Table III. Variation of k_r vs. Temperature for Radical $Me_2N\dot{N}P(O)(OEt)_2$ in Toluene-*tert*-Butylbenzene (50/50)

T, K	$10^{-6}k_r$, s^{-1}	$\Delta G^{\ddagger}$
339	3.2_7	9.8_3
344	3.8_1	9.8_8
349	5.7_0	9.7_5
355	7.6_3	9.7_3

the rotation around the N-N bond.

The first five lines of the spectrum of **1a·**, recorded at different temperatures, and the spin state to which they correspond are shown in Figure 2, assuming that the two methyl groups have coupling constants with like signs. The lines a, b, and c (Figure 2) belong to the same M_i and thus are not broadened by the exchange between the two methyl groups, while lines d and e have different M_i and are connected by the exchange process. At temperatures

$$\Delta\partial = \frac{\pi}{2 3^{1/2} k_r} \Delta H_r^2 \quad (\Delta H_r \text{ in frequency units}) \qquad (4)$$

above ca. 60 °C, lines d and e coalesce and the resulting line de has an excess width[15] given by eq 4. At 126 °C, $\Delta\partial = 0$, and the lines a and de have the expected $^1/_6$ intensity ratio.

In the temperature range ca. 65–100 °C the spectra can be described by the fast exchange limit, and analysis of the width of lines b and de by eq 4 leads to the k_r values reported in Table III. The free activation energy of the rotation, ΔG, was determined from Eyring's relationship, and the results of these calculations are presented in Table III.

Hindered rotation around the NN bond has been observed for a large number of hydrazyls.[4,9] However, for most of the hydrazyls studied, the ESR spectrum cannot be observed in the temperature range corresponding to a fast exchange between the substituents of the tervalent nitrogen, thus making difficult the measure of the free activation energy of the rotation process.

As far as we know, only the barrier of rotation for 1-benzoyl-2,2-bis(2,5-di-*tert*-butylphenyl)hydrazyl (**5·**) has been determined and was reported[16] to have a free activation energy of ca. 7.4 kcal mol^{-1}. As already mentioned, the higher $\Delta G^{\ddagger}$ observed for **1a·** (ca. 9.8 kcal mol^{-1}) compared to that observed for **5·** is certainly a consequence of electron delocalization which hampers the captodative effect and reduces the NN bond order in **5·**.

Registry No. 1a·, 99657-86-0; **1aH**, 10269-98-4; **1b·**, 99657-87-1; **1bH**, 99657-91-7; **1c·**, 99657-88-2; **1cH**, 75063-52-4; **1d·**, 99657-89-3; **1dH**, 99657-93-9; **1e·**, 99657-90-6; **1eH**, 99657-92-8; Me_2NNH_2, 57-14-7; t-$BuNHNH_2{\cdot}HCl$, 7400-27-3; $ClP(O)(OEt)_2$, 589-57-1; $ClP(O)Et_2$, 1112-37-4; $ClP(O)(OPh)_2$, 5382-00-3.

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Pyran Annelation: An Effective Route to a Tricyclic Dienone

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A new pyran annelation reaction was investigated. 2,6-Dimethyl-4*H*-pyran-4-one (**2**) was converted to 2-[(*p*-tolylsulfonyl)methyl]-6-methyl-4*H*-pyran-4-one (**7**) which was alkylated at the C-2 methylene position regioselectively, and the *p*-tolylsulfonyl group can be easily eliminated with an aluminum amalgam reduction. On the other hand, the pyran-4-one ring was easily transformed into a 1,5-diketone derivative. By joining and applying these selective alkylations and transformations, tricyclic dienone **22** was effectively synthesized from **2**.

The development of the synthetic methods of polycyclic natural products such as steroids and terpenes has been carried out by many organic chemists for 50 years. Among the many excellent synthetic procedures, isoxazole[1] and pyridine[2] annelations appear to be the predominant methods for this purpose.

