Notes

Generation of Cyclopentadienones from 2-Bromocyclopentenones

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Received April 6, 2001

Introduction

The generation of cyclopentadienone (**2**) from a bromocyclopentenone precursor was first reported by Hafner.[1] This report was quickly followed by a paper from DePuy and co-workers[2] who showed that the precursor that was used by Hafner to generate the reactive intermediate was 4-bromocyclopentenone (**1**) and not 5-bromocyclopentenone as proposed by Hafner. In fact, the latter was shown to decompose under the reaction conditions that were used to generate cyclopentadienone from 5-bromocyclopentenone.[3] DePuy and co-workers also beautifully demonstrated a number of interesting aspects of the chemistry of **2**.[2b]

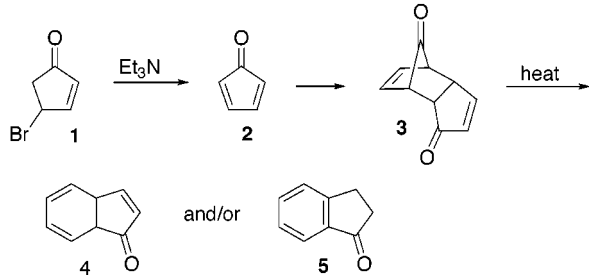
Cyclopentadienone is highly reactive and dimerizes to form **3** in virtually quantitative yield (Scheme 1). This compound can be decarbonylated to produce either **4** or **5** in good yield.[1,2,4]

While unsubstituted cyclopentadienone and various substituted analogues dimerize rapidly, reactions of these compounds as dienes or dienophiles are rather limited and have seen only a few applications in natural product synthesis.[5,6] However, more-highly substituted cyclopentadienones are isolable, and their ability to function as dienes is well-known.[7]

Results and Discussion

As part of our program involving the development of halogenated, cyclic, allylic cations in 4+3 cycloaddition reactions,[8] we attempted to brominate 2-bromocyclopentenone and use the resultant tribromide as a precursor to the oxyallylic cation **8** (Scheme 2). We learned that the tribromide **7** is difficult to handle. In an attempt to sort out exactly what occurred during studies involving cycloaddition reactions with furan, we allowed **6** to stir in a trifluoroethanol (TFE) solution of furan and triethylamine (TEA) for approximately one week at room temperature. During this time the slow formation of a new compound was made evident by TLC. Workup and chromatographic purification led to the identification of the compound as the cyclopentadienone dimer **3**, which was formed in 57% yield. To the best of our knowledge, the generation of cyclopentadienone from a 2-substituted cyclopentenone has not been reported.[9] We thus decided to optimize the reaction and explore its generality, albeit, at this stage only to a limited extent.

Scheme 1



Scheme 2

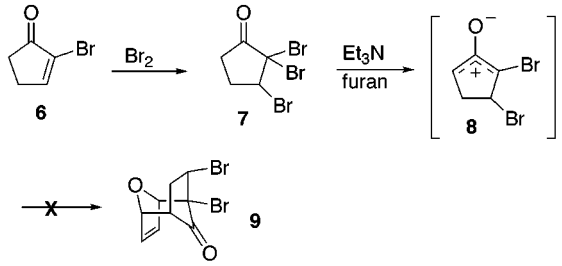


Table 1 shows the results of some of our work with 2-bromocyclopentenone in which we explored such variables as solvent, base, and temperature. The data suggest that relatively high temperatures are preferable to room temperature in this reaction (Table 1, cf. entries 1, 8, and 9). However, it is clear that prolonged heating could result in the formation of 1-indanone by thermal decarbonylation of **3** followed by isomerization (Table 1, entry 3).

The best choice for base at this point is triethylamine. As few as 1.2 equiv of this base produced **3** in high yield

(1) Hafner, D.; Goliasch, K. *Angew. Chem.* **1960**, *72*, 781.

(2) (a) DePuy, C. H.; Lyons, C. F. *Chem. Ind.* **1961**, 429−430. (b) DePuy, C. H.; Isaks, M.; Eilers, K. L.; Morris, G. F. *J. Org. Chem.* **1964**, *29*, 3503−3507.

(3) DePuy, C. H.; Ponder, B. W.; Fitzpatrick, J. D. *J. Org. Chem.* **1964**, *29*, 3508−3510.

(4) (a) DePuy, C. H.; Lyons, C. E. *J. Am. Chem. Soc.* **1960**, *82*, 631−633. (b) Hafner, K.; Goliasch, K. *Chem. Ber.* **1961**, *94*, 2909−2921. (c) Baggiolini, E.; Herzog, E. G.; Iwasaki, S.; Schorta, R.; Schaffner, K. *Helv. Chim. Acta* **1967**, *50*, 297−306.

(5) (a) Al-Busafi, S.; Whitehead, R. C. *Tetrahedron Lett.* **2000**, *41*, 3467−3470. (b) Bird, C. W.; Coffee, E. C. J.; Schmidl, B. W. C. *J. Chem. Soc., Chem. Commun.* **1993**, 613−620. (c) Nantz, M. H.; Fuchs, P. L. *J. Org. Chem.* **1987**, *52*, 5298−5299. (d) Baraldi, P. G.; Barco, A.; Benetti, S.; Pollini, G. P.; Polo, E.; Simoni, D. *J. Chem. Soc., Chem. Commun.* **1984**, 1049−1050. (e) Gaviña, F.; Costero, A. M.; Gil, P.; Luis, S. V. *J. Am. Chem. Soc.* **1984**, *106*, 2077−2080. (f) Gaviña, F.; Costero, A. M.; Palazón, B.; Luis, S. V. *J. Am. Chem. Soc.* **1981**, *103*, 1797−1798

(6) Applications in the synthesis of unnatural products are well-known. For example, see: (a) Eaton, P. E. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1421−1436. (b) *Carbocyclic Cage Compounds*; Osawa, E., Yonemitsu, O., Eds.; VCH: New York, 1992.

