The spectral data were identical with those of authentic 1,1,3,3-tetraphenyl-1-butene.

Preparative Photolysis of (4-Diphenylyl)diphenylmethylpotassium. A solution of 1.23 g (3.84 mmol) of diphenylyldiphenylmethane in 30 mL of dimethyl sulfoxide was treated with 20 mL (4.00 mmol) of 0.20 M dimsyl potassium and the solution degassed in the manner previously described. The solution was irradiated for 96 h, i.e., until the purple color had been replaced by a light brown, the reaction quenched with 2 mL of water, and the solvent removed in vacuo. The extracted from ether washing of the residue was washed three times with water, dried, and concentrated. Recrystallization from methanol yielded light yellow crystals (1.02 g, 3.12 g, 82%). Recrystallization from hexane yielded 0.88 g of colorless prisms, mp 92–93 °C. The spectral data: NMR ($CDCl_3$) δ 2.21 (s, 3 H, CH_3), 6.9–7.6 (m, 19 H, aromatic); IR ($CDCl_3$) 3060, 3052, 2990, 1601, 1500, 1491, 1450, 1030, 1012, 762, 733, 698 cm^{-1}. Anal. ($C_{26}H_{22}$) C, H.

Competitive Irradiation Experiments. Solutions of mixtures of the anions were prepared analogously to those for preparative photolysis of individual anions, using a 50% excess of base over the amount required to quantitatively deprotonate the hydrocarbons. For the diphenylyldiphenylmethyl/triphenylmethyl experiments, additional filter solutions were used as described in Table I, and irradiations were carried out in 50-mL vessels for 12 h. For the tetraphenylallyl/triphenylmethyl experiments, the irradiations were carried out in 5-mL irradiation tubes, irradiations were carried out for 2 h, and identical tubes were arranged so as to ensure virtually identical light absorption throughout the irradiation. Analyses of the mixtures were performed by gas chromatography using independently prepared products to calibrate the chromatograph. The amounts of starting materials used and products formed are listed in the appropriate tables.

Acknowledgment. We acknowledge the Research Corporation and the Division of Chemical Sciences of the Department of Energy for support of this work.

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A Novel Cycloaromatization Reaction. Regiocontrolled Synthesis of Substituted Methyl Salicylates[1]

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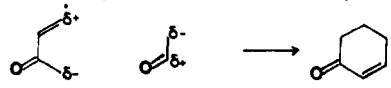
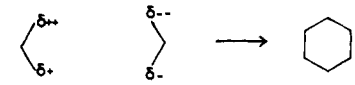
Abstract: A new method of constructing six-membered rings, involving the condensation of two three-carbon units, one with two nucleophilic sites and the other containing two electrophilic sites, is reported. The regiochemistry of the reaction is controlled by the differential reactivities of these sites. 1,3-Bis(trimethylsiloxy)-1-methoxybuta-1,3-diene (**1**) constitutes the three-carbon fragment with two nucleophilic sites. Condensation of **1** with various equivalents of β-dicarbonyl compounds and titanium tetrachloride gave substituted methyl salicylates. The regiochemistry is controlled by the order of reactivity of the electrophilic sites, which is conjugate position of enone > ketone > monothioacetal, acetal.

The two common methods of construction of six-membered rings (Diels–Alder and Robinson annelation) consist of the union of two framents, one with two carbon atoms and the other with four carbons. Regiochemistry in these reactions is essentially controlled by the direction of polarization within each fragment as represented schematically in eq 1 for the


(1)

Robinson annelation. In this paper we describe a new method of constructing six-membered rings, involving the condensation of two three-carbon units, one with two nucleophilic sites and the other containing two electrophilic sites. Furthermore, the regiochemistry of the reaction is controlled by the differential reactivities of these sites, as in eq 2.


(2)

Recently we reported in a preliminary communication[2] on the use of 1,3-bis(trimethylsiloxy)-1-methoxybuta-1,3-diene (**1**) as the equivalent of methyl acetoacetate dianion. It is evident from the reactions of **1** with a number of electrophiles that the nucleophilic site at C-4 is more reactive than that at C-2.[2] Compound **1** can therefore constitute one of the three-carbon

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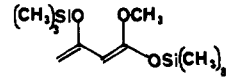
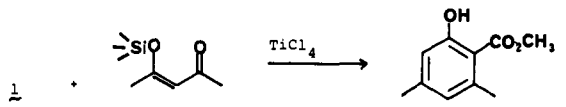


