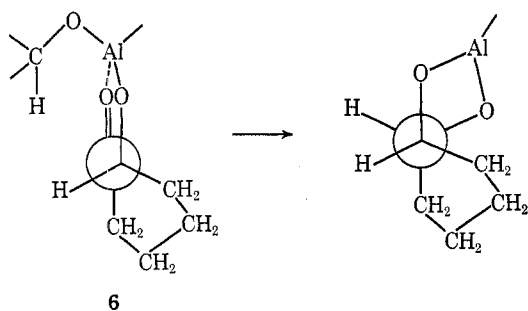those in the transition state leading to the *cis*-glycol, **6** (*cf.* **4**), decrease more rapidly.

6

Experimental Section

Materials.—Commercial toluene was distilled before use. Commercial aluminum isopropoxide was distilled and the solidified distillate was fused before each use. Weighing and transfer of aluminum isopropoxide were accomplished in a dry nitrogen atmosphere. 1,2-Cyclopentanedione was prepared by the method of Acheson,[7] except that the dione was extracted with chloroform rather than ether. 1,2-Cyclopentanedione was recrystallized from low-boiling petroleum ether before each use: mp 55–56° (lit.[7] mp 55–56°). Authentic *cis*- and *trans*-1,2-cyclopentanediols, used for identification of glycolic products, were prepared by the methods of Owen and Smith.[8]

Representative Reduction.—A solution of 4.1 g (20 mmol) of fused aluminum isopropoxide and 0.98 g (10 mmol) of 1,2-cyclopentanedione in 25 ml of toluene was heated in a 50-ml one-neck round-bottomed flask attached to a condenser capped by a drying tube. After 5 hr at 105°, the dark, red-brown reaction mixture was shaken with an equal volume of saturated, aqueous potassium sodium tartrate. Filtration removed 2.30 g of dark brown solids, which separated when the reaction mixture was shaken with the tartrate solution. The liquid phases of the filtrate were separated and the aqueous phase was extracted continuously with chloroform for 48 hr. Organic phases were combined and their volume was adjusted for glpc analysis. Analysis was accomplished with external standards of the authentic glycols and a 3-m column of 5% Carbowax 20M on 60/80 mesh, HMDS-treated Chromosorb W. A column temperature of 120° and a helium inlet pressure of 20 psi gave a satisfactory resolution of the isomeric glycols. Results are reported in Table I.

Registry No.—1,2-Cyclopentanedione, 3008-40-0; 1,2-cyclohexanedione, 765-87-7.

(7) R. M. Acheson, *J. Chem. Soc.*, 4232 (1956).
(8) L. N. Owen and P. N. Smith, *ibid.*, 4026 (1952).

3-(5-Methylfuryl-2)cycloalkanones.
A Synthesis of Bicyclic Dionenes

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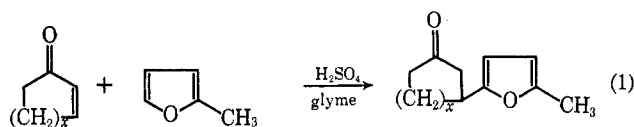
Although the reaction involving the condensation of *α,β*-unsaturated ketones with furan and its homologs is a well documented one,[1–4] there are no reports con-

(1) S. M. Sherlin, A. Y. Berlin, T. A. Serebrennikova, and F. E. Rabinovich, *Zh. Obshch. Khim.*, **8**, 7 (1938); *Chem. Abstr.*, **32**, 5397 (1938).
(2) K. Alder and S. Schmidt, *Chem. Ber.*, **76**, 183 (1943).
(3) Lambiotte and Co., French Patent 972,652 (1951); *Chem. Abstr.*, **47**, 1744 (1953).

