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Influence of the Localization of the Excitation Energy on the Photochemistry of α,β-Epoxy Ketones

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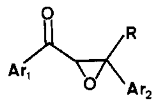
Depending on the localization of the energy, photolysis of α-epoxy ketones excited in their triplet state leads to β-diketones, α-diketones, or fragmentation products. Absorption spectra of ylide intermediates and phosphorescence spectra of α-epoxy ketones are reported.

Since the discovery of β-diketone formation by photolysis of an α-epoxy ketone,[1] a large amount of work has been published on the various aspects of the photochemical reactivity of this family of compounds.[2] While β-diketone formation is the predominant process, α-diketones[3] and epimerized epoxy ketones[4,5] as well as fragmentation[6] and cycloaddition products[7,8] can also be isolated from the reaction mixture. However, the factors directing the course of the photolysis remain unclear although it appears that epimerization and ylide formation occur preferentially from the triplet excited state of α-epoxy ketones.[5,8,9] Our purpose in this work was first to study the photochemical behavior of α-epoxy ketones 1-5 bearing a benzoyl group and preferentially excited in the triplet state and second to determine the effect of the localization of the excitation energy in the starting molecule on the course of the rearrangement and of the fragmentation reactions.

Results

The α-epoxy ketones 1-5 absorb UV light in a manner similar to that of the aromatic ketones bearing the identical chromophores in the absence of the oxirane ring.



	R	Ar_1	Ar_2
1	H	C_6H_5	α-Naphthyl
2	H	C_6H_5	β-Naphthyl
3	H	β-Naphthyl	β-Naphthyl
4	H	β-Naphthyl	C_6H_5
5	H	p-$CH_3OC_6H_4$	C_6H_5
6	CH_3	C_6H_5	C_6H_5

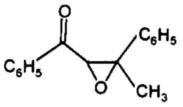


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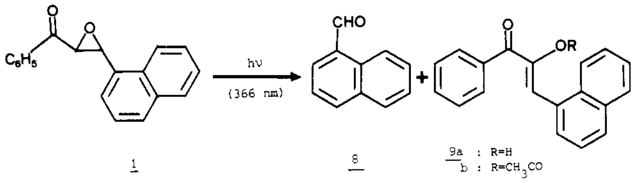
Table I. Phosphorescence Properties of α-Epoxy Ketones

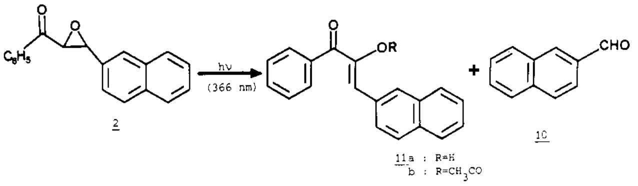
epoxy ketone	emitting excited states	λ_{0-0} emission, nm	E_T, kJ/mol (kcal/mol)
1	$^3(\pi,\pi^*)$	480	249 (59.6)
2	$^3(\pi,\pi^*)$	470	254 (60.8)
3	$^3(\pi,\pi^*)$	487.5	245 (58.6)
4	$^3(\pi,\pi^*)$	487.5	245 (58.6)
5	$^3(n,\pi^*)$	*a*	*a*
6	$^3(n,\pi^*)$	393	304 (72.7)
7	$^3(n,\pi^*)$	391.5	306 (73)

[a] Not determined (cf. text).

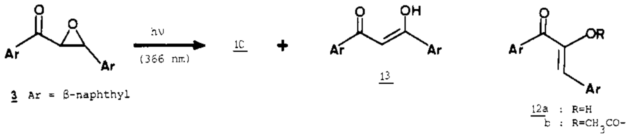
Scheme I



Scheme II



Scheme III



Phosphorescence spectra of these compounds in 2-methyltetrahydrofuran were recorded at 77 K after selective excitation of the benzoyl chromophore at 360 nm and were compared with those of *cis*- and *trans*-dypnone oxides 6 and 7 recorded under the sames conditions Figures 1 and 2 and Table I). Phosphorescence typical of the $^3(n,\pi^*)$ excited state of carbonyl compounds was observed for 5-7 while the emission from 1-3 is characteristic of that exhibited by the $^3(\pi,\pi^*)$ excited state of naphthalene. Furthermore, since the phosphorescence spectra of epoxy ketones 5-7 are very similar except that the 0-0 band was not observed in the case of 5, the triplet energies are very close for the three compounds.