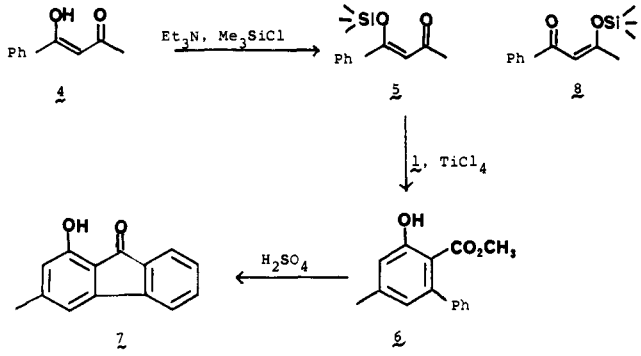
fragments of eq 2. We chose various equivalents of β-dicarbonyl compounds for the other three-carbon unit. Condensation of the two halves leads to cycloaromatization, resulting in a completely regiocontrolled synthesis of substituted methyl salicylates.

Compound **1** and 4-trimethylsiloxy-3-penten-2-one (**2**, obtained from acetylacetone) react in the presence of titanium tetrachloride[3] in dry dichloromethane at −78 °C to give methyl 4,6-dimethylsalicylate (**3**). Under these conditions, 2,4-pen-



tanedione itself, **1**, and titanium tetrachloride do not give an aromatic product, and only methyl acetoacetate and pentanedione are recovered on workup.[4]

Since this reaction does not show whether **1** initially attacks the carbonyl or silyl enol ether center of **2**, nor whether a β-silyloxy enone can be made regioselectively from an unsymmetrical β-diketone, we investigated enol silyl ether formation from benzoylacetone (**4**). With trimethylchlorosilane and base, **4** gave the β-siloxy enone **5**, which appears to be a mixture of geometric isomers but a single regioisomer from its ^{1}H NMR spectrum (chemical shifts similar to those of **4** itself[5]). Condensation of **5** and **1** gave only a single aromatic compound, **6** (mp 90.5–91.5 °C), whose regiochemistry was deduced from the high-field shift of the ester methyl group in its ^{1}H NMR spectrum (see Table I) due to the proximity of the phenyl group. This assignment was confirmed by conversion of **6** to the fluorenone **7** (mp 132–133 °C) under acidic con-

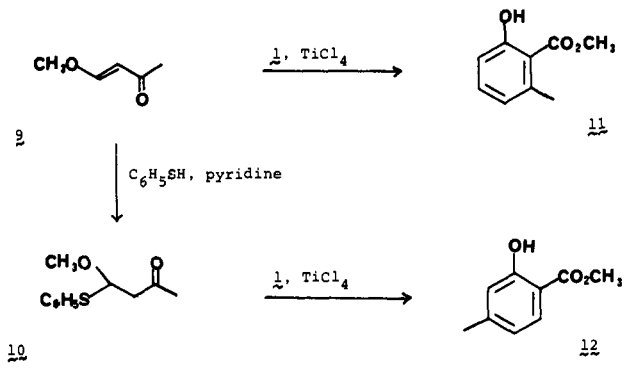


ditions. It seems that regioselective reaction can be achieved for unsymmetrical β-diketones, but the control is by no means obvious: either **1** reacts intially with the carbonyl group of **5**, or, if (as seems more likely from the reactions described below) the initial bond formation is to the β carbon of the enone, it appears that titanium tetrachloride must first cause isomerization of **5** to the regioisomer **8** (or its $TiCl_4$ complex).

We next examined the reaction of **1** with 4-methoxybut-3-en-2-one (**9**) and 4-methoxy-4-phenylthiobutan-2-one (**10**) and were pleased to find that the two electrophiles gave exclusively different regioisomers, **11** and **12**, respectively (Scheme I). In the condensation of **1** with **9**, because **9** is a very reactive compound and is polymerized readily by titanium tetrachloride, only a moderate yield (50%) of **11** was obtained.[6]

Mukaiyama has noted[3] that titanium dichlorodiisopropoxide (prepared by mixing equal amounts of titanium tetrachloride and tetraisopropoxide) is a more suitable catalyst for sensitive carbonyl compounds, and indeed we did find that this reagent gave a somewhat improved yield (59%). Nucleophilic addition of benzenethiol to **9** gives the β-oxo hemithioacetal **10**. Con-

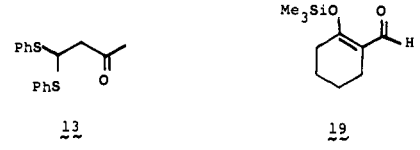
Scheme I



densation of **10** with **1** and titanium tetrachloride gave only the regioisomeric 4-methyl salicylate **12** (57%). However, the use of hemithioacetal as a carbonyl equivalent presents a problem because the liberated benzenethiol converted **10** under the reaction conditions to the dithioacetal **13**, which was also isolated. This problem has been circumvented by using β-keto acetals as indicated later.