cerned with its use as a starting point in the synthesis of molecules containing condensed ring systems. Therefore, we wish to report a two-step synthesis of 5,6-dihydro-7-methyl-1,4-indandione (**10**) and 2,3,4,6,7,8-hexahydro-8-methyl-1,5-naphthalenedione (**11**), in which the first step of each involves the condensation of 2-cyclopenten-1-one (**1**) or 2-cyclohexen-1-one (**2**) with 2-methylfuran.
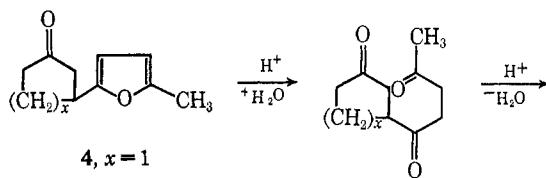

$$ (1) $$

1, *x* = 1	**4**, *x* = 1
2, *x* = 2	**5**, *x* = 2
3, *x* = 3	**6**, *x* = 3

4, *x* = 1	**7**, *x* = 1
5, *x* = 2	**8**, *x* = 2
6, *x* = 3	**9**, *x* = 3

$$ (2) $$
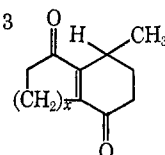
10, *x* = 1
11, *x* = 2
12, *x* = 3

When the alicyclic *α,β*-unsaturated ketones **1**, **2**, and **3** were allowed to react with 2-methylfuran in refluxing glyme containing a catalytic amount of sulfuric acid (eq 1), the 3-(5-methylfuryl-2)cycloalkanones **4**, **5**, and **6** were produced in yields of 36, 40, and 32%, respectively. Preparation of the dionenes **10** (47%) and **11** (35%) (eq 2) was best accomplished by refluxing **4** or **5** for 48 hr in aqueous acetic acid containing a trace of sulfuric acid. Although extended treatment (72 hr) of **6** under the same conditions yielded triketone **9**, no bicyclic dionene **12** could be isolated from this reaction.

When **5** was subjected to variations in the amount of time that it was heated under these acidic conditions, significant changes in the product composition from this reaction occurred. For example, while treatment for 24 hr yielded almost equal amounts of **8** and **11**, refluxing for 72 hr afforded both **11** and a single keto phenol **13**. Heating **5** for 96 hr produced a tarry reaction mixture from which only traces of **8** and **11** could be isolated, but from which a 20% yield of **13** was obtained.

The identification of **13** as 3,4-dihydro-5-hydroxy-8-methyl-1-(2H)-naphthalenone and not the alternative 3,4-dihydro-4-methyl-5-hydroxy-1-(2H)-naphthalenone (**16**) was based on the fact that the nmr spectrum of the isolated keto phenol displayed a methyl singlet at δ 2.45, and not the higher field methyl doublet anticipated for **16**. Additional proof for the structure of **13** was

(4) Y. K. Yur'ev, N. S. Zefirov, A. A. Shteinman, and V. I. Ruboedov *Zh. Obsch. Khim.*, **30**, 3755 (1960); *Chem. Abstr.*, **55**, 19890 (1961).

provided through the preparation of a known semi-carbazone[5] of its methyl ether 14.

The formation of 10 and 11 in eq 2 of the above sequence undoubtedly involves the *in situ* intramolecular cyclization of triketones 7 and 8, which themselves result from the acid-catalyzed cleavage[6,7] of the furan ring in 4 and 5. The sensitivity of 11 to autooxidation upon prolonged heating is not surprising, and the reported[8] extreme ease with which 4,8-dihydroxy-1-methylnaphthalene (17) is autooxidized probably accounts for its not being found among the products resulting from the reactions of 5.

13, x = 2; R = H
14, x = 2; R = CH₃
15, x = 1; R = H

16

17

18
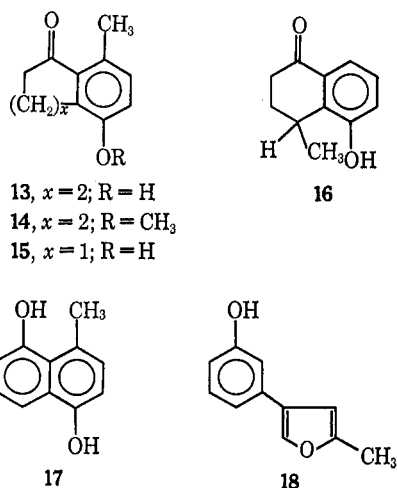
During the course of this investigation, the previously unreported 4-hydroxy-7-methyl-1-indanone (15) and *m*-(5-methylfuryl-2) phenol (18) were also prepared; the former by treating 10 with palladium on charcoal in refluxing mesitylene, and the latter by dehydrogenating 5 with elemental sulfur dissolved in diphenyl ether.

