sodium hydrosulfite in 30 mL of water was heated at reflux for 5 h. After cooling, the solution was saturated with potassium carbonate, extracted with 250 mL of chloroform, dried (sodium sulfate), and concentrated to give 1.05 g (44.4%) of **6** as an off-white solid, mp 110–115 °C. Two recrystallizations from chloroform/hexane afforded white crystals: mp 114–116 °C; IR (KBr) 1730 (ester C=O), 1625 (C=N), and 1540 cm^{-1} (C=C); UV max (CH$_3$OH) 225 nm (ϵ 12 300); NMR (CDCl$_3$) δ 10.62 (s, 1, NH), 3.61 (s, 3, COOCH$_3$), 2.85–2.18 and 1.97–1.49 ppm (m, 16, CH$_2$); mass spectrum *m/e* 236 (M$^+$).

Anal. Calcd for $C_{13}H_{20}N_2O_2$: C, 66.08; H, 8.53; N, 11.85. Found: C, 65.83; H, 8.53; N, 11.37.

Reaction of 2-Methoxy-3-oximinocyclohexene (8) with Methyl ω-Oximinocaproate (12). Hydrogen chloride was bubbled for 10–25 s through a solution of 0.710 g (5.00 mmol) of **8** and 0.800 g (5.00 mmol) of **12** in 50 mL of liquid sulfur dioxide at −10 °C. After stirring for 3 h, the sulfur dioxide was replaced by chloroform, and the solution was neutralized with ammonia, filtered, and evaporated to give 1.17 g (87.4%) of **3a**, mp 175–179 °C.

Reaction of 2,2-Dimethoxycyclohexanone Oxime (9)^5 with Methyl ω-Oximinocaproate (12).^{2} The same procedure was used as above to give **3a** in a 48.4% yield. **Reaction of 2-oximinocyclohexanone (10)^6 with Methyl ω-Oximinocaproate (12).** The same procedure as above was used to give **3a** in a 52.4% yield.

Reaction of 2-Methoxy-3-oximinocyclohexene (8) with Hydrogen Chloride. Using the same procedure as above, except in the presence of an equimolar amount of methanol, **8** was quantitatively recovered unchanged from the reaction mixture. The same result was obtained when hydrogen chloride was passed over the surface of a paste of **8** and methanol.

Reaction of 2,2-Dimethoxycyclohexanone Oxime (9) with Hydrogen Chloride. When the same procedure as above was used but in the absence of methanol, **9** was quantitatively converted into **8**. When hydrogen chloride was passed over the surface of solid **9**, **8** was obtained in an 85% yield.

Reaction of 2-Oximinocyclohexanone (10)^6 with Hydrogen Chloride. The same procedure as above was used in the presence of an equimolar amount of methanol to give **8** as the main product. When hydrogen chloride was passed over the surface of a paste of **8** and water, only tars were formed.

1-Hydroxy-2,4,5-trimethylimidazole 3-Oxide (13). A. Via Biacetyl Monoxime.^{7} Hydrogen chloride was passed over 10.0 g (99.0 mmol) of solid biacetyl monoxime for 45 min. Initially, an exothermic reaction occurred and within 10 min the solid mass was completely converted into a yellow-orange liquid. After cooling, the liquid was extracted with ether and analysis of the other solution by GLC and mass spectrometry showed only acetic acid. The oil was dissolved in chloroform and after neutralization with ammonia and filtration, evaporation of the filtrate afforded 4.00 g (56.3%) of crude **13**, mp 183–187 °C dec (lit. 203 °C dec,^{7} 189 °C dec.^{4} The structure was confirmed by IR and NMR.^{4}

B. Via Biacetyl Monoxime and Acetaldoxime. Hydrogen chloride was bubbled for 10 s through a solution of 0.510 g (5.00 mmol) of biacetyl monoxime and 0.300 g (5.00 mmol) of acetaldoxime in 50 mL of sulfur dioxide at −10 °C. Workup as above gave 0.530 g (74.8%) of **13**, mp 195–196 °C dec.

Attempts to prepare **13** by bubbling hydrogen chloride through a solution of biacetyl monoxime in sulfur dioxide, or biacetyl monoxime and acetonitrile in sulfur dioxide, gave a nearly quantitative recovery of starting materials.