It is evident from Scheme I that the order of reactivity of the electrophilic sites under titanium tetrachloride activation is conjugate position of enone > ketone > monothioacetal, acetal.[7] It is therefore possible to control completely the regiochemistry of the condensation. This is further demonstrated by the regiospecific synthesis of the isomeric tetralin derivatives **14** and **15** by elaboration of the same precursor, cyclohexanone (Scheme II).

Condensation of cyclohexanone enol silyl ether with methyl orthoformate and titanium tetrachloride produced the unstable β-oxo acetal **16**.[8] Reaction of **16** in situ with **1** and titanium tetrachloride gave **14** (41% overall). On the other hand, formylation of cyclohexanone and silylation of the hydroxymethylene product **17** to give β-siloxy enone **18** and reaction of this with **1** and titanium tetrachloride resulted in the regioisomeric tetralin derivative **15** (75%). Compounds **14** and **15** are easily differentiated by the aromatic proton signals in their ^{1}H NMR spectra. It is notable that, although **18** actually exists (as judged from its ^{1}H NMR spectrum) as a 4:1 mixture with the minor regioisomer **19** (−CH=O at δ 10.04), none of the product (**14**) expected from reaction of **19** with **1** is observed. This could be due to a vast difference in rate between



reaction of **18** and **19** with **1** and/or to isomerization of **19** to **18** by titanium tetrachloride.

Another way to control the regiochemistry is to start from isomeric carbonyl compounds. This is illustrated by synthesis of the phenanthrene derivatives **20** and **21**, starting from β- and

Scheme II

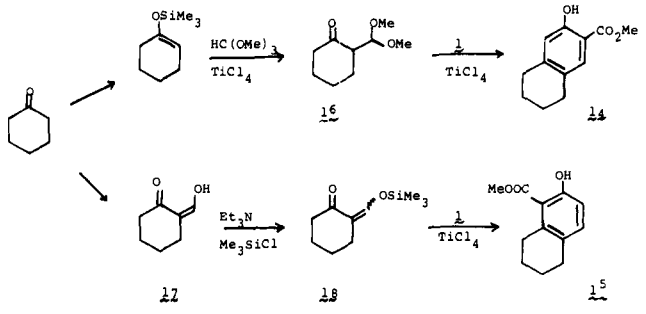
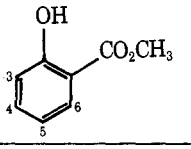


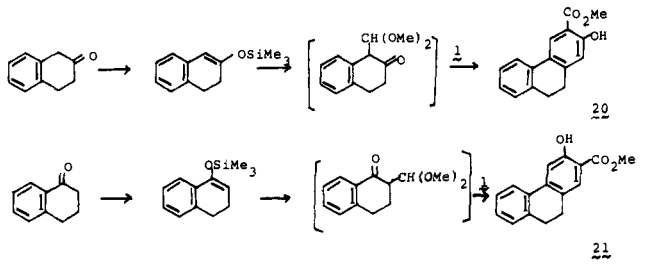
Table I. NMR Data for Salicylates[a]



compd	CO_2Me	4-Me	6-Me	3-H	4-H	5-H	6-H	OH	others
3	3.91	2.25	2.47	6.62 br[b]		6.50 br[b]		11.03	
6	3.38	2.30		6.68 br[b]		6.46 br[b]		10.61	7.15 br (5 H, Ph)
11	3.87		2.48	6.72 br[b] (d, J = 8)	7.17 (dd, J = 7.5, 8)	6.59 br[b] (d, J = 7.5)		11.00	
12	3.82	2.29		6.68 br		6.57 br (d, J = 8)	7.58 (d, J = 8)	10.68	
14	3.88			6.67			7.51	10.24	1.6-1.9 (4 H, β-CH_2), 2.5-2.9 (4 H, α-CH_2)
15	3.90			6.70 (d, J = 8.5)	7.07 (d, J = 8.5)			10.78	1.6-1.9 (4 H, β-CH_2), 2.55-3.1 (4 H, α-CH_2)
20	3.89			6.77[c]			8.10[d]	10.70	2.77 (4 H, CH_2), 7.1-7.4 (3 H, Ar), 7.5-7.8 (1 H[e])
21	3.85			7.26[d]			7.57[c]	10.58	2.75 (4 H, CH_2), 7.1-7.3 (3 H, Ar), 7.5-7.8 (1 H[e])
22	3.85	2.30		6.73 br[b]		6.52 br[b]		11.2 br	3.67 (3 H), 3.82 (2 H) (CH_2CO_2Me)