Experimental Section[9]

3-(5-Methylfuryl-2)cyclohexanone (5).—A solution of 2 (96.0 g, 1.0 mol) and 2-methylfuran (98.5 g, 1.2 mol) was dissolved in 500 ml of glyme containing 1 ml of concentrated sulfuric acid and heated at reflux for 8 hr. The solution was cooled, dried (NaHCO₃), concentrated, and distilled, giving 71.4 g (40%) of 5: bp 93–95° (2 mm); ir (neat) 5.85 and 12.80 μ; nmr (CCl₄) δ 5.80 (m, 2), 3.41–2.78 (m, 1), 2.78–2.22 (m, 4), 2.22 (s, 3), and 2.22–1.55 (m, 4). A semicarbazone of 5 was prepared, mp 171–173°.

Anal. Calcd for C₁₂H₁₇N₃O₂: C, 61.27; H, 7.24; N, 17.88. Found: C, 60.99; H, 7.33; N, 17.99.

3-(5-Methylfuryl-2)cyclopentanone (4) had bp 97–98° (4.5 mm); ir (neat) 5.75 and 12.80 μ; nmr (CCl₄) δ 5.83 (m, 2), 2.62–3.10 (m, 1), 2.50–1.80 (m, 6), and 2.22 (s, 3). A semicarbazone of 4 was prepared, mp 170.5–172°.

Anal. Calcd for C₁₁H₁₅N₃O₂: C, 59.73; H, 6.79; N, 19.00. Found: C, 59.70; H, 6.83; N, 19.03.

3-(5-Methylfuryl-2)cycloheptanone (6) had bp 111–112° (3.5 mm); ir (neat) 5.88 and 12.80 μ; nmr (CCl₄) δ 5.77 (m,2),

(5) W. Cocker, C. Lipman, and D. R. A. Whyte, *Chem. Ind.* (London), 237 (1950).

(6) A. P. Dunlop and F. N. Peters, "The Furans," American Chemical Society Monograph Series, No. 619, American Chemical Society, Washington, D. C., 1953, pp 640–658.

(7) G. Benson in "Organic Syntheses," Coll. Vol. II, John Wiley & Sons, Inc., New York, N. Y., 1943, p 220.

(8) N. P. Buu-Hoï and D. Lavit, *J. Org. Chem.*, 20, 1191 (1955).

(9) Microanalyses were performed by the Galbraith Laboratories, Knoxville, Tenn. Melting points are uncorrected. Nuclear magnetic resonance spectra were determined with a Varian Model A-60; pertinent chemical shifts are expressed in parts per million downfield from internal tetramethylsilane

3.10–2.22 (m, 4), 2.22 (s, 3), and 2.22–1.10 (m, 7). A semicarbazone of 6 was prepared, mp 176–178°.

Anal. Calcd for C₁₃H₁₉N₃O₂: C, 62.65; H, 7.63; N, 16.87. Found: C, 62.53; H, 7.62; N, 16.86.

3-(1,4-Dioxopentyl)cycloheptanone (9).—A solution of 6 (15.5 g, 0.08 mol), 15 ml of glacial acetic acid, 6 ml of water, and 5 drops of concentrated sulfuric acid was heated at reflux for 72 hr. After the solution had cooled, 0.3 g of sodium acetate was added and the solution was concentrated and distilled, giving 8.6 g of a light yellow oil: bp 130–140° (3 mm); ir (neat) 5.88 μ; mol wt (mass spectrum) 210. The crude triketone 9 partially crystallized on standing, and afforded an analytical sample upon recrystallization from hexane; mp 116.5–118°.

Anal. Calcd for C₁₂H₁₈O₃: C, 68.57; H. 8.57. Found: C, 68.66; H, 8.60.

