and 2 Hz, H-3'a), 5.09 (1 H, dd, J = 10.5 and 2 Hz, H-3'b), 5.76 (1 H, ddt, J = 15, 10.5, and 7.5 Hz, H-2'), 7.3 (15 H, m, Ar H); ^{13}C NMR ppm 20.90 (q, CH_3), 39.26 (t, C-1'), 65.73, 70.80, 72.34, 72.48 and 73.43 (t, -OCH_2-), 80.70 (d, C-3), 83.78 and 86.46 (d, C-4 and C-5), 84.64 (s, C-2), 118.93 (t, C-3'), 132.92 (d, C-2'), 170.55 (s, C=O). Anal. Calcd for $C_{32}H_{36}O_6$: C, 74.39; H, 7.02. Found: C, 74.19; H, 6.83.

1-(1-*O*-Acetyl-3,4,6-tri-*O*-benzyl-α-D-fructofuranosyl)-1-propene (9a). **8a** (200 mg, 0.38 mmol) was treated with $PdCl_2(CH_3CN)_2$ as described for **3**. A 95/5 mixture of **9a** and **8a** was obtained (196 mg, 98% yield).

9a: ^{1}H NMR δ 1.70 (3 H, dd, J = 6.5 and 1.5 Hz, CH_3), 1.95 (3 H, s, OAc), 3.60 (2 H, d, J = 4.5 Hz, H-6), 4.01-4.28 (3 H, m, H-3, H-4, and H-5), 4.15 (1 H, d, J = 11.5 Hz, H-1a), 4.25 (1 H, d, J = 11.5 Hz, H-1b), 4.52-4.58 (6 H, m, OCH_2Ph), 5.45 (1 H, dq, J = 15.5 and 1.5 Hz, H-1'), 5.80 (1 H, dq, J = 15.5 and 6.5 Hz, H-2'), 7.3 (15 H, m, Ar H).

1-(1-*O*-Acetyl-3,4,6-tri-*O*-benzyl-α-D-fructofuranosyl)-methanol (10a) and (3,4,6-Tri-*O*-benzyl-D-fructofuranosyl)methanol (11). **9** (120 mg, 0.23 mmol) in EtOH (1 mL) was submitted to ozonolysis and reduction of the ozonide as reported for **4**. Workup and chromatography (hexane-ethyl acetate, 2:1) afforded **10a** (30 mg, 26% yield) and **11** (65 mg, 60% yield).

10a: ^{1}H NMR δ 2.00 (3 H, OAc), 3.54 (2 H, d, J = 5.5 Hz, H-6a and b), 3.59 (2 H, d, J = 3 Hz, H-1'a and b), 4.07 (1 H, dd, J = 5 and 4 Hz, H-4), 4.15 (1 H, q, J = 5 Hz, H-5), 4.16 (1 H, d, J = 4 Hz, H-3), 4.18 (1 H, d, J = 10 Hz, H-1a), 4.33 (1 H, d, J = 10 Hz, H-1b), 4.53 (6 H, m, OCH_2Ph), 7.3 (15 H, m, Ar H).

11: ^{1}H NMR 3.43-3.76 (6 H, m, H-1, H-6, H-1'a and b), 4.02 (1 H, m, H-5), 4.26 (1 H, d, J = 6 Hz, H-3), 4.36 (1 H, dd, J = 7 and 6 Hz, H-4), 4.42-4.76 (6 H, m, OCH_2Ph), 7.3 (15 H, m, Ar H). Anal. Calcd for $C_{29}H_{32}O_6$: C, 73.09; H, 6.77. Found: C, 72.88; H, 6.92.

1-(1-*O*-(*tert*-Butyldimethylsilyl)-3,4,6-tri-*O*-benzyl-α-D-fructofuranosyl)-2-propene (8b). **7** (230 mg, 0.48 mmol) in dry CH_2Cl_2 (3 mL) was treated with freshly distilled Et_3N (0.1 mL, 0.72 mmol), ^{t}ButMe$_2$SiCl (88 mg, 0.58 mmol), and (dimethylamino)pyridine (6 mg). After 4 days at room temperature, usual workup and chromatography (hexane-ethyl acetate, 5/1 v/v) afforded **8b** (250 mg, 90% yield): oil; $[\alpha]_D$ +12.6° (c 1.3, $CHCl_3$); ^{1}H NMR δ 0.00 (3 H, s, SiMe), 0.03 (3 H, s, SiMe), 0.89 (9 H, s, Si-t-Bu), 2.47 (2 H, br d, H-1'a and b), 3.55-3.74 (3 H, m), 3.95 (1 H, d, J = 3 Hz, H-3), 4.02-4.25 (3 H, m), 4.50-4.64 (6 H, m, OCH_2Ph), 5.07 (1 H, dt, J = 15 and 1 Hz, H-3'a), 5.10 (1 H, dt, J = 7.5 and 1 Hz, H3'b), 5.88 (1 H, m, H-2'), 7.3 (15 H, m, Ar H); ^{13}C NMR ppm -5.51 (q, $SiCH_3$), 18.30 (s, $SiCMe_3$), 25.73 and 25.99 (q, t-Bu), 38.10 (t, C-1'), 64.04, 71.49, 72.09, 72.53 and 73.37 (t, -OCH_2-), 80.58 (d, C-3), 85.61 and 86.51 (d, C-4 and C-5), 85.97 (s, C-2), 118.02 (t, C-3'), 133.77 (d, C-2'). Anal. Calcd for $C_{36}H_{48}O_5Si$: C, 73.43; H, 8.22. Found: C, 73.58; H, 8.35.

