propyl 3-phenyl-2-propenyl ether, 13645-20-0; isopropyl 2-cyclohexenyl ether, 4982-24-5; 2-octanol, 123-96-6; 2-octanone, 111-13-7; 2-methylbenzyl alcohol, 98-85-1; 1-octanol, 111-87-5; 2,2-diphenylpropanol, 75-84-3; benzyl alcohol, 100-51-6; 4-*tert*-butylbenzyl alcohol, 877-65-6; 2-cyclohexen-1-ol, 822-67-3; *cis*-carveol, 1197-06-4; geraniol, 106-24-1; cholesterol, 57-88-5; 2-butanone, 78-93-3; propionaldehyde, 123-38-6; 2-furaldehyde, 98-01-1; trichloroacetaldehyde, 75-87-6; acetone, 67-64-1; cyclohexanone, 108-94-1; acetophenone, 98-86-2; 2,2-diphenylpropionaldehyde, 22875-82-7; benzaldehyde, 100-52-7; 4-*tert*-butylbenzaldehyde, 939-97-9; 2-cyclohexen-1-one, 930-68-7; carvone, 99-49-0; (*E*)-citral, 141-27-5; (*Z*)-citral, 106-26-3; 4-cholesten-3-one, 601-57-0; *p*-nitrobenzaldehyde, 555-16-8; *p*-anisaldehyde, 123-11-5; ethyl pyruvate, 617-35-6; cinnamaldehyde, 104-55-2; *p*-nitrobenzyl alcohol, 619-73-8; 4-methoxybenzyl alcohol, 105-13-5; ethyl lactate, 97-64-3; cinnamyl alcohol, 104-54-1; octanoic acid, 124-07-2; *p*-anisic acid, 100-09-4; dicyclohexenyl ether, 15129-33-6; myrcene, 123-35-3; limonene, 138-86-3; ocimene, 502-99-8.

Efficient Synthesis of 2-Methyl-1-cyclopentene-1-carboxylic Acid

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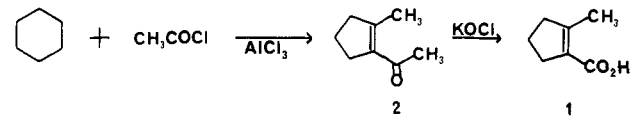
The utility of 2-methyl-1-cyclopentene-1-carboxylic acid (**1**) as a synthetic intermediate in our research efforts[1] as well as the efforts of other research groups[2] led us to develop a short, economical synthesis of this material. Previous syntheses[2,3] proved unsuitable for routine preparation of **1** in large quantities. A synthetic approach involving organocuprate addition to derivatives of 2-carbomethoxycyclopentanone reported previously by one of us[3d] and by Weiler and Sum[3e] appears to be quite sensitive to the purity of reagents and reaction scale.

The current approach was based on the recognition that a haloform-type oxidation of the known 1-acetyl-2-methylcyclopentene (**2**) should give the desired acid. The acetyl derivative **2** can be synthesized in a variety of ways. One common approach[4] utilizes an aldol cyclization of 2,7-octanedione,[5] but we have found that direct acetylation of cyclohexane provides an experimentally simple procedure that avoids the use of expensive starting materials or sensitive organometallic reagents. The conditions used for the acetylation reaction are a modification of the method reported by Tabushi.[9,10] It was found that treatment of the crude product with methanolic KOH prior to distillation gave material that did not discolor upon standing.

The haloform oxidation makes use of potassium hypochlorite formed by reaction of commercial calcium hypochlorite (Olin HTH) with potassium hydroxide and potassium carbonate.[11] Excess hypochlorite was destroyed by addition of sodium bisulfite, neutral materials were removed by ether extraction, and acid **1** was isolated by extraction after acidification to a Congo Red endpoint.[12]



2 **1**

Experimental Secton

1-Acetyl-2-methylcyclopentene (2). Aluminum trichloride (200 g, 1.5 mol) was added to 1 L of chloroform. Acetyl chloride (117.7 g, 1.5 mol) was added, and the mixture was stirred for 10 min, at which time cyclohexane (126.2 g, 1.5 mol) was added. The mixture was heated at reflux for 2 h, and then allowed to stir at room temperature for 2 days. The mixture was poured onto ice/HCl and the layers were separated. The aqueous layer was washed with CH_2Cl_2, and the combined organic layers were concentrated by rotary evaporation. The resulting material was dissolved in approximately 500 mL of methanol, 50 g of KOH was added, and the mixture was stirred overnight. The methanol was removed by rotary evaporation, and then the residue was dissolved in ether and washed with water and 10% NaOH. The ether layer was dried over $MgSO_4$, concentrated, and distilled (85–95 °C/27 torr) to yield 69.03 g (0.556 mol, 37% yield) of **2**: ^{1}H NMR ($CDCl_3$, 90 MHz) δ 1.6–2.0 (m, 2 H), 2.1–2.2 (m, allylic CH_3), 2.23 ($COCH_3$), 2.3–2.8 (m, 4 H); ^{13}C ($CDCl_3$, 50.31 MHz) δ 16.8 (CH_3), 21.5 (C-4), 30.3 ($COCCH_3$), 34.4 and 41.2 (C-3 and C-5), 135.8 (C-1), 154.1 (C-2), 198.3 (CO).