5,6-Dihydro-7-methyl-1,4-indandione (10).—A solution of 4 (16.4 g, 0.1 mol), 15 ml of glacial acetic acid, 6 ml of water, and 3 drops of concentrated sulfuric acid was heated at reflux for 48 hr. After the solution had cooled, 0.3 g of sodium acetate was added and the solution was concentrated and distilled, giving 9.8 g of a yellow oil, bp 110–130° (4 mm), which was shown by glc to contain 7.7 g of 10, an analytical sample of which was obtained by preparative glpc (5 ft × 0.25 in. 10% SE-30 on Chromosorb W): ir (neat) 5.95 and 8.37 μ; uv max (95% EtOH) 260 mμ; nmr (CCl₄) δ 1.26 (d, 3, J = 7 Hz); mol wt (mass spectrum) 164.

Anal. Calcd for C₁₀H₁₂O₂: C, 73.17; H, 7.32. Found: C, 72.86; H, 7.29.

2,3,4,6,7,8-Hexahydro-8-methyl-1,5-naphthalenedione (11).—A solution of 5 (17.8 g, 0.1 mol), 15 ml of glacial acetic acid, 6 ml of water, and 3 drops of concentrated sulfuric acid was heated at reflux for 48 hr. After the solution had cooled, 0.3 g of sodium acetate was added and the solution was concentrated and distilled, giving 6.8 g (35%) of 11: bp 120–125° (3.5 mm); mp 50–53.5°; ir (KBr) 6.0 μ; uv max (95% EtOH) 264 mμ (log ε 4.04); nmr (CCl₄) δ 1.15 (d, 3, J = 7 Hz); mol wt (mass spectrum) 178. An analytical sample of 8, mp 49–51°, was prepared by sublimation at 80–90° (5 mm).

Anal. Calcd for C₁₁H₁₄O₂: C, 74.16; H, 7.86. Found: C, 74.34; H, 8.10.

3,4-Dihydro-5-hydroxy-8-methyl-1-(2H)-naphthalenone (13).—A solution of 5 (17.8 g, 0.1 mol) was refluxed for 96 hr under conditions identical with those described for preparing 11. Attempted distillation of the tarry residue produced only a small forerun of liquid before a solid substance began to sublime into the distillation column. Further sublimation yielded 2.9 g of 13, which was purified by recrystallization from benzene followed by sublimation: mp 189–190.5°; ir (KBr) 3.20, 6.05, 6.37, 7.80, and 12.19 μ; uv max (95% EtOH) 205, 228, and 262 mμ; nmr (acetone-d₆) δ 6.92 (s, 2) and 2.45 (s, 3); mol wt (mass spectrum) 176.

Anal. Calcd for C₁₁H₁₂O₂: C, 75.00; H, 6.82. Found: C, 74.92; H, 6.81.

A sample of 13 was converted into its methyl ether 14 with dimethyl sulfate, and a semicarbazone of 14 was prepared, mp 235–237° (lit.[6] mp 233–234°).

4-Hydroxy-7-methyl-1-indanone (15).—A mixture of 10 (1.7 g, 0.01 mol) and 100 mg of 5% palladium on charcoal were placed in 5 ml of mesitylene and heated at reflux for 1 hr. When the mixture was cooled to room temperature, a solid crystallized. Crystallization from methanol followed by sublimation yielded 15: mp 194–195°; ir (KBr) 3.12, 5.99, 6.28, 7.80, and 12.21 μ; uv max (95% EtOH) 205, 226, and 259 mμ; nmr (acetone-d₆) δ 6.94 (s, 2), 3.11–2.75 (m, 2), 2.68–2.35 (m, 2), and 2.46 (s, 3); mol wt (mass spectrum) 162.

Anal. Calcd for C₁₀H₁₀O₂: C, 74.07; H, 6.17. Found: C, 74.23; H, 6.18.

