chemistry. A probable mechanism for its formation is shown in Scheme III. We propose that hydrogen abstraction by the carbonyl oxygen of the excited dienone derived from **7** affords the biradical **16** *via* a five-membered transition state. Piperitenone (**10**) is then formed by rearrangement to **17**, ring opening, and proton relocation.

The relatively complex mixture of products resulting from the photolysis of thymol (**7**) induced us to repeat the irradiation of durenol in triflic acid reported by Childs *et al.*[13] After closely following their conditions we were able to detect as many as six products by GLC analysis. Three products were isolated in a pure form and assigned the structures **6** (R = CH_3, 31%), **18** (16%), and **19** (7%). The unidentified products, two ketones (M_r 150, MS) and one phenol (M_r 136, MS), were produced in the yields 12, 2, and 2%, respectively. Thus, prolonged irradiation of either thymol or durenol gave similar and complex reaction mixtures. From a preparative point of view it is therefore advisable to carefully monitor the reactions in order to avoid excessive formation of secondary photoproducts, which will complicate the inevitable separation procedure.

Experimental Section

General Methods. Column chromatography separations were made on two types of columns: column A, dry packed with Merck 60 basic aluminum oxide, 0.063–0.200 mm, deactivated with 1% (wt) tartaric acid in ethanol and then dried; column B, dry packed with Merck 60 silica gel, 0.040–0.063 mm. The solvent, light petroleum bp 40–60 °C with increased amounts of ethyl acetate (0, 1.25, 2.5, 5, 10, 20, 40, and 80%), was delivered by a metering pump at a rate of 30 mL/min for 12.5 mm i.d. columns and 60 mL/min for 25 mm i.d. columns. Small amounts of acetonitrile (1% of the polar component) were added in some runs to minimize tailing. Irradiations were performed in a Rayonet reactor employing 16 lamps with emission maxima 254, 300, and 350 nm, respectively. The samples were contained in quartz tubes, which were sealed with plastic caps. In order to isolate sufficient quantities of the compounds for spectral data, material from several runs was combined and purified by column chromatography. Analytical GLC was performed on a Pye Unicam 204 instrument with an FID detector connected to a computing integrator. A 25-m Carbowax 20M capillary column was used. Melting points were determined on a hot-stage microscope and are uncorrected. Electronic absorption spectra were measured on a Varian Cary 19 spectrophotometer. A Finnigan Model 4021 spectrometer connected to an INCOS data system was used to record GC–MS spectra. Unless otherwise stated the ^1H (200 MHz) and ^{13}C (50.3 MHz) NMR spectra were recorded in deuteriochloroform with tetramethylsilane as an internal standard by using

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Bruker WP200 and Varian XL200 spectrometers. The samples for the NOE measurements were treated several times by the freeze-pump-thaw cycle before vacuum sealing the tubes. The NOE difference technique was used as described by Hall *et al.*[30] and the spectra were recorded with the decoupler turned off during pulse and aquisition preceded by 10 s of irradiation either in or out of resonance. The LIS experiments were carried out by adding a solution of $Eu(fod)_3$ in deuteriochloroform in small portions to the sample. Homo decoupling, resolution enhancement, and increased spectral resolution were used to determine the coupling constants.

Irradiation of 2-Isopropyl-5-methylphenol (7, Thymol). Thymol (500 mg), dissolved at 0 °C under nitrogen in triflic acid (17 mL, Fluka), was irradiated at 300 nm for 40 h at room temperature. The acid solution was then added to a slurry of a saturated solution of sodium hydrogen carbonate and dichloromethane kept at 0 °C. The aqueous layer was extracted with dichloromethane (3 × 50 mL) and the combined extracts were dried with anhydrous magnesium sulfate, filtered, and concentrated *in vacuo* to yield the crude photolysate (490 mg). The mixture was chromatographed on modified aluminum oxide (column A) and the eluent was divided into two portions: (1) 0.088 g, consisting mostly of ketones; (2) 0.400 g, consisting mostly of phenols. Rechromatography of portion 1 on silica gel (column B) afforded two compounds. One was identified as 1-isopropyl-4-methylbicyclo[3.1.0]hex-3-en-2-one (**8**, umbellulone): 43 mg (8.5%); MS, *m/e* 150 (M^+). The other was identical with 3-methyl-6-isopropylidenecyclohex-2-en-1-one (**10**): 26 mg (5%); MS, *m/e* 150 (M^+). The ^1H and ^{13}C NMR data of **8** and **10** are reported in Table I. Rechromatography of portion 2 on silica gel (column B) afforded the compounds **7**, **9**, **11**, **12**, **13**, **14**, and **15**. They are listed below in order of elution.