1-Hydroxy-2-*n*-propyl-3,4-dimethylimidazole 3-Oxide (15). Compound **15** was prepared from *n*-butyraldoxime and biacetyl monoxime as above (method B) in a 78.6% yield, mp 171–175 °C dec. Two recrystallizations from ethanol gave a white solid: mp 178.5–179.5 °C dec; IR (KBr) 3450 (OH), 1632 (C=C or C=N), and 1300–1200 cm^{-1} (nitrone); NMR (Me$_2$SO-d_6) δ 10.93 (s, 1, OH), 2.74–2.53 (t, 2, CH$_2$C=C), 2.00 (s, 6, CH$_3$), 1.73–1.43 (m, 2, CH$_2$), and 0.92–0.71 ppm (t, 3, CH$_3$CH$_2$); mass spectrum *m/e* 170 (M$^+$).

Anal. Calcd for $C_8H_{14}N_2O_2$: C, 56.45; H, 8.29; N, 16.46. Found: C, 56.48; H, 8.65; N, 16.08.

Registry No.—**1**, 62344-90-5; **3a**, 62549-82-0; **3b**, 62549-83-1; **4**, 62549-84-2; **5**, 62549-85-3; **6**, 62549-86-4; **8**, 52841-56-2; **9**, 52540-36-0; **10**, 24858-28-4; **12**, 62344-93-8; **13**, 2654-28-6; **15**, 41933-67-9; methanol, 67-56-1; cyclohexanone, 108-94-1; nitrosyl chloride, 2696-92-6; ethanol, 64-17-5; biacetyl monoxime, 57-71-6; acetaldoxime, 107-29-9; butyraldoxime, 110-69-0.

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(10) For NMR purposes, an aliquot was withdrawn at this point and sealed in a tube. The reaction was then followed by NMR by gradually raising the probe temperature.
(11) Higher yields of **3a** could be obtained by titrating the methanol solution directly with a methanolic 3 N sodium hydroxide solution.
(12) The procedure used was similar to that used by Wright (see ref 4).

Oxidation of Dibenzothiophene and Reaction of Dibenzothiophene 5,5-Dioxide with Aqueous Alkali

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Dibenzothiophene (1) has been oxidized with hydroperoxides, with hydroperoxides and catalysts, and with air in the presence of an organic solvent. The dibenzothiophene 5,5-dioxide (2) produced was converted to sodium 2-phenylphenolate (4) by reaction with aqueous alkali at 300 °C.

Thiophenes and condensed thiophenes are resistant to thermal extrusion of sulfur^{1,2} and the reaction of these structures under acidic or basic conditions seems unattractive as a route to sulfur-free products.^{3} However, unlike thiophenic systems, aliphatic sulfones form alkenes when treated with alkali at elevated temperatures.^{4} Wallace^5 found the general order of reactivity for a series of aliphatic sulfur derivatives toward elimination with potassium *tert*-butoxide to be sulfone > sulfoxide ≫ sulfide.

The decomposition of dibenzothiophene 5,5-dioxide (2) with alkali was noted by Weissgerber and Kruber^6 and Courtot and Chaix.^{7} Heimlich and Wallace^8 studied the

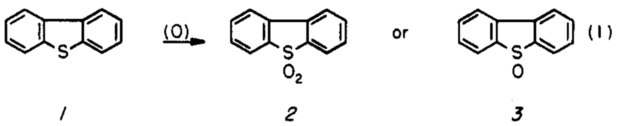
Table I. Oxidation of Dibenzothiophene (1) with Hydroperoxides[a]