On the other hand, functionalized heterocycles[3] are often used for the synthesis of the target organic compounds. These functionalized heterocycles are used not only as a masking group but also as the controlled reactive site. These functionalized heterocycles must have the following properties; i.e., a newly formed heterocycle, whose starting material has many reactive sites, must be entirely protected from some kinds of reactions and/or reagents and only one site should react with the reagent regioselectively. Moreover, by suitable treatment these heterocycles cannot only regenerate the compounds having the original partial structure but also they can be transformed into other useful synthetic intermediates.

In the course of our seeking novel synthetic methods using heterocycles, we selected 2,6-dimethyl-4*H*-pyran-4-one (γ-pyrone) (**2**) as a functionalized heterocycle and investigated a new annealation reaction.

In order to do this we required that (1) various substituents can be introduced regioselectively at the C-2 methyl position and (2) the 4*H*-pyran-4-one ring is convertable into a 1,5-diketone derivative.

We have already reported that 2-methyl-6-phenyl-4*H*-pyran-4-one (**1**) was regioselectively metalated at the C-2

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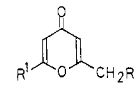
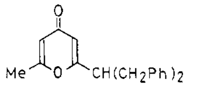


1: R^1=Ph, R^2=H
2: R^1=Me, R^2=H
3: R^1=Me, R^2=CH_2Ph
6: R^1=Me, R^2=Br, 58%
7: R^1=Me, R^2=SO_2-C_6H_4-CH_3-p, Quant.



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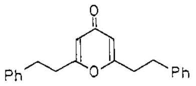


5

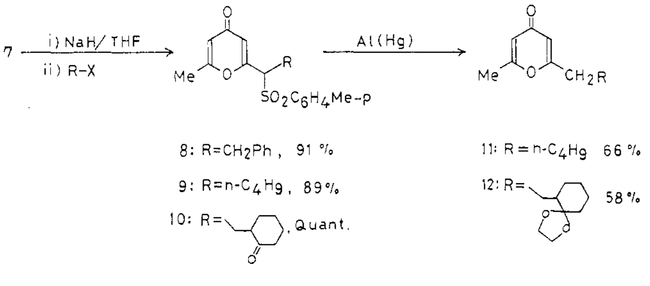
methyl position with sodium amide in liquid ammonia and afforded the alkylated or condensed products in good yield.[4]

However, pyran-4-one 2 is hard to dissolve in the usual aprotic solvents such as ethyl ether, tetrahydrofuran (THF), dioxane, dimethoxyethane (DME), benzene, and hexamethylphosphoric triamide (HMPA), or in protic solvents such as diisopropyl amine and liquid ammonia. In the case of the alkylation of 2 in liiquid ammonia, the desired pyran-4-one 3 was obtained in 32% yield, accompanied with 14.5% of dialkylated pyran-4-ones 4 and 5 (ratio of 4:5 = 73:27),[4] and 38% of starting material 2 was recovered.

Although pyran-4-one 2 dissolved in dimethyl sulfoxide (Me_2SO), treatment of 2 with dimsyl sodium in Me_2SO gave only a small amount (<5%) of the desired product 3 and 22% of the starting material 2 was recovered.

To solve this problem the procedure was changed as follows: pyran-4-one 2 was treated with *N*-bromosuccinimide (NBS) to give 2-(bromomethyl)-6-methyl-4*H*-pyran-4-one (6) in 58% yield which was treated with sodium *p*-toluenesulfinate in ethanol to give 2-methyl-6[(*p*-tolylsulfonyl)methyl]-4*H*-pyran-4-one (7) in quantitative yield.

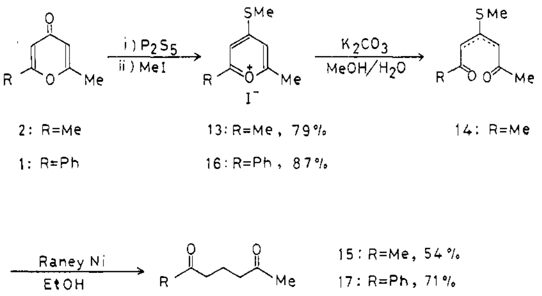
Sulfone 7 can be easily metalated at room temperature and then reacted with various electrophiles to give corresponding products 8, 9, and 10 in good yield.