1-(1-*O*-(*tert*-Butyldimethylsilyl)-3,4,6-tri-*O*-benzyl-α-D-fructofuranosyl)-1-propene (9b). **8b** (200 mg, 0.35 mmol) treated with $PdCl_2(CH_3CN)_2$ as reported for **3** afforded **9b** (184 mg, 92% yield): oil; $[\alpha]_D$ +10.9° (c 1, $CHCl_3$); ^{1}H NMR δ -0.03 (3 H, s, SiMe), -0.01 (3 H, s, SiMe), 0.86 (9 H, s, t-Bu), 1.70 (3 H, dd, J = 6.5 and 1.5 Hz, CH_3), 3.52-3.80 (4 H, m, H-1 and H-6), 3.99-4.14 (3 H, m, H-3, H-4, and H-5), 4.46-4.64 (6 H, m, OCH_2Ph), 5.54 (1 H, dd, J = 15.5 and 1.5 Hz, H-1'), 5.78 (1 H, dd, J = 15.5 and 6.5 Hz, H-2'), 7.3 (15 H, m, Ar H); ^{13}C NMR ppm -5.21 (q, $SiCH_3$), 18.07 (q, C-3'), 18.59 (s, $SiCMe_3$), 25.92 and 26.17 (q, t-Bu), 66.23, 71.73, 72.03, 72.94 and 73.49 (t, -OCH_2-), 80.45 (d, C-3), 85.54 and 88.14 (d, C-4 and C-5), 85.90 (s, C-2), 118.23 and 132.44 (d, C-1' and C-2'). Anal. Calcd for $C_{36}H_{48}O_5Si$: C, 73.43; H, 8.22. Found: C, 73.48; H, 8.37.

(1-*O*-(*tert*-Butyldimethylsilyl)-3,4,6-tri-*O*-benzyl-α-D-fructofuranosyl)methanol (10b). To **9b** (150 mg) were added 10 mL of a saturated solution of ozone in CH_2Cl_2 at -78 °C. After 5 min at -78 °C, PPh_3 (90 mg, 1.5 equiv) was added and the mixture was left to reach room temperature. The solvent was then removed under reduced pressure without warming, and the crude aldehyde was dissolved in Et_2O (5 mL) and reduced overnight with a solution of $Zn(BH_4)_2$[10] in Et_2O (10 mL, 0.18 M). Usual workup and chromatography (hexane-ethyl acetate, 4/1 v/v) afforded 110 mg (75% yield) of **10b**: oil; $[\alpha]_D$ +6.2° (c 1.5, $CHCl_3$); ^{1}H NMR δ 0.00 (3 H, s, SiMe), 0.04 (3 H, s, SiMe), 0.87 (9 H, s, t-Bu), 3.50 (1 H, dd, J = 16 and 5.5 Hz, H-6a), 3.58 (1 H, dd, J = 16 and 6 Hz, H-6b), 3.69 (1 H, d, J = 10 Hz, H-1a), 3.72 (2 H, s, H-1'a and b), 3.87 (1 H, d, J = 10 Hz, H-1b), 4.02 (1 H, dd, J = 5 and 3.5 Hz, H-4), 4.11 (1 H, d, J = 3.5 Hz, H-3), 4.13 (1 H, m, H-5), 4.41-4.65 (6 H, m, OCH_2Ph), 7.3 (15 H, m, Ar H); ^{13}C NMR ppm -5.61 (q, $SiCH_3$), 18.25 (s, $SiCMe_3$), 25.89 (q, t-Bu), 63.99, 64.08, 71.04, 71.89, 72.75 and 73.34 (t, -OCH_2-), 80.95 (d, C-3), 84.17 and 84.86 (d, C-4 and C-5), 86.13 (s, C-2). Anal. Calcd for $C_{34}H_{46}O_6Si$: C, 70.55; H, 8.01. Found: C, 70.32; H, 7.83.

(1-*O*-(*tert*-Butyldimethylsilyl)-3,4,6-tri-*O*-benzyl-α-D-fructofuranosyl)methyl Benzoate (12). **10b** (100 mg) in dry CH_2Cl_2 (1 mL) was treated with dry Py (0.2 mL) and freshly distilled benzoyl chloride (24 μL). After 2 h at room temperature, usual workup and chromatography (hexane-ethyl acetate, 4/1 v/v) afforded **12** (99 mg, 84% yield): oil; $[\alpha]_D$ +13.8° (c 1.4, $CHCl_3$); ^{1}H NMR δ 0.00 (3 H, s, SiMe), 0.03 (3 H, s, SiMe), 0.87 (9 H, s, t-Bu), 3.54 (1 H, dd, J = 10 and 5.5 Hz, H-6a), 3.62 (1 H, dd, J = 10 and 5.5 Hz, H-6b), 3.82 (1 H, d, J = 10 Hz, H-1a), 3.91 (1 H, d, J = 10 Hz, H-1b), 4.05-4.12 (2 H, m, H-3 and H-4), 4.26 (1 H, dt, J = 6 and 5.5 Hz, H-5), 4.38 (1 H, d, J = 11.5 Hz, H-1'a), 4.51-4.58 (6 H, m, OCH_2Ph), 4.63 (1 H, d, J = 11.5 Hz, H-1'b), 7.20-8.20 (20 H, m, Ar H); ^{13}C NMR ppm -5.51 (q, $SiCH_3$), 18.30 (s, $SiCMe_3$), 25.92 (q, t-Bu), 62.42, 64.09, 70.76, 71.97, 72.70 and 73.31 (t, -OCH_2-), 81.12 (d, C-3), 84.76 and 85.54 (d, C-4 and C-5), 84.87 (s, C-2), 165.18 (s, C=O). Anal. Calcd for $C_{41}H_{50}O_7Si$: C, 72.11; H, 7.38. Found: C, 72.33; H, 7.18.

