California Regional NMR Facility at the California Institute of Technology (supported by NSF Grant CHE 79-16324A1). We thank D. Busby and S. Pitzenberger for obtaining proton NMR spectra and K. Fang for high-resolution mass spectra. We are extremely grateful to Dr. F. A. L. Anet for use of his 395-MHz NMR spectrometer and for stimulating discussions on analysis of selenoether lactone **25** and editorial advice. We also thank Dr. C. E. Strouse and L. Goldsmith for technical assistance and X-ray analysis of *p*-bromobenzoate **13**.

Registry No. **6**, 148-53-8; **7**, 4383-05-5; **8**, 50827-57-1; **9**, 40338-61-2; **10**, 97654-83-6; **11** (isomer 1), 97654-84-7; **11** (isomer 2), 97654-98-3; **12**, 97654-85-8; **13**, 97654-86-9; **14**, 97654-87-0; **15**, 97654-88-1; **16**, 97654-89-2; **17**, 97718-46-2; **19**, 97654-90-5; **20** (isomer 1), 97654-91-6; **20** (isomer 2), 97718-47-3; **21** (isomer 1), 97654-92-7; **21** (isomer 2), 97718-48-4; **22**, 97654-93-8; **23**, 97654-94-9; **24**, 97654-95-0; **25**, 97673-90-0; **26** (isomer 1), 97654-96-1; **26** (isomer 2), 97718-49-5; **27**, 97654-97-2; **28**, 97673-91-1; ethyl vinyl ether, 352-93-2; *p*-bromobenzoyl chloride, 586-75-4.

Supplementary Material Available: A table of atomic positions and thermal parameters of lactone **14** and a discussion of the ^1H NMR analysis of selenoether lactone **25** at 200 and 500 MHz, including a table and spectra (11 pages). Ordering information is given on any current masthead page.

A New Class of Chiral Smectic Liquid Crystals: Substituted Biphenylylcyclohexylideneethanones Having an Axial Chirality

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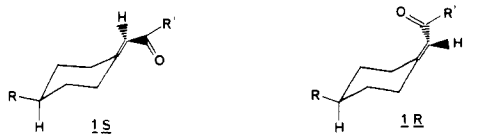
The introduction of a chiral cyclohexylideneethanone unit in a potential mesomorphic structure leads to the first family of optically active liquid crystals having an axial chirality. Racemic compounds **2** were synthesized by a Wittig-type coupling between β-keto phosphonates **6** (R^1 = *n*-C_5H_{11}) and substituted cyclohexanone **7** (R^2 = H, CH_3, *t*-Bu, OCH_3, O-*n*-C_5H_{11}, CO_2Et, $OCOC_6H_4CN$, $OCOC_6H_4Cl$). The optically active molecules **12** were prepared by a new route using the asymmetric coupling of a carbanion α to a chiral sulfoxide **9** (R^2 = *n*-C_5H_{11}, CH_2OEt) and a substituted biphenyl acid chloride (Ar = R′$C_6H_4C_6H_4$ with R′ = *n*-C_5H_{11}, CH_3O, *n*-$C_8H_{17}O$, CN) followed by a stereospecific pyrolytic elimination of the sulfoxide moiety. Derivatives containing only one aromatic ring were not mesomorphic in contrast to those having a biphenyl system.

Although optically active liquid crystals, mostly cholesteric, have been known for a long time,[1] the chirality has always been introduced by the way of one or more asymmetric centers, generally located in a side chain. There are no reports on any attempt to synthesize optically active liquid crystals having a molecular asymmetry,[13] although these molecules could be of interest in many applications such as dopants for nematic displays.

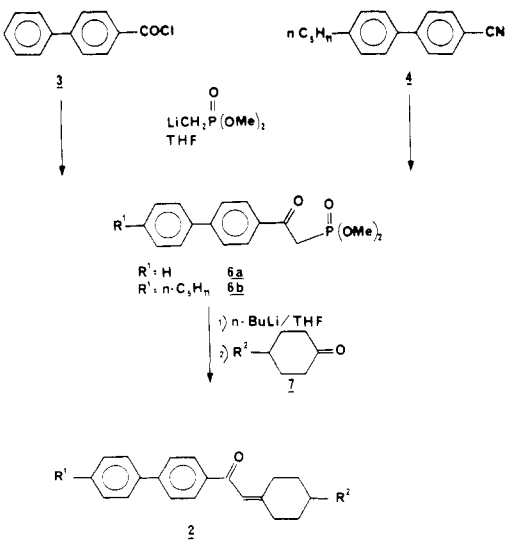
In the present work, we describe a new class of chiral liquid crystals having an axial chirality due to the presence of the chiral moiety cyclohexylideneethanone **1**.[14]



1S **1R**

These molecules which appeared to be chiral smectics or cholesteric (at room temperature in some cases) were synthesized in both racemic and optically active forms by two different routes. The optically active molecules were obtained from the asymmetric coupling of a carbanion α to a chiral sulfoxide group and substituted biphenyl acid chloride, followed by a stereospecific pyrolytic elimination of the sulfoxide moiety. This chirality transfer is a new methodology to prepare chiral cyclohexylideneethanones. However the unexpected photochemical unstability of these compounds did not allow a complete characterization of their mesomorphic phase.

Scheme I



Synthesis of Racemic Liquid Crystals 2

Because of the well-known ability of properly substituted biphenyls to give liquid crystals we chose to prepare first racemic type **2** molecules containing a biphenyl moiety (Scheme I).

The main step of the synthesis is the condensation of the β-keto phosphonates **6** with 4-substituted cyclo-

(1) (a) Kelker, H., Katz, R. "Handbook of Liquid Crystals"; Verlag Chemie: Weinheim/Berstr., West Germany, 1980; and references cited therein. (b) Gray, G. W.; Windsor, P. A. "Liquid Crystals and Plastic Crystals"; Wiley: New York, 1974; and references cited therein.

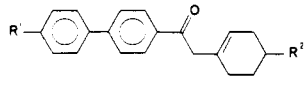
0022-3263/85/1950-4062$01.50/0

Table I. Mesomorphic Properties of Racemic Substituted Biphenylylcyclohexylideneethanones 2

	R^1	R^2	yield, %	transition temp,[a] °C
2a	H	p-$CNC_6H_4CO_2^-$	33	k 131–133 i
2b	n-C_5H_{11}	H	30	k 67 i (56 a)
2c	n-C_5H_{11}	CH_3	25	k 53 s 71 i
2d	n-C_5H_{11}	t-Bu	25	k 118–120 i (80 a)
2e	n-C_5H_{11}	OCH_3	35	s_A 95 i
2f	n-C_5H_{11}	O-n-C_5H_{11}	23	s 80 i
2g	n-C_5H_{11}	CO_2Et	17	k 64 s_1 66 i (19 s_2)
2h	n-C_5H_{11}	p-$CNC_6H_4CO_2^-$	35	k 128 i (110 n)
2i	n-C_5H_{11}	p-$ClC_6H_4CO_2^-$	34	k 125 i (97 n 77 s_A)

[a] k, crystal; n, nematic; i, isotropic; s, s_1, s_2, unidentified smectics; a, unidentified anisotropic phase.

Table II. Mesomorphic Properties of Racemic Biphenylylcyclohexenylethanones 17

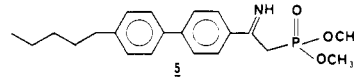


	R_1	R^2	transition temp,[a] °C
17f	n-C_5H_{11}	O-n-C_5H_{11}	s 112 i
17h	n-C_5H_{11}	p-$CNC_6H_4CO_2^-$	k 158 i (132 n 110 s_1 103 s_2)
17i	n-C_5H_{11}	p-$ClC_6H_4CO_2^-$	k 143 i (138 s)

[a] k, crystal; i, isotropic; n, nematic; s, s_1, s_2, unidentified smectics.

hexanones **7**. This reaction gave, with moderate yields, compounds **2** without any trace of isomers containing an endocyclic double bond as long as no excess of base was used. β-Keto phosphonates **6** were easily prepared from dimethyl (lithiomethyl)phosphonate and either the acid chloride **3** or the nitrile **4**.

It is interesting to notice that the reaction of dimethyl (lithiomethyl)phosphonate with the nitrile **4** proceeded through the formation of the imine **5**, which is quite stable and can be isolated very easily.



5

As shown in Table I, most of these molecules showed monotropic mesophases which are generally smectic. However molecules **2e** and **2f** deserve specific mention because they never crystallized but showed a smectic mesophase at room temperature and below. Molecule **2a** is the only one that did not show any mesomorphic properties, probably because of the absence of any substituent R^1 on the aromatic side. It is interesting to remark that in contrast, the molecule **2b** having no substituent R^2 on the cyclohexyl side showed a monotropic mesophase which was not identified. It must be also pointed out that the molecule **2d** having a *tert*-butyl group showed a monotropic mesophase; this is the first example of a liquid crystal having such a substituent.

We have also isomerized compounds **2**, in presence of bases such as sodium hydride or potassium *tert*-butoxide, to molecules **17** having an endocyclic double bond.