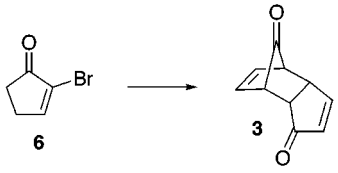
(7) For a review of cyclopentadienone chemistry, see: Ogliaruswo, M. A.; Romanelli, M. G.; Becker, E. I. *Chem. Rev.* **1965**, *65*, 262−367.

(8) (a) Harmata, M.; Shao, L. *Synthesis* **1999**, 1534−1540. (b) Harmata, M.; Shao, L.; Kürti, L.; Abeywardane, A. *Tetrahedron Lett.* **1999**, *40*, 1075−1078.

(9) For a process that appears to be related, see: Rizzo, C. J.; Bunlap, N. K.; Smith, A. B., III. *J. Org. Chem.* **1987**, *52*, 5280−5283.

10.1021/jo015671+ CCC: $20.00
Published on Web 07/03/2001

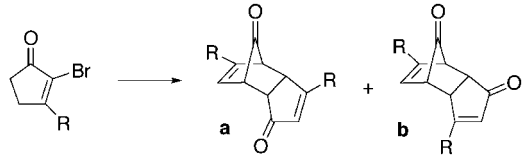
Table 1. Formation of 3 from 6 under Various Conditions



entry	solvent, [M][a]	base, no. of equiv.	temp. (°C)	time (h)	yield (%)
1	TFE, 0.3	TEA, 3	rt	48	43
2	ether, 2.4 $LiClO_4$, 0.3	TEA, 3	rt	3 min	[b]
3	TFE, 0.3	2,6-lutidine, 3	reflux	16	24[c]
4	TFE, 0.34	DBU, 1.2	reflux	2.25	57
5	ethanol, 0.35	TEA, 1.2	reflux	4	21
6	THF, 0.35	TEA, 5	reflux	2.75	35
7	THF[d]	TEA, 1.2	rt, reflux	0.33, 10	38
8	TFE, 0.5	TEA, 2	reflux	1	90
9	TFE, 0.7	TEA, 1.2	reflux	2.5	85

[a] Concentration of **3** in solvent. [b] Rapid decomposition was observed. [c] A 6% yield of 1-indanone was also isolated. [d] Containing 1 equiv of $LiClO_4$.

Table 2. Generation of Cyclopentadienone Dimers from 2-Bromocyclopentenones



entry	educt	R	time (h)	adduct	yield (%)	ratio (a:b)[a]
1	**10**	phenyl	2	**11**	72	3:1
2	**12**	3-methoxyphenyl	3.5	**13**	87	4.3:1
3	**14**	4-*tert*-butylphenyl	3	**15**	90	10.2:1
4	**16**	2,5-dimethylphenyl	5	**17**	97	5.6:1
5	**18**	phenylalkynyl	2.5	**19**	69	[b,c]

[a] Ratio determined by integration of crude ^1H NMR data. [b] Ratio less than 2:1 as determined by ^1H and ^{13}C NMR. [c] Only one isomer was isolated and characterized.

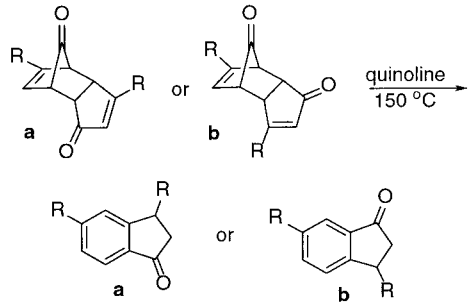
(Table 1, entry 9). However, we noted that reactions proceeded more quickly in the presence of larger amounts of base and prefer to use 2−3 equiv in performing the reaction. A slight increase in yield was observed when this was done (Table 1, entry 8).

While too few solvents have been examined to make generalizations, it seems that a polar, protic solvent such as TFE is well-suited for the reaction, while ethanol is surprisingly not. The use of THF resulted in a low yield of **3**. No improvement was observed when 1 equiv of $LiClO_4$ was included in the reaction mixture. Ethereal $LiClO_4$, a polar but aprotic medium, destroyed **6** rapidly.

With an acceptable procedure for the transformation of **6** into **3** in hand, we explored a small number of other substrates to begin to expand the scope of the reaction. The results are shown in Table 2. Our initial course was a safe one; we used 2-bromocyclopentenones that were substituted only with substituents bearing no acidic protons. However, the literature suggests that using precursors with potentially acidic hydrogens should not be a problem.[10]

The general reaction procedure consisted of reacting a 0.3 M trifluoroethanol solution of the starting material[11] with 3 equiv of triethylamine and heating to reflux. While the excess base was, in principle, not needed, reactions

Table 3. Indanone Formation from Cyclopentadienone Dimers



entry	educt	R	time (h)	adduct	yield (%)
1	**3**	H	5.25	**5**	54
2	**11a**	phenyl	5.5	**20a**	84
3	**11b**	phenyl	2.5	**20b**	65
4	**13a**	3-methoxyphenyl	4.25	**21a**	86
5	**15a**	4-*tert*-butylphenyl	5.5	**22a**	84
6	**17a**	2,5-dimethylphenyl	3.25	**23a**	77

appeared to proceed somewhat more cleanly and quickly when the reaction was performed in this way. After the reaction was shown to be complete by TLC, the mixture was cooled, the TFE removed, and ethyl acetate or chloroform was added in an amount that was 7−10 times the volume of TFE that was used. Extraction with aqueous acid, bicarbonate, and brine, followed by flash chromatographic purification (hexanes/ethyl acetate), afforded the products.

