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TETRAKIS(1-METHYLCYCLOPROPYL)ETHYLENE IN FOUR STEPS FROM α-METHYL-γ-BUTYROLACTONE

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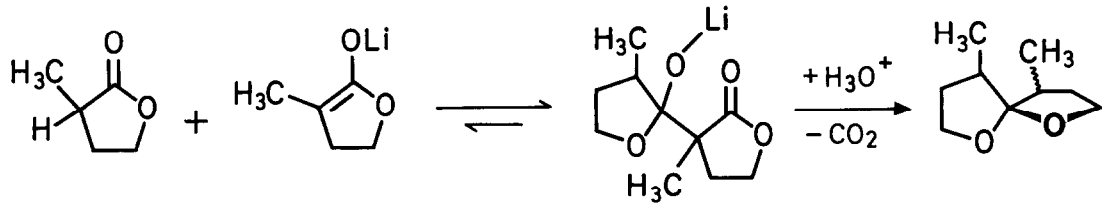
Summary: A short and efficient synthesis of bis(1-methylcyclopropyl)ketone (6) via the spiro-acetal 4 from α-methyl-γ-butyrolactone (1) has been found, and reductive dimerization of 6 by McMurry coupling yields tetrakis(1-methylcyclopropyl)ethylene (7) in competition with ring-opened products (8 and 9).

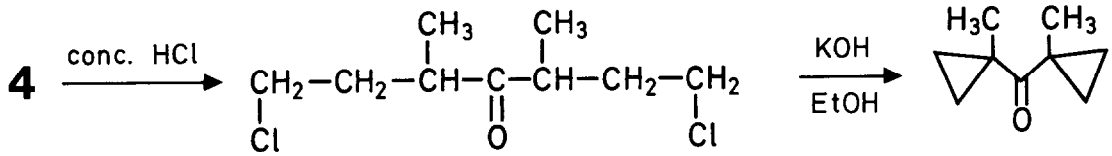
A recent communication[1] described the preparation of tetrakis(1-methylcyclopropyl)-ethylene (7) as a possible precursor to the still unknown tetra-tert-butylethylene. This synthesis required at least six steps, counting from 1-methylcyclopropanecarbonitrile, via derivatives of bis(1-methylcyclopropyl)ketone (6). We have independently arrived at olefin 7 directly from ketone 6 in the course of studies on reduction by low-valent titanium under McMurry[2] conditions. A previous preparation[3] of bis(1-methylcyclopropyl)ketone (with less than 10% overall yield of 6) obviously did not provide a sample sufficiently pure for physical characterization; therefore, we developed an efficient alternative synthesis of 6 from cheap starting material via spiro-acetal 4, an unnatural isomer of the biologically interesting chalcogran[4].

The base-catalyzed dimerization of lactones is well known[5,6] but had probably not been applied to α-substituted γ-lactones. We succeeded in coupling α-methyl-γ-butyrolactone (1), which is commercially available or can be made from γ-butyrolactone[7] and more conveniently from diethyl methylmalonate[8], to its lactone enolate 2 in hexane. The lactone 1 (0.39 mol), added at -78°C to a stirred hexane suspension of lithium diisopropylamide (0.21 mol), formed a copious precipitate (presumably 3) at room temperature overnight, which was then dissolved in 2n H_2SO_4 (600 mL) to generate the masked β-keto acid derived from 3. After removal of hexane in vacuo, the aqueous solution was heated to reflux (2 h) for decarboxylation. The subsequently obtained ethereal extracts were treated with 2n NaOH to remove the residual lactone, yielding 80% of the spiro-acetal 4 as a mixture[9] of two diastereomers with b.p. 64 - 64.5°C/ 12 torr. The major isomer is symmetric[10] according to the NMR spectra[11]. The proportion of the second (asymmetric) isomer may be further decreased by heating with acid, and the possible third (symmetric) isomer is never observed[10].



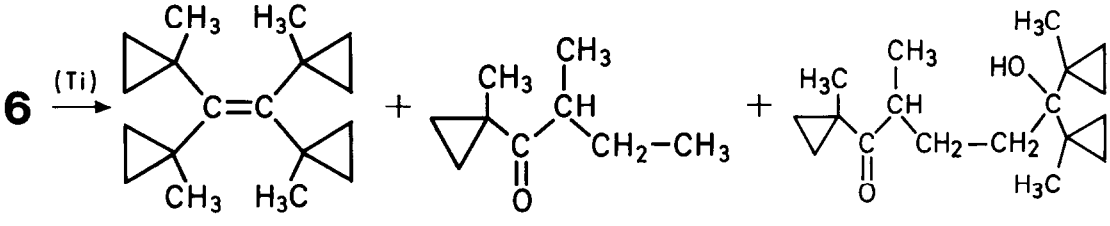
1 **2** **3** **4**

In contrast to the condensations of α-unsubstituted lactones[5,6], the addition of 1 to 2 is reversible and occurs slowly below 0°C; its equilibrium constant for formation of 3 becomes progressively unfavorable above room temperature and also on solvent change from hexane to diethyl ether, tetrahydrofuran (THF), or hexamethyl phosphoric triamide in THF[12].