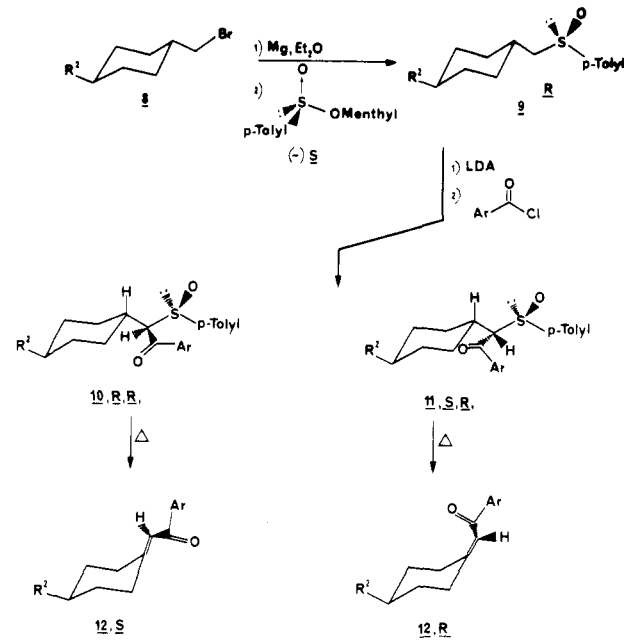
As shown in Table II, these molecules showed also mesomorphic phases, and the clarification points are generally 20–30 °C higher than in the preceeding series.

Again the compound **17f** could not be crystallized and showed a smectic phase at room temperature and below. The other molecules are monotropic mesophases.

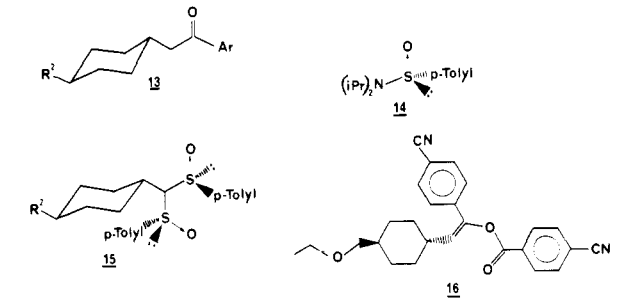
Synthesis of Optically Active Substituted Cyclohexylideneethanones 12

Optically active substituted cyclohexylideneethananones **12** were obtained by pyrolytic elimination of a chiral sulfoxide group.[2,3] (Scheme II).

Scheme II



Sulfoxides (*R*)-**9** were easily obtained from the corresponding Grignard and (−)-(*S*)-menthyl sulfinate by the standard procedure.[4] The corresponding carbanions prepared with LDA at −78 °C were acylated with acid chlorides, giving a mixture of the diastereoisomeric β-keto sulfoxides **10** and **11**. The reaction temperature during the addition of the acid chloride must be kept at −78 °C in order to avoid secondary reactions: deoxygenation of the sulfoxide[5] by the acid chloride and ligand exchange on the sulfur atom with LDA, giving the ketone **13** and the sulfinamide **14**, or with the carbanion of the starting of sulfoxide in excess, leading to the ketone **13** and the disulfoxide **15**.



However, when an electron-withdrawing group such as CN, is introduced on the aromatic ring of the acid chloride, the yield of the acylation reaction was only 10% (**10c** and **11c**), the main products resulting from the secondary reactions were **13c** (R_2 = CH_2OEt; Ar = p-NCC_6H_4) and the corresponding enol ester **16**.

In the whole series (Table III) the main stereoisomer **10** showed consistent characteristics with respect to the other stereoisomer **11**: the lowest R_f (in 20/80 acetone/n-hexane), the smallest chemical shift and the largest coupling constant for the proton α to the sulfoxide, and the highest

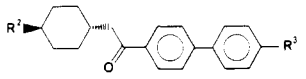
(2) Solladie, G.; Zimmermann, R.; Bartsch, R. *Tetrahedron Lett.* **1983**, *24*, 755.
(3) Solladie, G.; Zimmermann, R.; Bartsch, R.; Walborsky, H. M. *Synthesis*, in press.
(4) Solladie, G. *Synthesis* **1981**, 185.
(5) Amonoo-Neizer, E. H.; Ray, S. K.; Shaw, R. A.; Smith, B. C. *J. Chem. Soc.* 1965, 6250. Juge, S.; Kagan, H. B. *Tetrahedron Lett.* **1975**, *32*, 2733.

Table III. Optically Active β-Keto Sulfoxides 10 and 11

				major diastereoisomer (R,R)-10				minor diastereoisomer (S,R)-11			
	R^2	Ar	yield, %	%	R_f[a]	$[\alpha]^{20-22}_D$, deg	δ/J[3c]	%	R_f[b]	$[\alpha]^{20-22}_D$, deg	δ/J[c]
a	H	C_6H_5	60	70	0.26	+146	4.15/9	30	0.30		4.60/7
b	CH_2OEt	p-ClC_6H_4	70	75	0.24	+122	4.12/9	25	0.29	+21	4.53/6
c[d]	CH_2OEt	p-CNC_6H_4	10	60	0.22		4.18/9	40	0.29		4.70/6
d	n-C_5H_{11}	p-n-$C_5H_{11}C_6H_4$-p-C_6H_4	85	60	0.24	+73	4.20/9	40	0.32	+13	4.67/6
e	CH_2OEt	p-n-$C_5H_{11}C_6H_4$-p-C_6H_4	75	70	0.19	+48	4.22/9	30	0.24		4.60/6
f	n-C_5H_{11}	$MeOC_6H_4$-p-C_6H_4	86	60	0.20	+63	4.20/9	40	0.24	+15	4.60/6
g	CH_2OEt	p-$C_8H_{17}OC_6H_4$-p-C_6H_4	70	60	0.20	+45	4.10/9	40	0.25	+26	4.57/6
h	n-C_5H_{11}	p-CNC_6H_4-p-C_6H_4	60	75	0.13		4.27/10	25	0.18		4.57/6

[a] Solvent: 20/80 acetone/hexane. [b] Solvent: acetone. [c] 60-MHz ^1H NMR, δ of the proton α to the ketone and to the sulfoxide; J, hertz. [d] The two diastereoisomers were not separated.

Table IV. Mesomorphic Properties of Ketones 13



	R^2	R^3	transition temp,[a] °C
13h	n-C_5H_{11}	CN	k 139 n 153 i (138 s)
13d	n-C_5H_{11}	n-C_5H_{11}	k 84 s_1 99 s_2 148 i
13e	CH_2OEt	n-C_5H_{11}	k 75 s_1 78 s_2 123 i (55 s_3)

[a] k, crystal; i, isotropic; n, nematic, s, smectic.

optical rotation. All these experimental facts support the configuration of the main isomer as being the same in the whole series.

Furthermore, the carbanion of sulfoxide (*R*)-**9** was prepared under thermodynamic control. Our recent studies of the carbonation of such carbanion[2,3] demonstrated that under thermodynamic control the pro-*R* proton was preferentially abstracted while under kinetic control the pro-*S* proton was mainly metalated. Therefore the major diastereoisomer **10** must have the absolute configuration *RR*. This conclusion is strongly supported by the NMR data which show the major diastereoisomer *R,R* resulting from the carbonation[3] with respect to the other stereoisomer giving the highest coupling constant and highest field signal for the proton α to sulfoxide, consistent with the NMR of compounds **10** with respect to **11**.

It is interesting to notice that some of the ketones **13** obtained from the observed secondary reactions appeared to be smectic liquid crystals (Table IV).

The pyrolysis of sulfoxides **10** and **11** were conducted in refluxing toluene in presence of sodium bicarbonate during 31 min. This stereospecific elimination[3] of the sulfoxide moiety lead quantitatively to optically pure substituted biphenylylcyclohexylideneethanones **12**: diastereoisomers (*R,R*)-**10** giving molecules (*S*)-**12** showing in all cases a negative optical rotation and diastereoisomers (*S,R*)-**11** giving compounds (*R*)-**12** with a positive optical rotation (Table V).

It is important to remark that this pyrolysis performed in absence of sodium bicarbonate gave quantitatively the isomers **17** with the endocyclic double bond (NMR).

From the results listed in Table V it can be concluded that only molecules containing a biphenyl moiety exhibited liquid crystalline properties (molecules **12b** and **12c** are isotropic). Most of the molecules showed smectic phases. However ketone **12e** displayed also a cholesteric phase, while compound **12f** showed only cholesteric properties. This is also the first example of a cholesteric liquid crystal having an axial chirality.

Photochemical Stability of Cyclohexylideneethanones

Due to the presence of the highly conjugated chromophore, these molecules are particularly photochemically unstable. Qualitative experiments conducted on compound **2d** showed a rapid degradation in a few hours at the daylight even in Pyrex. Under irradiation with a UV lamp two main products are formed: the corresponding cyclohexenylethanone **17d**, resulting from double bond isomerization, and the corresponding biphenylcarboxylic acid, formed probably by oxidation of **17d**.

