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ONE POT SYNTHESIS OF 3,4-BIS(METHOXYCARBONYL)-2-TRIMETHYLSILYLFURANS BY DIELS-ALDER REACTION

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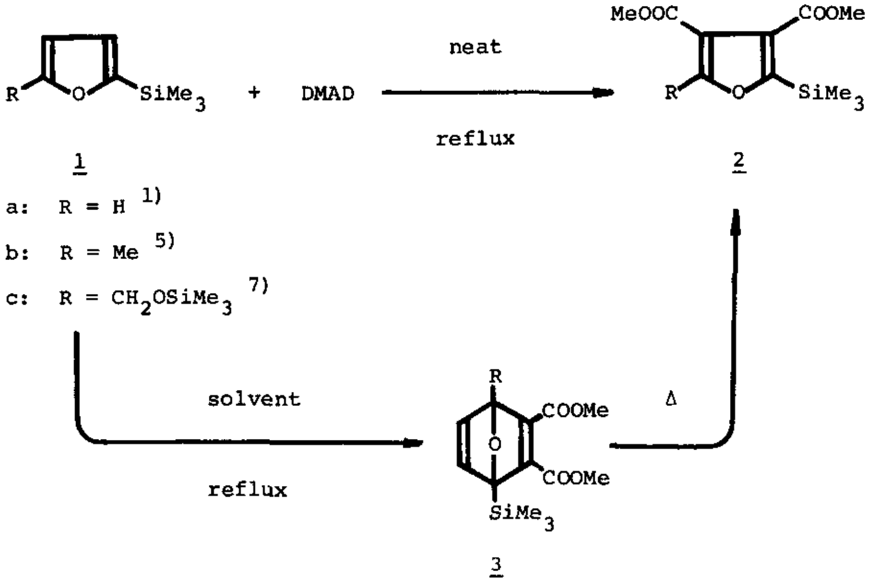
Abstract - 2-Trimethylsilylfurans (1a-c) were heated with dimethyl acetylenedicarboxylate to give 3,4-bis(methoxycarbonyl)-2-trimethylsilylfurans (2a-c). In organic solvents, 1a-c reacted with dimethyl acetylenedicarboxylate to give the corresponding oxabicyclo adducts.

2-Trimethylsilylfuan (1a) has been prepared by Benkeser et al. in 1948 and offered a few chemical reactions.[1] On the other hand, recently, Kuwajima et al. have shown to be transformed 5-substituted 2-trimethylsilylfurans into 5-substituted Δ^3-butenolides by oxidizing with peracetic acid.[2] Goldsmith et al. like the Kuwajima group, have converted 3- and 4-substituted 2-trimethylsilylfurans into 3- and 4-substituted Δ^2-butenolides by oxidizing with peracetic acid.[3] However, other synthetic application of trimethylsilylfurans has been scarcely investigated. It is supposed that the reactivities of their conjugated double bond system are affected by the trimethylsilyl group since trimethylsilyl group on furan ring possesses both properties of -M and +I effects to furan ring.[4] Accordingly, we were interested in comparing the behavior of furans with that of 2-trimethylsilylfurans in Diels-Alder reaction and we undertook to research the reaction of 2-trimethylsilylfurans with dimethyl acetylenedicarboxylate (DMAD). The mixture of 1a and DMAD was refluxed to give directly 3,4-bis(methoxycarbonyl)-2-trimethylsilylfuran (2a) [^{1}H-nmr ($CDCl_3$): δ 0.30 (s, 9H), 3.77 (s, 3H), 3.80 (s, 3H), 8.00 (s, 1H)], bp 103-105°C / 2 torr, 51 %, without giving the oxabicyclo adducts.



Similarly compounds 1b and 1c were treated with DMAD in a similar manner as above to provide 2b [^{1}H-nmr (CDCl$_3$): δ 0.30 (s, 9H), 2.50 (s, 6H), 3.80 (s, 6H)], bp 95-98°C / 1 torr, 56.2 %, and 2c [^{1}H-nmr (CDCl$_3$): δ 0.13 (s, 9H), 0.30 (s, 9H), 3.77 (s, 6H), 4.77 (s, 2H)], bp 142°C / 1 torr, 44.1 %, respectively.

In the above reactions, 2a-c could be formed by concomitant elimination of acetlene from the oxabicyclo adducts once formed. Then, in order to to grasp their oxabicyclo adducts, 1a-c were refluxed with DMAD in benzene and then the reaction mixture was treated with column chromatography (silica gel, CHCl$_3$). Compounds 1a and 1b gave dimethyl 4-trimethylsilyl-7-oxabicyclo[2.2.1]hepta-2,5-diene-2,3-dicarboxylate (3a) 50 %, [^{1}H-nmr (CCl$_4$): δ 0.13 (s, 9H), 3.60 (s, 3H), 3.67 (s, 3H), 5.30 (s. 1H), 7.00 (s, 2H)] and dimethyl 1-methyl-4-trimethylsilyl-7-oxabicyclo-[2.2.1]hepta-2,5-diene-2,3-dicarboxylate (3b) 57.5 %, [^{1}H-nmr (CCl$_4$): δ 0.17 (s, 9H), 1.73 (s, 3H), 3.70 (s, 6H), 6.83 (d, 1H), 7.00 (d, 1H)], respectively, however the starting material was recovered in a treatment of 1c under the same condition. Thereby, 1c was refluxed with DMAD in xylene to give dimethyl 1-trimethylsiloxymethyl-4-trimethylsilyl-7-oxabicyclo[2.2.1]hepta-2,5-diene-2,3-dicarboxylate (3c) 48 %, [^{1}H-nmr (CCl$_4$): δ 0.10 (s, 9H), 0.30 (s, 9H), 3.63 (s, 6H), 4.50 (s, 2H), 6.03 (d, 1H), 6.40 (d, 1H)]. Oxabicyclo adducts (3a-c) were heated at ca. 200°C for 1 h to give 2a-c quantitatively.

It has become apparent that the adducts of 2-trimethylsilylfurans with DMAD directly take place the retro Diels-Alder reaction to give 2a-c without passing hydrogenation process as those furans.[6] The reason why 3a-c easily occur Diels-Alder reaction to give 2a-c could be that some effects of the trimethylsilyl group on bridgehead accelerate cleavage of them. Thus the fact that 2a-c were obtained from 1a-c in one pot, shows that 2-trimethylsilylfurans are able to become synthetic intermediates for 3,4-disubstituted furans.

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