(1-*O*-Benzoyl-3,4,6-tri-*O*-benzyl-β-D-fructofuranosyl)-methanol (13). **12** (63 mg) was treated with AcOH, H_2O, and THF (3/1/1, 10 mL). After 36 h at room temperature, usual workup (extraction with ethyl acetate) and chromatography (hexane-ethyl acetate, 4/1 v/v) afforded **13** (50 mg, 95% yield): $[\alpha]_D$ +37.3° (c 1, $CHCl_3$); ^{1}H NMR δ 3.52 (1 H, dd, J = 10.5 and 3.5 Hz, H-6a), 3.66 (1 H, d, J = 12 Hz, H-1'a), 3.68 (1 H, dd, J = 10.5 and 3.5 Hz, H-6b), 3.83 (1 H, d, J = 12 Hz, H-1'b), 4.24 (1 H, d, J = 12 Hz, H-1a), 4.30 (1 H, d, J = 6 Hz, H-3), 4.32 (1 H, d, J = 12 Hz, H-1b), 4.44 (1 H, dd, J = 7 and 6 Hz, H-4), 4.46-4.75 (6 H, m, OCH_2Ph), 7.20-8.00 (20 H, m, Ar H); ^{13}C NMR ppm 63.13, 65.25, 69.54, 72.57, 72.92 and 73.31 (t, -OCH_2-), 80.03 (d, C-3), 83.17 and 85.42 (d, C-4 and C-5), 83.60 (s, C-2), 166.06 (s, C=O). Anal. Calcd for $C_{35}H_{36}O_7$: C, 73.92; H, 6.38. Found: C, 73.76; H, 6.52.

(10) Gensler, W. J.; Johnson, F.; Sloan, A. D. B. *J. Am. Chem. Soc.* **1960**, *82*, 6074.

Synthetic Elaboration of Diosphenols. 2.† Manifold Pathways in the Reaction of Cyclotene Dimethylthiocarbamate with Halide Ion

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We recently reported[1] that treatment of 1,2-cyclopentanedione dimethylthiocarbamate (**1**) with lithium chloride in acetonitrile/acetic acid gave 2-chloro-2-cyclopenten-1-one (**2a**) in 96% yield and that high yields of simple substitution were also obtained with other *3-unsubstituted* 1,2-cycloalkanediones by using lithium bromide and chloride (Figure 1).

We now report that the simple structural alteration of replacing the vinyl hydrogen of **1** by methyl causes the course of our reaction to be more complex. Thus, when cyclotene dimethylthiocarbamate (**3**) is treated with lithium chloride in boiling acetic acid, chlorine is attached not only to C-2 but also to C-5. This "abnormal" initial

† Part 1: see ref 1.

0022-3263/87/1952-5630$01.50/0

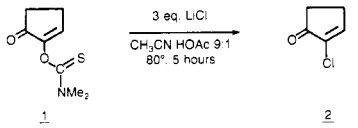
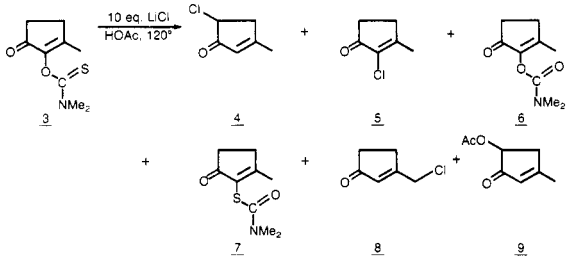


Figure 1.

Scheme I



product **4** is then partially isomerized to **8**, but not to the "normal" product **5**. Additionally, with **3** (but not with **1**), O–S interchange and thiocarbonyl hydrolysis are significant side reactions.

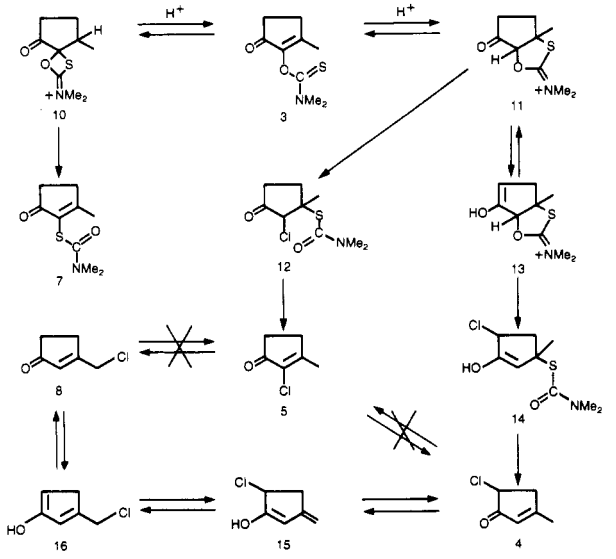
The sequence of events was deduced by periodically analyzing aliquots of a 0.2 M solution of **3** in boiling acetic acid containing 10 equiv of lithium chloride, by calibrated gas chromatography. After 1 h, when 30% of **3** remained,[2] four new compounds were present: 5-chloro-3-methyl-2-cyclopenten-1-one (**4**) (45%), 2-chloro-3-methyl-2-cyclopenten-1-one (**5**) (9%), 2-[(dimethylcarbamoyl)oxy]-3-methyl-2-cyclopenten-1-one (**6**) (7%), and 2-[(dimethylcarbamoyl)thio]-3-methyl-2-cyclopenten-1-one (**7**) (2%) (Scheme I).

