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DIELS-ALDER REACTIONS OF TRIMETHYLSILOXY-SUBSTITUTED BUTADIENES WITH DIMETHYL ACETYLENEDICARBOXYLATE

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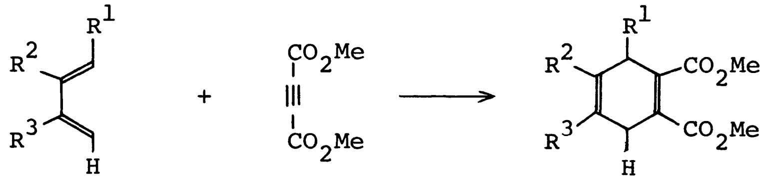
A variety of trimethylsiloxy-substituted butadienes, including novel 1-methoxy-1,3-bis(trimethylsiloxy)butadiene, react in a Diels-Alder process with dimethyl acetylenedicarboxylate. The adducts were converted, *via* elimination or oxidative aromatization, into four corresponding dimethyl hydroxy-substituted phthalates in good to moderate yields.

Utilization of extensively functionalyzed dienes in the Diels-Alder reaction has attracted much attention.[1-3] Several trimethylsiloxy-substituted butadienes, readily available by a silyl enol ether preparation from appropriate carbonyl compounds, are also expected to be of use for such transformations.[3]

We report here that trimethylsiloxy-substituted butadienes (**1a-c**) readily react in a Diels-Alder process with dimethyl acetylenedicarboxylate (**2**). The adducts (**3a-c**) isolated were transformed into dimethyl hydroxy-substituted phthalates by either facile elimination of trimethylsilanol or oxidative aromatization. Although the latter procedure met rather limited success at present, it would allow to conserve all functional groups in the diene component, and hence be of value.



2 **3a-c**

(1)

1a $R^1=OSiMe_3$; $R^2=R^3=H$
1b $R^1=R^3=OSiMe_3$; $R^2=H$
1c $R^1=H$; $R^2=R^3=OSiMe_3$

An equimolar (10 mmol) mixture of 1-(trimethylsiloxy)butadiene (**1a**)[4] and **2**, and a small amount of hydroquinone dissolved in dry benzene (20 ml) were heated at 50°C for two days. The solvent and unreacted materials were removed *in vacuo* at this temperature to leave substantially pure adduct **3a** (68% yield), which was characterized by NMR spectral data.[5] ^1H NMR (CCl_4, TMS) δ 0.08 (s, $SiMe_3$), 2.92 (m, CH_2), 3.68

(s, CO_2Me), 5.01 (m, CH-O), and 5.77 ppm (bs, CH=CH).

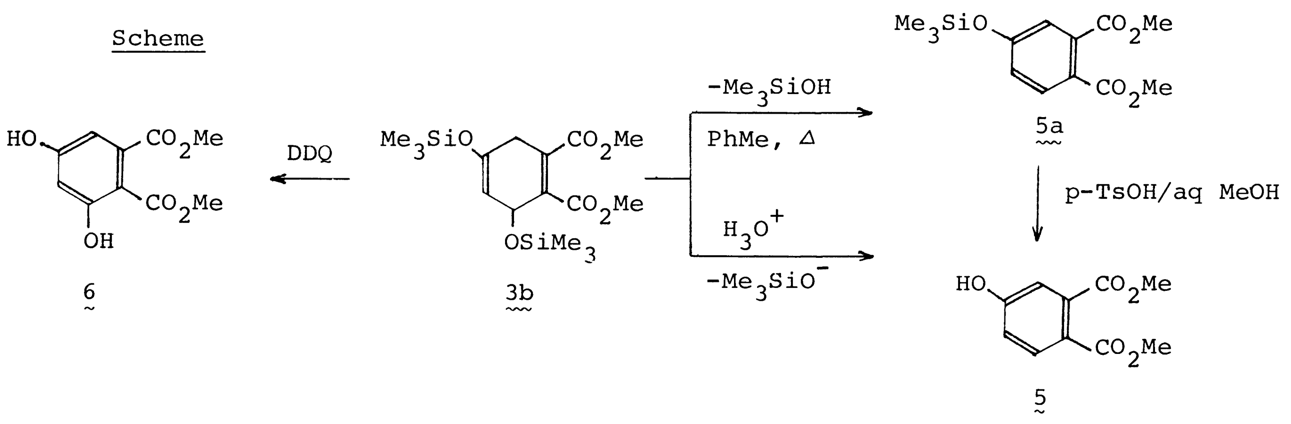
The same reaction was conducted in refluxing toluene for 4.5 h to give dimethyl phthalate (85% yield), which arose from an elimination of trimethylsilanol from intermediate 3a. The thermal elimination seems to be easier than that of acetic acid(6) and ethanol(7) from the corresponding intermediates, being recommended for the preparation of benzene rings.

Of particular interest was an oxidative aromatization of the adduct (3a) to give dimethyl 3-hydroxyphthalate (4) indicative of conserving a functional group in the diene component (1a). Among several oxidizing agents examined, chromic oxide was found to be satisfactory in this particular case. Thus, 3a was treated with three equivalents of dipyridine-chromium(VI) oxide at 0°C for 15 min to afford 4 in 60% yield after column chromatographic purification, mp 48.5-50.0°C (lit.(8) mp 48-51°C). 2,3-Dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) in benzene was also found to effect the oxidative aromatization of 3a to 4 (56% yield).