Interestingly, these dimerizations proceeded with reasonable regioselectivity and complete diastereoselectivity. Before we had definitive structural assignments, we took **11a** and treated it with triethylamine in refluxing TFE. No change was observed, and we concluded that the isomers that were observed were in fact regioisomers. We obtained crystal structures of **17a** and **17b**, and these data confirmed our assignments.[12] The structures of the other products were assigned on the basis of analogy. The product distributions that were observed are the result of kinetic control and can presumably be rationalized on the basis of FMO interactions, though a larger data set with a more diverse array of substituents will be useful in drawing more definitive conclusions.

To demonstrate that these cyclopentadienone dimers could be converted to products of further synthetic utility, they were refluxed in quinoline for several hours. This produced the expected indanones in good to excellent yields (Table 3).[13] The isomer corresponding to **4** (Scheme 1) presumably isomerizes rapidly in the presence of base.

Finally, at the behest of a referee, we carried out the reaction sequence shown in Scheme 3. Addition of *n*-butyllithium to **6** afforded **24** in low yield. Oxidation with PCC gave the ketone **25** without incident. When **25** was heated in trifluoroethanol in the presence of triethylamine, crude NMR and IR data suggested the formation of cyclopentadienone dimers as well as indanones. These

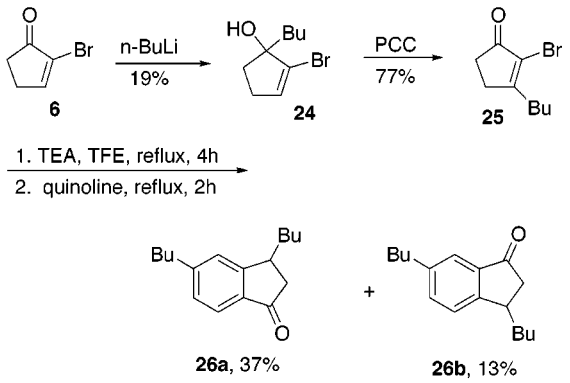
(10) Elliott, M.; Harper, S. H.; Kazi, M. A. *J. Sci. Food Agric.* **1967**, *18*, 167−171.

(11) The bromoenones were prepared by the addition of organolithium compounds to **6** followed by PCC oxidation. See the Experimental Section.

(12) A crystal structure was also obtained for **11a** and **3**. To the best of our knowledge, X-ray data on **3** have only appeared in the context of its participation in an inclusion complex. See: Toda, F.; Tanaka, K.; Marks, D.; Goldberg, I. *J. Org. Chem.* **1991**, *56*, 7332−7335.

(13) This type of transformation has also been accomplished by a metal-mediated process. See: Luh, T.-Y. *J. Organomet. Chem.* **1979**, *174*, 169−172.

Scheme 3



were not separable. The product mixture was heated in quinoline to afford the indanones **26a** and **26b** in 37 and 13% isolated yields, respectively, after two steps.

Conclusion

In summary, we have shown that several 2-bromocyclopentenones give rise to cyclopentadienones upon treatment with base in trifluoroethanol. To expand the scope of this intermolecular reaction, some of our future goals include exploring the alkylation chemistry of 2-halocyclopentenones and developing the chemistry of the cycloadducts and using the approach to study intramolecular cycloaddition reactions of cyclopentadienones with dienes and dienophiles. Results will be reported in due course.

Experimental Section

General. 2-Bromocyclopentenone was prepared as described in the literature.[14] THF and diethyl ether were distilled over sodium-benzophenone before use. 2,2,2-Trifluoroethanol was distilled over anhydrous $CaSO_4$ before use. Melting points were not corrected. 2-Cyclopentenone, bromine, phenyllithium, *n*-butyllithium, 3-bromoanisole, 4-*tert*-butylbromobenzene, 2,5-dimethylbromobenzene, phenylacetylene, and quinoline were used as supplied. Analytical TLC was performed on silica gel plates with F-254 indicator. ^{1}H NMR spectra were recorded at 250 and 300 MHz as $CDCl_3$ solutions with tetramethylsilane (0.05 vol %) as the internal reference. ^{13}C NMR spectra were obtained on the same instruments at 62.9 or 75 MHz with $CDCl_3$ (δ = 77 ppm) as the internal reference.

General Procedure for the Addition of Organolithiums to 2-Bromocyclopentenone. Into a flame-dried flask were placed 2-bromo-2-cyclopentenone (0.1 g, 0.62 mmol) and 3.0 mL of freshly distilled THF. The solution was cooled to −78 °C, and 1.2 equiv of aryllithium was slowly added.[15] The mixture ws stirred at −78 °C for 30 min, and the reaction was quenched with water (5 mL). The layers were separated, and the aqueous phase was extracted with Et_2O (3 × 10 mL). The combined organic phases were washed with brine, dried over $MgSO_4$ or Na_2SO_4, filtered, and evaporated. The crude product was purified by flash chromatography (silica gel, hexanes/EtOAc).

2-Bromo-1-phenyl-2-cyclopenten-1-ol: ^{1}H NMR (250 MHz, $CDCl_3$) δ 7.43−7.23 (m, 5H), 6.24 (t, J = 2.5 Hz, 1H), 2.61−2.32 (m, 5H); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 144.4, 134.6, 128.6, 128.3, 127.3. 124.9, 87.3, 40.7, 30.0. Anal. Calcd for $C_{11}H_{11}BrO$: C, 55.26; H, 4.64. Found: C, 55.30; H, 4.51.

