Tetrahedron Letters,Vol.23,No.12,pp 1279-1280,1982 0040-4039/82/121279-02$03.00/0
Printed in Great Britain

SYNTHESIS AND REACTIONS OF 1-BROMOCYCLOPROPYLTRIMETHYLSILANE DERIVATIVES

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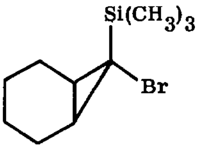
The title compounds derived from 1,1-dibromocyclopropanes are transformed into (1) cyclopropyltrimethylsilanes *via* 1-trimethylsilylcyclopropyllithium species, (2) 1-alkylidenecyclopropanes by the Peterson-olefination, and (3) 1-acetyl(or 1-allyl)cyclopropylsilanes with dibutylcopperlithium and acetyl chloride (or allyl bromide).

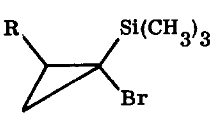
The note recorded by Krief and his coworkers[2] on the alkylidenecyclopropane synthesis using the title compounds prompted us to disclose our observations some time ago.

The title silanes were prepared simply by adding butyllithium to a mixture of 1,1-dibromocyclopropane and a slight excess of trimethylchlorosilane (TMSCl) at -95°C in tetrahydrofuran (THF).[3] The product I[4] (80% yield, 97% endo TMS), II[5] (69% yield, 95-97% C_6H_5-TMS cis), and III[5] (75% yield, 1:1 stereoisomeric mixture) were produced from the corresponding dibromides.

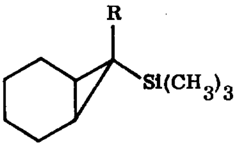
When I was allowed to react with butyllithium (1.2 eq) at -95°C in THF and the resulting cyclopropyllithium species IVb was quenched with acetic acid at -95°C, a 73:27 mixture of IVa[5] and its endo-TMS isomer was formed in 93% yield. Similarly, II[5] (95% C_6H_5-TMS cis) was transformed into Va and its cis isomer (78% yield, 83:17). Quenching with AcOD gave Vb and its isomer with D content of 92% (NMR). In view of the study of Walborsky and his coworkers bromine on cyclopropane rings should be lithiated with retention of configuration by means of organolithium reagents.[6] As protonation of carbanions also proceeds with the same stereochemical result in general, we can conclude that 1-trimethylsilylcyclopropyllithium intermediates such as IVb and Vc are configurationally unstable at -95°C and isomerize to thermodynamically favourable isomers.[7]



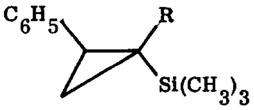
I



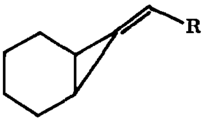
II R = C_6H_5
III R = $C_6H_5CH_2OCH_2$



IV a: R = H
b: R = Li

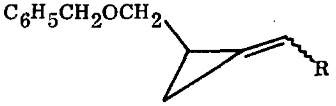


V a: R = H, b: R = D
c: R = Li
d: R = $COCH_3$
e: R = $CH_2CH{=}CH_2$



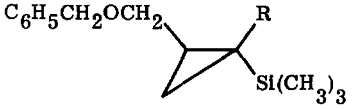
VI a: R = C_6H_5

b: R = $CH{=}CHCH_3$



VII a: R = C_6H_5

b: R = $CH{=}CHCH_3$



VIII a: R = $COCH_3$

b: R = $CH_2CH{=}CH_2$

We also have observed that the Peterson-olefination does occur using 1-trimethylsilylcyclopropyllithium-aldehyde adducts. For example, when IVb-heptanal adduct[8] was stirred with potassium hydride (excess) in THF (r.t., 1.3 h), 7-heptylidenenorcarane[5] [MS: m/e 192; ^{1}H-NMR (CCl_4): δ 5.77 (dt, J = 7, 2 Hz, 1H)] was produced in 96% yield. Without isolation, the IVb-benzaldehyde or -crotonaldehyde adducts were treated with potassium t-butoxide (THF, r.t., 2-10 h) to give VIa[5] (55% overall yield) or VIb[5] (45% overall yield) respectively. Starting with III, we obtained VIIa[5] (56%) and VIIb[5] (46%) from C_6H_5CHO and $CH_3CH{=}CHCHO$ respectively by means of potassium hydride.

Although alkylation[9] of IVb or Vc has failed, acetylation and allylation have been alternatively effected with II or III using dibutylcopperlithium.[10] Thus, II was treated with 4 mol of dibutylcopperlithium at -48°C in THF, and the resulting cuprate species was allowed to react with acetyl chloride or allyl bromide, hereby giving rise to Vd[5] (52%) or Ve[5] (77%) respectively. The stereochemistry of Vd and Ve was assumed to be C_6H_5-TMS trans based on the shielding effect of the phenyl group.[9] Similarly III was converted into VIIIa[5] (66%) or VIIIb[5] (68%). These trimethylsilylcyclopropanes are apparently versatile synthetic intermediates.[11]

References and Notes

1. Present address: Sagami Chemical Research Center, 4-4-1 Nishiohnuma, Sagamihara, Kanagawa 229, Japan
2. S. Halazy, W. Dumont, and A. Krief, Tetrahedron Lett., **22**, 4737 (1981).
3. T. Hiyama, A. Kanakura, H. Yamamoto, and H. Nozaki, Tetrahedron Lett., 3047 (1978).
4. D. Seyferth and R. L. Lambert, Jr., J. Organomet. Chem., **88**, 287 (1975); R. L. Lambert, Jr. and D. Seyferth, J. Am. Chem. Soc., **94**, 9246 (1972).
5. The compound was characterized spectrometrically (IR, ^{1}H-NMR, MS). II: bp 67-69°C/2 Torr; III: bp 115-118°C/0.05 Torr; IVa: bp 130-165°C (bath temp)/30-50 Torr; VIa: MS m/e 184, ^{1}H-NMR (CCl_4): δ 0.9-2.2 (m, 10H), 6.70 (br s, 1H), 7.0-7.7 (m, 5H); VIb: ^{1}H-NMR (CCl_4): δ 0.5-2.5 (m + d (δ 1.71)), 5.3-6.5 (m).
6. H. M. Walborsky, F. J. Impastato, and A. E. Young, J. Am. Chem. Soc., **86**, 3283 (1964).
7. Configurational isomerization of 1-phenylthio-2-methylcyclopropyllithium takes place similarly: B. M. Trost, D. E. Keeley, H. C. Arndt, J. H. Rigby, and M. J. Bogdanowicz, J. Am. Chem. Soc., **99**, 3080 (1977).
8. T. Hiyama, Y. Morizawa, H. Yamamoto, and H. Nozaki, Bull. Chem. Soc. Jpn., **54**, 2151 (1981).
9. K. Kitatani, T. Hiyama, and H. Nozaki, Bull. Chem. Soc. Jpn., **50**, 3288 (1977).
10. T. Hiyama, H. Yamamoto, K. Nishio, K. Kitatani, and H. Nozaki, Bull. Chem. Soc. Jpn., **52**, 3632 (1979).
11. M. Grignon-Dubois, J. Dunguès, and R. Calas, Synthesis, 737 (1976); T. H. Chan and I. Fleming, ibid., 761 (1979).

(Received in Japan 19 December 1981)