Analysis of the reaction mixture after 3 h revealed two new products: 3-(chloromethyl)-2-cyclopenten-1-one (**8**) (3%) and 5-acetoxy-3-methyl-2-cyclopenten-1-one (**9**) (3%), in addition to **3** (6%), **4** (48%), **5** (15%), **6** (13%), and **7** (7%). That **8** is derived from **4** was verified by treating the latter with lithium chloride in boiling acetic acid when rapid interconversion with **8** occurred, but no **5** was detected.

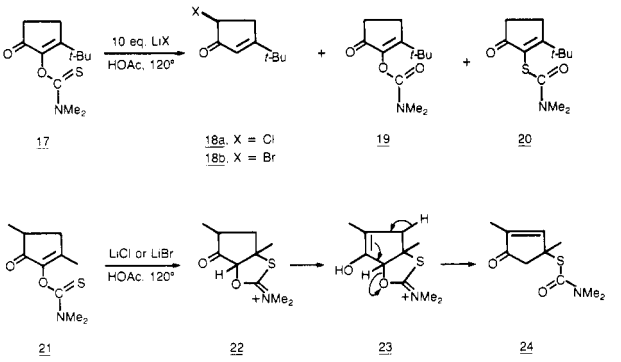
When the reaction was allowed to proceed for 30 h, only **5** (20%), **6** (13%), and **7** (6%) were observed. All other products eventually decompose to nonvolatile (or very water-soluble) substances, whereas the 2-substituted products are stable under the reaction conditions and their yield remains relatively constant after starting material has been consumed. Yields of the various products versus reaction time are plotted in Figure 2.

The following mechanistic scheme is consistent with these results (Scheme II). Fused cyclization to **11**, followed by attack of chloride at C-2, leads to **5**. This mode of displacement is relatively slow since it occurs at a neopentyl-type center; by default, the major pathway for attack of chloride ion is 1,3-substitution[3] on enol **13**. The interconversion of **4** and **8** occurs by way of 1,5-substitution[4] on dienols **15** and **16**, possibly through the intermediacy of an ion pair. The production of **6** and **7** is a consequence of the slow attack of chloride on **11** (at either C-2 or C-5), favoring reversion to **3** and then either thio-

Scheme II



Scheme III



carbonyl hydrolysis or spirocyclization.[5]

From a preparative point of view, this reaction offers an efficient route to **4** (64% yield based on 70% unrecovered **3**) from inexpensive materials. Since 5-halo-2-cyclopenten-1-ones are not generally accessible,[6] we have briefly examined the potential of this procedure for the preparatioin of analogues of **4**. Treatment of 3-*tert*-butyl-2-[(dimethylthiocarbamoyl)oxy]-2-cyclopenten-1-one (**17**) with 10 equiv of lithium chloride in boiling acetic acid for 3 h gave 3-*tert*-butyl-5-chloro-2-cyclopenten-1-one (**18a**) (45%), **19** (about 27%), and **20** (about 3%). Results with lithium bromide are capricious: treatment of **3** with 10 equiv of lithium bromide in boiling acetic acid for 1 h gave mainly **7**[7] but treatment of **17** under the same conditions for $1^1/_2$ h gave 5-bromo-3-*tert*-butyl-2-cyclopenten-1-one

(1) Ponaras, A. A.; Zaim, Ö. *J. Org. Chem.* **1986**, *51*, 4741.
(2) Reaction of 1 under these conditions is complete in 15 min.
(3) For pertinent examples in α-halo ketones and α,β-epoxy ketones, see: (a) Warnhoff, E. W.; Nakamura, A. *Tetrahedron Lett.* **1984**, *25*, 503. (b) Takahashi, T. T.; Satoh, J. Y. *Bull. Chem. Soc. Jpn.* **1975**, *48*, 69. (c) Neeman, M.; O'Grodnick, J. S. *Can. J. Chem.* **1974**, *52*, 2941. (d) Caton, M. P. L.; Darnbrough, G.; Parker, T. *Synth. Commun.* **1978**, *8*, 155.
(4) For pertinent examples, see the following and their contained references: (a) Burnett, R. D.; Kirk, D. N. *J. Chem. Soc., Perkin Trans. 1* **1973**, 1830. (b) Koga, T.; Tomoeda, M. *J. Chem. Soc., Perkin Trans. 1* **1973**, 1848.
(5) Thiono–thiolo rearrangement and thiocarbonyl hydrolysis are not significant side reactions with β-*un*substituted systems such as **1** (cf. ref 1) or when **3** and other β-substituted diosphenol dimethylthiocarbamates are treated with *iodide* ion (to be published). This fact implies that it is a slow chloride ion displacement (and not a slow fused cyclization) that drives spirocyclization. We thank reviewer 1 for pointing this out to us.
(6) Halogenation of the parent enone gives, in general, mixtures of positional isomers seldom (however, see ref 6d) containing much of the α′-halo enone (ref 6a–e). There are several nongeneral methods based on annulation reactions (inter alia., ref 6f,g): (a) Kosower, E. M.; Wu, G.-S. *J. Org. Chem.* **1963**, *28*, 633. (b) DePuy, C. H.; Isaks, M.; Eilers, K. L.; Morris, G. F. *J. Org. Chem.* **1964**, *29*, 3503. (c) Garbisch, E. W., Jr.; Sprecher, R. F. *J. Am. Chem. Soc.* **1969**, *91*, 6785. (d) Bloch, R. *Synthesis* **1978**, 140. (e) Novikov, V. L.; Shestak, O. P.; Kamernitskii, A. V.; Elyakov, G. B. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1982**, 476. (f) Martin, G.; Daviaud, G. *Bull. Soc. Chim. Fr.* **1970**, 3098. (g) Molines, H.; Wakselman, C. *Tetrahedron* **1976**, *32*, 2099.
(7) We have found in several other systems that lithium bromide is more effective than lithium chloride in promoting O–S interchange. The nature of this catalysis is currently under investigation.