The only photoproducts isolated and characterized upon irradiation of 1 in benzene at 366 nm were α-naphthaldehyde (8, 16%) and the α-diketone 9a (17%, Scheme I). We found it convenient to treat the crude photolysis mixture with acetic anhydride prior to workup and isolate the acetate 9b rather than the enol 9a.

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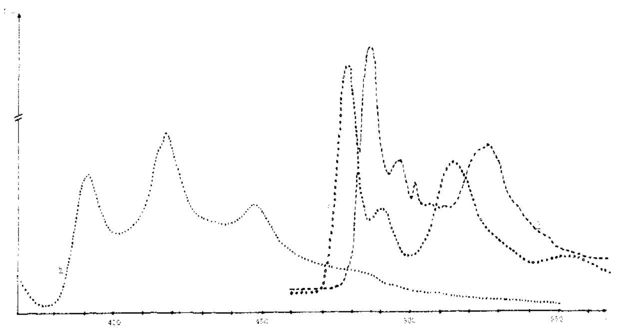


Figure 1. Phosphorescence spectra of epoxy ketones 1, 3, and 6 (λ_{ex} = 360 nm; 77 K).

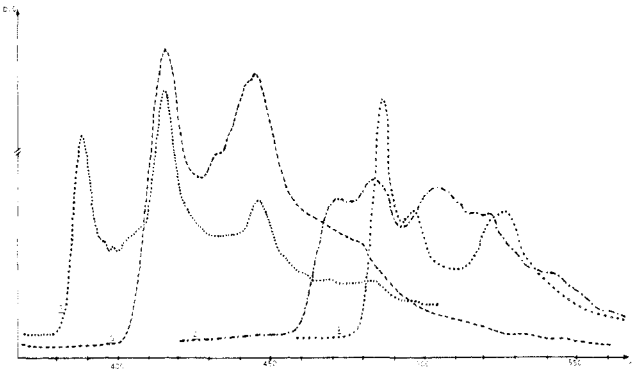
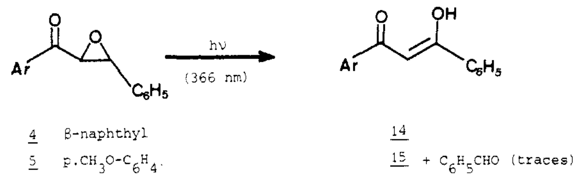


Figure 2. Phosphorescence spectra of epoxyketones 2, 4, 5, and 7 (λ_{ex} = 360 nm; 77 K).

Scheme IV



Interestingly, a very strong solvent effect on the composition of the reaction mixture was observed. For example, the chemical yield of naphthaldehyde increases considerably in more polar solvents such as acetonitrile (Table II). For verification that a triplet excited state was indeed involved in the reaction, sensitization and quenching experiments were conducted. It was found that benzophenone (E_T = 284 kJ/mol) was able to sensitize the reaction in acetonitrile to give a reaction mixture essentially identical in character with that obtained upon direct irradiation. In contrast, only a slow polymerization of the starting material was detected when 1 was photolyzed in the presence of *trans*-piperylene (E_T = 248 kJ/mol, Table II).

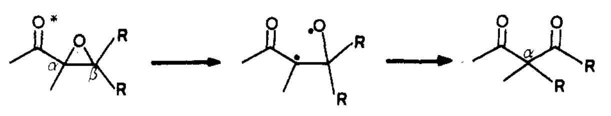
Similarly, β-naphthaldehyde 10 and α-diketone 11a were the major products of the photolysis of 2 in benzene (Scheme II), and here also a strong effect of solvent polarity on aldehyde formation was observed (Table II).

Although the fragmentation product 10 remains the major compound obtained upon photolysis of 3, it is noteworthy that instead of α-diketone 12a, β-diketone 13 was detected in the reaction mixture (Scheme III).

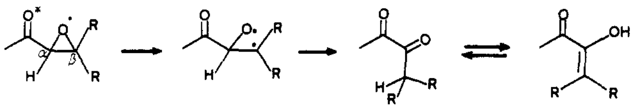
Contrasting photochemical behavior is observed with epoxy ketones 4 and 5 relative to that described above (Scheme IV). At most, only traces of fragmentation products are detected and β-diketones 14 and 15 are the major products.