8: R=CH_2Ph, 91%
9: R=n-C_4H_9, 89%
10: R=, Quant.
11: R=n-C_4H_9 66%
12: R= 58%

Alkylated sulfones 8, 9 and 10 were desulfurized with aluminum amalgam[5] to give 3, 11, and 12. These results showed that the first problem was successfully achieved.

On the other hand, the second problem was solved as follows: pyran-4-one 2 was treated with phosphorous pentasulfide (P_2S_5) in benzene[6] followed by methyl iodide to afford 2,6-dimethyl-4-(methylthio)pyrylium iodide (13)[6] in 79% yield. This pyrylium salt (13) was easily hydrolyzed with potassium carbonate in aqueous methanol solution to give ring-opened diketone 14. This diketone was, without isolation, desulfurized with Raney nickel (W-2)[7] or nickel borate[8] in ethanol followed by aqueous titanium trichloride[9] to give 1,5-diketone 15 in 43% overall yield from 2.

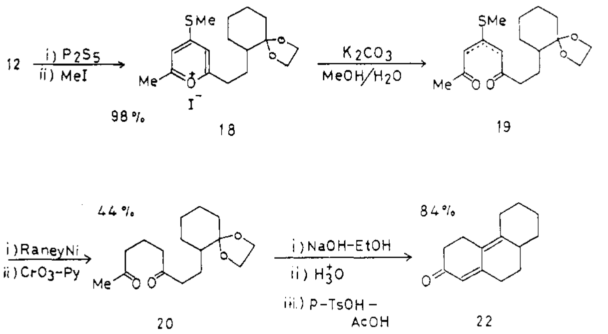


2: R=Me
1: R=Ph
13: R=Me, 79%
16: R=Ph, 87%
14: R=Me
15: R=Me, 54%
17: R=Ph, 71%

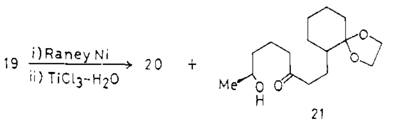
2-Methyl-6-phenyl-4*H*-pyran-4-one (1) was also treated with P_2S_5 followed by excess methyl iodide to give the corresponding pyrylium salt (16), and this salt was hydrolyzed with K_2CO_3–MeOH/H_2O followed by desulfurization with $TiCl_3$–H_2O to give 1-phenyl-1,5-hexanedione (17) in 62% overall yield from 1. Compound 17 was identified by comparison of the spectral data with those of the authentic sample which was synthesized by a known procedure.[10]

With the second problem also successfully solved, we applied these methods to the synthesis of the tricyclic dienone 22.

Compound 12 was treated with P_2S_5 in benzene followed by excess methyl iodide to give pyrylium salt 18 in quantitative yield. Salt 18 was treated with K_2CO_3 in aqueous methanol to afford the isomeric mixture of 19 which was desulfurized with Raney nickel (W-2) in ethanol solution followed by treatment with aqueous titanium trichloride to give 1,5-diketone derivative 20. But in this case the desulfurization of 19 with Raney nickel usually gave a mixture of 20 and an alcohol (21). Therefore, the mixture was treated with CrO_3–pyridine[11] to give 20.



18
19
20
22



21

The structure of 1,5-diketo ketal 20 was supported by the spectral results and the measurement of molecular formula by the high resolution mass spectrum.

By the known[12] procedure, diketo ketal 20 was treated with sodium hydroxide–ethanol, deketalized with acid, and then cyclodehydrated with *p*-toluenesulfonic acid–acetic acid to give the desired tricyclic dienone 22 in 84% yield.

As shown above, by combining two problems which are regioselective alkylation at the C-2 methyl position of 2

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and the transformation of **2** into a 1,5-diketone followed by cyclodehydration, this pyran annelation represents a useful synthetic method.

