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Three-Carbon Annelation Reagents: 3-Bromo-2-methoxy-1-butene, an Alkyl-Substituted Methoxyallyl Bromide

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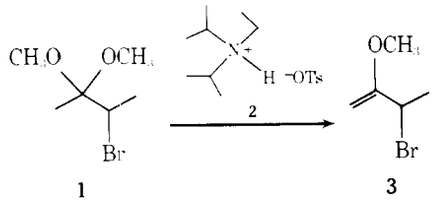
The utility of an electrophilic acetone synthon in the preparation of 1,4-dicarbonyl compounds and their derived cyclopentenones, furans, and pyrroles has been well demonstrated.[1,2] Our recent work on the use of 2-methoxyallyl bromide as a useful acetonyl alkylating agent has sparked our interest in the potential of various substituted derivatives, desiring to expand the scope and utility of the method. As polycyclic systems containing oxygenated methylcyclopentanes are widely found in nature, a methyl-substituted methoxyallyl bromide, 3-bromo-2-methoxy-1-butene (**3**), was chosen for the initial study. As **3** is a secondary allylic bromide, it was expected to be a less reactive alkylating agent than its parent, 2-methoxyallyl bromide.

The preparation of 3-bromo-2-methoxy-1-butene (**3**) was accomplished by the cracking of 3-bromo-2,2-dimethoxybutane (**1**) in the presence of a catalytic amount of diisopropylethylammonium tosylate (**2**) in a manner similar to that used for the preparation of 2-methoxyallyl bromide.[1] The resulting reagent contained approximately 76% of **3**, 2–5% of **1**, 3–8% of 3-bromo-2-butanone, less than 1% methanol, and little or no other "protic" impurities. In distinct contrast to our experience with 2-methoxyallyl bromide, none of the isomeric vinyl bromide was observed. Further purification by fractional distillation, though possible, was unnecessary for this work.



1 3

Imines of cycloalkanones were cleanly monoalkylated under standard (LDA/THF) conditions.[3,4] Imine **4a** gives a 4:1 mixture of imines **5** and **6**. The hydrolysis of the imine and enol ether functionalities requires some experimental care as subtle variation of conditions results in a large variation in product distribution. Treatment of **5** and **6** with acetic acid containing a few equivalents of water resulted in exclusive formation of furans **9** and **10** in 90% isolated yield.[5] Use of 1 M HCl in aqueous THF resulted in the predominant formation of pyrroles **11** and **12** in 80% overall yield.[6] The use of 1.5 M acetic acid in 50% aqueous THF proved optimum for hydrolysis to the diketones, providing **7a**, **8a**, and **9** in overall yields of 34, 22, and 25%, respectively. The ease of formation of furan **9** is noteworthy if predictable. The furans **9** and **10** could be hydrolyzed to diketones **7a** and **8a** with sulfuric acid[7] in high yield, allowing a good overall yield of diketone. Aldol cyclization[8] of the mixture of **7a** and **8a** gave the corresponding cyclopentenones which, under the reaction conditions, isomerized completely to the more substituted enone **14a**.

Alkylation of the imines of cycloheptanone and *N*-methyl-4-piperidone followed by hydrolysis and cyclization gave the expected cyclopentenones in good yield. Application of this annelation to the synthesis of hydroazulenes and tecomanine[9] will be reported in due course.

The reaction of **3** with singly and doubly activated esters and nitriles proceeded for the most part without difficulty. Diethyl 2-ethylmalonate (**15a**), dimethyl 2-methylmalonate (**15b**), and methyl cyanoacetate (**18**) were alkylated with **3** under standard (NaH/THF) conditions.[10] After a facile hydrolysis of the enol ethers, the resulting products were obtained in good yield. In these cases too, an S_N2' product was observed. Carbomethoxycyclohexane (**21**) and butyronitrile (**23**) could be cleanly alkylated under standard (LDA/THF) conditions.[11] Here no S_N2' products were observed.

In contrast to these successful alkylations, neither ethyl hexanoate nor methyl propionate could, in our hands, be alkylated with **3**, the competing Claisen condensation giving the observed products. Our attempts to directly alkylate ketone enolates have uniformly failed.