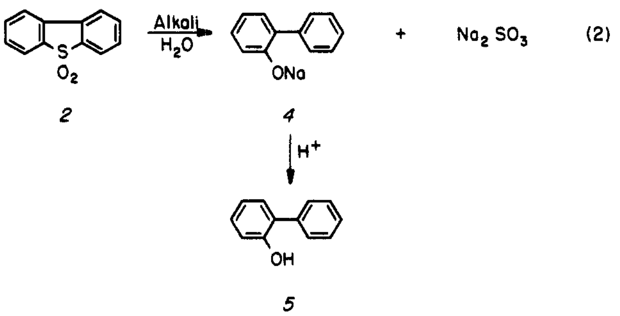
Hydroperoxide	Catalyst	mmol of catalyst	Product	Yield, %[b]
tert-Butyl	None		3	9[c]
tert-Butyl	$Mo(CO)_6$	1.9	2	98
tert-Butyl	$Mo(CO)_6$	0.019	2	98
tert-Butyl	MoO_3	1.9	2	98
Cumene	None		1	70[d]
Cumene	$Mo(CO)_6$	1.9	2	92
Cumene	V_2O_5	2.75	2	60[e]
Tetralin	None		3	45[f]
Tetralin	$Mo(CO)_6$	1.9	2	77
Tetralin	$Mo(CO)_6$	1.9	2	98[g]
Tetralin	V_2O_5	2.75	2	50[e]
Tetralin	MoO_3	3.4	2	68[e]
Tetralin	$Zr(O_2C_5H_7)_4$	1.0	2	73[h]

[a] The experiments were carried out for 6 h using dibenzothiophene (11 mmol) and hydroperoxide (22 mmol) in 100 mL of refluxing toluene. [b] Isolated product yields. [c] Trace amounts of 2 were present. [d] 2 or 3 could not be isolated after cooling, addition of petroleum ether, or fractional crystallization. [e] Trace amounts of 3 were present. [f] 21% of 2 was also formed. [g] Room temperature for 21 h. [h] *tert*-Butyl alcohol as solvent; room temperature for 24 h.

mechanism of oxidation of dibenzothiophene (1) in white oil with aqueous hydrogen peroxide–acetic acid mixtures, and Wallace and Heimlich[3] studied the mechanism of reaction for the alkaline decomposition of sulfone 2 and related compounds in white oil. The alkaline decomposition results indicate that the stability of the debenzothiophene nucleus is dependent on the oxidation state of the sulfur atom.[3] The percentage of sulfur-containing and sulfur-free products from the decomposition of sulfone 2 varied with the ratio of the base to 2, temperature, and reaction time. They observed the formation of 18% sodium-2-phenylbenzenesulfonate, 58% sodium-2-phenylphenolate (4), 2% biphenyl, and 19.5% dibenzofuran when sulfone 2 was treated with sodium hydroxide in white oil at 300 °C for 4 h. After similar treatment for 5.5 h, only sulfur-free products, 5% biphenyl and >90% dibenzofuran, were observed.

The present study explored the use of numerous reagents for oxidation of 1 (eq 1) and the aqueous, alkaline decomposition of 2 (eq 2). The investigation originated as a model compound study aimed toward desulfurization of coal and high molecular weight fractions from crude oil. Beneficiation of fossil fuels prior to combustion or removal of the atmospheric pollutants after combustion is recognized as the major environmental problem associated with the utilization of coal and residual fuel oil to meet fuel energy demand.[9,10] The sulfur in coal is generally classified as either inorganic or organic. Physical and chemical treatments that can remove much of the inorganic sulfur in coal have been reported.[10–12] The sulfur-containing organic structures of coal have not been well characterized, but numerous suggestions have appeared.[13] Substituted thiophenic structures have been suggested as one of the more probable resistant forms of organic sulfur in coals. These are resistant to thermal degradation, and when reaction does occur, the thiophene ring system gives a fair proportion of more highly condensed structures containing the original ring system.[2,13] The relative inertness of some of the organic sulfur in coal, the inferred polycyclic structure of coals, and the presence of condensed thiophenic structures in coal tar[6,13,14] are consistent with the selection of 1 as a model compound for a portion of the organic sulfur in coal.





Results and Discussion

To utilize an oxidation–alkali treatment approach as a practical sulfur extrusion method for condensed thiophenic systems in coal, a high yield, economical, rather specific oxidative technique for the organic sulfur should be available. Numerous procedures are known for the oxidation of sulfides;[15] however, thiophenic sulfur is resistant to oxidation under many of these conditions. Our results confirm and extend the work of Tolstikov[15] that notes the catalyzed hydroperoxide oxidation of benzothiophene derivatives to the corresponding sulfoxides or sulfones. Sulfone 2 was first prepared by the method of Gilman and Esmay,[16] but to develop an oxidation procedure, practical on a large scale, several methods were studied. Air should be the oxidant of choice for a commercial process. Nonetheless, the preparation of 2 was investigated by the reaction of 1 with hydroperoxides and hydroperoxides with catalysts as well as with air in the presence of an organic solvent.

