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DIKETENE AS A 3-BUTENOIC ACID SYNTHON IN TRANSITION METAL-CATALYZED ALKYLATION OF A TRIMETHYLSILYLMETHYL GRIGNARD REAGENT

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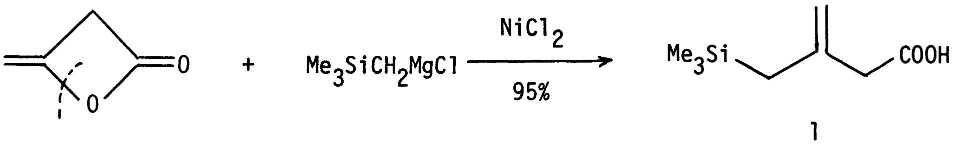
The reaction of $(CH_3)_3SiCH_2MgCl$ with diketene yields 3-trimethylsilylmethyl-3-butenoic acid (**1**) in the presence of a catalytic amount of $NiCl_2$(95%), $PdCl_2$(68%), $CoCl_3$(60%), or CuI(20%) under moderate conditions. The acid, **1**, is isomerized to the conjugated acid, 4-trimethylsilyl-3-methyl-2-butenoic acid (**2**) by means of an excess $LiN(SiMe_3)_2$. The rearrangement proceeds stereoselectively to **2**-(E) isomer by addition of diglyme or N,N,N',N'-tetramethylethylenediamine. This is the first example of the vinyl-oxygen bond cleavage of diketene.

The trimethylsilylmethyl-metal bond attracted much attention to inorganic chemists because of forming stable transition metal-alkyl compounds[1], however, there have been few studies to apply these particular metal-alkyls to organic synthesis.[2, 3c] We now report Me_3SiCH_2MgCl induces the first example of a highly selective vinyl-oxygen bond scission of diketene in the presence of catalytic amount of transition metal halides to give 3-trimethylsilylmethyl-3-butenoic acid (**1**), which is stereoselectively transformed into the (E) isomer of 4-trimethylsilyl-3-methyl-2-butenoic acid (**2**). Although many transition metal-mediated alkylations of carbanions have been investigated in recent years,[3] it is unprecedented that diketene behaves as an electrophilic reagent acting to be a "3-butenoic acid synthon".[4]

When a catalytic amount of nickel chloride(0.4g) was added at 0°C to a THF solution of Me_3SiCH_2MgCl, prepared from Me_3SiCH_2Cl (300 mmol), Mg(300 mmol), THF(130 ml), and a trace of iodine, a deep brown solution was obtained. After 10 min stirring at room temperature, a THF(25 ml) solution of diketene (300 mmol) was added dropwise at 0°C to give an orange-brown solution which turned to deep green after 5 hr at room temperature. Hydrolysis with excess 2N HCl followed by extraction with ether gave crude **1**, which was purified by chromatography (Silica gel 2cmϕ × 12cm; $CHCl_3$) to give pure **1** in 95% isolated yield as a pale yellow oil; NMR(CCl_4): δ ppm 0.18(9, s, CH_3Si), 1.65(2, d, CH_2Si), 2.96(2, s, CH_2CO), 4.72 and 4.48(each 1, m, olefinic), 11.48(1, brs, COOH). IR(CCl_4): ν(C=O) 1713, ν(C=C) 1637cm^{-1}. Anal. Calcd. for $C_8H_{16}O_2Si$: C, 55.77; H, 9.36. Found: C, 56.03; H, 9.28.



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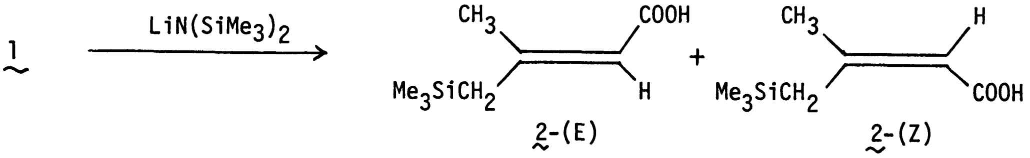
The above reaction was also catalyzed by CuI (20%), $PdCl_2$ (68%), and $CoCl_3$ (60%) and proceeded with $(Me_3SiCH_2)_2CuMgCl$(64%), however, the absence of these transition metal catalysts yielded a complex mixture of several products in which any trace of 1 was not detected. Other Grignard reagents, RMgX (R=CH_3, C_2H_5, n-C_4H_9, C_3H_5, CH_2=CH, or C_6H_5) did not give the corresponding 3-alkyl-3-butenoic acids under similar condition.[5]