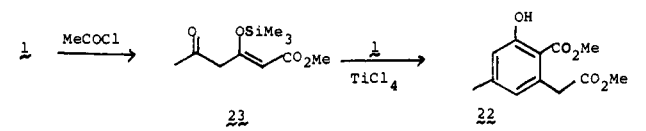
[a] Chemical shifts (δ) in $CDCl_3$. Peaks are singlets except where stated. Coupling constants in Hz. [b] These pairs of assignments may be reversed. [c] Phenanthrene H1. [d] Phenanthrene H4. [e] Phenanthrene H5.

Scheme III



α-tetralone, respectively (Scheme III). Our method may be useful for the synthesis of dihydrophenanthrene compounds with cytotoxic activity.[9]

An interesting variant on this cycloaromatization reaction was observed when **1** was reacted with acetyl chloride and titanium tetrachloride. A single aromatic product, **22**, was isolated. Although the yield was rather low (32%), **22** was obtained in a pure state simply by quenching the reaction mixture with aqueous sodium bicarbonate and extracting with ethyl ether. Presumably **22** is formed by acetylation of **1** to give **23**,



which then reacts with another molecule of **1**. The structure of **22** follows from its spectroscopic data; in particular it is shown to be a 4-methyl salicylate by the position of the aromatic methyl group in the ^1H NMR (δ 2.30). We have observed that a methyl group in the 4 position resonates at about δ 2.3, whereas the 6 position is deshielded by the ortho carboxylate group and a methyl in this position resonates at about δ 2.5 (see Table I). This regiochemistry for **22** is then explained by initial attack of **1** on the ketone group of **23**.

It is clear that the concept outlined in eq 2 is a viable one for the synthesis of cyclic compounds. There is no reason to believe that this strategy is limited to the synthesis of salicylates. We have evidence that substituted *o*-hydroxyacetophenones[10] and cyclic systems of more than six members[11] can be constructed by this approach.

Experimental Section

General. Melting and boiling points are uncorrected. Infrared spectra were obtained from films on NaCl plates for liquids and from solutions in 0.1-mm NaCl cells for solids, using a Perkin-Elmer 297 spectrophotometer. ^1H NMR spectra were recorded on Varian T-60 and T-60A instruments, with Me_4Si as internal standard. Mass spectra were obtained on a Hewlett-Packard 5984A or an LKB 9000 machine operating at 70 eV. Column chromatography was performed on silica gel 60 (Merck). Et_3N, *i*-Pr_2NH, and TMEDA were dried by distillation from CaH_2; hexane, CCl_4, and benzene from P_2O_5; CH_2Cl_2 from P_2O_5 and then from CaH_2. THF was distilled under nitrogen from sodium-benzophenone directly into the reaction vessel. Microanalyses were performed by Guelph Chemical Laboratories Ltd.

A. Synthesis of Silyl Enol Ethers. Cyclohexanone trimethylsilyl enol ether was prepared according to House.[12] Methyl acetoacetate was converted to methyl 3-trimethylsiloxybut-2-enoate by Danishefsky's method[13] in 85% yield, bp 71-72 °C (9 mm) [lit.[14] bp 67-68 °C (7 mm)]. NMR shows a 5:1 mixture of *E* and *Z* isomers: δ ($CDCl_3$) 0.28 (s, 9 H, Me_3Si), 1.90 (*Z*) and 2.27 (*E*) (each s, 3 H, MeC=C), 3.66 (s, 3 H, CO_2Me), 5.10 (*Z*) and 5.14 (*E*) (each s, 1 H, -CH=). IR (film): 1712, 1623 cm^{-1}.

