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NEW VERSATILE C_5 BUILDING BLOCKS FROM ETHYLENE AND TETRACHLOROCYCLOPROPENE[**]

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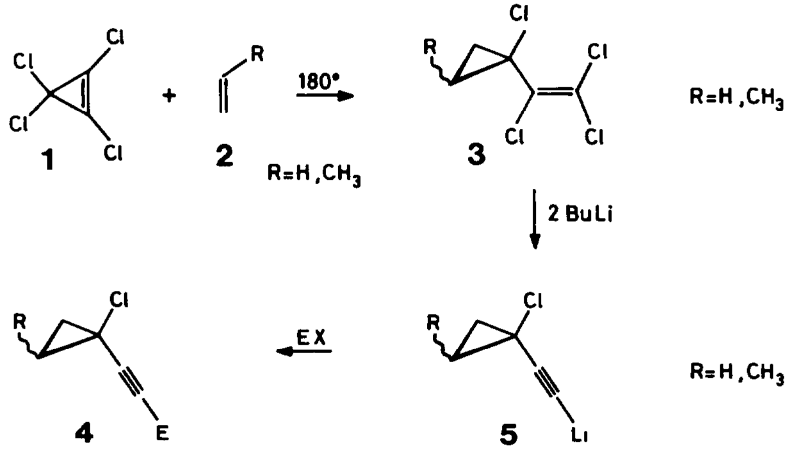
Summary: The perchlorovinylcarbene adducts of ethylene and propylene served as precursors to a wide spectrum of 1'-substituted cyclopropylacetylenes **4**, **8** and **9**, which are versatile polyfunctional molecules. E.g., the acetylenic ester **4c** underwent cycloaddition to 1,3-dienes giving otherwise unaccessible compounds.

As we have demonstrated earlier, tetrachlorocyclopropene (**1**) is an efficient source for tetrachlorovinylcarbene, which can be trapped intermolecularly by olefins to give 1-chloro-1-(trichlorovinyl)cyclopropanes in good to very good yields[1]. Single step transformations of these adducts give rise to synthetically useful vinylcyclopropanes[1], alkynylcyclopropanes[2] and esters of methylenecyclopropane carboxylic acids[3]. The application of this methodology to ethylene and propylene creates interesting new C_5 and C_6 functional molecules which can serve as versatile building blocks in organic synthesis.

The reactions of ethylene (**2** [R = H]) and propylene (**2** [R = CH_3]) with **1** were carried out in a 300 ml MONEL sampling cylinder. Tenfold ex-



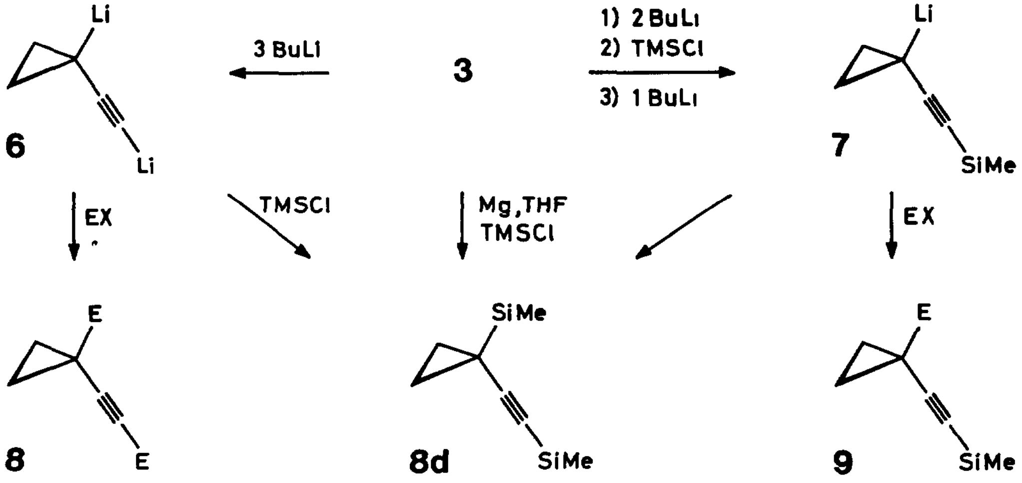
cesses of the gaseous olefins were condensed into the cylinder which had been charged with tetrachlorocyclopropene (**1**), tetrachloroethylene as a solvent and sodium bicarbonate as a hydrogen chloride scavenger. The vinylcyclopropanes **3** (R = H, CH_3) were isolated by distillation in 63% and 50% yield, respectively. The lithium acetylides **5** generated from **3** by metalation[2] with 2 equivalents of butyl lithium were reacted with various electrophiles to give the corresponding (1-chlorocyclopropyl)acetylene derivatives **4** (R = H, CH_3) (see table 1).