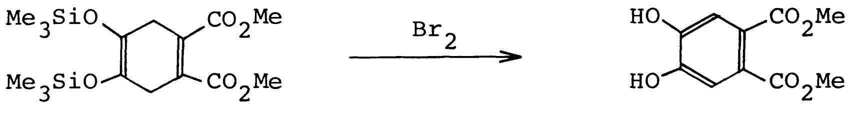
Attempted oxidation of 3b, which was obtained similarly from a reaction of 1,3-bis(trimethylsiloxy)butadiene (1b)(3b) with 2 in 90% crude yield, met difficulties, resulting in an extensive elimination of one of the trimethylsiloxy moiety in 3b to give dimethyl 4-hydroxyphthalate (5), mp 105-106°C, as a major product (lit.(9,10) mp 105.5-106.5°C). Use of DDQ gave at best a mixture of 5 and desired dimethyl 3,5-dihydroxyphthalate (6) in a ratio of 2:1 (60% combined yield).

It was also found that either thermal elimination followed by hydrolysis or direct acid-hydrolysis of 3b gave 5 in good yield. The latter hydrolysis indicates that 3b is sensitive to a nucleophile, which attacks a silicon atom bound to vinyloxy moiety to cause concomitant elimination of another trimethylsiloxy group (Scheme). There is one precedent of this type of elimination using 1-methoxy-3-(trimethylsiloxy)butadiene.(9)

Scheme



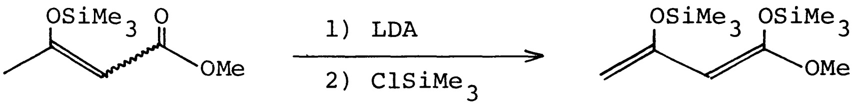
The reaction of 2,3-bis(trimethylsiloxy)butadiene (1c)(11) with 2 in refluxing toluene for 7 h gave 3c (73% yield), which was free from the elimination described above. Oxidation of 3c with equimolar amount of bromine in carbon tetrachloride which involves double β-elimination of bromotrimethylsilane gave dimethyl 4,5-dihydroxyphthalate (7) in 64% yield, mp 136-138°C.(12)



3c 7

(2)

Finally, the preparation of 6 was carried out *via* the Diels-Alder process accompanied by thermal elimination. Novel 1-methoxy-1,3-bis(trimethylsiloxy)-butadiene (1d) was prepared by a stepwise silyl enol ether preparation from methyl acetoacetate. Thus, enol trimethylsilyl ether of methyl acetoacetate (40 mmol, Z/E = 70/30), obtained by a conventional method, was treated sequentially with a slight excess of lithium diisopropylamide (LDA) in THF at -78°C and with chlorotrimethylsilane to afford 1d in 73% yield, bp 56-58°C/2.0 Torr.[13]

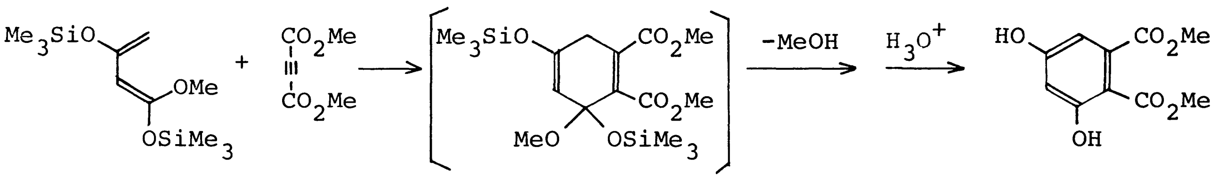


1d

(3)

Direct silylation of a dianion of methyl acetoacetate was found to result in exclusive formation of C-silylated isomer.[14]

The addition of 1d to 2 in refluxing toluene for 7 h, followed by acid hydrolysis, gave 6 in 53% yield, mp 124.5-126.5°C,[15] with concomitant formation of dimethyl 3-methoxy-5-hydroxyphthalate (8) (3% yield). The same reaction, but in benzene at 50°C for 30 h, gave 6 and 8 in 56% and 8% yield, respectively.



1d 2 3d 6

(4)

The results indicate that elimination of methanol is much favored both thermally and hydrolytically than that of trimethylsilanol from the intermediate adduct (3d).[16]

References and Notes

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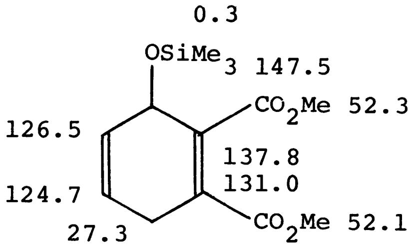
5) ^{13}C NMR (CDCl$_3$) chemical shifts in ppm from TMS were given as follows:



3a

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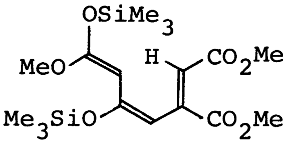
12) Identified as a known dimethyl ether, mp 85-87°C: Lit. mp 85.5-86.5°C, N. A. R. Hatam and D. A. Whiting, J. Chem. Soc., (C), 1921 (1969).

13) ^{1}H NMR (CCl$_4$, TMS) δ 0.14 and 0.20 (s, SiMe$_3$), 3.52 (s, OMe), 3.75 and 4.00 (d, =CH$_2$), and 4.30 ppm (s, =CH).

14) This was found by Mr. Shimizu of this laboratory.

15) Identified as a known dimethyl ether, mp 94.5-96.5°C: Lit, mp 95-97°C, E. Sondheimer, J. Am. Chem. Soc., 79, 5036 (1957).

16) It deserves mention that the diene 1d was found to react partially with dimethyl acetylenedicarboxylate in a Michael process giving compound 9, presumably due to a steric reason.



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