It is apparent that 3-bromo-2-methoxy-1-butene is a useful addition to the arsenal of annelating reagents. Its utilization, especially via alkylation of imine anions, should provide additional entries to the large number of methylcyclopentenone systems found in synthetic targets.

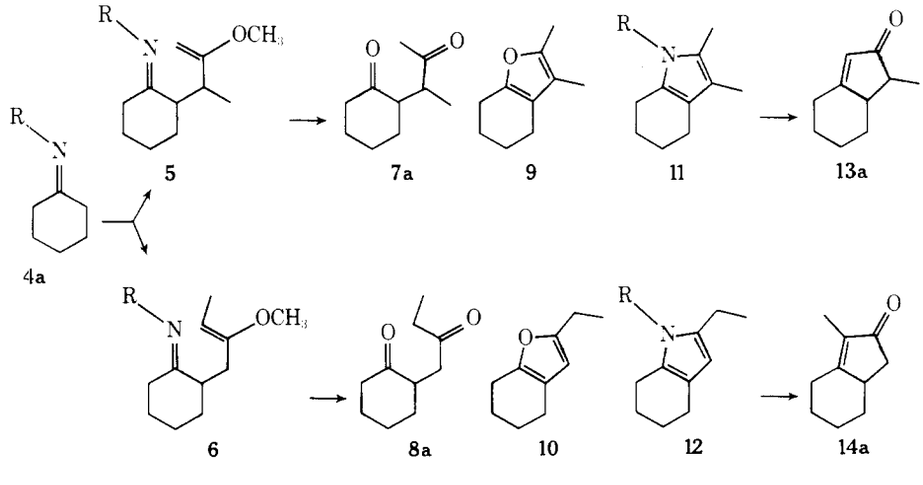


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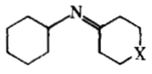
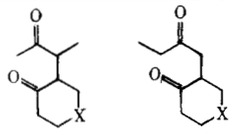
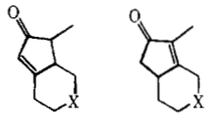
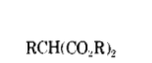
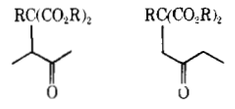
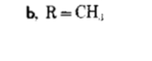
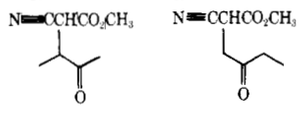
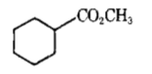
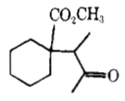
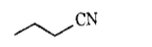
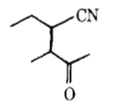
Table I

starting material	products	yield, %	S_N2/S_N2'	cyclopentenone	yield, %
 4a, X = CH_2 b, X = CH_2CH_2 c, X = NCH_3	 7 8	a, 79 b, 74 c, 65	80:20 83:17 *a*	 13 14	87 72 60
 15a, R = CH_2CH_3 b, R = CH_3	 16 17	a, 85 b, 88	83:17 86:14		
 18	 19 20	61	79:21		
 21	 22	87	*a*		
 23	 24	61	*a*		

[a] No S_N2' product was observed.

Experimental Section

All boiling points are uncorrected. ^1H NMR spectra were obtained on Varian T-60A and Varian HR220 spectrometers using tetramethylsilane as an internal standard. Infrared spectra were obtained on a Perkin-Elmer 467 grating infrared spectrometer. Mass spectra were obtained on a Varian-MAT CH-7 mass spectrometer. All starting materials were distilled before use. Tetrahydrofuran was dried over potassium benzophenone dianion and freshly distilled under nitrogen prior to use.

3-Bromo-2,2-dimethoxybutane (1). This was prepared from 3-bromo-2-butanone[12] by the method of Jacobson:[1] 94% yield; bp (40 torr) 85–87 °C; ^1H NMR (CCl_4) δ 1.3 (s, 3 H), 1.6 (d, 3 H), 3.1 (s, 6 H), 4.1 (q, 1 H); IR (neat) 2835, 1450, 1382, 1140, 1117, 1066, 1044, 862 cm^{-1}; mass spectrum (70 eV), *m/e* 196 (M^+, absent), 167 (24), 165 (24), 89 (100), 86 (33), 85 (42), 55 (20), 53 (37), 43 (83).