Table 1. (1-Chlorocyclopropyl)acetylene derivatives **4** from **3** via **5**.

Educt	EX	Product (E)[a]	Yield [%]	Isolation[b]
3(R = H)	H_2O	**4a** (H)	91	A
3(R = H)	CO_2	**4b** (CO_2H)	84	B
3(R = H)	$ClCO_2Me$	**4c** (CO_2Me)	95	C
3(R = H)	Me_3SiCl	**4d** ($SiMe_3$)	78	D
3(R = CH_3)	$ClCO_2Me$	**4e** (CO_2Me)	59	C

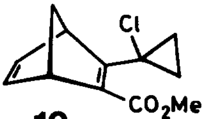
[a] All new compounds were fully characterized by spectroscopical methods (see table 3). [b] A Distillation, B Recrystallization, C· Kugelrohr-distillation, D: Prep. GC.

Metalation of **3** (R = H) with 3 equivalents of BuLi gave the dianion **6**, which upon electrophilic substitution yielded difunctional cyclopropylacetylenes of type **8** (e.g. **8d**, E = $SiMe_3$, 62%). The bistrimethylsilyl compound **8d** could be obtained more conveniently by heating **3** with magnesium in tetrahydrofurane in the presence of TMSCl (62% GC-isolated yield).



Further metalation of **4d** with subsequent electrophilic substitution opens the way to difunctional cyclopropylacetylenes **9** and others with almost any desirable combination of functional groups. The same objective could be achieved with a four step-one pot procedure metalation of **3** (2 eq. BuLi), addition of TMSCl (1 mol), metalation (1 eq. BuLi) and reaction with an electrophile, e.g. iodine gave **9f** (E = I) in 69% isolated yield.

Several of these cyclopropylacetylenes are valuable substrates for catalyzed[4] or uncatalyzed cycloaddition reactions. For instance the methyl 3-[1'-chlorocyclopropyl]propiolate **4c** (R = H) is a reasonably reactive dienophile. Its thermal reactions with various 1,3-dienes yielded [2+4]-cycloadducts, some of which underwent subsequent aromatization. E.g. **10** and **11** were obtained with cyclopentadiene and 1,3-cyclohexadiene respectively, addition to 1-methoxy-3-trimethylsiloxybutadiene occured with pronounced regioselectivity to give, after acidic work-up, the aromatic product **12** (see table 2).



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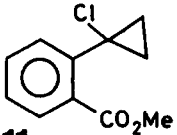

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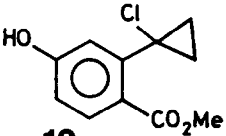

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Table 2. Cycloaddition products of methyl 3-[1'-chlorocyclopropyl]propiolate **4c** to various 1,3-dienes.

Product[a]	Yield [%]	Properties	Reaction conditions	Isolation[b]
10	90	colourl. liq.	80-90°C, 3 h	EE/PE 1 20
11	49	colourl. liq.	150°C, 24 h	EE/PE 1.20
12	63	cryst. m.p. 121°C	90°C, 24 h	EE/PE 7 3[c]

[a] Characterized by spectroscopic methods (see table 3).