2-Bromo-1-(3-methoxyphenyl)-2-cyclopenten-1-ol: ^{1}H NMR (250 MHz, $CDCl_3$) δ 7.29 (t, 1H, J = 8.0 Hz), 7.03−6.96 (m, 2H), 6.84 (dd, J = 0.9, 2.5 Hz, 1H), 6.26−6.24 (m, 1H), 3.82 (s, 3H), 2.64 (s, 1H, OH), 2.52−2.37 (m, 4H); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 159.6, 146.2, 134.6, 129.3, 128.4, 117.2, 112.5, 110.9, 87.2, 55.1, 40.6, 30.0; HRMS calcd for $C_{12}H_{13}BrO_2$ 268.0099, found 268.0089.

2-Bromo-1-(4-*tert*-butylphenyl)cyclopent-2-en-1-ol: ^{1}H NMR (250 MHz, $CDCl_3$) δ 7.34−1.29 (m, 4H), 6.20 (t, J = 2.4 Hz, 1H), 2.56 (s, 1H), 2.52−2.31 (m, 4H), 1.31 (s, 9H); ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 150.0, 141.3, 134.3, 128.8, 125.2, 124.6, 87.1, 40.3, 34.4, 31.3, 29.9. Anal. Calcd for $C_{15}H_{19}BrO$: C, 61.03; H, 6.49. Found: C, 61.23; H, 6.55.

2-Bromo-1-(2,5-dimethylphenyl)cyclopent-2-en-1-ol: mp 72−74 °C; ^{1}H NMR (250 MHz, $CDCl_3$) δ 7.24 (s, 1H), 7.01 (m, 2H), 6.22 (m, 1H), 2.43 (m, 11H); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 141.0, 134.8, 134.6, 132.7, 132.3, 128.9, 128.2, 126.9, 87.7, 38.3, 30.1, 21.1, 20.6. Anal. Calcd for $C_{13}H_{15}OBr$: C, 58.44; H, 5.66. Found: C, 58.60; H, 5.72.

2-Bromo-1-phenylethynyl-2-cyclopenten-1-ol: ^{1}H NMR (250 MHz, $CDCl_3$) δ 7.54−7.42 (m, 2H), 7.38−7.26 (m, 3H), 6.09 (t, 3H, J = 2.6 Hz), 3.00 (s, 1H), 2.73−2.61 (m, 1H), 2.55−2.37 (m, 3H); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 134.2, 133.5, 131.8, 131.6, 128.4, 128.1, 126.3, 122.1, 89.4, 85.3, 79.4, 40.1, 39.2, 29.8; HRMS calcd for $C_{13}H_{11}BrO - H^+$ 260.9915, found 260.9916.

2-Bromo-1-butyl-cyclopent-2-enol (24): colorless oil; ^{1}H NMR (250 MHz) δ 5.99 (t, J = 2.5 Hz, 1H), 2.48−2.34 (m, 1H), 2.29−2.15 (m, 2H), 2.06−1.93 (m, 1H), 1.89 (s, 1H), 1.76−1.51 (m, 2H), 1.41−1.16 (m, 4H), 0.92 (t, J = 6.84 Hz, 3H); ^{13}C NMR (62.9 Hz) δ 132.9, 129.1, 85.4, 38.9, 34.5, 29.7, 26.1, 22.9, 14.0.

General Procedure for the Synthesis of 2-Bromocyclopentenones. To a solution of 2-bromocyclopentenol (0.21 mmol) in 2.0 mL of CH_2Cl_2 (0.1M) was added 0.07 g (0.31 mmol, 1.5 equiv) of PCC, and the mixture was stirred at room temperature for 24 h. The solution was diluted with 5 mL of ether and filtered through a pad of silica gel. The filtrate was concentrated and the crude product purified by flash chromatography (silica gel, 10% EtOAc/hexanes).

2-Bromo-3-phenyl-2-cyclopenten-1-one (10): mp 99−101 °C; ^{1}H NMR (250 MHz, $CDCl_3$) δ 7.93−7.86 (m, 2H), 7.52−7.47 (m, 3H), 3.11−3.07 (m, 2H), 2.71−2.67 (m, 2H); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 201.4, 167.3, 133.9, 130.9, 128.5, 127.6, 121.5, 32.4, 30.5. Anal. Calcd for $C_{11}H_9BrO$: C, 55.72; H, 3.83. Found: C, 55.70; H, 3.69.

2-Bromo-3-(3-methoxyphenyl)-2-cyclopeten-1-one (12): mp 58−59 °C; ^{1}H NMR (250 MHz, $CDCl_3$) δ 7.45−7.33 (m, 3H), 7.03−7.00 (m, 1H), 3.83 (s, 3H), 3.03 (t, 2H, J = 4.8 Hz), 2.63 (t, 2H, J = 4.8 Hz); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 201.4, 167.2, 159.4, 135.1, 129.5, 121.6, 119.9, 116.4, 113.2, 55.3, 32.4, 30.6; HRMS calcd for $C_{12}H_{11}BrO_2$ 265.9942, found 265.9963.