Uncatalyzed reaction of 1 with *tert*-butyl hydroperoxide or tetralin hydroperoxide produced mainly dibenzothiophene 5-oxide (3), but 2 or 3 could not be isolated from the uncatalyzed reaction of 1 with cumene hydroperoxide. All experiments utilizing molybdenum hexacarbonyl or several other catalysts with the above hydroperoxides produced 2. These results are summarized in Table I. The tetralin hydroperoxide (approximately 30%) was prepared by bubbling air through tetrahydronaphthalene maintained at 70 °C. When 1 was added at the beginning of a tetralin hydroperoxide preparation (hydroperoxide formed ≫ 1 present) carried out for 96 h, approximately 30% of 1 was converted to a mixture of 2 and 3.

When an organic solvent capable of hydroperoxide formation, such as tetralin, decalin, or cyclohexane, was heated in an autoclave with 1 and compressed air, a large exotherm (starting at about 130 °C and resulting in observed temperature excursions of up to 80 °C in less than 2 min) was observed. The resulting reaction mixture contained solvent oxidation products, but little or no oxidized 1. Two methods were devised to overcome this behavior, which was interpreted to indicate the rapid formation and decomposition of solvent hydroperoxides. The first method required very careful temperature control, and involved interrupting the autoclave heating at about 130 °C, allowing the temperature to increase, and controlling the subsequent exotherm by means of cooling water in an internal cooling coil. Thus, by using this method, 1 with cyclohexane, methylcyclohexane, or *n*-heptane at 200 °C in the presence of compressed air gave a good yield of 2. A second method of regulating the reaction was by use of benzene as an inert diluent. With benzene as solvent, little or no 2 formed, but in a solvent mixture of benzene and tetralin or

Table II. Oxidation of Dibenzothiophene (1) with Air

Air, psi	Solvent (mL)	Solvent (mL)	Time, h	% yield of 2[a]
700	Cyclohexane (100)		6	>90[b,c]
700	Cyclohexane (100)		3[d]	0
800	Benzene (100)		5	<1[e]
770	Methylcyclohexane (100)		0.2	80[c]
800	*n*-Heptane (100)		0.3	80[c]
850	Benzene (90)	Tetralin (10)	1	67
850	Benzene (90)	Tetralin (10)	2	72
850	Benzene (90)	Tetralin (10)	4	86[c]
820	Benzene (90)	Tetralin (10)	5	>90
800	Benzene (80)	Cyclohexane (20)	3	25[f]
850	Benzene (50)	*tert*-Butyl alcohol (50)	0.2	60

[a] Gas chromatographic yields. [b] 1 (1 g, 5.4 mmol) used; all other reactions used 2.0 g (10.8 mmol) of 1. [c] Exotherm; temperature exceeded that reported for a short period of time. [d] Reaction temperature of 125 °C; all other reactions at 200 °C; however, refer to c. [e] Benzene oxidation products formed (e.g., biphenyl). [f] 15% 3 also formed.

benzene and *tert*-butyl alcohol, a good yield of 2 was realized. The reaction probably first involved combination of oxygen with solvent to form a hydroperoxide, followed by reaction with 1 to produce sulfoxide 3, and after further reaction, sulfone 2.[17] The data are summarized in Table II. This oxidation technique should be applicable to the formation of hydroperoxide intermediates and their uncatalyzed in situ use to oxidize a variety of thiophenic and other difficultly oxidizable sulfur-containing structures to the corresponding sulfones. This procedure has also been applied to the oxidation of organic sulfur in fossil fuels. Those results will be reported in a subsequent paper.