Sensitization and quenching experiments (Table II) confirm that triplet states are implicated in the photoconversion of 4 and 5 to β-diketones.

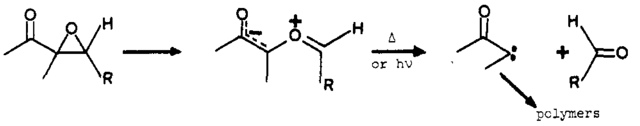
Scheme V



Scheme VI



Scheme VII



The significant increase in the chemical yields of aldehydes observed in polar solvents may reflect the enhanced participation of polar intermediates such as carbonyl ylides.[10] Since such ylides can be stabilized at very low temperature, we have examined the irradiation of ketones 1–7 and *trans*-chalcone oxide at 77 K in a matrix of 2-methyltetrahydrofuran.[11] In all cases, with the exception of 4, a color appears when the epoxy ketone substrate is excited at 366 nm.[9] Although the colored species observed are stable in the dark at 77 K, they undergo rapid bleaching upon irradiation with visible light or on warming.[12] The absorption spectra of these colored ylides are reported in Figure 3.

Although ylides have not been observed directly upon photolysis of 1–7 at room temperature, we have succeeded in trapping these photogenerated intermediates derived from 1–3 in the presence of selected dipolarophiles.[9b]

Discussion

It is known that intersystem crossing is very efficient for aromatic ketones.[13] Although we have not determined intersystem crossing efficiencies for the series of epoxy ketones studied here, the phosphorescence spectra, the behavior in direct or sensitized experiments, and the quenching of the photolysis by *trans*-piperylene suggest that only triplet excited states are involved in the photorearrangement of α-epoxy ketones 1–5. The same conclusions were reached in the case of the dypnone oxides 6 and 7.[14]

Three types of products in addition to polymers have been characterized: β-diketones, α-diketones, and aldehydes. Formation of β-diketones is best rationalized by a C_α–O bond cleavage followed by a C_β group migration[15] (Scheme V). The β-diketone is formed mainly in the enolized form provided a hydrogen is available in the α-position.

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Table II. Irradiation of Epoxy Ketones[a]

epoxy ketone substrates[b]	solvent (concn, M)	irradiation time, h	conversion, %	yield, %		
				naphthaldehyde	α-diketone	β-diketone
1 (0.7)	benzene	0.5	58	16	17	
1 (0.7)	acetonitrile	0.75	27	75	8	
1 (1.2)	acetonitrile + benzophenone (0.23)	2.5	97	72	traces	
1 (0.9)	acetonitrile + *trans*-piperylene (0.4)	2		0	0	
2 (0.5)	cyclohexane	1.5	93	13	9	
2 (1.2)	acetonitrile	5	95	70	traces	
3 (0.4)	acetonitrile	4	81	20		<3
4 (0.4)	acetonitrile or benzene	4	<5			
4 (0.4)	acetonitrile	50	55			30
4 (0.4)	benzene	50	30			35
4 (0.9)	acetonitrile + benzophenone (0.6)	80	20			20
4 (0.9)	acetonitrile + *trans*-piperylene (0.6)	80				0
5 (1.3)	acetonitrile	6.5	30			66
5 (1.3)	benzene + acetophenone (8.3)	6	20			45
5 (1.3)	acetonitrile + *trans*-piperylene (0.5)	7.5				0

[a] Room temperature; λ_{ex} = 366 nm. [b] Molar concentration times 10^2 given in parentheses.