2-Methyl-1-cyclopentene-1-carboxylic Acid (1). Commercial calcium hypochlorite (Olin HTH, 65% CaOCl, 35 g) was suspended in 140 mL of H_2O in a 250-mL Erlenmeyer flask. A solution of KOH (7 g, 0.125 mol) and K_2CO_3 (24.5 g, 0.177 mol) in 70 mL of H_2O was added. The flask was stoppered and shaken until the initial gelatinous precipitate liquefied. The potassium hypochlorite solution (containing approximately 0.14 mol of KOCl) was then filtered to remove the precipitated calcium salts and the filter cake was rinsed with 30 mL of water.

The resulting solution of potassium hypochlorite was cooled to 0 °C, and ketone **2** (10 g, 80.5 mmol) was added dropwise under

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(3) (a) King, L. E.; Robinson, R. *J. Chem. Soc.* **1941**, 465–470. (b) Wheeler, O. H.; Lerner, I. *J. Am. Chem. Soc.* **1956**, *78*, 63–64. (c) Takeda, A.; Shinhama, K.; Tsuboi, S. *Bull. Chem. Soc. Jpn.* **1977**, *50*, 1831–1835. (d) Harding, K. E.; Tseng, C.-Y. *J. Org. Chem.* **1978**, *43*, 3974–3977. (e) Sum, F.-W.; Weiler, L. *Can. J. Chem.* **1979**, *57*, 1431–1441. (f) Dieter, R. K.; Jenkitkasemwong, Y. *Tetrahedron Lett.* **1982**, *23*, 3747–3750.

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(5) (a) Commercially available 1,7-octadiyne can be hydrated to 2,7-octanedione in 80% yield by using conditions reported for the hydration of 1-octyne.[6] (b) Addition of 2 equiv of MeZnCl to adipyl chloride can be used to produce 2,7-octanedione in 65% yield.[7] (c) We have prepared 2,7-octanedione in 75% yield by oxidative cleavage of 1,2-dimethylcyclohexene with $KMnO_4/NaIO_4$, while ozonolysis of 1,2-dimethylcyclohexene has been reported to proceed in unspecified yield.[8]

(6) Thomas, R. J.; Campbell, K. N.; Hennion, G. F. *J. Am. Chem. Soc.* **1938**, *60*, 718–720. We investigated this approach on the basis of the report of this reaction by Bryson: Bryson, T. A.; Reichel, C.; Reichert, C.; Stevenson, S.; Gibson, M.; Dike, S.; Levine, E. Southeast/Southwest Regional Meeting of the American Chemical Society, Dec 1980; Paper 355. This reaction was first reported in 1962: Yen, V.-Q. *Ann. Chim. (Paris)* **1962**, *7*, 785–799.

(7) Blaise, E.-E.; Koehler, A. *Bull. Soc. Chem. Fr.* **1909**, *5*, 681–692.

(8) Meerwein, H. *Liebigs Ann. Chem.* **1914**, *405*, 129–160.

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(10) For other procedures for preparation of **2**, see inter alia: (a) Beak, P.; Berger, K. R. *J. Am. Chem. Soc.* **1980**, *102*, 3848–3856. (b) Shanhnazaryan, G. M. *Arm. Khim. Zh.* **1981**, *34*, 605; *Chem. Abstr.* **1981**, *95*, 203384. (c) Hudlicky, T.; Srnak, T. *Tetrahedron Lett.* **1981**, *22*, 3843–3846. (d) Danheiser, R. L.; Darini, D. J.; Fink, D. M.; Basak, A. *Tetrahedron* **1983**, *39*, 935–947. (e) Boaventura, M. A.; Drouin, J.; Conia, J. M. *Synthesis* **1983**, 801–804.

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(12) It is important that the solution be made strongly acidic before extraction or the isolated yield is drastically reduced.