Experimental Section

All melting points are uncorrected. IR spectra were taken on Model IR-S (Japan Spectrometric Co. Ltd.) and Hitachi 215 type spectrometers. ^{1}H NMR spectra were recorded with a Hitachi R-24 instrument. Mass spectra were obtained with a Hitachi RMU-7M spectrometer for high resolution mass spectra at 70 eV. Column chromatography was carried out with Merck silica gel 7734. Tetrahydrofuran (THF) was distilled from $LiAlH_4$ and dimethyl sulfoxide (Me_2SO) was distilled from calcium hydride.

2-Methyl-6-phenyl-4*H*-pyran-4-one (1) was synthesized from 1-phenyl-1,3,5-hexanetrione and concentrated sulfuric acid, mp 86–88 °C (lit.[4] mp 86–88 °C).

2,6-Dimethyl-4*H*-pyran-4-one (2) was synthesized by the reaction of 2-acetyl-5-hydroxy-3-oxo-4-hexanoic acid δ-lactone (dehydroacetic acid) with concentrated hydrochloric acid, mp 130–131 °C (lit.[13] mp 130–131 °C).

2-Methyl-6-phenethyl-4*H*-pyran-4-one (3). From 1.24 g (11 mmol) of **2**, 1.88 g (11 mmol) of benzyl bromide, and 11 mmol of sodium amide in 120 mL of liquid ammonia was obtained 694 mg (32.4%) of **3** as colorless crystals, mp 75–77 °C, accompanied with the mixture of dialkylated pyran-4-ones **4** and **5** (14.5%) (**4**:**5** = 73:27, by NMR) and 471 mg (38%) of **2** (recovered).[4]

Alkylation of 2 in Me_2SO. From 132 mg (5.5 mmol) of sodium hydride in 10 mL of dry Me_2SO was prepared dimsyl sodium by the usual method,[5] and to this solution were added 620 mg (5 mmol) of **2** in 5 mL of dry Me_2SO and 5 mL of dry THF at room temperature. The solution turned red immediately. After 30 min 955 mg (5 mmol) of benzyl bromide in 2 mL of dry THF was added dropwise to this solution, and the stirring was continued for an additional 30 min at room temperature. The reaction mixture was worked up as usual and the yellow residue was purified by silica gel column chromatography with benzene–ethyl acetate (2:1) as eluant to give 92 mg (4.3%) of **3**: mp 74–76 °C (lit.[4] mp 75–77 °C); NMR (in $CDCl_3$) 2.16 (s, 3 H), 2.50–3.00 (m, 4 H), 5.95 (s, 2 H), 7.15 ppm (m, 5 H). From this column chromatography only 137 mg (22%) of **2** was recovered.

2-Methyl-6-[(*p*-tolylsulfonyl)methyl]-4*H*-pyran-4-one (7). A mixture of **2** (3.10 g, 25 mmol), *N*-bromosuccinimide (NBS) (2.36 g, 13.3 mmol), and benzoyl peroxide (BPO) (2.21 g, 9.1 mmol) in 60 mL of dry benzene was heated to reflux for 1.5 h. And then 2.36 g of NBS and 2.21 g of BPO were added to the reaction mixture, the solution was heated to reflux for 1.5 h, and this procedure was repeated once again. After cooling, the reaction mixture was washed with 50 mL of a 3% Na_2SO_3 aqueous solution several times and worked up as usual to give a crude orange paste. This residue was purified by silica gel column chromatography with benzene–ethyl acetate (2:1) as eluant to afford 992 mg (58%) of 2-(bromomethyl)-6-methyl-4*H*-pyran-4-one (**6**): mp 109–110 °C (from *n*-hexane/ethyl acetate, 9:1); IR (in $CHCl_3$) 1670, 1615, 1405 cm^{-1}; NMR (in $CDCl_3$) 2.31 (s, 3 H), 4.22 (s, 2 H), 6.11 (br s, 1 H), 6.32 ppm (d, 1 H, J = 3.0 Hz); MS, *m/e* 202 (M^+) and 204 ($M^+ + 2$).