(*E*)-1,3-Bis(trimethylsiloxy)-1-methoxybuta-1,3-diene[15,16] (1). Under nitrogen at 0 °C, to dry diisopropylamine (6.8 mL, 48 mmol) in dry THF (100 mL) was added *n*-BuLi (32 ml of 1.5 M in hexane, 48 mmol), followed by dry TMEDA (6.4 mL). The solution was cooled to −78 °C and methyl 3-trimethylsiloxybut-2-enoate (7.6 g, 40 mmol) was added. The yellow anion was quenched after 10 min with Me_3SiCl (8 mL). The mixture was allowed to warm to 0 °C and concentrated on the rotary evaporator. The residue was triturated with dry hexane (400 mL) with cooling to precipitate salts and filtered. The filtrate was concentrated (finally under high vacuum) to give **1** as a yellowish oil (9.6-10.3 g, 91-98%, >95% pure by NMR). **1** had NMR δ ($CDCl_3$) 0.15 (s, 9 H, Me_3Si), 0.19 (s, 9 H, Me_3Si), 3.50 (s, 3 H, OMe), 3.90 (d, 1 H, J = 1.5 Hz, HC=) 4.10 (d, 1 H, J = 1.5 Hz, HC=), 4.42 (s, 1 H, HC=); IR (film) 1647 cm^{-1}. In spite of the fact that NMR only indicates a single isomer, two peaks (ratio 1:3) are observed in the GC-MS (Hewlett-Packard 5984A machine; column 2 m of 5% OV101 on Chromosorb 750; column temperature 50 °C + 20 °C/min): minor (retention time 3.5 min) *m/e* (rel intensity) 260 (M^+, 9), 245 (71), 229 (16), 156 (35), 147 (47), 73 (100); major (retention time 3.8 min) 260 (M^+, 7), 245 (35), 229 (13), 147 (64), 73 (88), 67 (100).

4-Trimethylsiloxypent-3-en-2-one (2). To a vigorously stirred mixture of acetylacetone (32 g, 0.32 mol), dry triethylamine (32.3 g, 0.32 mol), and dry hexane (100 mL), trimethylchlorosilane (35 g, 0.32

mol) was added dropwise. After addition was complete the reaction mixture was shaken overnight and filtered with hexane washings. Evaporation of volatiles from the filtrate and distillation gave **2** as a colorless oil (45.5 g, 83%): bp 69–71 °C (8 mm) [lit.[18] 66–68 °C (4 mm)]; IR as reported;[18] NMR (a 73:27 mixture of *E* and *Z* isomers) in C_6D_6 similar to that reported in PhCl.[19]

4-Trimethylsiloxy-4-phenylbut-3-en-2-one (5). Prepared as for **2** above (0.05-mol scale), **5** (94%) was a colorless oil: bp 105–107 °C (0.15 mm) [lit.[20] 110–111 °C (0.2 mm)]; NMR ($CDCl_3$) a 3:1 mixture of isomers, δ 0.22 (minor) and 0.34 (major) (each s, 9 H, Me_3Si), 2.20 (minor) and 2.38 (major) (each s, 3 H, Me), 5.91 (minor) and 6.21 (major) (each s, 1 H, -CH=), 7.2–7.9 (m, 5 H, Ph); IR (film) 1658, 1598, 1586, 1574 cm^{-1}.

2-(Trimethylsiloxymethylene)cyclohexanone (18). To a suspension of hexane-washed sodium hydride (5.0 g, 0.208 mol) in dry Et_2O (700 mL) was added 12.5 mL of ethanol. After evolution of hydrogen had subsided, ethyl formate (16.7 mL, 0.208 mol) was added, followed by cyclohexanone (20.0 g, 0.204 mol) in dry Et_2O (100 mL). After 2 h of stirring, the mixture was acidified with dilute HCl, the organic layer was separated, the aqueous layer was extracted with Et_2O (2 × 50 mL), and the combined organic fractions were dried ($MgSO_4$). Removal of volatiles gave crude 2-(hydroxymethylene)cyclohexanone (**17**, 22.2 g). To a mixture of this with dry Et_3N (40 mL) and dry hexane (60 mL) was added dropwise Me_3SiCl (50 mL). The mixture was stirred overnight and filtered with hexane washings and volatiles were evaporated from the filtrate to give crude **18.** Distillation gave pure **18** as a yellowish oil (16.0 g, 40% from cyclohexanone): bp 131–135 °C (19 mm); NMR ($CDCl_3$) δ 0.28 (s, 9 H, Me_3Si), 1.6–2.0 (m, 4 H, β-CH_2), 2.1–2.6 (m, 4 H, α-CH_2), 7.42 (t, 0.8 H, *J* = 2 Hz, SiOC*H*=CH_2), 10.04 (s, 0.2 H, CHO of the regioisomer **19**); IR (film) 1682, 1667, 1633, 1593 cm^{-1}.

1-Trimethylsiloxy-3,4-dihydronaphthalene was prepared from α-tetralone by House's method[13] in 93% yield: bp 91–95 °C (0.6 mm) [lit.[21] 90–95 °C (1.5 mm)]; NMR ($CDCl_3$) δ 0.26 (s, 9 H, Me_3Si), 2.1–2.5 (m, 2 H, CH_2CH=), 2.6–3.0 (m, 2 H, ArCH_2), 5.13 (t, 1 H, *J* = 4.5 Hz, CH_2C*H*=), 7.0–7.5 (m, 4 H, Ar).