3-Bromo-2-methoxy-1-butene (3). A mixture of 25 g of **1** and 0.45 g of **2**[1] was heated at 180–200 °C (bath temperature) while distilling off the produced methanol through a 150 × 15 mm Vigreux fractionating column. After about 1 h, the head temperature began to rise above 100 °C. At this point the oil bath was removed and an additional 0.10 g of **2** was added. Heat was then reapplied, and the distillation of methanol continued until the head temperature once gain rose above 100 °C. The reaction mixture was allowed to cool and then was distilled at 100 torr (bp 86–88 °C) through a 150 × 15 mm Vigreux fractionating column to yield 18.8 g of a product which contained ca. 76% (GC) of the desired **3**. The mixture was stored at −20 °C and used as obtained here for subsequent alkylations. There seems to be a tradeoff in eliminating all of the starting ketal, **1**, by addition of the second batch of **2**, and the formation of the 3-bromo-2-butanone impurity. An analytical sample was obtained by spinning band distillations: bp (47 torr) 68.0 °C; ^1H NMR (CCl_4) δ 1.73 (d, 3 H), 3.55 (s, 3 H), 3.93 (d, 1 H), 4.22 (d, 1 H), 4.40 (q, 1 H); IR (neat) 1661, 1626 cm^{-1}; mass spectrum (70 eV), *m/e* 166 (12), 164 (M^+, 12), 85 (100), 57 (23), 55 (31), 53 (95).

***N*-Cyclohexylidenecyclohexylamine (4a).** This was prepared by the procedure of Stork[3] in 95% yield.

***N*-Cycloheptylidenecyclohexylamine (4b).** This was prepared by the procedure of Stork[3] in 70% yield.

***N*-(1-Methyl-4-piperidylidene)cyclohexylamine (4c).** This was prepared by the procedure of Stork:[3] 90% yield; bp (10 torr) 138 °C; ^1H NMR (CCl_4) δ 1.0–1.8 (m, 10 H), 2.20 (s, 3 H), 2.1–2.4 (m, 8 H), 3.1 (br m, 1 H); IR (neat) 1660 cm^{-1}; mass spectrum (70 eV), *m/e* 194 (M^+, 13), 193 (26), 112 (59), 111 (20), 97 (20), 96 (24), 71 (100), 70 (26), 57 (26), 56 (65), 55 (25), 43 (72), 42 (43), 41 (28).

2-(1-Methyl-2-oxopropyl)cyclohexanone (7a),[13] 2-(2-Oxobutyl)cyclohexanone (8a),[13] and 4,5,6,7-Tetrahydro-2,3-dimethylbenzofuran (9). To an ice-cooled, nitrogen-filled flask containing 10 mL of dry THF was added 0.35 mL (2.5 mmol) of diisopropylamine and 1.03 mL (2.3 mmol) of a 2.2 M solution of butyllithium in hexane. After 10 min, 338 mg (1.9 mmol) of **4a** in 1 mL of THF was added and the mixture was stirred for 15 min, whereupon 0.53 mL (2.9 mmol) of **3** was added and the mixture was allowed to warm to 20 °C and was stirred for 10 h. Imines **5** and **6** could be isolated at this time, but they were routinely hydrolyzed directly by the addition of 10 mL of 3 M HOAc and stirring for 10 h. The resulting mixture was partitioned between ether and water. The organic layer was dried ($MgSO_4$), filtered, concentrated in vacuo, and distilled (bulb-to-bulb), yielding 293 mg of a mixture of **7a, 8a,** and **9.** Column chromatography on silica gel (ether/hexane) gave 72 mg (0.48 mmol, 25%) of **9** and 179 mg (1.06 mmol, 56%) of a 61:39 mixture (GC) of **7a** and **8a.** Preparative GC (OV17) gave analytical samples of **7a** and **8a.**

7a: bp (0.02 torr) 115–120 °C (bath); ^1H NMR ($CDCl_3$) δ 1.06 (d, 3 H), 1.3–2.5 (m, 8 H), 2.25 (s, 3 H), 2.6–2.9 (m, 2 H); IR (neat) 1712 cm^{-1}; mass spectrum (70 eV), *m/e* 168 (M^+, 23), 126 (43), 125 (52), 111 (44), 98 (22), 97 (95), 55 (70), 43 (100), 41 (34).