Conclusion

Although substituted cyclohexylideneethanones showed a low photochemical stability which prevents their use for application in the field of liquid crystals, this study has demonstrated that molecules having an axial chirality can exhibit liquid crystalline properties. The axial chirality arises from the presence of the chiral cyclohexylideneethanone unit **1** in which the plane defined by C_4, R, and H is perpendicular to the plane containing the double bond substituents. As a consequence, the geometry of the molecules is modified with respect to that of a saturated cyclohexane ring. The following results give some indication about the effect of such geometrical factors on the mesomorphic behavior of the molecules.

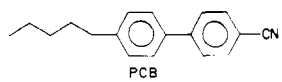
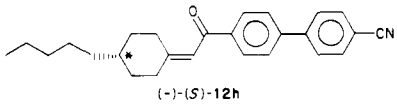
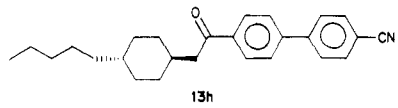
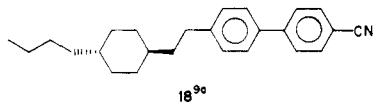
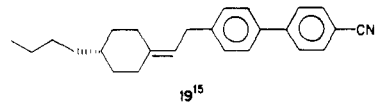
All the molecules listed in Table VI can be considered as derivatives of the well known PCB. We have shown in this paper that molecule **12h** displayed liquid crystal properties. Without the carbon–carbon double bond, compound **13h** is still a liquid crystal. In sharp contrast, the absence of the carbonyl group in compound **19** decreased considerably the mesomorphism. Finally, if the carbonyl group and the carbon–carbon are both replaced by saturated CH_2 groups the mesomorphic behavior is recovered. Therefore, the carbonyl group seems to play an important role for the liquid crystallinity of molecules

Table V. Mesomorphic Properties of Ketones 12

	R^2	Ar	starting sulfoxide	$[\alpha]^{20}_D$, deg (*c*)	transition temp,[a] °C
(−)-(*S*)-**12b**	CH_2OEt	p-ClC_6H_5	(*R,R*)-**10**	−3.0 (0.9)[b]	oil
(+)-(*R*)-**12c**	CH_2OEt	p-CNC_6H_4	(*S,R*)-**11**	+4.8 (5.0)[c,d]	k 46 i
(+)-(*R*)-**12d**	n-C_5H_{11}	p-n-$C_5H_{11}C_6H_4$-p-C_6H_4	(*S,R*)-**11d**	+1.0 (0.6)[c]	k 44 s_A 105 i
(−)-(*S*)-**12e**	CH_2OEt	p-n-$C_5H_{11}C_6H_4$-p-C_6H_4	(*R,R*)-**10e**	−0.6 (0.6)[c]	k 43 s 63 ch 67 i
(−)-(*S*)-**12f**	n-C_5H_{11}	p-$MeOC_6H_4$-p-C_6H_4	(*R,R*)-**10f**	−3.9 (0.2)[c]	k 65 ch 124 i
(+)-(*R*)-**12g**	CH_2OEt	p-$C_8H_{17}OC_6H_4$-p-C_6H_4	(*S,R*)-**11g**	+2.5 (0.2)[c]	k 102 s_A 123 i
(−)-(*S*)-**12h**	n-C_5H_{11}	p-CNC_6H_4-p-C_6H_4	(*R,R*)-**10h**	−4.4 (0.6)[c]	k 102 s 113 c 135 i

[a] k, crystal; i, isotropic; ch, cholesteric; s, smectic. [b] Solvent: acetone. [c] Solvent: chloroform. [d] Corrected to optically pure (*S,R*)-**11**.

Table VI

	transition temp,[a] °C
 PCB	k 22 n 35 i
 (-)-(S)-12h	k 102 s 113 ch 135 i
 13h	k 139 n 153 i (138 s)
 18^{9c}	k 71 s_A 74 n 182 i
 19^{15}	k 57 i (12 s)

[a] k, crystal; i, isotropic; ch, cholesteric; s, smectic.

containing a cyclohexylidene unit.

Experimental Section

Symbols s, n, and c indicate respectively smectic, nematic, and cholesteric mesophases while k and i refer to crystalline and isotropic phases.[1]

Transition temperatures were determined with a Leitz Orthoplan polarizing microscope equipped with an heating stage.

2-[1,1'-Biphenyl]-4-yl-1-(dimethoxyphosphinyl)-2-ethanone (6a). To a solution of dimethyl methylphosphonate (7.5 g, 60 mmol) in 20 mL of THF was added at −78 °C *n*-BuLi (60 mmol). After 30 min at −78 °C, 4-phenylbenzoyl chloride (6.5 g, 30 mmol) in 10 mL of THF was added. The reaction mixture was stirred 15 min at −78 °C and 1 h at room temperature. Then saturated ammonium chloride (15 mL) was added and stirring continued for 2 h. The product was finally extracted with chloroform (2 × 50 mL), the solvent evaporated, and the keto phosphonate **6a** purified by chromatography (Kieselgel; eluent, 10/90 to 50/50 AcOEt/Et_2O; R_f (20/80) 0.20): yield, 53%; mp 84–85 °C (after recrystallization from acetone/pentane); IR ($CHCl_3$) 1672, 1602, 1270 cm^{-1}; NMR ($CDCl_3$) δ 3.68 (d, J = 23 Hz, 2 H, CH_2), 3.82 (d, J = 11 Hz, 6 H, CH_3), 7.65 (m, 5 H Ar), 7.98 (A_2B_2, J = 8 Hz $\Delta\nu$ = 23 Hz, 4 H, Ar). Anal. Calcd for $C_{16}H_{17}O_4P$: C, 63.16; H, 5.46. Found: C, 63.33; H, 5.46.

2-(4'-*n*-Pentyl-[1,1'-biphenyl]-4-yl)-1-(dimethoxyphosphinyl)-2-ethanone (6b). *n*-BuLi (125 mmol) was added at −78 °C to a solution of dimethyl methylphosphonate (15.5 g, 125 mmol) in 100 mL of THF. After 10 min, 4'-cyano-4-pentyl-1,1'-biphenyl[6] (**4**) (5 g, 60 mmol) in 10 mL of THF was added at −78 °C, and the reaction was stirred 10 min at −78 °C and 1 h at room temperature. Saturated ammonium chloride solution (30 mL) was added, and acetic acid (50%, 100 mL) was added until the pH was acidic. The reaction mixture was stirred for 15 h, and then the solvent was evaporated and the residue extracted with 50/50 chloroform/ether (3 × 100 mL). The product was purified by chromatography (Kieselgel; eluent, 5/95 to 20/80 AcOEt/Et_2O; R_f (20/80) 0.32): yield, 80%; mp 47–49 °C (ether/hexane); IR ($CHCl_3$) 1673, 1607, 1255 cm^{-1}; NMR ($CDCl_3$) δ 0.7–1.95 (m, 9 H), 2.65 (t, J = 7 Hz, 2 H), 3.65 (d, J = 23 Hz, 2 H), 3.78 (d, J = 11 Hz, 6 H), 7.43 (A_2B_2, J = 8 Hz, $\Delta\nu$ = 16 Hz, 4 H), 7.90 (A_2B_2, J = 8 Hz, $\Delta\nu$ = 23 Hz, 4 H). Anal. Calcd for $C_{21}H_{27}O_4P$: C, 67.36; H, 7.27. Found: C, 67.27; H, 7.18.

If the decomposition of the reaction is done only with NH_4Cl, without any addition of acetic acid, the product obtained is a mixture of 50% **6** and 30% **5**. If the hydrolysis with NH_4Cl is limited to 30 min, a 90% yield of imine **5** was observed: mp 76–78 °C; IR ($CHCl_3$) 3490, 3340, 1675, 1622, 1570, 1250 cm^{-1}; NMR ($CDCl_3$) δ 0.8–2.00 (m, 9 H), 2.65 (t, J = 7 Hz, 2H), 3.72 (d, J = 11 Hz, 6 H), 4.13 (d, J = 12 Hz, 1 H), 5.88 (m, 2 H, exchanged with D_2O), 7.37 (A_2B_2, J = 8 Hz, $\Delta\nu$ = 15 Hz, 4 H), 7.58 (s, 4 H). Anal. Calcd for $C_{21}H_{28}NO_3P$: C, 67.54; H, 7.56. Found: C, 67.67; H, 7.73.

4-[(4-Cyanobenzoyl)oxy]cyclohexanone (7a). 4-Hydroxycyclohexanone[7] (1.5 g), pyridine (3 mL), and *p*-cyanobenzoyl chloride (3.0 g) in 10 mL of toluene were refluxed for 4 h. The product was purified by chromatography (Kieselgel; eluent, 10/90 CH_2Cl_2/Et_2O; R_f (50/50) 0.75): yield, 74%; mp 119–120 °C; IR ($CHCl_3$) 2240, 1715, 1615 cm^{-1}; NMR ($CDCl_3$) δ 2.1–2.8 (m, 8 H), 5.57 (m, 1 H), 8.08 (A_2B_2, J = 8 Hz, $\Delta\nu$ = 24 Hz, 4 H). Anal. Calcd for $C_{14}H_{13}NO_3$: C, 69.12; H, 5.39. Found: C, 69.21; H, 5.19.