2,5-Diisopropyl-4-methylphenol (13): 15 mg (3%); mp 51–52 °C (lit.[31] mp 52.7 °C); MS, *m/e* 192 (M^+); ^1H NMR δ 1.19 (d, 6 H, J = 6.9 Hz), 1.24 (d, 6 H, J = 6.9 Hz), 2.25 (s, 3 H), 3.13 and 3.05 (overlapping septets, 2 H, J = 6.9 Hz), 4.52 (s, 1 H), 6.64 (s, 1 H) and 6.93 (s, 1 H). The NOE observed was 9.3% for H_6 {OH} and 12.7% for H_3 {Me_4}. The LIS's were large on i-Pr_2 and H_6. Thus NOE and LIS established the substitution pattern.

2-Isopropyl-5-methylphenol (7): 180 mg (36%, starting material).

3-Methyl-5-isopropylphenol (12): 85 mg (17%); mp 40–42 °C. A sample which was recrystallized five times from pentane melted at 49–50 °C (reported[26] mp 49.5–50 °C); MS, *m/e* 150 (M^+); ^1H NMR δ 1.22 (d, 6 H, J = 6.9 Hz), 2.29 (s, 3 H), 2.82 (hept, 1 H, J = 6.9 Hz), 4.53 (s, 1 H), 6.48 (br s, 1 H), 6.52 (br s, 1 H) and 6.63 (br s, 1 H).

***m*-Cresol (11)**: 30 mg (6%). All physical constants as well as the gas chromatographic retention time of the *m*-cresol isolated from the reaction mixture were identical in every respect with those of an authentic sample.

2,5-Diisopropyl-3-methylphenol (14): 20 mg (4%); mp 59–60 °C; MS, *m/e* 192 (M^+); ^1H NMR δ 1.20 (d, 6 H, J = 6.9 Hz), 1.35 (d, 6 H, J = 7.1 Hz), 2.30 (br s, 3 H, J = 0.6, 0.6 Hz), 2.76 (hept, 1 H, J = 0.5, 0.6, 6.9 Hz), 3.26 (hept, 1 H, J = 7.1 Hz), 4.52 (s, 1 H), 6.42 (dq, 1 H, J = 0.5, 0.6, 1.85 Hz) and 6.59 (dt, 1 H, J = 0.6, 0.6, 1.85 Hz). The NOE observed was 17.4% for H_6 {OH}, 14.3% for H_4 {Me_3}, and 5.7% for H_4 and H_6 {CH of i-Pr_5}. Together with LIS studies the NOE established the substitution pattern.

3,5-Diisopropyl-4-methylphenol (15): 50 mg (10%); mp 90–91 °C (lit.[31] mp 92.7 °C); MS, *m/e* 192 (M^+); ^1H NMR δ 1.20 (d, 12 H, J = 6.8 Hz), 2.21 (s, 3 H), 3.18 (hept, 2 H, J = 6.8 Hz), 4.44 (s, 1 H) and 6.60 (s, 2 H). The structure of **15** was easily assigned due to symmetry reasons. The NOE's observed for H_2 and H_6 were 4.4% each {OH}. The LIS studies gave $\Delta\delta$ 0.63 of the aromatic protons at L/S = 0.6.

4-Methylbicyclo[3.1.0]hex-3-en-2-one (9): 10 mg (2%); MS, *m/e* 108 (M^+). The ^1H and ^{13}C NMR data are listed in Table I. Two minor products were also found, which were shown to be cresols by GC–MS analysis. One of the compounds (M_r 150) was substituted with one, while the other (M_r 192) was substituted with two isopropyl groups. No further characterization of these products was made.

^1H NMR of Protonated Thymol (7). Thymol was dissolved in triflic acid in an NMR tube. Tetramethylammonium chloride was added as an internal standard (3.1 ppm)[11] and deuterated acetone was used as external lock. ^1H NMR δ 1.22 (d, 6 H), 2.50 (s, 3 H), 3.07 (partly hidden hept, 1 H), 4.03 (d, 2 H), 7.06 (s, 1 H) and 8.06 (t, 1 H). No changes were observed upon cooling to −40 °C. Thus, the shift data can only be explained by a *para*-protonated species.