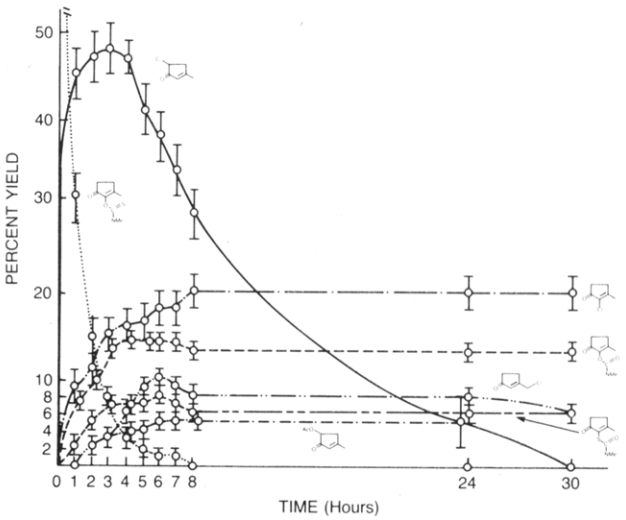


Figure 2.

(**18b**) (42%) and small amounts of **19** and **20**. Treatment of 3,5-dimethyl-2-[(dimethylthiocarbamoyl)oxy]-2-cyclopenten-1-one (**21**) with either lithium bromide or lithium chloride gave 2,4-dimethyl-4-[(dimethylcarbamoyl)thio]-2-cyclopenten-1-one (**24**) (about 35% in either case), which conceivably arises from the fused-cyclization intermediate **22** through enolization and 1,4-elimination (Scheme III).

This methodology appears to be unsatisfactory for the preparation of the homologous 6-halo-3-alkyl-2-cyclohexen-1-one systems; in several cases we have examined, aromatization and O–S interchange are the major reaction paths.

Experimental Section

General Methods. IR spectra were taken as thin films (for liquids) or as dilute chloroform solutions (for solids) with a Perkin-Elmer 1750 Fourier-transform instrument. ^{1}H NMR spectra were obtained in deuteriochloroform solution with Varian EM-360 or JEOL FX-90Q spectrometers. ^{13}C NMR spectra were obtained in deuteriochloroform solution with a JEOL FX-90Q spectrometer with complete proton decoupling. Low-resolution mass spectra were measured on a Finnegan 4500 instrument, with electron impact at 70 eV; high-resolution mass spectra were measured on a VG 7070F instrument, also with electron impact 70 eV. Elemental analyses were performed by M-H-W Laboratories, Phoenix, AZ. Gas chromatographic analyses were performed by using linear temperature programming on a Varian Model 3700 gas chromatograph equipped with a thermal conductivity detector and Hewlett-Packard Model 3380A integrator. Preparative liquid chromatography was performed at 3–7 atm pressure with Davisil grade 633 silica gel, 200–425 mesh.

Analytical Runs. GC response factors for compounds **3–9** (prepared below) versus 1,2,4-trichlorobenzene and *n*-octadecane were calculated, and then reactions of **3** were conducted in the presence of a small amount of one of these two internal standards. Direct injection of the reaction mixtures into the GC gave erratic results, so reaction aliquots were periodically removed, added to 3 volumes of water, neutralized with solid potassium bicarbonate, and extracted into methylene chloride before injection into the GC for analysis. Control experiments established that negligible amounts (<2%) of compounds **3–9** were lost to the aqueous phase by this procedure. GC conditions: 3.2 mm × 2 m column of 5% FFAP on 100/120 Chromosorb W, 110 °C for 10 min; 25 °C/min for 5 min; 235 °C, 5 min. Under these conditions the following retention times were observed: **4**, 5.72 min; **5**, 6.01 min; **8**, 6.32 min; **9**, 9.76 min; *n*-octadecane, 13.59 min; **6**, 14.02 min; **3**, 15.20 min; **7**, 15.76 min.