4-[(4-Chlorobenzoyl)oxy]cyclohexanone (7i). Was prepared by the same procedure as **7a** and purified by chromatography (Kieselgel; eluent, 60/40 $CHCl_3$/hexane; R_f 0.14): yield, 91%; mp 75.5 °C; IR ($CHCl_3$) 1712, 1599 cm^{-1}; NMR ($CDCl_3$) δ 2.0–2.77 (m, 8 H), 5.45 (m, 1 H), 7.76 (A_2B_2, J = 8 Hz). Anal. Calcd for $C_{13}H_{13}ClO_3$: C, 61.79; H, 5.19. Found: C, 61.89; H, 5.09.

4-(*n*-Pentyloxy)cyclohexanone (7f). 4-(*n*-Pentyloxy)cyclohexanol (2 g) (obtained by reduction of the corresponding phenol)[8] was dissolved in acetone (100 mL) and cooled at 0 °C. A mixture of chromic anhydride (2 g), concentrated sulfuric acid (2 mL), and water (10 mL) was added slowly under vigorous stirring. The reaction mixture was stirred for 15 min at room temperature and then filtered on Celite. The solvent was evaporated and the product purified by chromatography (Kieselgel; eluent, 50/50 Et_2O/hexane; R_f 0.47): yield, 95%; IR ($CHCl_3$) 1708 cm^{-1}; NMR ($CDCl_3$) δ 0.85–2.8 (m, 17 H), 3.47 (t, J = 6 Hz, 2 H), 3.67 (m, 1 H). Anal. Calcd for $C_{11}H_{20}O_2$: C, 71.70; H, 10.94. Found: C, 71.98; H, 11.10.

Racemic Substituted Cyclohexylideneethanones 2. General Procedure. Keto phosphonate **6** (4.05 mmol) in DME (10 mL) was added to NaH (4 mmol) in DME (10 mL). After the mixture was stirred for 2 h at room temperature under argon, substituted cyclohexanone **7** (4.05 mmol) in DME (3 mL) was added. The reaction mixture was stirred in dark for 24 h, then decomposed by adding a saturated NH_4Cl solution (3 mL) and water (5 mL), and extracted with methylene chloride (4 × 30 mL) and ether (2 × 30 mL). The organic layers were washed with water (1 × 30 mL) and a sodium chloride solution (1 × 30 mL). After drying over sodium sulfate and after the solvent was removed, the product was purified by chromatography (Kieselgel; eluent, 10/90 Et_2O/hexane) and recrystallized from hexane.

2a: yield, 33%; mp 131–133 °C; R_f (50/50 Et_2O/hexane) 0.46; IR ($CHCl_3$) 1718, 1658, 1608 cm^{-1}; NMR ($CDCl_3$) δ 1.90–2.40 (m, 8 H), 5.43 (m, 1 H), 6.87 (s, 1 H), 7.40–7.90 (m, 5 H), 7.93 (A_2B_2, J = 8 Hz, $\Delta\nu$ = 20 Hz, 4 H), 8.00 (A_2B_2, J = 10 Hz, $\Delta\nu$ = 24 Hz, 4 H). Anal. Calcd for $C_{28}H_{23}NO_2$: C, 79.89; H, 5.50. Found: C, 79.80; H, 5.49.

2b: yield, 30%; mp (°C) k 67 i (56 a); R_f (50/50 Et_2O/hexane) 0.73; IR ($CHCl_3$) 1655, 1611 cm^{-1}; NMR ($CDCl_3$) δ 0.8–2.6 (m, 19 H), 2.67 (t, J = 7 Hz, 2 H), 6.68 (s, 1 H), 7.45 (A_2B_2, J = 8 Hz, $\Delta\nu$ = 17 Hz, 4 H), 7.90 (A_2B_2, J = 8 Hz, $\Delta\nu$ = 21 Hz, 4 H).

2c: yield, 25%; mp (°C) k 53 s 71 i; R_f (50/50 Et_2O/hexane) 0.73; IR ($CHCl_3$) 1655, 1604 cm^{-1}; NMR ($CDCl_3$) δ 0.7–2.5 (m, 20 H with d at 0.94, J = 5 Hz, 3 H), 2.67 (t, J = 7 Hz, 2 H), 3.62 (m, 1 H), 6.72 (s, 1 H), 7.50 (A_2B_2, J = 9 Hz, $\Delta\nu$ = 17 Hz, 4 H), 7.93 (A_2B_2, J = 6 Hz, $\Delta\nu$ = 20 Hz, 4 H).

2d: yield, 25%; mp (°C) k 118 i (80 a); R_f (50/50 Et_2O/hexane) 0.75; IR ($CHCl_3$) 1655, 1608 cm^{-1}; NMR ($CDCl_3$) δ 0.7–2.4 (m, 26 H with s at 0.87, 9 H), 2.63 (t, J = 7 Hz, 2 H), 3.70 (m, 1 H), 6.62 (s, 1 H), 7.38 (A_2B_2, J = 8 Hz, $\Delta\nu$ = 17 Hz, 4 H), 7.82 (A_2B_2, J = 8 Hz, $\Delta\nu$ = 21 Hz, 4 H).

2e: yield, 35%; mp (°C) s_A 95 i; R_f (50/50 Et_2O/hexane) 0.62; IR ($CHCl_3$) 1656, 1607 cm^{-1}; NMR ($CDCl_3$) δ 0.7–2.4 (m, 16 H), 2.67 (t, J = 7 Hz, 2 H), 3.50 (s, 3 H), 3.4–3.6 (m, 2 H), 6.83 (s, 1 H), 7.3–8.6 (m, 8 H, 2 × A_2B_2).

2f: yield, 23%; mp (°C) s 80 i; R_f (50/50 Et_2O/hexane) 0.69; IR ($CHCl_3$) 1662, 1611 cm^{-1}; NMR ($CDCl_3$) δ 0.7–2.9 (m, 25 H),

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2.62 (t, J = 7 Hz, 2 H), 3.7–3.3 (m, 4 H with t at 3.40, J = 6 Hz, 2 H), 6.58 (s, 1 H), 7.26 (A_2B_2, J = 8 Hz, $\Delta\nu$ = 16 Hz, 4 H), 7.72 (A_2B_2, J = 8 Hz, $\Delta\nu$ = 21 Hz, 4 H).

2g: yield, 17%; mp (°C) k 64 s_1 66 i (19 s_2); R_f (50/50 Et_2O/hexane 0.50; IR ($CHCl_3$) 1720, 1657, 1607 cm^{-1}; NMR ($CDCl_3$) 0.7–2.6 (m, 20 H with t at 1.27, J = 7 Hz, 3 H), 2.67 (t, J = 7 Hz, 2 H), 3.3–3.6 (m, 1 H), 4.18 (q, J = 7 Hz, 2 H), 6.73 (s, 1 H), 7.47 (A_2B_2, J = 8 Hz, $\Delta\nu$ = 16 Hz, 4 H), 7.88 (A_2B_2, J = 8 Hz, $\Delta\nu$ = 19 Hz, 4 H). Anal. Calcd for $C_{28}H_{34}O_3$: C, 80.34; H, 8.19. Found: C, 80.28; H, 8.19.

2h: yield, 35%; mp (°C) k 128 i (110 n); R_f (50/50 Et_2O/hexane) 0.48; IR ($CHCl_3$) 2235, 1717, 1658, 1607 cm^{-1}; NMR ($CDCl_3$) δ 0.7–2.4 (m, 17 H), 2.65 (t, J = 7 Hz, 2 H), 3.10 (m, 1 H), 5.40 (m, 1 H), 6.82 (s, 1 H), 7.50 (A_2B_2, J = 8 Hz, $\Delta\nu$ = 21 Hz, 4 H), 7.93 (A_2B_2, J = 8 Hz, $\Delta\nu$ = 21 Hz, 4 H), 8.00 (A_2B_2, J = 8 Hz, $\Delta\nu$ = 25 Hz, 4 H). Anal. Calcd for $C_{33}H_{33}O_3$: C, 80.62; H, 6.77. Found: C, 80.63; H, 6.72.

2i: yield, 34%; mp (°C) k 125 i (97 n 77 s_A); R_f (50/50 Et_2O/hexane) 0.71; IR ($CHCl_3$) 1708, 1657, 1606 cm^{-1}; NMR ($CDCl_3$) δ 0.8–3.10 (m, 19 H), 5.27 (m, 1 H), 6.73 (s, 1 H), 7.42 (A_2B_2, J = 8 Hz, $\Delta\nu$ = 16 Hz, 4 H), 7.72 (A_2B_2, J = 9 Hz, $\Delta\nu$ = 34 Hz, 4 H), 7.85 (A_2B_2, J = 8 Hz, $\Delta\nu$ = 19 Hz, 4 H).