2-Bromo-3-(4-*tert*-butylphenyl)-2-cyclopenten-1-one (14): mp 81−83 °C; ^{1}H (250 MHz, $CDCl_3$) δ 7.91 (dt, J = 2.0, 8.5 Hz, 2H), 7.52 (dt, J = 2.0, 8.5 Hz, 2H), 3.12−3.08 (m, 2H), 2.70−2.66 (m, 2H), 1.37 (s, 9H); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 201.6, 167.0, 154.7, 131.1, 127.6, 125.5, 120.8, 35.0, 32.4, 31.0, 30.4. Anal. Calcd for $C_{15}H_{17}BrO$: C, 61.45; H, 5.84. Found: C, 61.42; H, 5.89.

2-Bromo-3-(2,5-dimethylphenyl)-cyclopent-2-enone (16): mp 107−108 °C; ^{1}H NMR (250 MHz, $CDCl_3$) δ 7.15 (m, 2H), 6.93 (s, 1H), 2.98 (m, 2H), 2.72 (m, 2H), 2.35 (s, 3H), 2.23 (s, 3H); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 201.2, 173.8, 135.4, 135.2, 131.0, 130.4, 129.9, 126.4, 124.4, 33.3, 32.9, 20.8, 19.0. Anal. Calcd for $C_{13}H_{13}BrO$: C, 58.89; H, 4.94. Found: C, 58.85; H, 4.98.

2-Bromo-3-phenylethynyl-2-cyclopentenone (18): ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.58 (m, 2H), 7.41 (m, 3H), 2.85 (t, 2H, J = 4.5 Hz), 2.62 (t, 2H, J = 4.5 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 200.9, 153.5, 132.2, 130.2, 128.6, 121.4, 109.0, 84.37, 32.7, 31.3; HRMS calcd for $C_{13}H_9BrO$ 259.9837, found 259.9846.

2-Bromo-3-butyl-cyclopent-2-enone (25): colorless oil; ^{1}H NMR (250 MHz) δ 2.70−2.68 (m, 2H), 2.59−2.52 (m, 4H), 1.64−1.52 (m, 2H), 1.48−1.33 (m, 2H), 0.96 (t, J = 7.2 Hz, 3H); ^{13}C NMR (62.9 Hz) δ 201.4, 177.1, 122.7, 33.0, 32.3, 30.2, 28.6, 22.5, 13.6.

General Procedure for the Synthesis of Cyclopentadienone Dimers. A 10 mL round-bottomed flask was charged with 1.1 mmol of a bromoketone and 2.5 mL of trifluoroethanol.

(14) Smith, A. B., III; Branca, S. J.; Guaciaro, M. A.; Wovkulich, P. M.; Korn, A. *Org. Synth.* **1983**, *61*, 65−70.

(15) Addition of the bromoketone to the organolithium also produced good results.

(16) Neither combustion nor HRMS analysis (decarbonylation) was obtained for this compound.

(17) Sammour, A.; Elkasaby, M. *U. A. R. J. Chem.* **1971**, *13*, 409−420.

To the solution was added 2 or 3 equiv, and the mixture was refluxed. The reaction was monitored by TLC, and upon completion, the mixture was cooled and the trifluoroethanol was removed on a rotary evaporator. To the residue was added 25 mL of a polar solvent (ethyl acetate, chloroform, or dichloromethane). This solution was washed with water, 1 N HCl, saturated bicarbonate solution, and brine (5 mL each). The solution was dried (Na_2SO_4), and the solvent was removed in vacuo. The product was purified by flash chromatography (hexanes/EtOAc).

3,5-Diphenyl-3a*R,4*S**,7*S**,7a*S**-tetrahydro-4,7-methano-1*H*-indene-1,8-dione (11a):** mp 196 °C; ^{1}H NMR (250 MHz, $CDCl_3$) δ 7.49−7.34 (m, 5H), 7.09−6.94 (m, 3H), 6.84−6.81 (m, 2H), 6.66 (dd, J = 1.4, 3.7 Hz, 1H), 6.54 (d, J = 1.0 Hz, 1H), 4.21−4.16 (m, 1H), 3.80 (dt, J = 1.3, 4.8 Hz, 1H), 3.65−3.61 (m, 1H), 3.26 (dd, J = 4.8, 6.4 Hz, 1H); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 205.6, 198.0, 171.7, 140.7, 133.4, 133.2, 132.8, 131.5, 129.0, 128.1, 128.0, 127.2, 125.0, 121.0, 51.4, 50.6, 46.1, 41.0. Anal. Calcd for $C_{22}H_{16}O_2$: C, 84.59; H, 5.16. Found: C, 84.70; H, 5.29.

3,6-Diphenyl-3a*S,4*S**,7*S**,7a*R**-tetrahydro-4,7-methano-indene-1,8-dione (11b):** mp 194−196 °C; ^{1}H NMR (250 MHz, $CDCl_3$) δ 7.68−7.64 (m, 2H), 7.51−7.26 (m, 8H), 6.58 (d, J = 1.1 Hz, 1H), 6.26 (dd, J = 1.5, 3.8 Hz, 1H), 4.14−4.10 (m, 1H), 3.86 (dt, J = 1.4, 4.9 Hz, 1H), 3.60−3.56 (m, 1H), 3.29 (dd, J = 4.9, 6.3 Hz, 1H); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 204.6, 197.4, 171.4, 142.3, 133.4, 133.3, 132.4, 131.6, 129.2, 128.5, 127.2, 125.9, 119.8, 52.0, 51.1, 45.1, 42.8. Anal. Calcd for $C_{22}H_{16}O_2$: C, 84.59; H, 5.16. Found: C, 84.40; H, 5.37.