[b] Chromatography on silica gel, EE = diethyl ether, PE = petrolether,

[c] After treatment with HCl/MeOH.

The chemistry presented here once more demonstrates the synthetic utility of small functional molecules containing a cyclopropyl group in combination with a multiple bond system[5].

Table 3. 270 MHz-^{1}H-NMR (δ values, TMS int.) and IR spectroscopic data of all new compounds.

4a, NMR ($CDCl_3$): 1.33(m, 4H), 2.40(s, 1H). - IR ($CDCl_3$): 3310(νH-C≡), 3100, 3010(νH-$C_{cyclopr.}$), 2120, 2090(νC≡C).

4c, NMR ($CDCl_3$): 1.46(m, 2H), 1.52(m, 2H), 3.78(s, 3H). - IR (KBr): 2220 (νC≡C), 1710(νC=O), 1220(νC-O).

4d, NMR ($CDCl_3$): 0.16(s, 9H), 1.31(m, 4H). - IR (film): 3090, 3010(νH-$C_{cyclopr.}$), 2160(νC≡C).

4e, NMR ($CDCl_3$): 0.87 - 0.96(m, rel. int. 3), 1.00 - 1.05(m, rel. int. 1), 1.27 - 1.36(m, 9), 1.55 - 1.61(m, 4), 1.94 - 2.06(m, 2), 3.79, 3.80(2s, 6). - IR (film): 2220(νC≡C), 1710(νC=O).

8d, NMR ($CDCl_3$): 0.03(s, 9H), 0.10(s, 9H), 0.66(m, 2H), 0.93(m, 2H). - IR (film). 3100, 3010(νH-$C_{cyclopr.}$), 2160(νC≡C).

9f, NMR ($CDCl_3$, 60 MHz): 0.20(s, 9H), 1.40(m, 4H). - IR (film): 2160(νC≡C).

10, NMR ($CDCl_3$): 1.14(m, 2H), 1.39(m, 2H), 2.07(AB, 2H, $^3J_{AB}$ = 6.6 Hz), 3.75(m, 1H), 3.80(s, 3H), 3.94(m, 1H), 6.84(m, 2H, $^3J_{5-H,6-H}$ = 7.8 Hz). - IR (film): 1710(νC=O), 1625(νC=C).

11, NMR ($CDCl_3$): 1.24(m, 2H), 1.49(m, 2H), 3.97(s, 3H), 7.32(dt, 1H, ^3J = 7.2 Hz, ^4J = 1.4 Hz), 7.45(dt, 1H, ^3J = 7.2 Hz, ^4J = 1.4 Hz), 7.55(m, 1H, ^3J = 7.2 Hz, ^4J = 1.4 Hz), 7.75(m, 1H, ^3J = 7.2 Hz, ^4J = 1.4 Hz). - IR (film): 1720(νC=O).

12, NMR (d_6-acetone): 1.26(m, 2H), 1.41(m, 2H), 3.75(s, 3H), 6.64(ABX, 1H, $^3J_{AB}$ = 8.4 Hz, $^4J_{AX}$ = 2.4 Hz), 6.82(d(AX), 1H, $^4J_{AX}$ = 2.4 Hz), 7.51(d(AB), 1H, $^3J_{AB}$ = 8.4 Hz), 8.87(s, 1H). - IR (KBr): 3350(νO-H), 1700(νC=O).

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[2] Th. Liese, A. de Meijere, Angew. Chem. **94**, 65 (1982), Angew. Chem. Int. Ed. Engl. **21**, 65 (1982).

[3] Th. Liese, G. Splettstoßer, A. de Meijere, Angew. Chem. **94**, in press (1982), Angew. Chem. Int. Ed. Engl. **94**, in press (1982).

[4] Work in progress in collaboration with Prof. U. Schuchardt, University of Campinas, Sao Paulo, Brazil.

[5] For further examples see: A. de Meijere, Angew. Chem. **91**, 867 (1979); Angew. Chem. Int. Ed. Engl. **18**, 809 (1979) and ref. cited therein.

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