***m*-(5-Methylfuryl-2)phenol (18).**—A mixture of 5 (7.0 g, 0.04 mol) and 2.55 g (0.08 mol) of powdered sulfur were placed in 70 ml of diphenyl ether and heated together for 2.5 hr at 245–255°. The reaction mixture was cooled, diluted with ether, and extracted with dilute sodium hydroxide. The alkaline extracts were saturated with sodium chloride, acidified with dilute acid, and extracted with ether. Concentration of the ether extracts followed by distillation yielded 2.6 g (37%) of 18: bp 147–151° (3 mm); ir 3.01, 6.30, and 12.95 μ; nmr (CCl₄) δ 2.21 (s, 3), 5.85 (m, 1), 6.33 (d, 1), 6.45–6.85 (m, 2), and 6.97–7.18 (m, 3). This material slowly crystallized to a light yellow solid, mp 45–49°. Several crystallizations from hexane–benzene produced a sample suitable for analysis, mp 51–53°.

Anal. Calcd for $C_{11}H_{10}O_2$: C, 75.86; H, 5.75. Found: C, 75.85; H, 5.73.

The Coupling of Phenyllithium with *trans*- and *cis*-1-Chloro-2-butene[1]
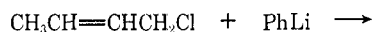
Ronald M. Magid and Richard D. Gandour

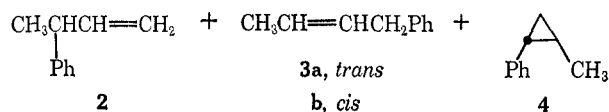*Department of Chemistry, William Marsh Rice University, Houston, Texas 77001*

The recent report by Wawzonek, *et al.*,[2] on the reaction of 1-chloro-2-butene with phenyllithium prompts us to communicate our results on the same system, and to point out that the apparent loss of geometrical integrity[2] is due solely to the use of impure starting materials.

According to Wawzonek, *et al.*,[2] the addition of *trans*-1-chloro-2-butene (1a) to phenyllithium yields 3-phenyl-1-butene (2), *trans*- and *cis*-1-phenyl-2-butene (3a and 3b), and *trans*-1-methyl-2-phenylcyclopropane (4) in an 18:54:16:11 distribution; similarly, *cis*-1-chloro-2-butene (1b) is alleged to give the same products in the distribution 23:7:67:3.

$$CH_3CH{=}CHCH_2Cl \ + \ PhLi \ \longrightarrow$$

1a, *trans*
b, *cis*

$$CH_3\underset{\underset{Ph}{|}}{CHCH}{=}CH_2 \ + \ CH_3CH{=}CHCH_2Ph \ + $$

2   3a, *trans*   b, *cis*   4

The commercially available crotyl chloride assumed by these workers to be *trans*-1-chloro-2-butene is, in fact, a mixture of 1a, 1b, and 3-chloro-1-butene (1c). The first two components have the same retention times on most glpc columns, but can be separated on β,β'-oxydipropionitrile.[3] A pure sample (>99%) of *trans*-1-chloro-2-butene (1a) can be obtained by preparative glpc of the commercial material (*ca.* 85% 1a, 15% 1b, and 1% 1c). Similarly, the reaction mixture (*ca.* 5% 1a, 92% 1b, and 3% 1c) from treatment of *cis*-1-hydroxy-2-butene[4a] with thionyl chloride[4b] can be separated by preparative glpc, yielding pure (>99%) *cis*-1-chloro-2-butene (1b).

The results from the reactions of 1a, 1b, and the commercial mixture of 1a and 1b with phenyllithium are summarized in Table I. *No geometric isomerization*

occurs during the course of the reaction. Control experiments establish that neither 1a nor 1b isomerizes during the reaction, nor is either converted into allylic bromide by reaction with lithium bromide present in the phenyllithium solution; all of the products are stable under the reaction conditions. The clean stereochemistry, therefore, makes it unnecessary to invoke[2] the ionization mechanism[5] which we have argued against earlier.[6]

Cyclopropane 4 undoubtedly arises *via* a mechanism analogous with that established previously for allyl chloride,[6] concluding with the addition of phenyllithium across the double bond of 3-methylcyclopropene. The fact that 4 is nearly exclusively *trans* should not be taken as evidence against this mechanism in the light of the known directing effects of a methyl group on the Diels–Alder reactions of cyclopropenes.[7]

We have also investigated the coupling reaction of phenyllithium with 3-chloro-1-butene and with 3-chloro-2-methyl-1-propene-3,3-d_2; we will report these results, as well as those from all of the dimethyl allyl chlorides, in a future publication.