2-Trimethylsiloxy-3,4-dihydronaphthalene[22] was prepared from β-tetralone by Danishefsky's method[13] in 85% yield: bp 99–102 °C (0.7 mm); NMR ($CDCl_3$) δ 0.26 (s, 9 H, Me_3Si), 2.1–2.5 (m, 2 H, CH_2), 2.7–3.1 (m, 2 H, CH_2), 5.62 (s, 1 H, CH=), 6.8–7.1 (m, 4 H, Ar); IR (film) 1641 cm^{-1}.

B. Synthesis of Salicylates. Methyl 4,6-Dimethyl-2-hydroxybenzoate (3). To a mixture of **1** (1.04 g, 4 mmol) and **2** (0.69 g, 4 mmol) in dry CH_2Cl_2 (5 mL) under nitrogen at −78 °C was added $TiCl_4$ (0.45 mL, 4 mmol). The mixture immediately became dark red; after 3 h, it was added to aqueous $NaHCO_3$ and extracted with Et_2O. The extracts were dried ($MgSO_4$) and solvents evaporated to give **3** (0.51 g, 66%) as a colorless solid. One recrystallization from methanol gave large, colorless prisms, mp 79.5–80 °C (lit.[23] 79.5–80 °C).

Methyl 3-hydroxy-5-methyl(1,1′-biphenyl)-2-carboxylate (6) was prepared from **1** and **5** in a similar way to the above, except that after 1 h at −78 °C the mixture was kept at 0 °C for 3 h. The product was a 5:2 mixture of **6** and benzoylacetone (**4**); these were separated by column chromatography with CCl_4 as eluant to give recovered **4** (28%), R_f 0.26, and **6** (65%), R_f 0.36: mp 88–90 °C (raised to 90.5–91.5 °C by recrystallization from methanol); IR ($CHCl_3$) 3200 br, 1666, 1613, 1574 cm^{-1}; MS *m/e* (rel intensity) 242 (M^+, 25), 210 (100), 182 (31). No further conversion was observed when the reaction mixture was left overnight at room temperature. Anal. ($C_{15}H_{14}O_3$) C, H.

1-Hydroxy-3-methyl-9*H*-fluoren-9-one (7). **6** (60 mg, 0.25 mmol) was dissolved in concentrated H_2SO_4 (3 mL). After 1 h, the red solution was poured into ice water and extracted with Et_2O. The extract was dried ($MgSO_4$) and evaporated to give **7** as yellow needles (50 mg, 100%): mp 132–133 °C (from hexane); NMR ($CDCl_3$) δ 2.29 (s, 3 H, Me), 6.44 (s, 1 H, H2), 6.67 (s, 1 H, H4), 7.0–7.6 (m, 4 H, Ar), 7.74 (br s, 1 H, OH); IR ($CHCl_3$) 3420 br, 1685, 1630, 1603 cm^{-1}; MS *m/e* (rel intensity) 210 (M^+, 100), 182 (17). Anal. ($C_{14}H_{10}O_2$) C, H.

4-Methoxy-4-phenylthiobutan-2-one (10). Benzenethiol (39.7 g, 0.36 mol), **9** (36.1 g, 0.36 mol), dry CCl_4 (100 mL), and piperidine (0.3 mL) were stirred overnight at room temperature, the CCl_4 was evaporated, and the product was distilled, giving **9** (3.6 g, 10%), bp 35 °C (0.6 mm), and **10** (52.6 g, 70%), bp 125–127 °C (0.6 mm): NMR ($CDCl_3$) δ 2.10 (s, 3 H, MeCO), 2.82 (d, 2 H, *J* = 6.5 Hz, $COCH_2$), 3.45 (s, 3 H, MeO), 5.05 (t, 1 H, *J* = 6.5 Hz, C*H*CH_2), 7.2–7.6 (m, 5 H, Ph); IR (film) 1720 cm^{-1}; MS *m/e* (rel intensity) 210 (M^+, 95), 180 (100), 154 (92), 153 (96), 137 (94), 110 (83), 109 (86), 102 (85), 101 (47).