If the condensation of keto phosphonate **6** on cyclohexanones **7** is conducted in presence of an excess of NaH (1.1 equiv) or if the cyclohexylideneethanones **2** are treated in refluxing DME or THF with 0.1 equiv of NaH or *t*-BuOK, the corresponding cyclohexenylethanones **17** were obtained.

17f: yield, 35%; mp (°C) s 112 i; R_f (50/50 Et_2O/hexane) 0.69; IR ($CHCl_3$) 1677, 1610 cm^{-1}; NMR ($CDCl_3$) δ 0.7–2.4 (m, 24 H), 2.62 (t, J = 7 Hz, 2 H), 3.27–3.67 (m from t at 3.40, J = 6 Hz, 2 H, s at 3.57, 2 H, and m, 1 H), 5.43 (m, 1 H), 7.33 (A_2B_2, J = 8 Hz, $\Delta\nu$ = 16 Hz, 4 H), 7.83 (A_2B_2, J = 7 Hz, $\Delta\nu$ = 20 Hz, 4 H).

17h: from **2h** isomerization in a quantitative yield; mp (°C) k 158 i (132 n 110 s_1 103 s_2); R_f (50/50 Et_2O/hexane) 0.49; IR ($CHCl_3$) 2235, 1720, 1669, 1608 cm^{-1}; NMR ($CDCl_3$) δ 0.8–2.40 (m, 15 H), 2.67 (t, J = 7 Hz, 2 H), 3.68 (s, 2 H), 5.33 (m, 1 H), 5.62 (m, 1 H), 7.45 (A_2B_2, J = 8 Hz, $\Delta\nu$ = 15 Hz, 4 H), 7.90 (A_2B_2, J = 9 Hz, $\Delta\nu$ = 21 Hz, 4 H), 7.92 (A_2B_2, J = 7 Hz, $\Delta\nu$ = 23 Hz, 4 H).

17i: yield, 50%; mp (°C) k 143.5 i (138 s); R_f (50/50 Et_2O/*n*-hexane) 0.60; IR ($CHCl_3$) 1700, 1668, 1599 cm^{-1}; NMR ($CDCl_3$) δ 0.7–2.5 (m, 15 H), 2.68 (t, J = 6 Hz, 2 H), 3.70 (s, 2 H), 5.33 (m, 1 H), 5.60 (m, 1 H), 7.23–8.23 (m, 3 × A_2B_2, 12 H). Anal. Calcd for $C_{32}H_{33}ClO_3$: C, 76.71; H, 6.64. Found: C, 76.66; H, 6.76.

***trans*-4-(Ethoxymethyl)-1-(bromomethyl)cyclohexane (8b).** (1) A solution of *trans*-cyclohexanedimethanol (29 g, 0.2 mol) in THF (200 mL) was added dropwise to a suspension of NaH (9 g) in THF (100 mL) containing ethyl iodide (40 g, 0.26 mol) under reflux. The reaction mixture was refluxed for 16 h, decomposed with water (20 mL), and extracted with chloroform (2 × 100 mL). The organic layer was washed with a saturated NaCl solution (1 × 50 mL) and dried over sodium sulfate. The solvent was evaporated, and the residue was crystallized by adding *n*-hexane. The solid was washed with ether (2 × 50 mL); the resulting solid was the starting diol. The ether extracts were evaporated, and the residue was chromatographed (Kieselgel; eluent, 50/50 Et_2O/hexane and pure Et_2O) to yield 30% of 4-(ethoxymethyl)-1-(hydroxymethyl)cyclohexane and 32% of 1,4-bis(ethoxymethyl)cyclohexane: R_f (80/20 Et_2O/hexane) [monoether] 0.39, [diol] 0.04, [diether] 0.80; IR ($CHCl_3$) [monoether] 3615 cm^{-1}; NMR ($CDCl_3$) [monoether] δ 0.7–2.1 (m, 14 H with t at 1.18, J = 7 Hz, and OH at 1.85), 3.18–3.70 (m, 6 H with q at 3.48, J = 7 Hz, 2 H).

(2) Bromine was added dropwise to a solution of the preceeding monoether (10 mmol) and triphenylphosphine (11 mmol) in DMF (30 mL) at 0 °C till a yellow coloration was obtained. The reaction was then stirred 1 h at room temperature. After evaporation of the solvent the residue was first filtered on silica gel (20/80 ether/hexane) and then chromatographed (Kieselgel; eluent, 5/95 Et_2O/hexane; R_f 0.66): yield, 80% pure **8b**; NMR ($CDCl_3$) δ 0.67–2.13 (m, 13 H with t at 1.15, J = 7 Hz, 3 H), 3.10–3.67 (m, 6 H with q at 3.43, J = 7 Hz, 2 H).

Cyclohexylmethyl *p*-Tolyl Sulfoxides (*R*)-9. General Procedure. The Grignard of the corresponding 4-substituted (bromomethyl)cyclohexane (30 mmol) was prepared from magnesium (40 mmol) in ether (15 mL). To avoid coupling reactions the ether was distilled over *n*-pentylmagnesium bromide under argon. The Grignard is then rapidly added at 0 °C to a suspension of (−)-*S*-methyl *p*-toluenesulfinate[4] (30 mmol) in ether (25 mL). The reaction mixture was stirred after the addition for 10 min and decomposed with a saturated solution of NH_4Cl (10 mL) and water (10 mL). Extraction with ether (2 × 80 mL) and chloroform (1 × 80 mL). The organic layers were washed with a saturated solution of NaCl (1 × 50 mL) and dried over sodium sulfate. The sulfoxide was finally purified by chromatography (Kieselgel; eluent, 30/70 Et_2O/*n*-hexane 30/70; R_f (50/50 Et_2O/hexane) [sulfinate] 0.64, [menthol] 0.45).

(*R*)-9a (R^2 = H): yield, 68%; R_f (50/50 Et_2O/hexane) 0.28; mp 69–71 °C; $[\alpha]^{22}_D$ + 187° (*c* 1.4, acetone); IR ($CHCl_3$) 1602, 1081, 1010 cm^{-1}; NMR ($CDCl_3$) δ 0.8–2.2 (m, 11 H), 2.42 (s, 3 H), 2.56 (dd, J_{AB} = 12 Hz, J_{AX} = 3 Hz, 1 H), 2.82 (dd, J_{BA} = 12 Hz, J_{BX} = 4.5 Hz, 1 H), 7.50 (A_2B_2, J = 8 Hz, $\Delta\nu$ = 12 Hz, 4 H). Anal. Calcd for $C_{14}H_{20}OS$: C, 71.14; H, 8.53. Found: C, 70.95; H, 8.68.

(*R*)-9b (R^2 = n-C_5H_{11}) from 4-*n*-pentyl-1-(bromomethyl)-cyclohexane:[9a] yield, 72%; R_f (50/50 ether/hexane) 0.25; mp 89–90 °C; $[\alpha]^{22}_D$ +169° (*c* 0.6, acetone); IR ($CHCl_3$) 1600, 1086, 1022, 1011 cm^{-1}; NMR ($CDCl_3$) δ 0.77–2.20 (m, 21 H), 2.43 (s, 3 H), 2.57 (dd, J_{AB} = 13 Hz, J_{AX} = 6 Hz, 1 H), 2.87 (dd, J_{BA} = 13 Hz, J_{BX} = 4 Hz, 1 H), 7.55 (A_2B_2, J = 8 Hz, $\Delta\nu$ = 12 Hz, 4 H). Anal. Calcd for $C_{19}H_{30}OS$: C, 74.56; H, 9.39. Found: C, 74.45; H, 9.87.

(*R*)-9c (R^2 = CH_2OEt): yield, 49%; R_f (50/50 ether/hexane) 0.25; mp 80–82 °C; $[\alpha]^{22}_D$ +168° (*c* 2.0, acetone); IR ($CHCl_3$) 1597, 1101, 1050 cm^{-1}; NMR ($CDCl_3$) δ 0.83–2.33 (m, 13 H with t at 1.17, J = 7 Hz, 3 H), 2.40 (s, 3 H), 2.56 (dd, J_{AB} = 12 Hz, J_{AX} = 4 Hz, 1 H), 2.83 (dd, J_{BA} = 12 Hz, J_{BX} = 5 Hz, 1 H), 3.21 (d, J = 6 Hz, 2 H), 3.45 (q, J = 7 Hz, 2 H), 7.43 (A_2B_2, J = 8 Hz, $\Delta\nu$ = 13 Hz, 4 H). Anal. Calcd for $C_{17}H_{26}O_2S$: C, 69.34; H, 8.90. Found: C, 69.24; H, 8.97.

Acid Chlorides (ArCOCl) Preparation. General Procedure. Carboxylic acid (5 mmol) and oxalyl chloride (10 mmol) were dissolved in benzene (10 mL) and stirred for 0.5 h. One drop of DMF catalyzed the reaction. The acid chloride was recrystallized in *n*-hexane.