Thymol in Triflic Acid. Control Experiments. Thymol was stored at room temperature in the dark in triflic acid. After seven days 97% of the unchanged thymol (**7**) could be recovered from the reaction mixture and only a minimal amount of *m*-cresol (<1%) was detected by GLC analysis. When a sample, wrapped in black paper, was kept inside the Rayonet reactor with lit lamps for 96 h about 10% of *m*-cresol was formed. After workup this sample was investigated by GC–MS. Surprisingly, no isopropylated phenols (*m/e* 192) could be found. A third control experiment was then run. A sample containing 30 mg of thymol in 3 mL of triflic acid was divided in three equal parts. The first part was stored in the dark at 0 °C. Propene was added to the second part by bubbling gas through the solution for 2 min. The uptake was 95 mg and the sample was stored at 0 °C. The third part was irradiated for 2 h in a quartz tube taped together with a long-stemmed thermometer to the side of an immersion well equipped with a 450-W Hanovia mercury lamp. During irradiation the immersion well was placed in a large dewar flask filled with ice water and the thermometer reading did not exceed 5 °C. All three samples were worked up after 2 h and analyzed by GC–MS. A search for the mass fragments *m/e* 108 (*m*-cresol) and *m/e* 192 (isopropylated products) was performed. The dark samples showed no trace of *m*-cresol (detection level <0.02%). Moreover, no isopropylated products could be detected in the sample with added propene. In the irradiated sample which was carried to 35% conversion of starting material only a trace of *m*-cresol was present but substantial amounts of the isopropylated phenols (>5% of the total reaction mixture, *i.e.*, 14% of the formed products) could be detected.

Irradiation of Umbellulone (8). A solution of the ketone **8** (50 mg) was irradiated in the same manner as thymol (**7**) for a period of 40 h. Samples for GLC analysis were removed after 0.2, 1.0, 2.0, 3.0, 5.0, and 20 h (see Figure 1, part b). The gas chromatographic retention times of the formed products corresponded to those of the products formed in the irradiation of thymol. After 40 h of irradiation the mixture was shown to contain **8** (10%), **7** (39%), **9** (2%), **10** (5%), **11** (6%), **12** (21%), **13** (2%), **14** (3%), and **15** (12%).

Photolysis of *m*-Cresol. A solution of **11** (200 mg) was irradiated with the same conditions as described above. After 20 h of irradiation the reaction mixture was worked up and examined by GLC. One of the products had a retention time identical with 4-methylbicyclo[3.1.0]hex-3-en-2-one (**9**) and was isolated by column chromatography on column A. The other products were not investigated.

Irradiation of 2,3,5,6-Tetramethylphenol (Durenol). Starting from 150 mg of durenol, the procedure as described in ref 12 was exactly followed. Six products were detected by GLC analysis. Column chromatography of the crude mixture on column A afforded **6** and a mixture of two ketones (M_r 150) in the ratio 1:6.

1,3,4,5-Tetramethylbicyclo[3.1.0]hex-3-en-2-one (6, R = CH_3): 46 mg (31%); MS, *m/e* 150 (M^+); ^1H NMR δ 0.92 (d, 1 H, J = 3.0 Hz), 1.32 (s, 3 H), 1.33 (obscured, 1 H, J = 3.0 Hz), 1.35 (s, 3 H), 1.56 (q, 3 H, J = 1.0 Hz) and 1.99 (q, 3 H, J = 1.0 Hz). The later fractions from column A was rechromatographed on column B to give **18**, **19**, and the starting material (42 mg, 28%).

2,3,4,6-Tetramethylphenol (18): 24 mg (16%); MS, *m/e* 150 (M^+); ^1H NMR δ 2.15 (s, 3 H), 2.20 (br s, 9 H), 4.46 (s, 1 H) and 6.78 (s, 1 H).

2,3,4,5-Tetramethylphenol (19): 10 mg (7%); MS, *m/e* 150 (M^+); ^1H NMR δ 2.13 (s, 3 H), 2.17 (s, 3 H), 2.19 (s, 3 H), 2.22 (s, 3 H), 4.55 (s, 1 H) and 6.49 (s, 1 H). The two isomers **18** and **19** were distinguished by LIS studies. By adding $Eu(fod)_3$ to the two compounds the aromatic proton showed a much larger shift ($\Delta\delta$ 0.67) in **19** than in **18** ($\Delta\delta$ 0.10) at L/S = 0.6. Minor amounts

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(2%) of an additional phenol (M_r 136) were detected but could not be isolated in a pure form.