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a nitrogen atmosphere to the vigorously stirred solution. A small amount of CH_2Cl_2 was used to rinse the last traces of **2** into the reaction mixture. The mixture was stirred vigorously overnight and allowed to warm gradually to room temperature. The reaction was quenched by the addition of $NaHSO_3$ (10 g) and extracted with ether to remove any remaining ketone **2**. The aqueous solution was acidified to a Congo Red endpoint by the addition of 12 M HCl and extracted five times with 100 mL of CH_2Cl_2. The combined extracts were dried over $MgSO_4$ and concentrated to yield 8.12 g (80% yield) of acid **1**: ^1H NMR ($CDCl_3$, 90 MHz) δ 1.6–2.1 (m, 2 H), 2.1–2.2 (m, allylic CH_3), 2.3–2.8 (m, 4 H); ^{13}C NMR ($CDCl_3$, 50.31 MHz) δ 16.6 (CH_3), 21.3 (C-4), 33.3 and 41.2 (C-3 and C-5), 126.9 (C-1), 159.3 (C-2), 172.2 (CO_2H). This material was generally used without further purification. Purification could be effected by chromatography with silica gel (ethyl acetate:hexane, 15:85) or by crystallization from a solution of slowly evaporating methylene chloride. Recrystallization from hexane or sublimation gives analytically pure material: mp 129.5–130.0 °C (lit.[3d] 129–130 °C).

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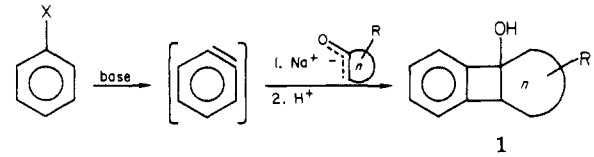
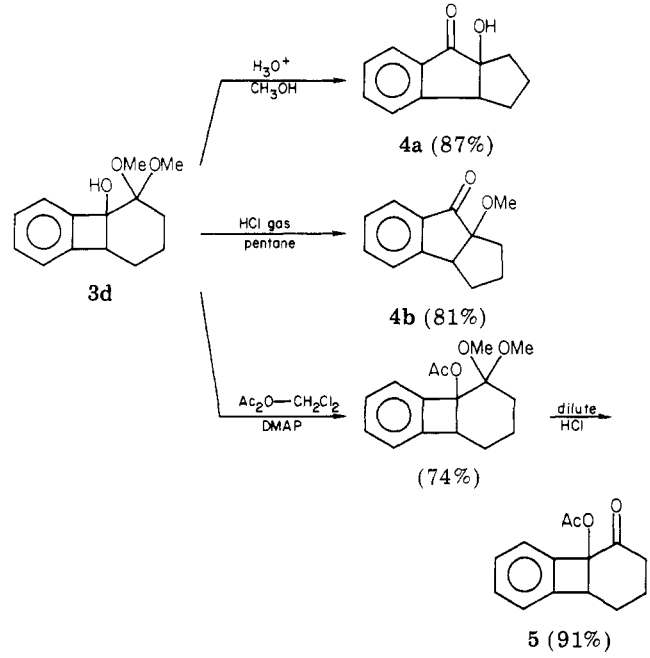
Registry No. **1**, 67209-77-2; **2**, 3168-90-9; $CH_3C(O)Cl$, 75-36-5; cyclohexane, 110-82-7.

Scheme I



1

Scheme II



Arynic Condensation of Ketone Enolates. 16.[1] Efficient Access to a New Series of Benzocyclobutenols

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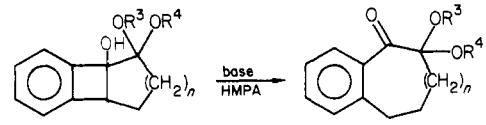
Benzocyclobutenes constitute an important family of starting materials for the synthesis of a large variety of very interesting polycyclic compounds,[2] and convenient access to these structures is always appreciated.

Our laboratory has been interested in the synthesis of benzocyclobutenes for some years and we have already published[3] that benzocyclobutenols **1** could be easily obtained through arynic condensations of ketone enolates (Scheme I).

However these reactions suffer from some limitations. Indeed with a few exception,[4] alcohols **1** were obtained only from cyclic ketone enolates for which $5 \leq n \leq 7$.[5] Linear ketone enolates never led to the desired alcohols with these conditions.

Scheme III



3d,f-i

6d, n = 2 (71%)
6e, n = 2 (83%)
6f, n = 3 (80%)
6g, n = 3 (96%)
6h, n = 4 (90%)
6i, n = 8 (90%)

As part of our program aimed at improving these results as well as at obtaining benzocyclobutenols bearing a function on the saturated ring, we undertook the study of arynic condensations of functionalized ketone enolates. We report here the first results obtained with 1,2-diketone monoketal enolates.

Preliminary experiments showed that instead of $NaNH_2$,[6] the complex base[7] $NaNH_2$–Bu-*t*-ONa must be used to generate the benzyne. The results obtained are grouped in Table I. Unexpectedly the presence of the ketal group dramatically favors the formation of the benzocyclobutenols **3** which were obtained, in good to excellent yields for medium sized cyclic ketone enolates **2c–h** as well as for a linear one (**2a**). With a large ring and a linear ketone enolate, **2i** and **2b** respectively, alcohols **3** were still formed

(1) For part 15, see: Essiz, M.; Guillaumet, G.; Brunet, J. J.; Caubere, P. *J. Org. Chem.* **1980**, *45*, 240.

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