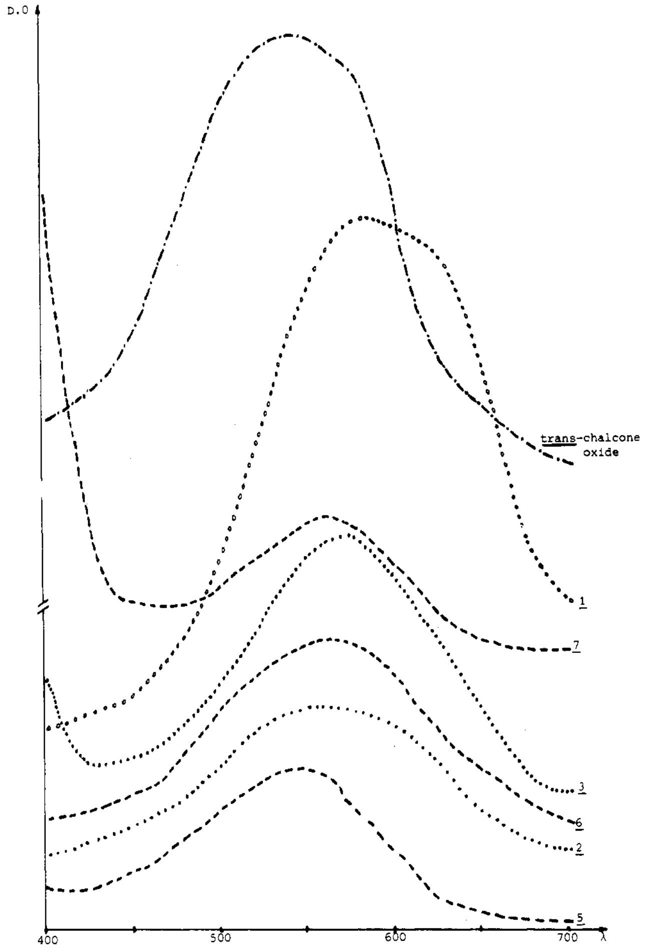

Figure 3. Absorption spectra of the ylides formed by irradiation of α-epoxy ketones. The irradiations were carried out at 77 K (λ_{ex} = 366 nm).

α-Diketones, as has been shown for phenalenone oxide,[3] arise from C_β–O bond cleavage followed by a C_α group migration (Scheme VI). In solution, they are also at least partially enolized.

In order to rationalize the enhancement of aldehyde formation in more polar media, fragmentation of an ylide intermediate is invoked[12c] (Scheme VII).

Since no phosphorescence characteristic of the aroyl group can be seen in the emission spectra of the epoxy ketones 1 and 2 measured at 77 K, the excitation energy must be transferred from the selectively excited aroyl moiety to the naphthyl group bound at the 3-position of the oxirane ring. Furthermore, the absence of β-diketone formation during the photolysis of solutions of 1 and 2 indicates that energy transfer is also very efficient at room temperature. This is not surprising if we consider the exothermicity of the energy transfer for these epoxy ketones. After energy transfer, 1* and 2* become equivalent to excited styrene oxides, and we detect the two expected C_β–O and C_α–C_β type bond cleavage characteristic of such systems. α-Diketone formation arises as explained earlier from the C_β–O bond cleavage; the ylide photolysis products are explained on the basis of C_α–C_β bond cleavage in the triplet excited state.

At 77 K, the phosphorescence observed for 4 arises from the $^3(\pi,\pi^*)$ state localized largely on the naphthoyl substituent on the molecule. Energy transfer from the excited naphthoyl group to the phenyl group attached to the β extremity of the oxirane is precluded by the endothermicity of such a process (>80 kJ/mol). At room temperature, only β-diketone formation is observed, which is characteristic of the C_α–O bond cleavage. Since such C_α–O bond cleavage occurs from an (n,π^*) excited state[2] and since the $^3(\pi,\pi^*)$ is lower in energy than the $^3(n,\pi^*)$ excited state, the low photoreactivity of 4 is not unexpected.[3]

At 77 K, epoxy ketone 5 shows phosphorescence emission typical of a $^3(n,\pi^*)$ excited state. That such a state can be populated at room temperature is confirmed by the easy β-diketone formation. However, it is known that a *p*-methoxy substituent on a benzoyl group bumps the $^3(\pi,\pi^*)$ state to a lower energy than the corresponding $^3(n,\pi^*)$ state.[16] The benzaldehyde formed in very small amounts is attributed to cleavage of the C_α–C_β bond from the $^3(\pi,\pi^*)$ state although it is not the lowest triplet excited state. Such an interpretation involving two states in thermal equilibrium has already been proposed to explain the Norrish II reactivity of substituted butyrophenones.[16]

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Furthermore, the observation of a ylide at 77 K indicates that the C_α–C_β cleavage can occur even when the excitation energy is localized on the aroyl group.[17]

At least at 77 K, ylide formation appears to be a general process of deactivation of α,β-epoxy ketones substituted on the β-carbon by an aryl group. As seen in Figure 3, the position of the ylide absorption maximum is sensitive to the nature of the substituents and seems to correlate with the charge-delocalizing ability of the substituents; a bathochromic shift is observed for the β-naphthyl groups, and this effect is greater for the 1-naphthyl isomer. This can be easily explained if we assume that β-aryl groups delocalize positive charge in the ylide intermediate.