4′-Methoxy-[1,1′-biphenyl]-4-carboxylic acid chloride[9b] from the corresponding acid:[9c] yield 90%; mp (°C) k 100 i (81 s); IR ($CHCl_3$) 1775, 1732, 1603 cm^{-1}; NMR ($CDCl_3$) δ 3.85 (s, 3 H), 7.25 (A_2B_2, J = 9 Hz, $\Delta\nu$ = 35 Hz, 4 H), 7.83 (A_2B_2, J = 8 Hz, $\Delta\nu$ = 26 Hz, 4 H).

4′-(*n*-Octyloxy)-[1,1′-biphenyl]-4-carboxylic acid chloride[10a] from the corresponding acid:[9] yield, 90%; mp (°C) k 92 i (92 s); IR ($CHCl_3$) 1777, 1736, 1605 cm^{-1}; NMR ($CDCl_3$) δ 0.8–2.00 (m, 15 H), 4.03 (t, J = 6 Hz, 2 H), 7.37 (A_2B_2, J = 9 Hz, $\Delta\nu$ = 35 Hz, 4 H), 8.00 (A_2B_2, J = 8 Hz, $\Delta\nu$ = 28 Hz, 4 H).

4′-*n*-Pentyl-[1,1′-biphenyl]-4-carboxylic acid chloride[10b] from the corresponding acid:[10c] yield, 90%; mp 42–44 °C; IR ($CHCl_3$) 1775, 1732, 1604 cm^{-1}; NMR ($CDCl_3$) δ 0.8–1.90 (m, 9 H), 2.67 (t, J = 7 Hz, 2 H), 7.41 (A_2B_2, J = 8 Hz, $\Delta\nu$ = 15 Hz, 4 H), 7.91 (A_2B_2, J = 7 Hz, $\Delta\nu$ = 26 Hz, 4 H).

4′-Cyano-[1,1′-biphenyl]-4-carboxylic acid chloride:[10d] yield, 85%; mp 126–128 °C; IR ($CHCl_3$) 2230, 1775, 1731, 1603 cm^{-1}; NMR ($CDCl_3$) δ 7.80 (s, 4 H), 8.03 (A_2B_2, J = 8 Hz, $\Delta\nu$ = 29 Hz, 4 H).

β-Keto Sulfoxides (*R*,*R*)-10 and (*S*,*R*)-11. General Procedure. *n*-Butyllithium (10 mmol) was added at 0 °C to a solution of diisopropylamine (10 mmol) (distilled over sodium hydroxide) in THF (10 mL), and the reaction mixture was stirred for 10 min. After the mixture was cooled to −78 °C, sulfoxide **9** (5 mmol) in THF (5 mmol) was added dropwise, 10 min later the corresponding acid chloride (5 mmol) in THF (8 mL) was added very slowly, and stirring was continued for 30 min. The reaction mixture was decomposed by saturated ammonium chloride (3 mL) and extracted with chloroform (3 × 50 mL), and the organic layers were washed with a saturated sodium chloride solution (1 × 30

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mL). Diastereoisomers[11] **10** and **11** were separated by column chromatography (Kieselgel; eluent, 5/10/85 acetone/Et_2O/hexane). Solvent evaporation must be done at room temperature to avoid the very easy pyrolytic examination of the sulfoxide group.

(*R*,*R*)-10a: R_f (20/80 acetone/*n*-hexane) 0.26; mp 140–148 °C dec; $[\alpha]^{21}_D$ +146° (*c* 0.3, acetone); IR ($CHCl_3$) 1667, 1598, 1038, 1048 cm^{-1}; NMR ($CDCl_3$) δ 0.7–1.87 (m, 11 H), 2.18 (s, 3 H), 4.15 (d, J = 9 Hz, 1 H), 7.13 (A_2B_2, J = 8 Hz, $\Delta\nu$ = 19 Hz, 4 H), 7.32 (A_2B_2, J = 9 Hz, $\Delta\nu$ = 14 Hz, 5 H).

(*S*,*R*)-11a: R_f (20/80 acetone/*n*-hexane) 0.30; NMR ($CDCl_3$) δ 0.7–1.87 (m, 11 H), 2.17 (s, 3 H), 4.60 (d, J = 7 Hz, 1 H), 6.90–7.50 (2 × A_2B_2, 9 H).

(R,R)-10b: R_f (20/80 acetone/*n*-hexane) 0.24; mp 136–144 °C dec; $|\alpha|^{19}_D$ +122° (*c* 0.6, acetone); IR ($CHCl_3$) 1670, 1593, 1097, 1050 cm^{-1}; NMR ($CDCl_3$) δ 0.9–2.4 (m, 13 H with t at 1.17, J = 7 Hz, 3 H), 2.23 (s, 3 H), 3.22 (d, J = 5 Hz, 2 H), 3.45 (q, J = 7 Hz, 2 H), 4.12 (d, J = 9 Hz, 1 H), 7.20 (A_2B_2, J = 8 Hz, $\Delta\nu$ = 15 Hz, 4 H), 7.35 (A_2B_2, J = 8 Hz, $\Delta\nu$ = 15 Hz, 4 H).

(*S*,*R*)-11b: R_f (20/80 acetone/*n*-hexane) 0.29; oil; $[\alpha]^{19}_D$ +21° (*c* 0.4, acetone); IR ($CHCl_3$) 1666, 1592, 1097, 1035 cm^{-1}; NMR ($CDCl_3$) δ 0.9–2.4 (m, 13 H with t at 1.17, J = 7 Hz, 3 H), 2.27 (s, 3 H), 3.22 (d, J = 5 Hz, 2 H), 3.45 (q, J = 7 Hz, 2 H), 4.53 (d, J = 6 Hz, 1 H), 7.32 (A_2B_2, J = 9 Hz, $\Delta\nu$ = 19 Hz, 4 H), 7.43 (A_2B_2, J = 8 Hz, $\Delta\nu$ = 14 Hz, 4 H).

(*R*,*R*)-10c and (*S*,*R*)-**11c**. These two diastereoisomers were not separated because of the low yield (10%) of the reaction leading mainly to the subproducts **13c**, **14**, and **16**. R_f (20/80 acetone/*n*-hexane) [**10c**] 0.22, [**11c**] 0.29; IR ($CHCl_3$) [of the mixture] 2235, 1671, 1609, 1600, 1084, 1036 cm^{-1}; NMR ($CDCl_3$) [of the mixture] δ 0.7–2.4 (m, 16 H with t at 1.17, J = 7 Hz, 3 H, and s at 2.28, 3 H), 3.23 (d, J = 5 Hz, 2 H), 3.48 (q, J = 7 Hz, 2 H), 4.18 (d, J = 9 Hz, **10c**) 4.70 (d, J = 6 Hz, **11c**), 7.0–8.0 (m, 8 H).

13c: yield, 12%; R_f (20/80 acetone/hexane) 0.45; mp 64–66 °C; IR ($CHCl_3$) 2235, 1685, 1609 cm^{-1}; NMR ($CDCl_3$) δ 0.70–2.30 (m, 13 H with t at 1.17, J = 7 Hz, 3 H), 2.85 (d, J = 6 Hz, 2 H), 3.05 (d, J = 6 Hz, 2 H), 3.45 (q, J = 7 Hz, 2 H), 7.93 (A_2B_2, J = 9 Hz, $\Delta\nu$ = 16 Hz, 4 H).

16: yield, 40%; R_f (20/80 acetone/*n*-hexane) 0.37; mp 129–134 °C; IR ($CHCl_3$) 2230, 1738, 1610 cm^{-1}; NMR ($CDCl_3$) δ 0.9–2.3 (m, 13 H, with t at 1.17, J = 7 Hz, 3 H), 3.21 (d, J = 5 Hz, 2 H), 3.45 (q, J = 7 Hz, 2 H), 5.97 (d, J = 11 Hz, 1 H), 7.62 (s, 4 H), 8.13 (A_2B_2, J = 8 Hz, $\Delta\nu$ = 25 Hz, 4 H).

14: yield, 30%; R_f (20/80 acetone/hexane) 0.40; liquid;[12] IR ($CHCl_3$) 1599, 1084, 1040, 951 cm^{-1}; NMR ($CDCl_3$) δ 1.27 (dd, J_1 = 18 Hz, J_2 = 7 Hz, 12 H), 2.40 (s, 3 H), 3.57 (m, 2 H), 7.47 (A_2B_2, J = 9 Hz, $\Delta\nu$ = 16 Hz, 4 H).

15 (R^2 = *n*-C_5H_{11}): R_f (10/20/70 acetone/Et_2O/*n*-hexane) 0.28; oil; IR ($CHCl_3$) 1608, 1048 cm^{-1}; NMR ($CDCl_3$) δ 0.7–2.0 (m, 21 H), 2.40 (s, 6 H), 3.65 (m, 1 H), 7.50 (A_2B_2, J = 8 Hz, $\Delta\nu$ = 24 Hz, 8 H).

(*R*,*R*)-10d: R_f (20/80 acetone/*n*-hexane) 0.24; oil; $[\alpha]^{19}_D$ +73° (*c* 0.5, acetone); IR ($CHCl_3$) 1663, 1604, 1087, 1028 cm^{-1}; NMR ($CDCl_3$) δ 0.7–2.00 (m, 30 H), 2.22 (s, 3 H), 2.63 (t, J = 7 Hz, 2 H), 4.20 (d, J = 9 Hz, 1 H), 6.93–7.83 (m, 3 × A_2B_2, 12 H).