Preparation of Diosphenol Dimethylthiocarbamates and Related Substances. 3-Methyl-2-[(dimethylthiocarbamoyl)oxy]-2-cyclopenten-1-one (3). A 10-mL sample of 1 M aqueous lithium hydroxide solution was added at room temperature to a magnetically stirred solution of 1.12 g (10 mmol) 3-methyl-1,2-cyclopentadione (cyclotene) in 5 mL of chloroform, and then a solution of 1.36 g (11 mmol) of dimethylthiocarbamoyl chloride (Aldrich) in 5 mL of chloroform was added. After the mixture was stirred for 3 h, the chloroform phase was removed, and the aqueous phase was extracted with 10 mL of chloroform. The combined organic extracts were washed with saturated sodium chloride solution and evaporated, giving 1.90 g of a solid whose NMR spectrum indicated that it was substantially pure. Recrystallization from 10 mL of a mixture of cyclohexane/ethyl acetate (1:1) gave 1.57 g (79%) of white crystals: mp 93–93.5 °C; IR 1722, 1665, 1541 cm^{-1}; ^{1}H NMR δ 1.98 (s, 3 H), 2.50 (m, 4 H), 3.26 (s, 3 H), 3.36 (s, 3 H); MS, *m/z* 199 (18, $M^{\bullet+}$), 88 (72, $Me_2NC{=}S^+$), 72 (100, Me_2NCO^+). Anal. Calcd for $C_9H_{13}NO_2S$: C, 54.25; H, 6.58. Found: C, 54.21; H, 6.56.

3-Methyl-2-[(dimethylcarbamoyl)oxy]-2-cyclopenten-1-one (6). A 1.18-g (11-mmol) portion of dimethylcarbamoyl chloride was added to a solution of 1.12 g (10 mmol) of cyclotene in 5 mL of dry pyridine, and the mixture was stirred at room temperature for 5 h and then quenched with several drops of water. The mixture was poured into 50 mL of ice–water and extracted with three 25-mL portions of methylene chloride. The combined organic extracts were washed successively with 50-mL portions of aqueous copper sulfate solution, water, 1 M aqueous NaOH solution, and brine. The dried extract was evaporated to give a yellow solid, which was recrystallized from ether to give pale yellow crystals: mp 60–62 °C; IR 1718, 1666 cm^{-1}; ^{1}H NMR δ 1.98 (s, 3 H), 2.47 (m, 4 H), 2.99 (s, 3 H), 3.02 (s, 3 H); MS, *m/z* 183 (54, $M^{\bullet+}$), 72 (100, Me_2NCO^+). Anal. Calcd for $C_9H_{13}NO_3$: C, 59.01; H, 7.15. Found: C, 58.92; H, 7.17.

2-[(Dimethylcarbamoyl)thio]-3-methyl-2-cyclopenten-1-one (7). In analogy to procedures used for Newman–Kwart rearrangements,[8] a mixture of 1.99 g (10 mmol) of **3** and 20 mL of *n*-tetradecane was heated at 255 °C (under nitrogen) for 2 h. The dark mixture was cooled to room temperature, diluted with an equal volume of pentane, and chilled in a dry ice/acetone bath to precipitate a solid, which after washing with cold pentane was recrystallized from cyclohexane/ethyl acetate (2:1) to give white crystals: mp 80–81 °C; IR 1713, 1670, 1610 cm^{-1}; ^{1}H NMR δ 2.20 (s, 3 H), 2.63 (m, 4 H), 3.03 (s, 6 H); MS, *m/z* 199 (13, $M^{\bullet+}$), 72 (100, Me_2NCO^+). Anal. Calcd for $C_9H_{13}NO_2S$: C, 54.25; H, 6.58. Found: C, 54.14; H, 6.60.

3-*tert*-Butyl-2-[(dimethylthiocarbamoyl)oxy]-2-cyclopenten-1-one (17). The procedure used for the preparation of **3** was repeated, replacing cyclotene by 3-*tert*-butyl-1,2-cyclopentanedione and then stirring 5 h at room temperature. The crude product (2.35 g) was chromatographed on 105 g of silica gel packed in a mixture of cyclohexane/ethyl acetate (3:1), giving 1.31 g (54%) of a solid. Crystallization from ether gave white crystals: mp 92–94 °C; IR 1722, 1713, 1639, 1547 cm^{-1}; ^{1}H NMR δ 1.24 (s, 9 H), 2.2–2.8 (m, 4 H), 3.14 (s, 3 H), 3.38 (s, 3 H); HRMS, *m/z* 241.1134, calcd for $C_{12}H_{19}NO_2S$ 241.1137.

3-*tert*-Butyl-2-[(dimethylcarbamoyl)oxy]-2-cyclopenten-1-one (19). A solution of 154 mg (1 mmol) of 3-*tert*-butyl-1,2-cyclopentanedione in 10 mL of anhydrous ether was added dropwise to an ice-cold suspension of 60 mg (1.5 mmol) of sodium hydride (60% mineral oil suspension) in 5 mL of ether. After 5 min, a solution of 129 mg (1.2 mmol) of dimethylcarbamoyl chloride in 5 mL of ether was added dropwise, then the ice bath was removed, and the reaction mixture was stirred overnight. The mixture was poured into 25 mL of ice–water, and the ether phase was separated, washed with brine, dried, and evaporated. The crude product (145 mg) was chromatographed on 70 g of silica gel packed in a mixture of cyclohexane/ethyl acetate (2:1), giving 24 mg (15%) of recovered diosphenol followed by 89 mg (40%) of the title compound. Recrystallization from pentane gave white crystals: mp 90–92 °C; IR 1731, 1709, 1641 cm^{-1}; ^{1}H NMR δ 1.19 (s, 9 H), 2.2–2.6 (m, 4 H), 2.89 (sl br s, 6 H). Anal. Calcd for $C_{12}H_{19}NO_3$: C, 63.98; H, 8.50. Found: C, 63.90; H, 8.39.