3,5-Bis(3-methoxyphenyl)-3a*R,4*S**,7*S**,7a*S**-tetrahydro-4,7-methano-1*H*-indene-1,8-dione (13a):** ^{1}H NMR (250 MHz, $CDCl_3$) δ 7.31 (t, 1H, J = 7.9 Hz), 7.12 (d, 1H, J = 7.8 Hz), 7.00−6.95 (m, 1H), 6.92−6.89 (m, 2H), 6.65−6.61 (m, 2H), 6.51−6.49 (m, 2H), 6.36 (t, 1H, J = 2.0 Hz), 4.13 (t, 1H, J = 5.2 Hz), 3.77−3.75 (m, 4H), 3.63−3.59 (m, 1H), 3.51 (s, 3H), 3.23 (dd, J = 5.0, 6.2 Hz, 1H); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 205.6, 197.9, 171.6, 160.0, 159.4, 140.6, 134.7, 134.3, 133.8, 130.0, 129.1, 121.4, 119.5, 117.7, 117.2, 114.3, 112.5, 110.2, 55.3, 54.8, 51.6, 50.6, 46.2, 41.1. Anal. Calcd for $C_{24}H_{20}O_4$: C, 77.40; H, 5.41. Found: C, 77.28; H, 5.42.

3,6-Bis(3-methoxyphenyl)-3a*S,4*S**,7*S**,7a*R**-tetrahydro-4,7-methano-1*H*-indene-1,8-dione (13b):** ^{1}H NMR (250 MHz, $CDCl_3$) δ 7.39 (t, 1H, J = 7.9 Hz), 7.25−7.21 (m, 3H), 7.13 (t, 1H, J = 2.3 Hz), 7.06−6.97 (m, 2H), 6.93 (t, 1H, J = 2.3 Hz), 6.83 (ddd, J = 0.8, 2.5, 8.2 Hz, 1H), 6.56 (d, 1H), 6.26 (dd, 1.4, 3.8 Hz, 1H), 4.09 (t, 1H, J = 5.0 Hz), 3.85 (s, 3H), 3.83 (m, 1H), 3.82 (s, 3H), 3.59−3.55 (m, 1H), 3.27 (dd, 1H, J = 5.0, 6.3 Hz); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 204.0, 197.3, 171.3, 160.1, 159.7, 142.3, 134.8, 134.3, 133.7, 130.2, 129.6, 120.3, 119.7, 118.5, 117.0, 114.5, 112.8, 111.3, 55.4, 55.3, 52.1, 51.4, 45.1, 42.9; HRMS calcd for $C_{24}H_{20}O_4$ 372.1361, found 372.1341.

3,5-Bis(4-*tert*-butylphenyl)-3a*R,4*S**,7*S**,7a*S**-tetrahydro-4,7-methano-1*H*-indene-1,8-dione (15a):** mp 213−217 °C dec; ^{1}H NMR (250 MHz, $CDCl_3$) δ 7.37 (s, 4H), 6.91−6.93 (m, 2H), 6.68−6.71 (m, 2H), 4.17−4.20 (m, 1H), 3.77−3.79 (m, 1H), 3.62−3.58 (m, 1H), 3.23 (dd, J = 5.1, 6.2 Hz, 1H), 1.36 (s, 9H), 1.19 (s, 9H); ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 205.7, 198.3, 171.8, 155.2, 151.0, 140.6, 132.6, 130.5, 130.0, 127.2, 125.7, 124.8, 124.7, 119.7, 51.3, 50.5, 46.0, 41.0, 34.9, 34.3, 31.04, 30.97. Anal. Calcd for $C_{30}H_{32}O_2$: C, 84.87; H, 7.60. Found: C, 84.64; H, 7.60.

3,6-Bis(4-*tert*-butylphenyl)-3a*S,4*S**,7*S**,7a*R**-tetrahydro-4,7-methano-1*H*-indene-1,8-dione (15b):** mp 213−215 °C dec; ^{1}H NMR (250 MHz, $CDCl_3$) δ 7.59 (dt, J = 1.6, 7.1 Hz, 2H), 7.48 (dt, J = 1.6, 7.1 Hz, 2H), 7.35 (s, 4H), 6.55 (d, J = 0.8 Hz, 1H), 6.23 (dd, J = 1.1, 3.2 Hz, 1H), 4.11−4.07 (m, 1H), 3.83 (dt, J = 1.1, 4.1 Hz, 1H), 3.57 (dt, J = 0.9, 3.4 Hz, 1H), 3.27 (dd, J = 4.2, 5.3 Hz, 1H), 1.36 (s, 9H), 1.30 (s, 9H); ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 204.8, 197.7, 171.3, 155.5, 151.7, 142.2, 132.6, 130.6, 130.2, 127.2, 126.2, 125.7, 125.5, 119.1, 52.2, 51.2, 45.2, 42.9, 35.1, 34.6, 31.2, 31.1. Anal. Calcd for $C_{30}H_{32}O_2$: C, 84.87; H, 7.60. Found: C, 84.70; H, 7.60.

3,5-Bis(2,5-dimethylphenyl)-3a*R,4*S**,7*S**,7a*S**-tetrahydro-4,7-methano-indene-1,8-dione (17a):** mp 163−165 °C; ^{1}H NMR (250 MHz, $CDCl_3$) δ 7.11−6.96 (m, 4H), 6.87 (d, J = 8.8 Hz, 1H), 6.53 (dd, J = 1.7, 3.6 Hz, 1H), 6.40 (d, J = 0.9 Hz, 1H), 6.33 (s, 1H), 4.23−4.18 (m, 1H), 3.68−3.64 (m, 2H), 3.25−3.20 (m, 1H), 2.31 (s, 3H), 2.26 (s, 3H), 1.97 (s, 3H), 1.93 (s, 3H); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 206.2, 198.5, 172.7, 141.2, 137.7, 135.6, 134.9, 133.9, 133.3, 132.9, 131.6, 131.2, 130.8, 129.2, 128.4, 128.0, 126.0, 52.9, 50.9, 45.5, 43.4, 22.1, 20.9, 20.8, 20.6. Anal. Calcd for $C_{26}H_{24}O_2$: C, 84.75; H, 6.57. Found: C, 85.00; H, 6.71.

