white crystalline matter separated. This was collected by filtration and was recrystallized from ethanol. Yield, 3.3 g. (50%), m.p. 147–148°, $[\alpha]^{29}\text{D}$ +3.4° (*c* 1, pyridine).

Anal. Calcd. for $C_{21}H_{27}O_{10}N$: C, 55.62; H, 6.00; N, 3.09 Found: C, 55.12; H, 5.93; N, 3.33. $[\alpha]\text{D}$ showed that the above crystal was the β-isomer (IV).

The filtrate was concentrated under reduced pressure to a small volume and was placed in a refrigerator, whereupon crystals separated. Repeated recrystallization from ethanol yielded 3.0 g. of fine needles (45%), m.p. 102–105°, $[\alpha]^{29}\text{D}$ +104° (*c* 1, pyridine).

Anal. Found: C, 55.39; H, 5.95; N, 3.30. The constants showed that the crystal was the α-isomer[2] (III).

Methyl 3,4,6-tri-O-acetyl-2-amino-2-deoxy-β-D-glucopyranoside hydrochloride (VI). An amount of 5 g. of IV was dissolved in 100 ml. of methanol, and to this was added 1 g. of palladium-on-barium sulfate catalyst. The solution was stirred for few minutes, with dry hydrogen gas bubbling through, and to this was added half of 0.011 mole of dry methanolic hydrogen chloride. Another half portion of methanolic hydrogen chloride was added after 1.5 hr., and the reaction was completed within 3 hr. After removal of catalyst, the solution was concentrated under reduced pressure to a small volume, and to this was added a large amount of ether. A white crystalline substance separated. Recrystallization was effected from ethanol-ether. Yield, 3.0–3.2 g. (78–83%). Methyl 3,4,6-tri-O-acetyl-2-amino-2-deoxy-β-D-glucopyranoside hydrochloride (VI) melted at 216–227° (dec.). $[\alpha]^{25}\text{D}$ +10° (*c* 1, water).

Anal. Calcd. for $C_{13}H_{22}O_8NCl$: C, 43.89; H, 6.23; N, 3.94 Found: C, 43.99; H, 6.35; N, 4.11.

Methyl 3,4,6 - tri - *O* - acetyl - 2 - amino - 2 - deoxy - α-D-glucopyranoside hydrochloride (V) melted at 225–233° (dec.). $[\alpha]^{23}\text{D}$ +157.8° (*c* 1, water).

Anal. Found: C, 43.79, H 6.28, N 3.85. Reported constants,[2] m.p. 230–238°, $[\alpha]^{26}\text{D}$ +154° (*c* 1.8, water).

Methyl 3,4,6-tri-O-acetyl-2-amino-2-deoxy-β-D-glucopyranoside (VIII). Five grams of VI was dissolved in a small amount of 50% aqueous methanol and the solution was passed through a column (20 × 2 cm. diam.) of Amberlite IRA 400 (OH^-) and the effluent was concentrated under reduced pressure. The product was a sirup, dried over phosphorus pentoxide, and was used in the next reaction. Methyl 3,4,6-tri-*O*-acetyl-2-amino-2-deoxy-α-D-glucopyranoside (VII) was also a sirup.

Methyl 3,4,6-tri-O-acetyl-2-deoxy-2-sulfamino-β-D-glucopyranoside sodium salt (X). VIII was dissolved in 60 ml. of anhydrous pyridine and to this was added the sulfation reagent[2,5] which was freshly prepared by the slow addition of 3 ml. of sulfur trioxide to 50 ml. of anhydrous pyridine previously cooled to −15°. The reaction mixture was shaken for 20 hr. at room temperature with the exclusion of moisture. A pale-yellow sirupy substance was obtained. This was poured into 700 ml. of water containing 4 g. of sodium bicarbonate, and the resultant solution was concentrated under reduced pressure. It was extracted three times with ethyl acetate-methanol, and the extract was concentrated under reduced pressure to a sirup. Methyl 3,4,6-tri-*O*-acetyl-2-deoxy-2-sulfamino-α-D-glucopyranoside (IX) could not be obtained in crystalline form.