8a: bp (0.02 torr) 115–120 °C (bath); ^1H NMR (CCl_4) δ 1.02 (t, 3 H), 1.4–2.8 (m, 13 H); IR (CCl_4) 1714 cm^{-1}; mass spectrum (70 eV), *m/e* 168 (M^+, 53), 139 (99), 121 (39), 111 (49), 97 (54), 93 (23), 57 (100), 55 (82), 41 (43), 39 (22), 29 (79), 27 (29).

9: bp (0.02 torr) 115–120 °C (bath); ^1H NMR ($CDCl_3$) δ 1.83 (s, 3 H), 1.6–2.0 (m, 4 H), 2.20 (s, 3 H), 2.1–2.7 (m, 4 H); IR (neat) 1610, 1578, 1452 cm^{-1}; mass spectrum (70 eV), *m/e* 150 (M^+, 53), 149 (18), 135 (16), 123 (10), 122 (100), 107 (13), 91 (12), 79 (18), 77 (11), 43 (32).

7-Methylbicyclo[4.3.0]non-6-en-8-one (14a).[14] Aldol cyclization of **7a** and **8a** was accomplished by treating 39 mg of a mixture of **7a** and **8a** (3:1) with 4 mL of 2% ethanolic KOH at reflux for 30 min.[8] Partitioning between ether and water, drying with $MgSO_4$, and bulb-to-bulb distillation gave 30 mg of a single product, **14a:** 87% yield; bp (0.02 torr) 120 °C (bath); ^1H NMR ($CDCl_3$) δ 1.68 (br s, 3 H), 1.0–2.9 (m, 13 H); IR (CCl_4) 1701, 1650 cm^{-1}; mass spectrum (70 eV), *m/e* 150 (M^+, 87), 122 (100), 121 (28), 108 (30), 107 (45), 94 (22), 93 (79), 91 (30), 79 (59), 77 (35), 53 (21), 41 (23), 39 (30).

8-Methylbicyclo[5.3.0]dec-7-en-8-one (14b). This was prepared from **7b** and **8b** in a manner similar to that used for **14a:** 72% yield; bp (0.02 torr) 120 °C (bath); ^1H NMR (CCl_4) δ 1.60 (br s, 3 H), 1.0–2.2 (m, 8 H), 2.3–2.7 (m, 5 H); IR (neat) 1703, 1644 cm^{-1}; mass spectrum (70 eV), *m/e* 164 (M^+, 91), 136 (77), 122 (31), 121 (73), 108 (100), 93

(58), 91 (32), 80 (23), 79 (80), 77 (44), 67 (30).

3,9-Dimethyl-3-azabicyclo[4.3.0]non-9-en-8-one (14c). This was prepared from **7c** in a manner similar to that used for **14a:** 60% yield; bp (0.02 torr) 100 °C (bath); ^{1}H NMR (CCl_4) δ 1.66 (br s, 3 H), 2.30 (s, 3 H), 0.8–3.1 (m, 7 H), 3.27 (br s, 1 H), 3.60 (br s, 1 H); IR (CCl_4) 1708, 1665 cm^{-1}; mass spectrum (70 eV), *m/e* 165 (M^+, 62), 164 (54), 137 (58), 122 (100), 94 (32), 79 (39), 77 (20), 53 (21), 44 (47), 42 (69), 41 (24), 39 (21).

General Procedure for the Alkylation of Doubly Activated Esters and Nitriles. To a refluxing suspension of 6 mmol of NaH (hexane washed) in 25 mL of THF was slowly added 5 mmol of active methylene compound. After hydrogen evolution was complete, 6 mmol of **3** was added and the refluxing was continued for 14 h. Upon cooling, the reaction mixture was acidified with dilute aqueous HCl, stirred for 15 min to hydrolyze the enol ether, and extracted with ether. The organic layer was dried over $MgSO_4$, filtered, concentrated in vacuo, and purified by bulb-to-bulb distillation. Analytical samples were obtained by preparative GC (OV17). The following alkylated products were obtained.