3-*tert*-Butyl-2-[(dimethylcarbamoyl)thio]-2-cyclopenten-1-one (20). A mixture of 67 mg (0.28 mmoles) of 3-*tert*-butyl-1,2-cyclopentanedione and 3 mL of *n*-tetradecane was heated under nitrogen at reflux (255 °C) for 3 h and then processed as in the preparation of **7** to give 22 mg (33%) of white crystals: mp

(8) (a) Newman, M. S.; Karnes, H. A. *J. Org. Chem.* **1966**, *31*, 3980. (b) Kwart, H.; Evans, E. R. *J. Org. Chem.* **1966**, *31*, 410.

129–131 °C; IR 1670, 1718 cm^{-1}; ^1H NMR δ 1.31 (s, 9 H), 2.3–3.0 (m, 4 H), 3.00 (sl br s, 6 H); HRMS, m/z 241.1125, calcd for $C_{12}H_{19}NO_2S$ 241.1137.

3,5-Dimethyl-2-[(dimethylthiocarbamoyl)oxy]-2-cyclopenten-1-one (21). The procedure used for the preparation of **3** was repeated, replacing cyclotene by 3,5-dimethyl-1,2-cyclopentanedione and stirring 3 h at room temperature. The crude product was chromatographed on silica gel and crystallized from ether, giving white crystals: mp 47–48 °C; IR 1720, 1665, 1540 cm^{-1}; ^1H NMR δ 1.23 (d, J = 7 Hz, 3 H), 1.98 (sl br s, 3 H), 2.2–3.0 (m, 3 H), 3.30 (s, 3 H), 3.40 (s, 3 H). Anal. Calcd for $C_{10}H_{15}NO_2S$: C, 56.32; H, 7.08. Found: C, 56.32; H, 7.10.

Preparative Runs Involving Diosphenol Dimethylthiocarbamates. 5-Chloro-3-methyl-2-cyclopenten-1-one (4). A 12.9-g (65-mmol) sample of **3** was added, in one portion, to a boiling solution of 27.3 g (650 mmol) lithium chloride in 325 mL of acetic acid, and the resulting solution was heated at reflux for 1 h. The reaction mixture was poured into 2 kg of ice–water and neutralized with solid potassium bicarbonate. The mixture was extracted with two 1-L portions of methylene chloride. Drying and evaporation gave a thick liquid, which was chromatographed on 350 g of silica gel packed in cyclohexane/ethyl acetate (2:1), giving ca. 3.5 g of a pale liquid. Vacuum distillation afforded pure material: bp 69–70 °C (0.35 mm); IR 1714, 1626 cm^{-1}; ^1H NMR δ 2.17 (s, 3 H), 2.3–2.8 (m, 2 H), 4.22 (dd, J = 6.5, 3 Hz, 1 H), 5.92 (narr m, 1 H); ^{13}C NMR δ 19.2, 43.4, 53.9, 127.7, 176.3, 201.7; HRMS, m/z 130.0186, calcd for C_6H_7ClO 130.0186.

The title compound is hitherto unreported; its ^{13}C NMR spectrum is very similar to that reported[6e] for 5-bromo-3-methyl-2-cyclopenten-1-one.

2-Chloro-3-methyl-2-cyclopenten-1-one (5). A 1.99-g (10 mmol) sample of **3** was added, in one portion, to a boiling solution of 4.2 g (100 mmol) lithium chloride in 50 mL of acetic acid, and the resulting solution was heated at reflux for 16 h. Workup as above gave 1.0 g of a thick dark liquid, which was chromatographed on 70 g of silica gel packed in cyclohexane/ethyl acetate (2:1), giving 230 mg (18%) of **5**, which was recrystallized from pentane to give white crystals: mp 37–38 °C; IR 1714, 1621 cm^{-1}; ^1H NMR δ 2.13 (s, 3 H), 2.3–2.8 (m, 4 H); HRMS, m/z 130.0178, calcd for C_6H_7ClO 130.0186.

The title compound has been reported without physical or spectral data.[9]

3-(Chloromethyl)-2-cyclopenten-1-one (8) and 5-Acetoxy-3-methyl-2-cyclopenten-1-one (9). A 70-g (350-mmol) sample of **3** was added, in one portion, to a boiling solution of 147 g (3.5 mol) of lithium chloride in 1.5 L of acetic acid, and the resulting solution was heated at reflux for 3 h. Workup as above gave ca. 30 g of a dark liquid, which was chromatographed on 600 g of silica gel packed in cyclohexane/ethyl acetate (6:1), giving first, 12.2 g of a mixture of **4** and **5**, then 1.5 g of crude **8**, and finally 2.0 g of pure **9**. Vacuum distillation of crude **8** afforded material, bp 67–68 °C (0.4 mm), which was further purified by chromatography on 50 g of silica gel packed in cyclohexane/ethyl acetate (6:1), giving 1.0 g of pure **8**: IR 1713, 1681, 1626 cm^{-1}; ^1H NMR δ 2.36–2.74 (m, 4 H), 4.30 (s, 2 H), 6.06 (narr m, 1 H). Compound **9** had the following spectra: IR 1782, 1744, 1718, 1620 cm^{-1}; ^1H NMR δ 2.10 (2 s, 6 H), 2.6–3.3 (m, 2 H), 5.04 (dd, J = 5, 1 Hz, 1 H), 5.95 (narr m, 1 H).