Methyl 2-deoxy-2-sulfamino-β-D-glucopyranoside sodium salt (XII). The above obtained sirup (X) was dissolved in methanol and was decolorized, and to this was added 0.05 mole of sodium methoxide to effect deacetylation. The reaction mixture was kept at room temperature for 20 hr., and the solvent was removed under reduced pressure to give a sirup. To this was added a large amount of ethanol, and the solution was stored overnight in a refrigerator. The amorphous precipitate was collected by centrifugation. Repeated recrystallizations from methanol-ethanol yielded 2 g. (4%, based on VI) of white powder which was very hygroscopic. The product was negative for the ninhydrin test and the Elson-Morgan reaction but was positive for both the tests after hydrolysis with 2.5 *N* hydrochloric acid at 100°. M.p. 193–197° (dec.), $[\alpha]^{25}\text{D}$ +5.0° (*c* 1, water).

Anal. Calcd. for$C_7H_{14}O_8NSNa \cdot H_2O$: C, 26.8; H, 5.1; N, 4.5; S, 10.2; Na, 7.3. Found: C, 27.3; H, 5.3; N, 4.3; S, 10.3; Na, 7.4. This compound seems to be a monohydrate. Methyl 2-deoxy-2-sulfamino-α-D-glucopyranoside sodium salt (monohydrate) (XI) melted at 175–178° (dec.), $[\alpha]^{25}\text{D}$ +105.9° (*c* 1, water).

Anal. Found: C, 27.3; H, 5.3; N, 4.4; S, 10.1; Na, 7.7. The reported constants[2] for the compound (XI) are m.p. 159–161°, $[\alpha]^{27}\text{D}$ +103.1° (*c* 2.1, water).

BIOCHEMICAL LABORATORY
COLLEGE OF AGRICULTURE
KYOTO UNIVERSITY
KYOTO, JAPAN

The Synthesis of Dicyclopropyl Ethers[1]

BERNARD T. GILLIS AND KARL F. SCHIMMEL[2]

Received August 15, 1961

The direct synthesis of the previously unknown class of compounds, dicyclopropyl ethers, was made possible by the recent availability of a series of divinyl ethers.[3] The addition of carbenes to monovinyl ethers was previously noted by Doering[4] to proceed more rapidly than similarly substituted olefins. Consequently, the divinyl ethers were expected to allow isolation of reasonable yields of dicyclopropyl ethers upon reaction with carbenes, even though the divinyl ethers could not be used in excess as are mono-unsaturated reactants.

The generation of dichlorocarbene from chloroform in the presence of the unsubstituted divinyl ether (I) by the action of potassium *tert*-butoxide resulted in polymerization of the divinyl ether. Similarly, bromoform and benzal dichloride with potassium *tert*-butoxide in the reaction gave the same results. The use of *n*-butyllithium and methylene dichloride was also unsuccessful as the butyllithium also caused polymerization of the divinyl ether. However, the slow addition of ethyl trichoroacetate to sodium methoxide in a petroleum ether solution of I yielded the desired bis(2,2-dichlorocyclopropyl) ether (III). Compound III was a very high boiling viscuous compound which was purified by evaporative distillation at low pressure.

As I was so sensitive toward polymerization, a more stable divinyl ether was sought. The synthetically available diisobutenyl ether (II) exhibited a high degree of stability toward base and was consequently used. According to previous observations, the higher substitution of this ether

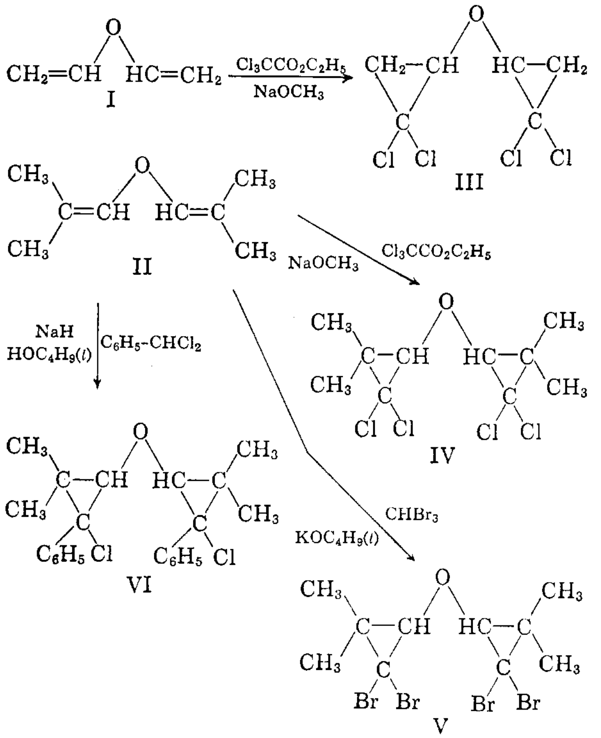
---

(1) This research was sponsored by a Frederick Gardner Cottrell Grant from Research Corporation.