The bromide **6** (400 mg) was reacted with sodium *p*-toluenesulfinate (500 mg) in 5 mL of refluxing ethanol for 1 h to give a quantitative yield (545 mg) of **7**: mp 177–177.5 °C (from ethyl acetate/chloroform, 20:1); IR (in $CHCl_3$) 1670, 1630, 1405, 1325, 1160 cm^{-1}; NMR (in $CDCl_3$) 2.10 (s, 3 H), 2.50 (s, 3 H), 4.25 (s, 2 H), 6.15 (s, 2 H), 7.50 (d, 2 H, J = 9 Hz), 7.90 ppm (d, 2 H, J = 9 Hz). Anal. Found: C, 60.25; H, 5.06. Calcd for $C_{14}H_{14}O_4S$: C, 60.42; H, 5.07.

2-Methyl-6-[1-(*p*-tolylsulfonyl)-2-phenylethyl]-4*H*-pyran-4-one (8). Sulfone **7** (2.78 g, 10 mmol) in 30 mL of dry THF was treated with 252 mg (10.5 mmol) of sodium hydride at room temperature. After H_2 gas evolution ceased, 1.71 g (10 mmol) of benzyl bromide in 10 mL of dry THF was added dropwise and the stirring was continued for an additional 2 h. The reaction mixture was quenched with diluted hydrochloric acid and the residue was purified by silica gel column chromatography with benzene/ethyl acetate (2:1) as eluant to give **8** in 91% yield (3.35 g): IR (in $CHCl_3$) 1670, 1630, 1410 cm^{-1}; NMR (in $CDCl_3$) 2.7–3.2 (m, 2 H), 2.07 (s, 3 H), 2.46 (s, 3 H), 4.10–4.60 (m, 1 H), 6.05 (br s, 2 H), 7.35 (d, 2 H, J = 9 Hz), 7.65 ppm (d, 2 H, J = 9 Hz).

Desulfurization of 8. A mixture of the above alkylated product (**8**) (3.35 g) and 1.94 g of aluminum amalgam[5] in 200 mL of 10% aqueous THF was stirred at 0 °C for 4 h. The solid was filtered off and the filtrate was concentrated and purifed by silica gel column chromatography with benzene/ethyl acetate (2:1) as eluant. The obtained yellow oil was crystallized from *n*-hexane/benzene (4:1) to afford 1.12 g (58%) of **3**: mp 75–77 °C (lit.[4] mp 75–77 °C); IR (in $CHCl_3$) 1670 and 1610 cm^{-1}; NMR (in $CDCl_3$) 2.15 (s, 3 H), 2.5–3.0 (m, 4 H), 5.95 (s, 2 H), 7.00–7.25 ppm (m, 5 H).

2-Methyl-6-*n*-pentyl-4*H*-pyran-4-one (11). By a similar procedure as the case of **3**, from 2.78 g (10 mmol) of **7** and 1.37 g (10 mmol) of *n*-butyl bromide, 2.97 g (89%) of **9** was synthesized and desulfurized with 1.90 g of aluminum amalgam to give 1.06 g (66%) of **11**:[4] IR (neat) 1660 and 1610 cm^{-1}; NMR (in $CDCl_3$) 0.90 (t, 3 H), 1.10–1.73 (m, 6 H), 2.20 (s, 3 H), 2.45 (t, 2 H), 5.96 ppm (s, 2 H); MS, *m/e* found M^+ 180.2488, calcd for $C_{11}H_{16}O_2$ M 180.2462.