Diethyl 2-Ethyl-2-(1-methyl-2-oxopropyl)malonate (16a):[15] 71% yield; bp (0.05 torr) 118 °C (bath); ^{1}H NMR (220 MHz, $CDCl_3$) δ 0.90 (t, 3 H), 1.20 (t, 6 H), 1.24 (d, 3 H), 2.02 (q, 2 H), 2.24 (s, 3 H), 3.21 (q, 1 H), 4.21 (q, 4 H); IR ($CHCl_3$) 1715 cm^{-1}; mass spectrum (70 eV), *m/e* 258 (M^+, absent), 213 (25), 187 (72), 170 (35), 142 (43), 141 (77), 139 (46), 115 (29), 114 (22), 97 (23), 69 (25), 43 (100), 29 (53).

Diethyl 2-Ethyl-2-(2-oxobutyl)malonate (17a): 14% yield; bp (0.05 torr) 118 °C (bath); ^{1}H NMR (220 MHz, $CDCl_3$) δ 0.64 (t, 3 H), 0.84 (t, 3 H), 1.02 (t, 6 H), 1.82 (q, 2 H), 2.20 (q, 2 H), 2.84 (s, 2 H), 3.98 (q, 4 H); IR (neat) 1710 cm^{-1}; mass spectrum (70 eV), *m/e* 258 (M^+, absent), 187 (24), 141 (36), 139 (34), 127 (22), 83 (20), 57 (73), 55 (31), 29 (100), 27 (21).

Dimethyl 2-Methyl-2-(1-methyl-2-oxopropyl)malonate (16b): 76% yield; bp (0.05 torr) 120 °C (bath); ^{1}H NMR ($CDCl_3$) δ 1.20 (d, 3 H), 1.52 (s, 3 H), 2.21 (s, 3 H), 3.41 (q, 1 H), 3.71 (s, 6 H); IR (neat) 1730 cm^{-1}; mass spectrum (70 eV), *m/e* 216 (M^+, 1), 185 (20), 174 (27), 145 (32), 142 (71), 125 (50), 115 (48), 114 (84), 113 (23), 83 (39), 59 (47), 55 (37), 43 (100).

Methyl 2-(1-Methyl-2-oxopropyl)-2-cyanoacetate (19):[16] 48% yield; bp (0.05 torr) 110 °C (bath); ^{1}H NMR ($CDCl_3$) δ 1.44 (dd, 3 H), 2.29 (d, 3 H), 3.30 (m, 1 H), 3.83 (s, 3 H), 3.95 (m, 1 H); IR (neat) 2250, 1750, 1720 cm^{-1}; mass spectrum (70 eV), *m/e* 169 (M^+, 3), 68 (7), 43 (100), 28 (6), 15 (9).

Methyl 2-(2-Oxobutyl)-2-cyanoacetate (20): 13% yield; bp (0.05 torr) 110 °C (bath); ^{1}H NMR ($CDCl_3$) δ 1.10 (t, 3 H), 2.50 (q, 2 H), 3.1 (d, 2 H), 3.85 (s, 3 H), 4.1 (t, 1 H); IR (CCl_4) 2261, 1752, 1720 cm^{-1}; mass spectrum (70 eV), *m/e* 169 (M^+, 5), 140 (7), 138 (9), 112 (27), 80 (7), 59 (6), 57 (100), 29 (17).