(*S*,*R*)-11d: R_f (20/80 acetone/*n*-hexane) 0.32; oil; $[\alpha]^{20}_D$ +13° (*c* 0.3, acetone); IR ($CHCl_3$) 1659, 1604, 1082, 1035 cm^{-1}; NMR ($CDCl_3$) δ 0.7–2.10 (m, 30 H), 2.22 (s, 3 H), 2.63 (t, J = 7 Hz, 2 H), 4.67 (d, J = 6 Hz, 1 H), 7.03–7.87 (m, 3 × A_2B_2, 12 H).

(*R*,*R*)-10e: R_f (20/80 acetone/N-hexane) 0.19; mp 135–138 °C; $[\alpha]^{20}_D$ +48° (*c* 0.4, acetone; IR ($CHCl_3$) 1662, 1603, 1085, 1045 cm^{-1}; NMR ($CDCl_3$) δ 0.7–2.0 (m, 22 H with t at 1.15, J = 7 Hz, 3 H), 2.15 (s, 3 H), 2.60 (t, J = 7 Hz, 2 H), 3.18 (d, J = 5 Hz, 2 H), 3.42 (q, J = 7 Hz, 2 H), 4.22 (d, J = 9 Hz, 1 H), 6.93–7.70 (m, 3 × A_2B_2, 12 H).

(*S*,*R*)-11e: R_f (20/80 acetone/*n*-hexane) 0.24. This diastereoisomer was not separated from the mixture. The NMR was deduced from the mixture: NMR ($CDCl_3$) δ 0.7–2.0 (m, 22 H with t at 1.15, J = 7 Hz, 3 H), 2.15 (s, 3 H), 2.60 (t, J = 7 Hz, 2 H), 3.18 (d, J = 5 Hz, 2 H), 3.42 (q, J = 7 Hz, 2 H), 4.60 (d, J = 6 Hz, 1 H), 6.9–7.8 (m, 3 × A_2B_2, 12 H).

(*R*,*R*)-10f: R_f (20/80 acetone/*n*-hexane) 0.20; mp 147–151 °C dec; $[\alpha]^{20}_D$ +63° (*c* 0.2, acetone); IR ($CHCl_3$) 1659, 1600, 1085, 1034 cm^{-1}; NMR ($CDCl_3$) δ 0.7–2.20 (m, 21 H), 2.22 (s, 3 H), 3.87 (s, 3 H), 4.20 (d, J = 9 Hz, 1 H), 6.93–7.74 (m, 3 × A_2B_2, 12 H).

(*S*,*R*)-11f: R_f (20/80 acetone/*n*-hexane) 0.24; oil; $[\alpha^{19}_D$ +15° (*c* 0.3, acetone); IR ($CHCl_3$) 1657, 1602, 1035 cm^{-1}; NMR ($CDCl_3$) δ 0.7–2.20 (m, 21 H), 2.22 (s, 3 H), 3.83 (s, 3 H), 4.60 (d, J = 6 Hz, 1 H), 6.85–7.77 (m, 3 × A_2B_2, 12 H).

(*R*,*R*)-10g was not obtained pure because it could not be separated from the starting sulfoxide **9**. The NMR was deduced from the spectrum of the mixture of diastereoisomers: R_f (20/80 acetone/*n*-hexane) 0.20; NMR ($CDCl_3$) δ 0.7–2.5 (m, 28 H with t at 1.16, J = 7 Hz, 3 H), 2.28 (s, 3 H), 3.14 (d, J = 5 Hz, 2 H), 3.38 (q, J = 7 Hz, 2 H), 3.95 (t, J = 6 Hz, 2 H), 4.10 (d, J = 9 Hz, 1 H), 6.8–7.8 (m, 3 × A_2B_2, 12 H).

(*S*,*R*)-11g: R_f (20/80 acetone/*n*-hexane) 0.25; oil; $[\alpha]^{19}_D$ +26° (*c* 1.1, acetone); IR ($CHCl_3$) 1659, 1604, 1085, 1035 cm^{-1}; NMR ($CDCl_3$) δ 0.7–2.53 (m, 28 H with t at 1.16, J = 7 Hz, 3 H), 2.28 (s, 3 H), 3.14 (d, J = 5 Hz, 2 H), 3.38 (q, J = 7 Hz, 2 H), 3.95 (t, J = 6 Hz, 2 H), 4.57 (d, J = 6 Hz, 1 H), 6.83–7.73 (m, 3 × A_2B_2, 12 H).

(*R*,*R*)-10h: R_f (20/80 acetone/*n*-hexane) 0.13; mp 138–145 °C; $[\alpha]^{12}_D$ +45° (*c* 0.6, acetone); IR ($CHCl_3$) 2230, 1665, 1607, 1085, 1045 cm^{-1}; NMR ($CDCl_3$) δ 0.75–2.20 (m, 21 H), 2.20 (s, 3 H), 4.27 (d, J = 10 Hz, 1 H), 7.27 (A_2B_2, J = 8 Hz, $\Delta\nu$ = 18 Hz, 4 H), 7.62 (A_2B_2, J = 9 Hz, $\Delta\nu$ = 12 Hz, 4 H), 7.75 (s, 4 H).

(*S*,*R*)-11h: R_f (20/80 acetone/*n*-hexane) 0.18; NMR ($CDCl_3$) δ 0.75–2.2 (m, 21 H), 2.20 (s, 3 H), 4.67 (d, J = 5 Hz, 1 H), 7.00–7.95 (m, 3 × A_2B_2, 12 H).

When the reaction temperature was not very well controlled during the addition of the acid chloride, ketones **13** could be isolated.

13h: R_f (20/80 acetone/*n*-hexane) 0.36; mp k 139 n 153 i (138 s); IR ($CHCl_3$) 2230, 1677, 1609 cm^{-1}; NMR ($CDCl_3$) δ 0.7–2.4 (m, 20 H), 2.83 (d, J = 6 Hz, 2 H), 7.75 (s, 4 H), 7.90 (A_2B_2, J = 8 Hz, $\Delta\nu$ = 20 Hz, 4 H).

13d: R_f (10/90 Et_2O/*n*-hexane) 0.55; mp k 84 s_1 99 s_2 148.5 i; IR ($CHCl_3$) 1671, 1607 cm^{-1}; NMR ($CDCl_3$) δ 0.6–2.10 (m, 30 H), 2.68 (t, J = 7 Hz, 2 H), 2.85 (d, J = 6 Hz, 2 H), 7.50 (A_2B_2, J = 8 Hz, $\Delta\nu$ = 17 Hz, 4 H), 7.93 (A_2B_2, J = 8 Hz, $\Delta\nu$ = 20 Hz, 4 H). Anal. Calcd for $C_{30}H_{42}O$: C, 86.06; H, 10.11. Found: C, 85.83; H, 10.13.

13e: R_f (20/80 acetone/*n*-hexane) 0.67; mp k 75 s_1 78 s_2 123 i (55 s_3); IR ($CHCl_3$) 1670, 1604 cm^{-1}; NMR ($CDCl_3$) δ 0.7–2.1 (m, 22 H with t at 1.20, J = 7 Hz, 3 H), 2.72 (t, J = 7 Hz, 2 H), 2.90 (d, J = 6 Hz, 2 H), 3.27 (d, J = 6 Hz, 2 H), 3.50 (q, J = 7 Hz, 2 H), 7.55 (A_2B_2, J = 8 Hz, $\Delta\nu$ = 16 Hz, 4 H), 7.37 (A_2B_2, J = 8 Hz, $\Delta\nu$ = 21 Hz, 4 H).

Pyrolysis of β-Keto Sulfoxides. General Procedure. β-Keto sulfoxide (0.5–1.0 mmol.) and sodium bicarbonate (200 mg) in toluene (15 mL) were heated under reflux for 15–30 min. After filtration and solvent evaporation, the product was purified by chromatography (Kieselgel; eluent, 10/90 Et_2O/hexane). Quantitative yields were obtained.

(−)-(*S*)-12b: R_f (50/50 Et_2O/*n*-hexane) 0.60; oil; $[\alpha]_D$ −3.0° (*c* 0.9, acetone); IR ($CHCl_3$) 1659, 1615, 1593 cm^{-1}; NMR ($CDCl_3$) δ 0.7–2.6 (m, 11 H with t at 1.18, J = 7 Hz, 3 H), 3.27 (d, J = 6 Hz, 2 H), 3.47 (q, J = 7 Hz, 2 H), 3.73 (m, 1 H), 6.62 (s, 1 H), 7.72 (A_2B_2, J = 9 Hz, $\Delta\nu$ = 29 Hz, 4 H).