Methyl 2-Hydroxy-6-methylbenzoate (11). $TiCl_4$ (2.2 mL, 20 mmol) and Ti(O-*i*-Pr)$_4$ (6.0 mL, 20 mmol) were mixed under nitrogen (resulting volume 8 mL) and 1.0 mL (5 mmol) of the resulting $TiCl_2$(O-*i*-Pr)$_2$ was transferred rapidly to a stirred mixture of **1** (1.30 g, 5 mmol) and **9** (0.50 g, 5 mmol) in dry CH_2Cl_2 (10 mL) under nitrogen at −40 °C. After 1 h at −40 °C and 2 h at 0 °C, the mixture was poured into aqueous $NaHCO_3$ and extracted with Et_2O. The extracts were dried ($MgSO_4$), solvents were evaporated, and the residue was columned (CH_2Cl_2) to give **11** (0.49 g, 59%) as colorless leaves, mp 31–32 °C (lit.[24] 32 °C). Using $TiCl_4$ alone for this reaction (method as for **3**) gave **11** in 50% yield. $SnCl_4$ was also used as the Lewis acid, but the yield was somewhat lower.

Methyl 2-Hydroxy-4-methylbenzoate (12). Using **1, 10,** and $TiCl_4$ (4 mmol of each) as described for **3** gave after column chromatography with CCl_4 as eluant **12** (57% based on **10**) as a colorless oil (lit.[25] mp 27–28 °C) [R_f 0.28; mass spectrum *m/e* (rel intensity) 166 (M^+, 51), 134 (100)] and 4,4-di(phenylthio)butan-2-one (**13,** 86% based on **10**) [R_f 0.16; NMR ($CDCl_3$) δ 2.07 (s, 3 H, MeCO), 2.85 (d, 2 H, *J* = 6.5 Hz, $COCH_2$CH), 4.85 (t, 1 H, *J* = 6.5 Hz, C*H*CH_2), 7.0–7.5 (m, 10 H, Ph)]. GC–MS (see **1,** column temperature 130 °C + 16 °C/min) showed two peaks, both of which had M^+ corresponding to loss of benzenethiol from the di(phenylthio)ketone and were therefore probably geometric isomers of 4-phenylthiobut-3-en-2-one: major peak (retention time 4.9 min) *m/e* (rel intensity) 178 (M^+, 62), 163 (100), 135 (35), *m/e* (isobutane chemical ionization) 179 (MH^+); the minor peak (retention time 5.1 min) had similar EI and CI spectra.

Methyl 3-Hydroxy-5,6,7,8-tetrahydronaphthalene-2-carboxylate (14). To trimethyl orthoformate (0.53 g, 5 mmol) in dry CH_2Cl_2 (5 mL) under nitrogen at −78 °C were added $TiCl_4$ (0.56 mL, 5 mmol) and cyclohexanone silyl enol ether (0.85 g, 5 mmol). After 2 h at −78 °C[26] a further 0.56 mL of $TiCl_4$ was added, followed by **1** (1.30 g, 5 mmol) in dry CH_2Cl_2 (5 mL). After a further 2 h at −78 °C and 4 h at −23 °C the mixture was worked up as for **3**; column chromatography with CH_2Cl_2 as eluant gave **14** (0.42 g, 41%), colorless plates, mp 40–42 °C (lit.[27] 42 °C), R_f 0.70. No trace of **15** was observed.

Methyl 2-hydroxy-5,6,7,8-tetrahydronaphthalene-1-carboxylate (15) was prepared from **1** and **18** as described for **3.** The product was purified by column chromatography (CH_2Cl_2) to give **15** (75%), mp 41–42 °C (lit.[28] 42–43 °C), R_f 0.72. No trace of **14** was observed.

Methyl 2-hydroxy-9,10-dihydrophenanthrene-3-carboxylate (20) was prepared from β-tetralone silyl enol ether, trimethyl orthoformate, and **1** as described for **14,** except that the mixture was stirred overnight at room temperature. Column chromatography with CH_2Cl_2 as eluant gave **20** (72%) as colorless needles: mp 78–78.5 °C (from cyclohexane); R_f 0.66; IR ($CHCl_3$) 3200 br, 1676 cm^{-1}; MS *m/e* (rel intensity) 254 (M^+, 91), 222 (100), 194 (8), 165 (88). Anal. ($C_{16}H_{14}O_3$) C, H. The identity of this compound was confirmed by hydrolysis to the known acid: 2-hydroxy-9,10-dihydrophenanthrene-3-carboxylic acid had mp 218–219 °C (from $CHCl_3$) (lit.[29] 219–220 °C); NMR [$(CD_3)_2CO$] δ 2.82 (s, 4 H, CH_2), 6.80 (s, 1 H, H-1), 7.1–7.4 (m, 3 H, Ar), 7.6–7.8 (m, 1 H, H-5), 8.22 (s, 1 H, H-4), 10.0 (v br, 2 H, OH). No isomeric products were observed.