3-*tert*-Butyl-5-chloro-2-cyclopenten-1-one (18a). A 120-mg (0.5 mmol) sample of **17** was added to a boiling solution of 210 mg (5 mmol) of lithium chloride in 2.5 mL of acetic acid, and the resulting solution was heated at reflux for 3 h. Workup as in the preparation of **4** gave 0.1 g of an oil, which was chromatographed on 15 g of silica gel packed in cyclohexane/ethyl acetate (3:1), giving 39 mg (45%) of **18a** (oil) followed by 38 mg of a 9:1 mixture of **19** and **20** (as determined by NMR and GC comparison with an authentic mixture). Compound **18a** had the following spectra, closely analogous to **4**: IR 1719, 1601 cm^{-1}; ^1H NMR δ 1.20 (s, 9 H), 2.64 (A part of ABMX, $|J_{ab}|$ = 16 Hz, J_{am} = 3 Hz, J_{ax} = 1.5 Hz, 1 H), 3.15 (B part of ABMX, $|J_{ab}|$ = 16 Hz, J_{bm} = 6.5 Hz, J_{bx} = 1.5 Hz, 1 H), 4.24 (M part of ABMX, dd J_{bm} = 6.5, J_{am} = 3 Hz, 1 H), 5.94 (X part of ABMX, t, J_{ax} = J_{bx} = 1.5 Hz, 1 H); ^{13}C NMR δ 28.3, 35.5, 38.8, 54.2, 124.6, 188.0, 202.9. Anal. Calcd for $C_9H_{13}ClO$: C, 62.62; H, 7.59. Found: C, 62.63; H, 7.43; HRMS, m/z 172.0647, calcd for $C_9H_{13}ClO$ 172.0655.

5-Bromo-3-*tert*-butyl-2-cyclopenten-1-one (18b). The procedure used above was followed, replacing lithium chloride by lithium bromide and heating for only 1.5 h. Workup and chromatography gave 45 mg (42%) of **18b** (oil): IR 1714, 1699, 1601 cm^{-1}; ^1H NMR δ 1.20 (s, 9 H), 2.88 (A part of ABMX, $|J_{ab}|$ = 18 Hz, J_{am} = 3 Hz, J_{ax} = 1.5 Hz, 1 H), 3.30 (B part of ABMX, $|J_{ab}|$ = 18 Hz, J_{bm} = 6 Hz, J_{bx} = 1.5 Hz, 1 H), 4.32 (M part of ABMX, dd, J_{bm} = 6, J_{am} = 3 Hz, 1 H), 5.93 (X part of ABMX, t, J_{ax} = J_{bx} = 1.5 Hz, 1 H).

The spectrum of this substance is clearly different from that of 4-bromo-3-*tert*-butyl-2-cyclopenten-1-one reported by Garbisch.[5c]

2,4-Dimethyl-4-[(dimethylcarbamoyl)thio]-2-cyclopenten-1-one (24). A 230-mg (1-mmol) sample of **21** was added to a boiling solution of 420 mg (10 mmol) of lithium chloride in 5 mL of acetic acid, and the resulting solution was heated at reflux for 1.5 h. Workup as in the preparation of **4** gave 0.11 g of an oil, which was chromatographed on 15 g of silica gel packed in cyclohexane/ethyl acetate (3:1), giving 79 mg (37%) of **24**: mp 60–62 °C; IR 1712, 1656 cm^{-1}; ^{1}NMR δ 1.72 (s, 3 H), 1.77 (d, J = 1.5 Hz, 3 H), 2.54, 2.81 (AB q, $|J_{ab}|$ = 19 Hz, 2 H), 2.92 (s, 6 H), 7.38 (t, J = 1.5 Hz, 1 H); ^{13}C NMR δ 9.9, 27.7, 36.6, 49.8, 51.4, 140.7, 160.8, 166.8, 206.2; MS, m/z 213 (21, $M^{\cdot+}$), 109 (78, $M^{\cdot+}$ – $Me_2NC(=O)S$), 81 (49, 109 – CO), 72 (100, Me_2NCO^+); HRMS, m/z 213.0814, calcd for $C_{10}H_{15}NO_2S$ 213.0824.

Interconversion of 4 and 8. A solution of 1.17 g (9 mmol) of **4** and 780 mg (90 mmol) of lithium chloride in 45 mL of acetic acid was heated at reflux as the appearance of **8** was monitored by GC. During this reaction, neither **5** nor 2-chloro-4-methyl-2-cyclopenten-1-one was observed. (An authentic sample of the latter compound was made by treatment of 2-[(dimethylthiocarbamoyl)oxy]-4-methyl-2-cyclopenten-1-one with lithium chloride in acetonitrile/acetic acid.) After 2 h the reaction was worked up as usual, and the crude product was chromatographed on 120 g of silica gel packed in cyclohexane/ethyl acetate (6:1), giving **4** followed by **8**. Similarly, a solution of 261 mg (2 mmol) of **8** and 840 mg (20 mmol) of lithium chloride in 10 mL of acetic acid was heated at reflux for 7 h when GC analysis showed partial conversion to **4**.

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^{13}C Kinetic Isotope Effects in the Acid-Catalyzed Disproportionation and Rearrangements of 4,4′-Dichloro[2,2′,6,6′-$^{13}C_4$]hydrazobenzene

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In acid solution, 4,4′-dichlorohydrazobenzene (**1**) undergoes disproportionation into 4-chloroaniline (**2**) and 4,4′-dichloroazobenzene (**3**) and also rearrangement to an *o*- and *p*-semidine (**4** and **5**, respectively) (Scheme I).

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