The acid 1 can be isomerized successfully to an α,β-unsaturated acid 2, which has a possibility to act as an isoprenoid acid synthon, by means of excess $LiN(SiMe_3)_2$. High stereoselectivity to 2-(E) was attainable by controlling the reaction media and additives as summarized in Table 1. The strong coordination of diglyme or N,N,N',N'-tetramethylethylenediamine(TMEDA) resulted in a drastic increase of the E/Z ratio of 2 (E/Z = 98/2, run 6): 2-(E); after chromatographic purification (Silica gel, n-hexane then benzene); Mp 45-47°, NMR(CCl_4): δ ppm 0.06(9, s, CH_3Si), 1.73(2, s, CH_2Si), 2.14(3, d, CH_3, J=1 HZ), 5.46(1, m, olefinic), 11.87(1, br., COOH). IR(CCl_4): ν(C=O)1685, ν(C=C)1622cm^{-1}. Anal. Calcd. for $C_8H_{16}O_2Si$: C, 55.77; H, 9.36, Found: C, 56.07; H, 9.27.

On the contrary, the trimethylsilyl ester of acid 1 rearranged mainly to a 2-(Z)-rich mixture in 60% yield (E/Z=15/85, run 7) with excess $LiN(SiMe_3)_2$ in a HMPA-THF mixed solvent (11/10 vol. ratio): 2-(Z); after chromatographic purification (Silica gel, n-hexane), pale yellow oil, NMR(CCl_4): δ ppm 0.02(9, s, CH_3Si), 1.82(3, d, CH_3, J=0.9Hz), 2.35(2, s, CH_2Si), 5.50(1, m, olefinic), 11.21(1, br., COOH). IR(CCl_4): ν(C=O)1679, ν(C=C)1617cm^{-1}. Anal. Calcd. for $C_8H_{16}O_2Si$: C, 55.77; H, 9.36: Found: C, 55.95; H, 9.66.

The application of 1,2-(E), and 2-(Z) to develop new carbon-carbon bond formation reactions is under active investigation.

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Table I. Rearrangement of **1** to **2** with Lithium Bis(trimethylsilyl)amide(LBTMSA)

Run	**1** (mmol)	LBTMSA (mmol)	Solvent	Reaction Conditions	**2** Yield(%)[a]	**2** E/Z[b]
1	4.76	9.51	THF(15 ml)	reflux 1 hr	90	45:55
2	5.22	15.60	THF(25 ml)+ HMPA(15 ml)	-50° for addition of **1**, then reflux 15 min.	82	71:29
3	5.22	15.62	THF(9 ml) + HMPA(17 ml)	-30° for addition of **1**, then reflux 5 min.	76	73:27
4	5.22	15.60	DME(30 ml)	-45° for addition of **1**, then reflux 20 min.	74	68:32
5	2.61	8.25	Diglyme(10 ml)	-78° for addition of **1**, then 20° for 45 min.	90	93: 7
6	2.60	8.20	Ethyl ether(20 ml) +n-hexane(26 ml) +HMPA(1.5 ml) +TMEDA(2 ml)	-70° for addition of **1**, then 20° for 1hr.	91	98: 2
7	3.74[c]	7.28	THF(10 ml)+ HMPA(11 ml)	-50° for addition of **1**, then reflux 10 min	60	15:85

[a] Isolated crude yield. [b] Determined by NMR; relative ratio of the 3-methyl proton signals.

[c] Used $(CH_3)_3SiCH_2C(=CH_2)CH_2COOSi(CH_3)_3$ instead of **1**.

References and Footnotes

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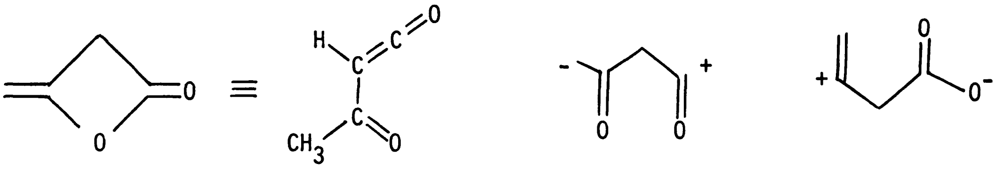
(4) The most common reaction of diketene is its role as an acetylketene eguivalent **3**.



3 **4** **5**

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The present reaction is the first example that diketene behaves as a pure 3-butenoic acid synthon (**5**).

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