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Registry No. 7, 89-83-8; **7H**, 97878-19-8; 8, 24545-81-1; 10, 491-09-8; 11, 108-39-4; 12, 3228-03-3; 13, 15269-16-6; 14, 76138-70-0; 15, 15269-17-7; 18, 3238-38-8; 19, 488-70-0; H_2, 1333-74-0; durenol, 527-35-5.

Regioselectivity in α-Cleavage Reactions: Arylalkylcyclopropenethiones

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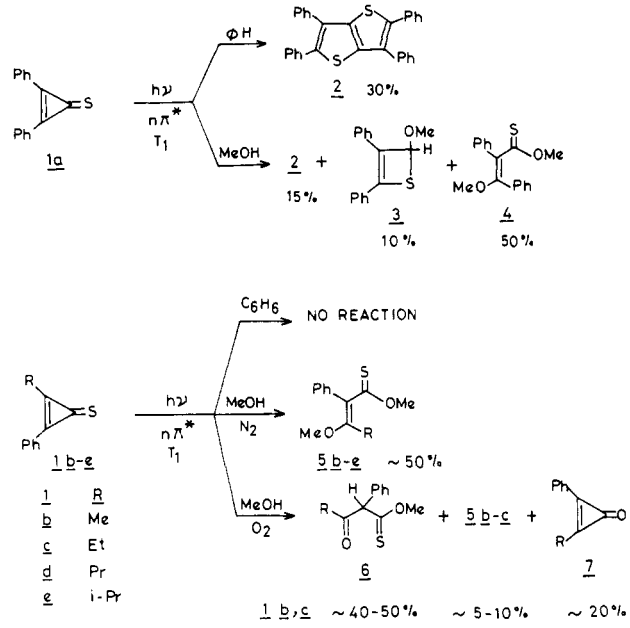
Photoreactions of several arylalkylcyclopropenethiones (**1b–e**) have been investigated. The products formed have been rationalized on the basis of α-cleavage as the primary photoprocess. The photochemical α-cleavage is presumed to originate from the lowest excited nπ* triplet state. A regioselective α-cleavage reaction has been observed and this unusual regioselectivity is explained on the basis of close approach of the ground-state energy surface of the diradical/carbene, the primary intermediates, to the excited triplet-state surface of cyclopropenethiones. Reactions originating from both triplet and singlet thioketene carbene have been observed upon photolysis of arylalkylcyclopropenethiones.

The Norrish type I α-cleavage reaction has recently been established as one of the primary photoreactions of strained thiocarbonyls.[1] Cyclobutanethiones[2] and diphenylcyclopropenethiones[3] have been shown to undergo α-cleavage from the lowest triplet state. A natural extension of the above investigation is the study of selectivity in the α-cleavage processes. Selectivity in α-cleavage reactions of ketones has been extensively investigated.[4] Introduction of different substituents on the α and α′ carbons of ketones results in a preferential α-cleavage that gives the more stable of the two diradicals. In this context thiones with different α,α′ substituents were chosen for investigation and alkyl- and phenyl-substituted cyclopropenethiones **1** appeared to be suitable substrates. Earlier we had shown[3] that diphenylcyclopropenethione in benzene affords 2,3,5,6-tetraphenylthieno[3,2-*b*]-thiophene upon excitation (Scheme I, of top). However, in methanol two additional products namely 2-methoxy-3,4-diphenylthiete (10%) and methyl 3-methoxy 2-phenylthiocinnamate (50%) were isolated. These products have been rationalized on the basis of the Norrish type I α-cleavage process, and 1,3-diradical and thioketene carbene have been postulated to be the primary intermediates. Results on the photobehavior of methyl-, ethyl-, propyl-, and isopropylphenylcyclopropenethiones **1b–e** presented below show some similarity with those of diphenylcyclopropenethione. The most interesting aspect of the present study is related to the observed unusual selectivity in the α-cleavage.

Scheme I. Photoproducts upon Irradiation of Diphenylcyclopropenethione and Arylalkylcyclopropenethiones



Results

Cyclopropenethiones **1a–e** chosen for investigation were prepared by standard procedures[5] and were characterized by their spectral properties. The data summarized in Table I are consistent with the literature reports. Of these, electronic absorption spectra are relevant to understanding their excited behavior. The electronic absorption spectrum

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