2-[2-[2,2-(Ethylenedioxy)cyclohexyl]ethyl]-6-methyl-4*H*-pyran-4-one (12). To a suspension of 240 mg of sodium hydride in 30 mL of THF was added 1.50 g of sulfone **7**, and the mixture was stirred at room temperature for 1 h. To this solution was added 3.00 g of 2-oxocyclohexylmethyltrimethylammonium iodide[14] and heated to reflux for 1 h. The reaction mixture was poured into water and extracted with ether, dried over anhydrous magnesium sulfate, and concentrated to give 3.73 g of red oil, which was purified by silica gel column chromatography to afford the desired alkylated product **10** (2.07 g) in quantitative yield: IR (in $CHCl_3$) 1715, 1675, 1630, 1330, 1155 cm^{-1}; NMR (in $CDCl_3$) 1.30–2.60 (m, 11 H), 2.07 (s, 3 H), 2.46 (s, 3 H), 4.10–4.60 (m, 1 H), 6.05 (br s, 2 H), 7.35 (d, 2 H, J = 9 Hz), 7.90 ppm (d, 2 H, J = 9 Hz); MS, *m/e* 388 (M^+) and 233 (M^+ – Ts).

Compound **10** (1.0 g), 500 mg (excess) of ethylene glycol, 20 mg of *p*-toluenesulfonic acid, and 100 mL of benzene were mixed, and the mixture was heated to reflux to remove water by azeotropic distillation (about 40 mL of water-containing benzene). The benzene solution was washed with diluted sodium bicarbonate solution and 30 mL of brine, dried over anhydrous magnesium sulfate, and concentrated to give 1.14 g (quantitative yield) of ketal: mp 166.5–167 °C; IR (in $CHCl_3$) 1670, 1625, 1410, 1325, 1150 cm^{-1}; NMR (in $CDCl_3$) 1.10–2.20 (m, 11 H), 2.09 (s, 3 H), 2.46 (s, 3 H), 3.90 (s, 4 H), 4.47 (dd, 1 H, J = 12 and 4 Hz), 6.11 (s, 2 H), 7.34 (d, 2 H, J = 9 Hz), 7.69 ppm (d, 2 H, J = 9 Hz); MS, *m/e* 432 (M^+) and 277 (M^+ – Ts). Anal. Found: C, 63.98; H, 6.54. Calcd for $C_{23}H_{28}O_6S$: C, 63.87; H, 6.53.

To 600 mg of ketal in 40 mL of 10% aqueous THF solution was added 300 mg of aluminum amalgam[5] with stirring at 0 °C for 4 h. The reaction mixture was filtered and the solid was washed with THF. The filtrate was concentrated, and the residue was washed with 20 mL of water and 30 mL of ether. The ether layer was separated and worked up as usual to give 420 mg of orange oil, which was purified by the usual procedure to give pure **12** (225 mg, 58%): IR (in $CHCl_3$) 1670 and 1625 cm^{-1}; NMR (in $CDCl_3$) 1.3–2.7 (m, 13 H), 2.15 (s, 3 H), 3.95 (s, 4 H), 6.07 ppm (s, 2 H); MS, *m/e* 278 (M^+).

Conversion of 2 into 2,6-Heptanedione (15). To 3.10 g (25 mmol) of pyran-4-one **2** in 50 mL of dry benzene was added 5.55 g (25 mmol) of phosphorous pentasulfide, and the mixture was heated to reflux for 1 h. After cooling, the reaction mixture was diluted with 80 mL of cold water and stirred for 30 min. The benzene layer was separated and evaporated to afford 2.84 g (81%) of thiopyran, which was recrystallized from isopropyl alcohol; mp 144–145 °C (lit.[6] mp 145 °C).

To the thiopyran (1.0 g) in 30 mL of acetone was added excess methyl iodide (3.5 g) at room temperature, and the mixture was heated to reflux for 2 h. After cooling, the resulting crystals were washed with acetone to afford crude thiopyrylium salt **13** (1.96 g, 98%) which was recrystallized from ethanol to give pure product, mp 176–177 °C dec (lit.[6] mp 176–177 °C dec). A solution of 1.96 g of salt **13** in 40 mL of water was cooled to 0 °C and K_2CO_3