According to the stereochemical rules for electrocyclic processes, ylide formation, if concerted, should occur by disrotatory opening of the oxirane.[18] The stereochemistry of the cycloadducts formed in the presence of dipolarophiles does indeed result from disrotatory opening of the oxirane.[19] Such a finding is interesting since a triplet state seems to be involved in the reaction, thus requiring a spin inversion along the reaction coordinate. Furthermore, from calculations performed on ethylene oxide excited in the triplet state, only the disrotatory opening of the C–C bond is able to compete with the more favorable C–O bond cleavage.[20] The presence of a β-aryl substituent might favor such a concerted process.

Experimental Section

Proton magnetic resonance spectra were recorded with Varian A-60 A and Brucker WP 60 spectrometers; chemical shifts are reported as parts per million (δ scale) from tetramethylsilane. Infrared spectra were recorded with Perkin-Elmer 137 and Pye Unicam instruments. Ultraviolet spectra were recorded with a Beckman Acta C III spectrophotometer. Mass spectra were recorded at the Faculty of Pharmacy of Reims. Elemental analyses were performed by the microanalytical laboratory of Reims University. Phosphorescence spectra were recorded at the University of Paris VI.

Epoxy Ketones. Epoxy ketones **1**–**5** were prepared from ethylenic ketones by the standard procedure.[21]

1-Phenyl-3-(1-naphthyl)-2,3-epoxy-1-propanone (1): yield 60–70%; mp 112 °C; IR ($CHCl_3$) 1690, 1600, 1450, 1390, 1280, 1000, 890, 800 cm^{-1}; NMR ($CDCl_3$) δ 4.22 (d, 1 H, J = 2 Hz), 4.65 (d, 1 H, J = 2 Hz), 7.20–8.05 (m, 12 H); UV (EtOH) λ_{max} 223, 250, 285 nm (ϵ 54 800, 13 000, 8500). Anal. Calcd for $C_{19}H_{14}O_2$: C, 83.19; H, 5.14. Found: C, 83.17; H, 5.22.

1-Phenyl-3-(2-naphthyl)-2,3-epoxy-1-propanone (2): yield 70–85%; mp 80 °C; IR ($CHCl_3$) 1690, 1600, 1410, 1285, 1230, 1140, 1010, 860, 820 cm^{-1}; NMR (CCl_4) δ 4.15 (d, 1 H, J = 2 Hz), 4.25 (d, 1 H, J = 2 Hz), 7.20–8.10 (m, 12 H); UV (MeOH) λ_{max} 223, 246 nm (ϵ 64 000, 19 800). Anal. Calcd for $C_{19}H_{14}O_2$: C, 83.19; H, 5.14. Found: C, 83.33; H, 5.34.

1,3-Bis(2-naphthyl)-2,3-epoxy-1-propanone (3): yield 70–85%; mp 183 °C; IR ($CHCl_3$) 1690, 1610, 1530, 1480, 1275, 1150, 880, 840 cm^{-1}; NMR ($CDCl_3$) δ 4.35 (d, 1 H, J = 2 Hz), 4.55 (d, 1 H, J = 2 Hz), 7.40–8.40 (m, 14 H); UV (MeOH) λ_{max} 220, 250, 283 nm (ϵ 46 200, 30 000, 10 700).

1-(2-Naphthyl)-3-phenyl-2,3-epoxy-1-propanone (4): yield 70–90%; mp 124 °C; IR ($CHCl_3$) 1690, 1600, 1460, 1410, 1280, 1180, 1130, 905, 820 cm^{-}1; NMR ($CDCl_3$) δ 4.11 (d, 1 H, J = 2 Hz), 4.36 (d, 1 H, J = 2 Hz), 7.15–8.10 (m, 11 H), 8.30 (1 H); UV (MeOH) λ_{max} 220, 252, 290 nm (ϵ 23 000, 29 300, 7900). Anal. Calcd for $C_{19}H_{14}O_2$: C, 83.19; H, 5.14. Found: C, 83.37; H, 5.04.