1-Carbomethoxy-1-(1-methyl-2-oxopropyl)cyclohexane (22). To a solution of 2.6 mmol of LDA (generated in situ) in 10 mL of THF at 0 °C was added 351 mg (2.47 mmol) of carbomethoxycyclohexane. After 0.5 h, 0.50 mL (3.0 mmol) of **3** was added and the mixture was slowly allowed to warm to room temperature. After 12 h, 5 mL of 3 M aqueous acetic acid was added. After an additional 12 h, the reaction mixture was diluted with ether and water. The organic layer was washed with water, dried over $MgSO_4$, filtered, and concentrated in vacuo; bulb-to-bulb distillation afforded 456 mg (2.15 mmol, 87%) of the alkylated product **22:** bp (0.02 torr) 130 °C (bath); ^{1}H NMR (CCl_4) δ 1.04 (d, 3 H), 0.9–1.8 (m, 10 H), 2.05 (s, 3 H), 2.69 (q, 1 H), 3.66 (s, 3 H); IR (CCl_4) 1734 cm^{-1}; mass spectrum (70 eV), *m/e* 212 (M^+, 1), 141 (100), 109 (44), 81 (44), 72 (29), 43 (60).

3-Methyl-4-cyano-2-hexanone (24). To a solution of 2.4 mmol of LDA (generated in situ) in 5 mL of THF at −78 °C was added 0.16 mL (2.0 mmol) of butyronitrile. After 0.5 h, 0.33 mL (2.0 mmol) of **3** in 3 mL of HMPA was added and stirring was continued for an additional 0.5 h. The reaction mixture was slowly warmed to room temperature over the course of 6 h, acidified with dilute aqueous HCl, stirred for 15 min to hydrolyze the enol ether, and diluted with ether and water. The organic layer was separated, washed with water, dried over $MgSO_4$, filtered, and concentrated in vacuo. The crude alkylated product was purified by bulb-to-bulb distillation to afford 0.17 g (1.2 mmol, 61%) of products **24,** that GC analysis (OV17 at 100 °C) and NMR, IR, and mass spectra showed were diastereoisomers, in a ratio of 52:48.

24a: bp (5 torr) 100 °C (bath); ^{1}H NMR (CCl_4) δ 1.15 (t, 3 H), 1.30 (d, 3 H), 1.55 (q, 2 H), 2.20 (s, 3 H), 2.6–2.9 (m, 2 H); IR ($CHCl_3$) 2220, 1712 cm^{-1}; mass spectrum (70 eV), *m/e* 139 (M^+, 1), 72 (12), 68 (10), 43 (100).

24b: bp (5 torr) 100 °C (bath); ^{1}H NMR (CCl_4) δ 1.15 (t, 3 H), 1.30 (d, 3 H), 1.55 (q, 2 H), 2.20 (s, 3 H), 2.6–2.9 (m, 2 H); IR ($CHCl_3$) 2220, 1712 cm^{-1}; mass spectrum (70 eV), *m/e* 139 (M^+, 1), 82 (5), 72 (19), 70 (16), 68 (13), 55 (8), 43 (100), 42 (5), 41 (8).

Acknowledgment. We wish to thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

Registry No.—**1,** 67722-23-0; **3,** 67722-24-1; **4a,** 10468-40-3; **4b,** 6114-69-8; **4c,** 67722-22-9; **7a,** 67722-25-2; **7b,** 67722-26-3; **7c,** 67722-27-4; **8a,** 29943-11-1; **8b,** 59574-62-8; **9,** 67722-28-5; **14a,** 24730-98-1; **14b,** 67722-29-6; **14c,** 67722-30-9; **15a,** 133-13-1; **15b,** 609-02-9; **16a,** 67722-31-0; **16b,** 67722-32-1; **17a,** 67722-33-2; **18,** 105-34-0; **19,** 67722-34-3; **20,** 67722-35-4; **21,** 4630-82-4; **22,** 67722-36-5; **23,** 109-74-0; **24** isomer 1, 67722-37-6; **24** isomer 2, 67722-38-7.

References and Notes

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Concerning the Electronic Effects of Substituted Methyl Groups

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The nature of the substituent effect(s) exerted by substituted methyl groups attached to aromatic or other unsaturated systems continues to be an area of considerable interest.[1] This contribution was prompted by the recent work of Shapiro[2] which purported to demonstrate that in a series of para-substituted benzyl systems, hyperconjugative interactions at the para position were of minor importance. This conclusion contrasted with persuasive evidence to the contrary, particularly that from systems in which the C–X bond was geometrically defined with respect to the π system[1] and from PES studies of benzyl systems.[3]

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