Methyl 3-hydroxy-9,10-dihydrophenanthrene-2-carboxylate[30] **(21)** was prepared as described for **20,** using α-tetralone silyl enol ether, in 31% yield after column chromatography eluted with CH_2Cl_2, as yellow plates: mp 130.5–131 °C (from cyclohexane); R_f 0.67; IR ($CHCl_3$) 3210 br, 1675 cm^{-1}; MS *m/e* (rel intensity) 254 (M^+, 94), 222 (100), 194 (24), 165 (82). Anal. ($C_{16}H_{14}O_3$) C, H. No isomeric products were observed.

Methyl (3-Hydroxy-2-methoxycarbonyl-5-methylphenyl)acetate (22). To a well-stirred mixture of acetyl chloride (0.315 g, 4 mmol), $TiCl_4$ (0.44 mL, 4 mmol), and dry CH_2Cl_2 (4 mL) under nitrogen at −78 °C was added **1** (1.04 g, 4 mmol). After 3 h the mixture was worked up as for **3.** Evaporation of the Et_2O extracts gave colorless needles of **22** (0.15 g, 32%): mp 82–83 °C (after one recrystallization from cyclohexane); IR ($CHCl_3$) 3440 br, 1734, 1668, 1627, 1576 cm^{-1}; MS *m/e* (rel intensity) 238 (M^+, 57), 207 (30), 206 (80), 179 (54), 178 (100), 174 (64), 163 (88). Anal. ($C_{12}H_{14}O_5$) C, H.

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The Bicycle Rearrangement. Relationship to the Di-π-methane Rearrangement and Control by Bifunnel Distortion. Mechanistic and Exploratory Organic Photochemistry[1,2]

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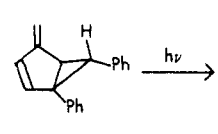
Abstract: The generality of the bicycle rearrangement was extended and the mechanism was further investigated by study of the photochemistry of 3,4-benzo-2-methylene-6,6-dimethylbicyclo[3.1.0]hex-3-ene, 2,2-dimethyl-1-methylene-1,2-dihydronaphthalene, 4,4-dimethyl-1-methylene-1,4-dihydronaphthalene, 2,2-dimethylspiro[cyclopropan-1,1′-indene], and 1,1-dimethyl-2-methylene-1,2-dihydronaphthalene. Direct irradiation of the benzobicyclohexene led to the spiroindene as the major product with a quantum yield of 0.040. The minor photoproduct was the 2,2-dimethyldihydronaphthalene, formed with a quantum yield of 0.0033. Both products arise from a mechanism in which the isopropylidene moiety bicycles along the 1-methylenindene π system. The 2,2-dimethyldihydronaphthalene derives from an intermediate cyclopropyldicarbinyl diradical, arising in the bicycling process, opening its three ring. Irradiation of the 2,2-dimethyldihydronaphthalene led exclusively to the benzobicyclohexene without formation of the spiroindene isomer; the efficiency here was 0.086. This reaction is only formally the reverse of the benzobicyclohexene photolysis and utilizes a different state of the cyclopropyldicarbinyl diradical as an intermediate. The lack of formation of spiroindene product from the 2,2-dimethyldihydronaphthalene is discussed in terms of a distorted bifunnel effect. The photolysis of the 4,4-dimethyldihydronaphthalene led to the benzobicyclohexene with an efficiency of 0.22; here, again, a bicycle mechanism is used. The spiroindene isomer and the 1,1-dimethyldihydronaphthalene were unreactive. Also, the triplets throughout were unreactive. Singlet excited state rate constants were derived for each of the reactions. Correlation diagrams, consisting of a triptych with benzobicyclohexene, dihydronaphthalene, and spiro compound at the three branches, reveal a HOMO–LUMO crossing on the benzobicyclohexene branch. The positioning of the crossing, again, accounts for the unidirectionality of the reactions. At the SCF-CI level a distorted bifunnel was encountered and the hypersurfaces concur in predicting the photochemistry. The distorted funnel concept was developed along with other related photochemical theory.

Introduction

Present-day photochemistry has two main objectives. One is the quest for new and general types of photochemical reactions. The other is the search for theory elaborating the factors controlling excited-state transformations. Among the reactions we have been subjecting to study, the bicycle rearrangement[3] is one of the most fascinating, both because of its generality and also because of its utility in defining new photochemical theory.

Equation 1 describes a typical example of the photochemical bicycle rearrangement, an example of particular interest because the reaction is seen to be stereospecific. One of our main



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