TABLE I

THE REACTION OF 1-CHLORO-2-BUTENE WITH PHENYLLITHIUM[a]

Starting chloride	Total yield, %[b]	Product distribution, %[c]			
		2	3a	3b	4
1a	55	22.6	66.0	0[d]	11.4
1b	42	23.5	0[d]	71.8	4.7
1a + 1b[e]	63	15.7	62.3	12.4	9.7

[a] The allylic chloride was added to a slight excess of phenyllithium in ether, and the reaction mixture was refluxed for 2 hr. [b] Total yields were determined by quantitative glpc using ethylbenzene as an internal standard. [c] The product distribution was determined by glpc of the crude reaction mixture. [d] None present by the limits of glpc detection. [e] Commercially available crotyl chloride (Aldrich Chemical Co., Inc.).

Experimental Section

Instruments.—Analytical glpc was performed on a Perkin-Elmer Model 800 gas chromatograph (flame ionization detector) and utilized the following columns: A, β,β'-oxydipropionitrile (15%) on 80/100 Chromosorb P, $^1/_8$ in. × 10 ft; B, a $^1/_8$ in. × 30 ft column composed of a 20-ft section of diethyleneglycol succinate (20%) on 80/100 Chromosorb P, HMDS and a 10-ft section of Bentone 34 (10%) on 80/100 Chromosorb P, HMDS. All yields were determined by glpc using an internal standard; areas were measured with a Disc integrator. Preparative glpc was performed on a Varian Aerograph Model 202-1B gas chromatograph (thermal conductivity detector) and utilized the following columns: C, β,β'-oxydipropionitrile (15%) on 80/100 Chromosorb P, $^3/_8$ in. × 10 ft; D, XF-1150 (10%) on 45/60 Chromosorb P, $^3/_8$ in. × 10 ft.

Nmr spectra were obtained on a Varian Associates A-56/60A spectrometer; ir spectra were obtained on a Beckman IR-8.

Materials.—Crotyl chloride was purchased from Aldrich Chemical Co., Inc.; preparative glpc (column C) yielded pure (>99%, column A) *trans*-1-chloro-2-butene (1a). Pure (>99%, column A) *cis*-1-chloro-2-butene (1b) was obtained by preparative glpc (column C) of the reaction mixture[4b] from *cis*-crotyl alcohol[4a] and thionyl chloride. Phenyllithium in ether was prepared in the usual manner and was standardized by the Gilman method.[8] All reactions involving lithium reagents were run under an argon atmosphere.

Reaction of 1-Chloro-2-butene with Phenyllithium.—Pure *trans*-1-chloro-2-butene (1a, 0.90 g, 0.01 mol) in 5 ml of ether was added dropwise over 15 min to 15 ml (0.012 mol) of 0.8 *N*

(1) Support of this work by the Robert A. Welch Foundation is gratefully acknowledged as is the assistance of the National Science Foundation in the purchase of a Varian Associates A-56/60A Spectrometer.

(2) S. Wawzonek, B. J. Studnicka, and A. R. Zigman, *J. Org. Chem.*, **34**, 1316 (1969).

(3) L. J. Brubacher, L. Treindl, and R. E. Robertson, *J. Amer. Chem. Soc.*, **90**, 4611 (1968).

(4) (a) L. F. Hatch and S. S. Nesbitt, *ibid.*, **72**, 727 (1950); (b) S. H. Sharman, F. C. Caserio, J. C. Leak, and W. G. Young, *ibid.*, **80**, 5965 (1958).

(5) S. J. Cristol, W. C. Overhults, and J. S. Meek, *ibid.*, **73**, 813 (1951).

(6) R. M. Magid and J. G. Welch, *ibid.*, **90**, 5211 (1968).

(7) (a) G. L. Closs, L. E. Closs, and W. A. Böll, *ibid.*, **85**, 3796 (1963); (b) M. A. Battiste, *Tetrahedron Lett.*, 3795 (1964).

(8) H. Gilman and A. H. Haubein, *J. Amer. Chem. Soc.*, **66**, 1515 (1944).