The nonaqueous reaction of 2 with alkali has been previously noted.[3,6,7] For effective contact of the alkaline reagents with the organic sulfur of coal or a water-insoluble compound, a reaction medium capable of dissolving the alkali should be beneficial. Accordingly, the model compound study of 2 with aqueous alkali was carried out. Treatment of 2 with aqueous sodium hydroxide at elevated temperatures was accomplished in a stirred autoclave. The major product isolated from the neutralized reaction mixture was 2-phenylphenol (5), consistent with one of the products previously isolated from alkaline fusion reactions.[6] Experiments were completed using a number of other aqueous alkaline mixtures and in each case phenol 5 was observed. Analysis of the aqueous layer shortly after workup revealed the presence of sulfur primarily as sulfite. A small amount of sulfate (probably formed from the oxidation of sulfite during workup) was also found to be present. Although a 5-h reaction time was standard for the alkali treatment of 2 at 300 °C, the reaction proceeds rapidly. At 200 °C the reaction of 2 with aqueous sodium hydroxide was quite slow. These results are summarized in Table III.

Experimental Section

Melting points are uncorrected. Infrared spectra were recorded using a Perkin-Elmer 521 spectrometer[18] and all GC analyses were accomplished using a Hewlett-Packard 7620A research chromatograph equipped with a 10 ft × 0.125 in. 3% Apiezon L on Chromosorb G column. Commercial samples of most reagents were employed. We thank Climax Molybdenum Co. for a generous sample of molybdenum hexacarbonyl and Oxirane Chemical Co. for a generous sample of *tert*-butyl hydroperoxide. Tetralin hydroperoxide[19] was prepared by passing a stream of air through tetrahydronaphthalene maintained at 70 °C. All hydroperoxides were analyzed for active oxygen content prior to use. The iodometric method combined with an electrometric end point detection procedure[20] was used to determine the percentage of hydroperoxide present.

The following experimental procedures are representative of those used in the hydroperoxide and air oxidation of 1 as well as the alkaline reaction of 2.

***tert*-Butyl Hydroperoxide Oxidation of Dibenzothiophene (1) with Molybdenum Hexacarbonyl as Catalyst.** A solution of 2.02 g (11.0 mmol) of 1, 5.0 mg (0.019 mmol) of $Mo(CO)_6$, and 2.75 g (22.0 mmol) of 72% *tert*-butyl hydroperoxide in 100 mL of toluene was stirred at reflux under nitrogen for 6 h. (If larger amounts of $Mo(CO)_6$ catalyst are used, a blue solid may precipitate and must be filtered off before isolating the product.) The pale yellow solution was cooled in the refrigerator overnight and a colorless solid separated. [Removal of toluene and/or addition of petroleum ether (bp 38–47 °C) was usually necessary to obtain complete separation of 2 or 3 in those reactions utilizing cumene hydroperoxide or tetralin hydroperoxide.] The product was filtered off and dried under vacuum to give 2.30 g (98%) of colorless 2, mp 232–234 °C (lit.[16] mp 232–233 °C). The infrared spectrum (KBr disk) of the product was identical with that of authentic 2 and a mixture melting point of the product with an authentic specimen of 2 was not depressed.

Table III. Reaction of Dibenzothiophene 5,5-Dioxide (2) with Alkali[a]

Alkali	mmol alkali	% 2 recovered	% 2-phenylphenol (5)[b]
None[c]		53	0[d]
NaOH	83	0	100
NaOH	83	0	99[e]
NaOH	83	0	98[f]
NaOH	83	89	4[g]
NaOH	33.2	0	84
NaOH	16.6	26	61
CaO	83	76	15
Na_2CO_3	83	0	89
Na_2CO_3	33.2	0	81
Na_2CO_3	16.6	0	84
Na_2CO_3	8.3	29	61

[a] 2 (3.6 g, 16.6 mmol) used in all reactions; alkali in 125 mL of H_2O; reaction time 5 h and temperature 300 °C unless otherwise noted. [b] Isolated yields; sulfur present after reaction primarily as SO_3^{2-}. [c] Temperature was 410 °C. [d] 41% 1 isolated. [e] Reaction time 1 h at temperature. [f] Reaction mixture heated to 300 °C and cooled immediately. [g] Reaction time 1 h at 200 °C.