(+)-(*R*)-12c: [pyrolysis of the mixture of diastereoisomers, 20% ee] R_f (50/50 Et_2O/*n*-hexane) 0.44; mp 46 °C; $[\alpha]^{21}_D$ +4.8° (*c* 5.0, $CHCl_3$) [corrected to optically pure (*S*,*R*)-**11**; IR ($CHCl_3$) 2235, 1662, 1615 cm^{-1}; NMR ($CDCl_3$) δ 118 (t, J = 7 Hz, 3 H), 1.5–2.57 (m, 8 H), 3.28 (d, J = 5 Hz, 2 H), 3.48 (q, J = 7 Hz, 2 H), 3.80 (m, 1 H), 6.67 (s, 1 H), 7.97 (A_2B_2, J = 8 Hz, $\Delta\nu$ = 16 Hz, 4 H).

(+)-(*R*)-12d: R_f (50/50 Et_2O/hexane) 0.79; mp k 44 s_A 105 i; $[\alpha]^{21}_D$ +1.0° (*c* 0.6, $CHCl_3$); IR ($CHCl_3$) 1649, 1603 cm^{-1}; NMR ($CDCl_3$) δ 0.8–2.5 (m, 28 H), 2.63 (t, J = 7 Hz, 2 H), 3.60 (m, 1 H), 6.67 (s, 1 H), 7.45 (A_2B_2, J = 9 Hz, $\Delta\nu$ = 18 Hz, 4 H), 7.88

(11) Yields and diastereoisomeric ratios are listed in Table III.

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(A_2B_2, J = 8 Hz, $\Delta\nu$ = 22 Hz, 4 H).

(-)-(*S*)-**12e**: R_f (50/50 Et_2O/hexane) 0.65; mp k 43 s 63 c 67 i; $[\alpha]^{22}_D$ -0.6° (*c* 0.6, $CHCl_3$); IR ($CHCl_3$) 1652, 1603 cm^{-1}; NMR ($CDCl_3$) δ 0.8-2.5 (m, 20 H with t at 1.20, J = 7 Hz, 3 H), 2.68 (t, J = 7 Hz, 2 H), 3.30 (d, J = 5 Hz, 2 H), 3.50 (q, J = 7 Hz, 2 H), 3.70 (m, 1 H), 6.70 (s, 1 H), 7.45 (A_2B_2, J = 9 Hz, $\Delta\nu$ = 17 Hz, 4 H), 7.88 (A_2B_2, J = 8 Hz, $\Delta\nu$ = 21 Hz, 4 H).

(-)-(*S*)-**12f**: R_f (50/50 Et_2O/hexane) 0.66; mp k 65 c 124 i; $[\alpha]^{22}_D$ -3.9° (*c* 0.2, $CHCl_3$); IR ($CHCl_3$) 1655, 1608 cm^{-1}; NMR ($CDCl_3$) δ 0.7-2.60 (m, 19 H), 3.60 (m, 1 H), 3.87 (s, 3 H), 6.70 (s, 1 H), 7.33 (A_2B_2, J = 10 Hz, $\Delta\nu$ = 37 Hz, 4 H), 7.90 (A_2B_2, J = 8 Hz, $\Delta\nu$ = 23 Hz, 4 H).

(+)-(*R*)-**12g**: R_f (50/50 Et_2O/hexane) 0.55; mp k 102 s_A 123 i; $[\alpha]^{19}_D$ +2.5° (*c* 0.2, $CHCl_3$); IR ($CHCl_3$) 1652, 1605 cm^{-1}; NMR ($CDCl_3$) δ 0.87-2.5 (m, 26 H with t and 1.18, J = 7 Hz, 3 H), 3.27 (d, J = 5 Hz, 2 H), 3.48 (q, J = 7 Hz, 2 H), 3.65 (m, 1 H), 4.00 (t, J = 6 Hz, 2 H), 6.70 (s, 1 H), 7.30 (A_2B_2, J = 9 Hz, $\Delta\nu$ = 36 Hz, 4 H), 7.87 (A_2B_2, $\Delta\nu$ = 22 Hz, 4 H).

(-)-(*S*)-**12h**: R_f (50/50 Et_2O/hexane) 0.56; mp k 102 s 113 c 135 i; $[\alpha]^{21}_D$ -4.4° (*c* 0.6, $CHCl_3$); IR ($CHCl_3$) 2230, 1676, 1658, 1609 cm^{-1}; NMR ($CDCl_3$) δ 0.8-2.5 (m, 19 H), 3.60 (m, 1 H), 6.70 (s, 1 H), 7.77 (s, 4 H), 7.88 (A_2B_2, J = 8 Hz, $\Delta\nu$ = 24 Hz, 4 H).

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Registry No. **2a**, 94110-63-1; **2b**, 94110-64-2; **2c**, 94110-65-3; **2d**, 94110-66-4; **2e**, 94110-67-5; **2f**, 94110-68-6; **2g**, 94136-09-1; **2h**, 94110-69-7; **2i**, 94110-70-0; **6a**, 51638-45-0; **6b**, 94110-77-7; **7a**, 94110-78-8; **7f**, 82492-51-1; **7i**, 94110-79-9; **8b**, 97974-03-3; (*R*)-**9a**, 97974-04-4; (*R*)-**9b**, 94110-80-2; (*R*)-**9c**, 94110-81-3; (*R,R*)-**10a**, 97974-05-5; (*R,R*)-**10b**, 97974-07-7; (*R,R*)-**10c**, 97974-08-8; (*R,R*)-**10d**, 97974-09-9; (*R,R*)-**10e**, 97974-10-2; (*R,R*)-**10f**, 97974-11-3; (*R,R*)-**10g**, 97974-12-4; (*R,R*)-**10h**, 97974-13-5; (*S,R*)-**11a**, 97974-06-6; (*S,R*)-**11b**, 98048-31-8; (*S,R*)-**11c**, 98048-32-9; (*S,R*)-**11d**, 98048-33-0; (*S,R*)-**11e**, 98048-34-1; (*S,R*)-**11f**, 98048-35-2; (*S,R*)-**11g**, 98048-36-3; (*S,R*)-**11h**, 98048-37-4; (-)-(*S*)-**12b**, 94110-71-1; (+)-(*R*)-**12c**, 94110-72-2; (+)-(*R*)-**12d**, 94110-73-3; (-)-(*S*)-**12e**, 94110-74-4; (-)-(*S*)-**12f**, 94110-75-5; (+)-(*R*)-**12g**, 97974-18-0; (-)-(*S*)-**12h**, 94110-76-6; **13c**, 97974-14-6; **13d**, 97974-17-9; **13e**, 97996-90-2; **13h**, 97996-89-9; **14**, 98048-38-5; **15**, 97974-16-8; **16**, 97974-15-7; **17f**, 94110-68-6; **17h**, 97974-01-1; **17i**, 97974-02-2.

Thermolysis of 4-Methyl-4-(1-propenyl)malonyl Peroxide: Mechanistic Limits to Chemiluminescence Efficiency

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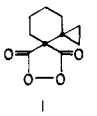
The preparation and thermal chemistry of 4-methyl-4-(1-propenyl)malonyl peroxide (**3**) is described. Thermolysis in acetonitrile at 84 °C gives 2,4-dimethylbut-2-en-4-olide in 45% yield and an oligomeric ester derived from an intermediate α-lactone in 55% yield. The reaction of **3** can be catalyzed by aromatic hydrocarbons such as perylene. Under these conditions weak chemiluminescence results. The mechanism for light generation is identified as chemically initiated electron-exchange luminescence (CIEEL). Application of the CIEEL mechanism to **3** reveals an important limitation to light generation by this path.

Chemical reactions that generate visible light often arouse interest. This phenomenon is observed to occur naturally in bioluminescent organisms[1] and it can be created synthetically in the laboratory.[2] The organic substances that are known to exhibit chemiluminescence with measurable efficiency are limited to structures containing a peroxide linkage. This constraint is related directly to the energy required to generate light. The exothermic conversion of the oxygen-oxygen bond of the peroxide to some other functional group is one of the few transformations capable of releasing sufficient energy to generate a visible photon.

Satisfaction of the energy requirement outlined above is necessary but not a sufficient criterion for the design of an efficient chemiluminescent reaction. Successful routing of the released energy to the creation of an electronically excited state product must also occur. The details of this routing are revealed by studying the mechanism of chemiluminescent reactions. Our previous efforts in this regard have revealed a general pathway we identified as chemically initiated electron-exchange luminescence (CIEEL).[3]

Malonyl peroxides are endowed with many of the features required for the efficient generation of chemical light by the CIEEL path.[4] In their simplest form, these substances lack an efficient path for energy release. Recently, we reported investigations of the chemiluminescence of cyclopropyl-substituted malonyl peroxide **1**[4] and 4-methyl-4-phenylmalonyl peroxide (**2**).[5] Both of these



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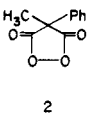

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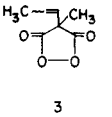

3

high-energy compounds do generate light by the CIEEL route. Herein we report our investigation of the thermal and chemiluminescent properties of 4-methyl-4-(1-propenyl)malonyl peroxide (**3**). This peroxide is weakly chemiluminescent. The investigation of **3** reveals clear mechanistic limits to light generation by the CIEEL route.

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