1-(*p*-Methoxyphenyl)-3-phenyl-2,3-epoxy-1-propanone (5): yield 80–85%; mp 79–80 °C; IR ($CHCl_3$) 1690, 1610, 1580, 1520, 1465, 1430, 1355, 1320, 1270, 1250, 1180, 1035, 895, 855, 705 cm^{-1}; NMR ($CDCl_3$) δ 3.82 (s, 3 H), 4.01 (d, 1 H, J = 2 Hz), 4.20 (d, 1 H, J = 2 Hz), 6.85 (d, 2 H, J = 8.5 Hz), 7.28 (s, 5 H), 7.95 (d, 2 H, J = 8.5 Hz); UV (EtOH) λ_{max} 286, 216 nm (ϵ 20 000, 16 000).

α-Diketones. The procedure used has been described.[22]

1-Phenyl-3-(1-naphthyl)-1,2-propanedione (9a): yield 40%; IR ($CHCl_3$) 3500, 1720, 1680, 1600, 1510, 1450, 1270, 700 cm^{-1}; NMR ($CDCl_3$) δ 4.56 (s, 1.56 H), 7.10–8.10 (m, 12.22 H), 10.5 (s, 0.22 H); UV (EtOH) λ_{max} 220, 244, 270 nm (ϵ 25 000, 6800, 4000).

1-Phenyl-3-(2-naphthyl)-1,2-propanedione (11a): yield 70%; mp 156 °C; IR ($CHCl_3$) 3400, 1650, 1610, 1390, 1270, 1140, 980 cm^{-1}; NMR ($CDCl_3$) δ 6.55 (s, 1 H), 7.55–8.00 (m, 12 H), 8.30 (s, 1 H); UV (EtOH) λ_{max} 224, 244, 345 (ϵ 49 400, 14 000, 13 700); UV (EtOH + 1 drop of 1 M NaOH) λ_{max} 210, 232, 395 (ϵ 76 000, 25 000, 13 700); mass spectrum, m/e 274 (M^+), 141, 105 (base).

1,3-Bis(2-naphthyl)-1,2-propanedione (12a): yield 75%; mp 135 °C; IR ($CHCl_3$) 3400, 1620, 1470, 1400, 1380, 1280, 1200 cm^{-1}; NMR ($CDCl_3$) δ 6.65 (1 H), 7.40–8.10 (m, 13 H), 8.30 (2 H); UV (MeOH) λ_{max} 220, 248, 348 nm (ϵ 40 500, 13 200, 6900); UV (MeOH + 1 drop of 1 M NaOH) λ_{max} 210, 248, 400 (ϵ 136 000, 14 000, 5800).

General Procedure for Acetylation of α-Diketones. To a solution of α-diketone (3 mM) in pyridine (15 mL) was added 5 mL of acetic anhydride; the resulting solution was stirred overnight. The usual workup furnished the enol acetate.

1-Phenyl-3-(1-naphthyl)-2-acetyl-2-propen-1-one (9b): yield 85%; mp 145 °C; IR ($CHCl_3$) 1760, 1660, 1600, 1510, 1450, 1370, 1335, 1270, 1200, 1130, 1010, 960 cm^{-1}; NMR ($CDCl_3$) δ 2.15 (s, 3 H), 7.20–8.10 (m, 13 H); UV (MeOH) λ_{max} 220, 252, 334 nm (ϵ 65 600, 22 100, 15 300). Anal. Calcd for $C_{21}H_{16}O_3$: C, 79.73; H, 5.10. Found: C, 79.79; H, 5.05.

1-Phenyl-3-(2-naphthyl)-2-acetyl-2-propen-1-one (11b): yield 75%; mp 148 °C; IR ($CHCl_3$) 1760, 1660, 1600, 1450, 1370, 1340, 1200, 1130, 1020, 820 cm^{-1}; NMR ($CDCl_3$) δ 2.36 (s, 3 H), 7.03 (s, 1 H), 7.30–8.10 (m, 12 H); UV (MeOH) λ_{max} 220, 250, 330 nm (ϵ 49 500, 21 300, 11 600). Anal. Calcd for $C_{21}H_{16}O_3$: C, 79.73; H, 5.10. Found: C, 79.68; H, 5.19.