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(1.0 g) was added. The mixture was stirred for 2 h and then was extracted with benzene. The benzene solution was dried over anhydrous magnesium sulfate and concentrated to give an orange oil (**14**). This orange oil dissolved in 60 mL of absolute ethanol and was heated to reflux with an excess of freshly prepared Raney nickel (W-2) for 1 h. Solid was filtered off, the filtrate was concentrated, and the residue was again stirred with 1.5 mL of 20% of aqueous $TiCl_3$ in 10 mL of acetone for 1 h at room temperature[11] and then poured into 30 mL of brine, extracted with benzene, dried over anhydrous magnesium sulfate, and concentrated to give 1.02 g of a brown oil. The resulting residue was purified by silica gel column chromatography with benzene/ethyl acetate (4:1) to afford 890 mg (54%) of **15**: IR (in $CHCl_3$) 1715 cm^{-1}; NMR (in $CDCl_3$) 1.5–2.5 (m, 6 H), 2.08 ppm (s, 6 H).

1-Phenyl-1,5-hexanedione (17). Diketone 17 was also synthesized by a similar procedure to that of 15; overall yield 62%. This compound (17) was identified by comparison of the spectral results with those of an authentic sample, which was synthesized by a known route:[10] IR (in CCl_4) 1715, 1675, 1600, 755, 690 cm^{-1}; NMR (in CCl_4) 1.90 (m, 2 H), 2.00 (s, 3 H), 2.42 (t, 2 H), 2.86 (t, 2 H), 7.28 (m, 3 H), 7.72 ppm (m, 2 H).

Synthesis of (Methylthio)pyrylium Iodide 18. A mixture of 500 mg of **12** and 400 mg of phosphorous pentasulfide in 5 mL of dry benzene was heated to reflux for 1 h, followed by filtering off the solid. The resulting benzene solution was concentrated to give 532 mg of crude thio derivative. To this thio derivative which was dissolved in 15 mL of ethyl acetate was added excess methyl iodide (1.0 g); and the mixture was heated to reflux for 1 h and concentrated to afford 765 mg (98%) of **18** as a red oil: IR (in $CHCl_3$) 1675, 1635, 1515, 1460 cm^{-1}; NMR (in $CDCl_3$) 1.3–2.6 (m, 13 H), 2.94 (s, 3 H) 3.10 (s, 3 H), 4.00 (s, 4 H), 7.70–8.30 ppm (m, 2 H).

Synthesis of Diketo Ketal 20. A mixture of 765 mg of **18**, 266 mg of potassium carbonate, and 50 mL of 50% aqueous methanol was stirred at 0 °C for 30 min. The mixture was concentrated and then dissolved in 20 mL of water and extracted with two 25-mL portions of benzene. The benzene solution as worked up as usual to give 591 mg of orange oil **19** which was almost one spot on this layer chromatography (benzene/ethyl acetate, 4:1, as eluant): IR (in $CHCl_3$) 1715, 1680, 1565, 1360 cm^{-1}; NMR (in $CDCl_3$) 1.1–2.0 (m, 13 H), 2.16 and 2.25 (two singlets, total integration 3 H), 2.40–2.70 (m, 2 H), 3.80 (s, 2 H), 3.93 (s, 4 H), 6.02 ppm (s, 1 H).

A solution of 591 mg of this orange oil in 90 mL of absolute ethanol was heated to reflux for 3 h with excess Raney nickel (W-2). The solid was filtered and washed with ethanol (30 mL), concentrated to give the crude product (525 mg), which was treated with 0.5 mL of 20% aqueous titanium trichloride in 2.5 mL of acetone for 1 h at room temperature, and then worked up as in the case of **15** to give two components. The first component (R_f 0.39) on thin layer chromatography (solvent benzene/ethyl acetate (9:1)) was the desired diketo ketal **20** (178 mg, 36%) and the latter one (R_f 0.10) was an alcohol (**21**) (90 mg, 18%).

Spectral data of 20: IR (in $CHCl_3$) 1715 cm^{-1}; NMR (in $CDCl_3$) 1.1–2.0 (m, 13 H), 2.12 (s, 3 H), 2.2–2.6 (m, 6 H), 3.94 (s, 4 H); HRMS, *m/e* found M^+ 282.3767, calcd for $C_{16}H_{26}O_4$ M 282.3792.