5 **6**

The colourless 1,7-dichloro-3,5-dimethyl-4-heptanone[13] (5) was prepared in the usual way[5,6] in 88% yield by boiling the spiro-acetal 4 for 30 min with a ten-fold amount (by volume) of conc. hydrochloric acid, followed by dilution and ether extraction. This crude material (0.156 mol in 70 mL of ethanol) was added slowly with stirring at +80°C to ethanolic KOH (1.43 mol in 320 mL) and then refluxed for 75 min, yielding 73 - 83% of the target ketone[9,14] 6 (overall yield from 1 better than 50%).



7 **8** **9**

Reductive coupling[2] of 6 to give the olefin 7 could be best achieved after pretreatment of the commercial McMurry reagent ($TiCl_3/LiAlH_4$ 4:1) in THF with one additional[15] equivalent of $LiAlH_4$. Although 7 is formed in a rather low yield of 13% and in a mixture with two major products (31% of 8 and 29% of 9)[9], it can be readily obtained in a probably purer state[9,16] than before: Several of the previously[1] assigned mass spectral and infrared peaks are missing in our sample[16].

Bis(1-methylcyclopropyl)ketone (6) thus appears to represent a borderline case for successful reductive coupling.

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References and Footnotes

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9) Elemental analyses within ±0.23 for C and ±0.27 for H for 4, 6, 7, 9, and for 6-(2,4-dinitrophenyl)hydrazone.

10) Compare: P. Deslongchamps, D. D. Rowan, N. Pothier, G. Sauvé and J. K. Saunders, Can. J. Chem. 59, 1105-1121, 1132-1139 (1981).

11) Diastereomeric mixture of 4, ^{1}H NMR (CCl_4): m at δ 3.70 (4 H), 1.90 (6 H), 0.97 (6 H); IR (film): 1460, 1070, 992, 922 cm^{-1}. - ^{13}C NMR ($CDCl_3$, main isomer): δ 114.7 (C-5), 65.8 (2 CH_2O), 37.5 (2 CH), 33.0 (2 CH_2), 13.0 (2 CH_3).

12) Preliminary results indicate that our method may be much less efficient with other γ-butyrolactones, even with the use of i-C_3H_7-MgN(i-C_3H_7)$_2$ (compare: G. E. Coates and D. Ridley, J. Chem. Soc. A 1967, 56-59) as a base providing a coordinating cation in hydrocarbon solutions.

13) 5: B.p. 126.5-127.5°C/12 torr with slight decomposition. - IR (film): 1710 cm^{-1}. - ^{1}H NMR (CCl_4): δ 3.45 (m, CH_2Cl), 3.00 (mc, CH), 1.92 (very broad m,

CH_2), 1.13 (d, J = 7 Hz, CH_3).

14) 6: B. p. 59.5-60.5°C/12 torr or 76°C/24 torr (lit.[1,3]: no data). - IR (film): 3088, 1687, 1060 cm^{-1}. - ^1H NMR (CCl_4): δ 1.43 (s, CH_3), 1.00 and 0.47 (2 CH_2, AA'BB'). - ^{13}C NMR ($CDCl_3$): δ 210.4 (CO), 25.6 (2 quart. C), 20.7 (2 CH_3), 15.3 (4 CH_2). - 2,4-Dinitrophenylhydrazone[9] of 6: m.p. 148-149°C.

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16) Tetrakis(1-methylcyclopropyl)ethylene (7). Commercial $TiCl_3/LiAlH_4$ (4:1, 11.7 g) was added to the suspension of $LiAlH_4$ (0.69 g) in 75 mL of anhydrous THF at 3°C and then refluxed for 1 h under nitrogen gas. The ketone 6 (5.00 g) in 20 mL of THF was slowly added at +15°C and the mixture stirred for two days at +50°C. Distillation of the crude product obtained from hydrolysis and ether extraction gave, after a forerun containing 8, a mixture of 7 and 9 with b.p. 63-92°C/0.09 torr, which on chromatography (silica gel/CCl_4), distillation and final crystallization from methanol yielded 7 with m.p. 132-134°C[9] (lit.[1]: 126-130°C). - IR (KBr): 3103, 3070, 3015, 2992, 2968, 2953, 2932, 2900, 2865, 2730, 1452, 1419, 1382, 1290(w), 1255(w), 1168(w), 1113, 1093(w), 1072, 1053, 1042(w), 1029, 1020, 989, 946, 931, 914, 902, 847, 840, 795, 743(w), 736 cm^{-1}. - MS (70 eV): m/e = 244 (12%, M^+), 216 (13), 201 (46), 189 (100), 173 (15), 161 (15), 159 (44), 147 (17), 145 (36), 133 (36), 131 (20), 119 (42), 107 (24), 105 (38), 95 (21), 93 (22), 91 (33), 81 (24), 79 (18), 77 (24), 69 (14), 67 (12), 65 (11), 55 (40). - ^1H NMR (CCl_4, 60 MHz at +30°C): δ 1.22 (s, CH_3), 0.43 (pseudo-s, 2 H). - ^{13}C NMR ($CDCl_3$ at +53.5°C): δ 142.6 (olefin. C), 25.9 (4 CH_3), 19.7 (quart. C), 17.0 (8 CH_2).

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