1,3-Bis(2-naphthyl)-2-acetyl-2-propen-1-one (12b): yield 55%; mp 115 °C; IR ($CHCl_3$) 1760, 1655, 1470, 1370, 1280, 1200, 1100, 1020 cm^{-1}; NMR ($CDCl_3$) δ 2.38 (s, 3 H), 6.87 (s, 1 H), 7.40–8.10 (m, 13 H), 8.46 (s, 1 H); UV (MeOH) λ_{max} = 220, 274, 320 nm (ϵ = 44 600, 17 800, 14 200); mass spectrum, m/e 366 (M^+) 323, 155, 127 (base).

β-Diketones. The procedure used has already been described.[23]

1,3-Bis(2-naphthyl)-1,3-propanedione (13): yield 20%; mp 173 °C; IR (KBr) 1600, 1530, 1430, 1390, 1370, 1195, 1140, 1070, 955, 925 cm^{-1}; NMR ($CDCl_3$) δ 7.10–8.20 (m, 13 H), 8.22 (s, 2 H), 16.95 (s, 1 H); UV (MeOH) λ_{max} 218, 367 nm (ϵ 66 500, 35 600); UV (MeOH + 1 drop of 1 M NaOH) λ_{max} 218 nm (72 900).

1-(2-Naphthyl)-3-phenyl-1,3-propanedione (14): yield 25%; mp 101 °C; IR ($CHCl_3$) 1600, 1570, 1430, 1300, 1195, 1130, 865 cm^{-1}; NMR ($CDCl_3$) δ 7.25–8.22 (m, 12 H), 8.50 (s, 1 H), 16.87 (s, 1 H); UV (MeOH) λ_{max} 216, 240, 355 nm (ϵ 36 500, 17 100, 26 000); UV (MeOH + 1 drop of 1 M NaOH) λ_{max} 216, 240 nm (ϵ 54 800, 24 400).

1-(*p*-Methoxyphenyl)-3-phenyl-1,3-propanedione (15): yield 30%; mp 129–131 °C (lit.[8] mp 129–130 °C); IR ($CHCl_3$) 3450, 1605, 1570, 1510, 1460, 1310, 1260, 1180, 1120, 1035, 850 cm^{-1}; NMR ($CDCl_3$) 3.86 (s, 3 H), 6.73–8.06 (m, 10 H), 16.91 (s, 1 H); UV (MeOH) λ_{max} 205, 354 nm (ϵ 10 900, 22 900); UV (MeOH + 1 drop of 1 M NaOH) λ_{max} 208, 354 (ϵ 33 500, 19 400); mass spectrum, m/e 254 (M^+, base), 177, 147, 135, 105.

Photochemical Reactions. Deoxygenated solutions ($\simeq 10^{-2}$ M; cf. Table II) were irradiated in a Pyrex vessel at room temperature by using a Philips HPW 125-W lamp.

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(17) However, as pointed out by one referee, formation of benzaldehyde from fragmentation of the β-diketone **15** cannot be completely excluded [cf.: ref 15c; D. Veierov, Y. Mazur, and E. Fischer, *J. Chem. Soc., Perkin Trans. 2*, 1659 (1980)]. Nevertheless, since in the various cases studied here, aldehydes appear only when ylides are detectable, they are more probably formed from such an intermediate.

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The yield of α-naphthaldehyde was determined by VPC (internal reference, eicosene) using two columns: SE 30, 2% on HMDS WAW, 1.5 m; Carbowax HMDS (treated with 3% H_3PO_4), 15% on HMDS WAW 60/80, 2 m. Benzaldehyde was detected by VPC using two columns: SE 30, 1% on WAW 60/80, 1 m; the previous Carbowax column.

When α-diketones were formed, the irradiation mixture was treated overnight with acetic anhydride–pyridine. After the usual workup, the products were purified by TLC and recrystallized. β-Diketones and keto enol acetates were identified by comparison with authentic samples.

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Registry No. **1**, 73354-52-6; **2**, 73354-53-7; **3**, 73354-54-8; **4**, 60857-46-7; **5**, 40327-51-3; **6**, 19804-64-9; **7**, 19804-81-0; **8**, 66-77-3; **9a**, 78498-88-1; **9b**, 78498-89-2; **10**, 66-99-9; **11a**, 78498-90-5; **11b**, 78498-91-6; **12a**, 78498-92-7; **12b**, 78498-93-8; **13**, 51583-97-2; **14**, 57114-80-4; **15**, 6327-79-3.