3,6-Bis(2,5-dimethylphenyl)-3a*S,4*S**,7*S**,7a*R**-tetrahydro-4,7-methano-indene-1,8-dione (17b):** mp 163−165 °C; ^{1}H NMR (250 MHz, $CDCl_3$) δ 7.26 (s, 1H), 7.23−7.19 (m, 2H), 7.08−7.00 (m, 2H), 7.01 (m, 1H), 6.43 (d, J = 1.0 Hz, 1H), 6.06 (dd, J = 1.4, 3.8 Hz, 1H), 4.20−4.16 (m, 1H), 3.81−3.78 (m, 1H), 3.37−3.34 (m, 1H), 3.25 (dd, J = 5.0, 6.3 Hz, 1H), 2.39 (s, 3H), 2.36 (s, 3H), 2.34 (s, 3H), 2.30 (s, 3H); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 205.2, 197.8, 173.0, 142.9, 138.2, 136.0, 135.6, 133.5, 133.3, 132.5, 131.7, 131.0, 130.8, 130.0, 128.7, 128.0, 124.8, 53.7, 51.5, 45.2, 44.7, 21.2, 21.2, 20.99, 20.96. Anal. Calcd for $C_{26}H_{24}O_2$: C, 84.75; H, 6.57. Found: C, 85.00; H, 6.71.

3,5-Bis(phenylethynyl)-3a,4,7,7a-tetrahydro-4,7-methano-1*H*-indene-1,8-dione (19):[16] ^{1}H NMR (250 MHz, $CDCl_3$) δ 7.49−7.42 (m, 2H), 7.39−7.31 (m, 3H), 7.21−7.09 (m, 6H), 6.55 (d, 1H, J = 3.6 Hz), 6.51 (s, 1H), 3.72 (t, 1H, J = 5.0 Hz), 3.57 (d, 1H, J = 4.4 Hz), 3.53 (t, 1H, J = 3.9 Hz), 3.09 (dd, 1H, J = 5.0 Hz); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 205.4, 197.2, 154.5, 141.2, 132.4, 132.1, 131.7, 131.5, 130.0, 129.4, 128.6, 128.5, 128.1, 124.0, 122.2, 121.4, 106.7, 95.1, 84.0, 83.8, 53.8, 51.1, 44.5, 44.3.

General Decarbonylation Procedure: Synthesis of Indanones. In a flame-dried flask, 15−40 mg of the diketone was dissolved in 1 mL of quinoline. The reaction mixture was stirred at 150−160 °C and monitored by TLC until the starting material was consumed. The reaction mixture was cooled to room temperature, diluted with ether, and added to a separatory funnel. The mixture was washed three times with 3 N HCl, and then twice with water to remove the quinoline. The organic phase was dried with $MgSO_4$, and the solvent was removed under reduced pressure. The crude product was purified by column chromatography (5−15% EtOAc/hexanes) to yield a clean product.

3,5-Diphenyl-1-indanone (20a):[17] mp 153−155 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.87 (d, J = 8.0 Hz, 1H), 7.66−7.64 (m, 1H), 7.56−7.52 (m, 2H), 7.44−7.22 (m, 7H), 7.18−7.15 (m, 2H), 4.62 (dd, J = 3.9, 8.0 Hz, 1H), 3.28 (dd, J = 8.0, 19.2 Hz, 1H), 2.74 (dd, J = 3.9, 19.2 Hz, 1H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 205.4, 158.6, 148.2, 143.6, 140.0, 135.7, 129.0, 128.9, 128.4, 127.7, 127.5, 127.3, 127.0, 125.3, 123.8, 47.2, 44.6; HRMS calcd for $C_{21}H_{16}O$ 284.1201, found 284.1190.

3,6-Diphenyl-1-indanone (20b): mp 126−128 °C; ^{1}H NMR (250 MHz, $CDCl_3$) δ 8.24 (d, J = 1.7 Hz, 1H), 7.81 (dd, J = 1.9, 8.0 Hz, 1H), 7.64−7.59 (m, 2H), 7.49−7.22 (m, 7H), 7.19−7.14 (m, 2H), 4.61 (dd, J = 3.8, 8.0 Hz, 1H), 3.29 (dd, J = 8.1, 19.2 Hz, 1H), 2.75 (dd, J = 3.9, 19.2 Hz, 1H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 205.9, 156.8, 143.6, 141.3, 139.9, 137.4, 134.2, 129.0, 127.9, 127.7, 127.2, 127.0, 121.5, 47.2, 44.2; HRMS calcd for $C_{21}H_{16}O$ 284.1201, found 284.1206.