Spectral data of 21: IR (in $CHCl_3$) 3400 and 1715 cm^{-1}; NMR (in CCl_4) 1.0–1.9 (m, 18 H), 2.35 (t, 4 H), 3.52 (m, 1 H), 3.88 ppm (s, 4 H).

CrO_3–Pyridine Oxidation Method. Compound 18 (3.18 g) was again treated with potassium carbonate and the resulting orange oil (2.35 g) was treated with excess Raney nickel (W-2) in refluxing ethanol for 10 h. The reaction mixture was worked up as described above, and 1.56 g of a mixture of **20** and **21** (by TLC) was obtained. On the other hand, chromium trioxide (2.50 g) was added to a stirred solution of 9 mL of dry pyridine and 80 mL of methylene chloride. After 15 min the resulting deep burgandy solution was added to 1.56 g of the desulfurized mixture in 10 mL of methylene chloride, and the solution was stirred for an additional 1 h. The reaction mixture was filtered and the filtrate was washed with a 5% sodium hydroxide solution and then a 5% NaCl solution, dried over anhydrous magnesium sulfate, and concentrated to give a brown oil. This brown oil was purified by silica gel column chromatography with a benzene/ethyl acetate (9:1) mixture to give pure **20**[12] (906 mg, 43% overall yield from **12**) as a pale yellow oil.

Synthesis of Tricyclic Dienone 22. A mixture of **20** (218 mg), 2 mL of aqueous sodium hydroxide solution, and 10 mL of ethanol was heated to reflux for 2 h. The reaction mixture was acidified with diluted hydrochloric acid; ethanol was removed under reduced pressure, and the residue was extracted with benzene (2 × 30 mL), dried over anhydrous magnesium sulfate, and concentrated to give 171 mg of an orange residue which was dissolved in 20 mL of acetic acid and 400 mg of *p*-toluenesulfonic acid. The mixture was heated at 100 °C for 2 h. Acetic acid was driven off under reduced pressure and 30 mL of water + 30 mL of benzene were added to the residue. The benzene solution was worked up as usual to give pure tricyclic dienone **22** (131 mg, 84%): IR (in $CHCl_3$) 1655, 1620, 1590 cm^{-1}; NMR (in CCl_4) 1.10–2.95 (m, 17 H), 5.50 ppm (s, 1 H); MS, *m/e* found M^+ 202.2944, calcd for $C_{14}H_{18}O$ M 202.2956.

Registry No. **1**, 1013-99-6; **2**, 1004-36-0; **3**, 56150-33-5; **4**, 56150-34-6; **5**, 56150-35-7; **6**, 99809-37-7; **7**, 99809-38-8; **8**, 99809-39-9; **9**, 99809-40-2; **10**, 99809-41-3; **10** (ketal), 99809-42-4; **11**, 99809-53-7; **12**, 99809-43-5; **13**, 6276-12-6; **14** (R = Me), 90097-35-1; **14** (R = Ph, isomer 1), 99809-48-0; **14** (R = Ph, isomer 2), 99809-54-8; **15**, 13505-34-5; **15** (desulfonated), 99809-46-8; **16**, 99809-47-9; **17**, 6303-82-8; **17** (desulfonated), 99809-49-1; **18**, 99809-50-4; **19** (isomer 1), 99809-51-5; **19** (isomer 2), 99809-55-9; **20**, 38275-06-8; **20** (desulfonated), 99809-52-6; **21**, 99809-45-7; **22**, 18074-70-9; (2-oxocyclohexyl)methyltrimethylammonium iodide, 71666-50-7; thiopyran, 1004-37-1; 2-methyl-6-[2-[2,2-(ethylenedioxy)cyclohexyl]ethyl]-4*H*-thiopyran, 99809-44-6; 2-methyl-6-phenyl-4*H*-thiopyran, 1014-00-2.