Air Oxidation of Dibenzothiophene (1) in Tetralin–Benzene. Compound 1 (2.0 g, 10.8 mmol) was dissolved in a mixture containing 90 mL of benzene and 10 mL of tetralin and the resulting solution was added to the liner of a stainless steel stirred autoclave. The system was pressurized to 820 psi with air and the reaction mixture was stirred and heated at 200 °C for 5 h. After cooling to room temperature, the autoclave was vented and the resulting solution was analyzed directly by GC analysis (comparison against known concentrations of authentic mixtures indicated that a nearly quantitative conversion of 1 to 2 occurred). The solvent was removed by use of a rotary evaporator (steam bath) and 20 mL of 2-propanol was added to the residue obtained. The sulfone crystallized and was filtered off. The infrared spectrum (KBr disk) of the crude product was identical with that of authentic 2 and a mixture melting point of the product with an authentic specimen of 2 was undepressed at 232–234 °C.

Decomposition of Dibenzothiophene 5,5-Dioxide (2) with

Aqueous Sodium Hydroxide. To the liner of a stainless steel autoclave was added 3.6 g (16.6 mmol) of **2** and 125 mL of H_2O containing 3.4 g (83 mmol) of NaOH. The mixture was stirred under nitrogen for 5 h at approximately 300 °C. The autoclave was cooled to room temperature and vented, and the reaction products were removed by pipet. The autoclave liner and stirrer were rinsed with three 50-mL portions of $CHCl_3$. The aqueous alkaline reaction mixture was neutralized (pH 7) with 2 N HCl and extracted three times with 50-mL portions of $CHCl_3$ rinse from above. The $CHCl_3$ extracts were combined, dried (Na_2SO_4 and decolorizing carbon), and filtered. After removal of solvent from the dried solution, 2.82 g (100 mol %) of nearly colorless, crystalline **5** was isolated, mp 54–56 °C (lit.[21] mp 57–58 °C). The infrared spectrum of the product (KBr disk) was identical with that of authentic **5** and a mixture melting point of the product with an authentic specimen of **5** was not depressed. Recrystallization of the product from petroleum ether gave 2.75 g of product, mp 56–57 °C.

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Registry No.—**1**, 132-65-0; **2**, 1016-05-3; **5**, 90-43-7.

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Diterpenoid Total Synthesis, an A → B → C Approach. 9. Structure and Stereochemistry of Tricyclic Intermediates[1]

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Michael addition of the sodium enolate of a *tert*-butyl β-keto ester to a 4,4,10-trisubstituted 8-formyl-Δ^8-7-octalone (**2**)[2] was shown earlier to afford adducts of general structure **3** which upon exposure to acid undergo *tert*-butyl ester cleavage, decarboxylation, and cyclodehydration to produce tricyclic enediones **6** or **8**. Spectroscopic evidence, primarily ^{1}H NMR, is presented to demonstrate that the double bond in these enediones is normally in the 13,14 position (**6**) rather than the 8,14 position (**8**) when C-13 carries fewer than two substituents, and that the relative configuration of the carbon skeleton is trans-syn-cis in **6** and by inference trans-syn in **8**. Intramolecular ketals **20** and **22**, in which the C-10–C-9–C-8 configuration can only be anti-cis or syn-cis, were synthesized from enedione **6g** by routes which do not alter the configuration at these sites. Relation of ketal **20** to saturated diketone **17**, which must be either trans-anti-trans or trans-syn-cis because it does not epimerize in base, confirms the trans-syn-cis configuration of these substances. Stereoselectivity in the Michael addition producing adducts **3** therefore leads exclusively to the 9α orientation of the β-keto ester side chain. In cases where more than one stereoisomeric adduct **3** is formed, it is shown that the configurational difference is only at C-11.

In previous publications we have described a new synthetic approach to the elaboration of a variety of perhydrophenanthrenoid diterpenoids,[3] and have partially illustrated its generality and versatility in total syntheses of racemic sugiol,[4,5] ferruginol,[4,5] nimbiol,[5] dehydroabietic acid,[6] carnosic acid,[1a,7,8] carnosol,[1a,8] and hinokiol.[9] A central stage in this sequence comes with addition of ring C to an A/B precursor in the form of a suitably substituted *trans*-7-decalone (**1**).[2] The decalone is condensed with ethyl formate and the resulting 8-hydroxymethylene derivative is dehydrogenated with 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ) to produce an 8-formyl-Δ^8-7-octalone (**2**, Scheme I). Owing to its double conjugation this olefin is highly receptive to nucleophilic attack,[3] and reaction with the enolate of a suitably activated ketone affords an adduct of general structure **3** in which R^4 and in some cases also R^5 represent potential C-13 substitu-