3,5-Bis(3-methoxyphenyl)-1-indanone (21a): mp 97−99 °C; ^{1}H NMR (250 MHz, $CDCl_3$) δ 7.85 (d, J = 8.0 Hz, 1H), 7.63 (dd, J = 1.3, 8.1 Hz, 1H), 7.46 (s, 1H), 7.36−7.20 (m, 2H), 7.14−7.11 (m, 1H), 7.08−7.06 (m, 1H), 6.91 (dd, J = 2.5, 8.2 Hz, 1H), 6.80−6.69 (m, 3H), 4.58 (dd, J = 3.8, 8.0 Hz, 1H), 3.84 (s, 3H), 3.76 (s, 3H), 3.26 (dd, J = 8.0, 19.2 Hz, 1H), 2.73 (dd, J = 3.9, 19.2 Hz, 1H); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 205.3, 160.0, 159.9, 158.3, 148.0, 145.2, 141.5, 135.7, 130.0, 129.9, 127.3, 125.3, 123.7, 120.0, 119.9, 113.7, 113.5, 113.4, 112.0, 55.3, 55.2, 47.0, 44.5; HRMS calcd for $C_{23}H_{20}O_3$ 344.1412, found 344.1416.

3,5-Bis(4-*tert*-butylphenyl)-1-indanone (22a): mp 203−205 °C; ^{1}H NMR (250 MHz, $CDCl_3$) δ 7.85 (d, J = 8.0 Hz, 1H), 7.64 (dd, J = 1.0, 8.0 Hz, 1H), 7.53−7.43 (m, 5H), 7.34−7.25 (m, 2H), 7.11−7.06 (m, 2H), 4.59 (dd, J = 3.8, 8.0 Hz, 1H), 3.25 (dd, J = 8.0, 19.2 Hz, 1H), 2.73 (dd, J = 3.9, 19.2 Hz, 1H), 1.34 (s, 9H), 1.30 (s, 9H); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 205.7, 158.8, 151.6, 149.8, 147.9, 140.5, 137.2, 135.4, 127.3, 127.2, 127.0, 125.9, 125.8, 125.1, 123.7, 47.2, 44.0, 34.6, 34.5, 31.3, 31.2; HRMS calcd for $C_{29}H_{32}O$ 396.2453, found 396.2479.

3,5-Bis(2,5-dimethylphenyl)-1-indanone (23b): mp 47−49 °C; ^{1}H NMR (250 MHz, $CDCl_3$) δ 7.56 (d, J = 7.91 Hz, 1H), 7.41−7.37 (m, 1H), 7.37 (d, J = 7.2 Hz, 1H), 7.15−6.93 (m, 5H), 6.66 (s, 1H), 4.82 (dd, J = 4.0, 8.0 Hz, 1H), 3.27 (dd, J = 8.1, 19.1 Hz, 1H), 2.61 (dd, J = 4.0, 19.1 Hz, 1H), 2.36 (s, 3H), 2.32 (s, 3H), 2.19 (s, 3H), 2.17 (s, 3H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 205.7, 158.0, 149.2, 140.7, 136.0, 135.7, 135.4, 132.7, 131.9, 130.5,

130.1, 129.2, 128.7, 127.6, 127.5, 123.2, 46.1, 20.9, 20.8, 19.8, 19.4; HRMS calcd for $C_{25}H_{24}O$ 340.1827, found 340.1811.

3,5-Dibutyl-indan-1-one (26a): yellow oil; ^{1}H NMR (250 MHz) δ 7.64 (d, J = 7.8 Hz, 1H), 7.29 (s, 1H), 7.19 (d, J = 7.8 Hz, 1H), 3.33−3.26 (m, 1H), 2.83 (dd, J = 7.5, 19.0 Hz, 1H), 2.70 (t, J = 7.6 Hz, 2H), 2.34 (dd, J = 3.30, 19.0 Hz, 1H), 1.95−1.88 (m, 1H), 1.70−1.30 (m, 9H), 0.97−0.90 (m, 6H); ^{13}C NMR (62.9 Hz) δ 206.0, 159.2, 150.7, 134.7, 128.1, 125.2, 123.4, 43.3, 38.1, 36.2, 35.8, 33.4, 29.8, 22.7, 22.4, 14.0, 13.9; IR (neat) 3018, 2958, 2930, 2858, 1710, 1609, 756 cm^{-1}; HRMS calcd for $C_{17}H_{24}O$ 244.1827, found 244.1830.

3,6-Dibutyl-indan-1-one (26b): yellow oil; ^{1}H NMR (250 MHz) δ 7.54 (s, 1H), 7.45−7.38 (m, 2H), 3.34−3.26 (m, 1H), 2.85 (dd, J = 7.4, 19.0 Hz, 1H), 2.66 (t, J = 7.5 Hz, 2H), 3.35 (dd, J = 3.2, 19.0 Hz, 1H), 1.92−1.86 (m, 1H), 1.67−1.26 (m, 9H), 0.95−0.89 (m, 6H); ^{13}C NMR (62.9 Hz) δ 206.7, 159.7, 142.4, 136.9, 135.3, 125.3, 122.8, 43.5, 37.9, 35.9, 35.2, 33.5, 29.8, 22.8, 22.2, 14.0, 13.9; IR (neat) 3020, 2963, 2932, 2862, 1703, 1216 cm^{-1}; HRMS calcd for $C_{17}H_{24}O$ 244.1827, found 244.1834.

Acknowledgment. This work was supported by the National Science Foundation, to whom we are grateful. We thank the National Science Foundation for partial support of the NMR (PCM-8115599) facility at the University of Missouri—Columbia and for partial funding for the purchase of a 500 MHz spectrometer (CHE-89-08304). We thank Dr. Dmitri Zagorevski for mass spectral data and the University of Missouri Research Board for its continued support of the Mass Spectrometry Facility.

Supporting Information Available: X-ray data for **3**, **11a**, **17a**, and **17b**, and copies of proton and carbon spectra for the alcohol precursors of the 2-bromocyclopentenones and of **10**−**26**. This material is available free of charge via the Internet at http://pubs.acs.org.

JO015671+