Decaryiol, a New Cembrane Diterpene from the Marine Soft Coral *Sarcophyton decaryi*

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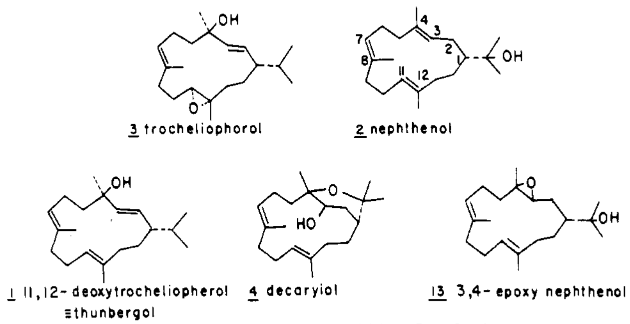
The petroleum ether extract of the soft coral *Sarcophyton decaryi* yielded the cembrane-type diterpenes thunbergol (**1**), decaryiol (**4**), and 3,4-epoxynephthenol (**13**) in addition to nephthenol and trocheliophorol as reported previously. Compounds **4** and **13** are new and were characterized by spectral data, degradative studies by ozonolysis, and chemical transformations. Nephthenol reacts with tetrabromocyclohexadienone to give **11**, the 3-bromo analogue of decaryiol. Compounds **4** and **11** rearrange to an enol ether (**10**), thereby proving the cembranoid structure of **4**. 3,4-Epoxynephthenol (**13**), the second new cembranoid, is believed to be the biogenetic precursor of decaryiol (**4**), and, indeed, **13** could be transformed into **4** by acid catalysis.

Sarcophyton decaryi (Tixier-Durivault, 1946) is one of many soft corals which populate the coral reefs of the Gulf of Eilat. More than 150 species of these alcyonaceans which form large patches on the reef table have already been reported.[1] Many of the soft corals contain cembranoid diterpenes, some of which are toxic to fish and are believed to play a role in the protection of the soft corals from predators. Other cembranoids have been reported to have biological activities.[2]

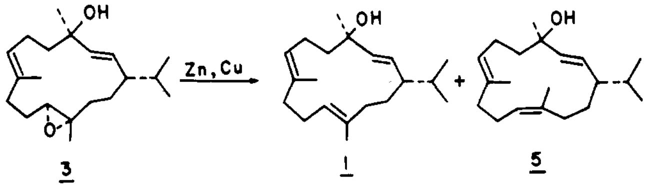
Repeated chromatography of the petroleum ether extract of *S. decaryi* (Sephadex LH-20 and silica gel; see Experimental Secion) yielded, apart from large amounts of glycerides and steroids, five cembranoid diterpenes which were, in order of their polarity, thunbergol (**1**), nephthenol (**2**), trocheliophorol (**3**), 3,4-epoxynephthenol (**13**), and **4**, which was named decaryiol (Chart I). Structure elucidation of two of these compounds, nephthenol (**2**) and the then unknown trocheliophorol (**3**), was described by us in a recent report.[3]

Chart I



Diterpenenoids of Sarcophyton decaryi (The Red Sea)

Scheme I



Thunbergol, one of the reported 2,7,11-cembratrien-4-ol isomers, was first obtained from the North American Douglas fir *Pseudotsuga menziesii*.[6] The close relationship between thunbergol and trocheliophorol (**3**) can be seen in the ^1H and ^{13}C NMR spectra (see Table I and the Experimental Section). Furthermore, microozonolysis[4] of **1** gave levulinaldehyde and, in addition, 2-methyl-2-hydroxypentane-1,5-dial, also obtained from **3**. Deoxygenation of **3** with Zn/Cu couple[5] gave two olefinic isomers (see Scheme I) in the ratio 9:1 as determined by ^{13}C NMR. The (11*E*)-11,12-deoxytrocheliophorol isomer was identical in all respects with thunbergol. Presumably **3** arises from thunbergol by regiospecific epoxidation, well-known among the marine soft coral metabolites.[7]

Comparison of the ^{13}C NMR spectra of compounds **1**, **3**, and **5** made possible the almost full line assignment (see Table I). Assignments were based on the peak multiplicities (SFORD), chemical shift considerations,[8] and com-

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