(2) Abstracted from the doctoral thesis of Karl F. Schimmel, Duquesne University, 1961.

(3) B. T. Gillis and K. F. Schimmel, *J. Org. Chem.*, **25**, 2187 (1960).

(4) W. von E. Doering and W. A. Henderson, *J. Am. Chem. Soc.*, **80**, 5274 (1958).



would have the additional advantage of greater reactivity toward carbene additions.[4] The method used for the preparation of III was also satisfactory for the synthesis of bis(2,2-dichloro-3,3-dimethylcyclopropyl) ether (IV), which was a white crystalline solid, melting point 132–133°. The addition of dibromocarbene, generated from bromoform and potassium *tert*-butoxide, to II furnished bis-(2,2-dibromo-3,3-dimethylcyclopropyl) ether (V), which melted at 123°. The best results for the synthesis of bis(2-chloro-2-phenyl-3,3-dimethylcyclopropyl) ether (VI) were obtained by the addition of benzal dichloride to a petroleum ether solution of II containing an equivalent amount of sodium hydride and a small amount of *tert*-butyl alcohol. The crystalline VI melted 144–145°.

In all the carbene addition reactions of the divinyl ethers, no attempts were made to isolate the labile mono-adducts. Compounds III, IV, V, and VI all exhibited infrared spectra in which vinyl ether absorption was absent and medium absorption in the 1000–1021-cm.$^{-1}$ region, purportedly characteristic of a cyclopropane ring, was present.

EXPERIMENTAL[5]

Bis(2,2-dichlorocyclopropyl) ether (III). To a solution containing 14 g. (0.20 mole) of divinyl ether[6] and 24.5 g. (0.42 mole) of sodum methoxide in olefin free petroleum ether was slowly added with stirring 76.8 g. (0.2 mole) of ethyl trichloroacetate. After the addition was complete, the solution was stirred for 48 hr., poured into water, and the organic phase was separated. The aqueous phase was extracted with ether and the ether layer was combined with the organic phase and the total solution was dried over anhydrous sodium sulfate. The solution was then filtered and the low boiling components were removed on a steam bath. The remaining material was evaporatively distilled to yield 7 g. (16%) of III, b.p. 85–90° (0.2 mm.), n_D^{25} 1.4978, d^{20} 1.3855.

Anal. Calcd. for $C_6H_6Cl_4O$: C, 30.65; H, 2.84; Cl, 60.00. Found: C, 30.57, H, 2.84; Cl, 59.85.

Bis(2,2-dichloro-3,3-dimethylcyclopropyl) ether (IV). To a solution containing 12.6 g. (0.1 mole) of diisobutenyl ether[7] and 11.88 g. (0.22 mole) of sodium methoxide in olefin free petroleum ether was slowly added with stirring 42 g. (0.22 mole) of ethyl trichloroacetate. After the addition was complete, the solution was stirred for 48 hr., poured into water, and the organic phase was separated. The aqueous layer was extracted with chloroform and the combined chloroform extract and organic phase were dried over anhydrous sodium sulfate. The solution was then filtered and the low boiling components were removed by vacuum concentration. A white solid crystallized, which on recrystallization from ether yielded 5.8 g. (20%) of IV, m.p. 132–133°.

Anal. Calcd. for $C_{10}H_{14}Cl_4O$: C, 41.12; H, 4.83; Cl, 48.57. Found: C, 41.26; H, 4.94; Cl, 48.29.

Bis(2,2-dibromo-3,3-dimethylcyclopropyl) ether (V). To a solution containing 12.6 g. (0.1 mole) of diisobutenyl ether and 24.6 g. (0.22 mole) of potassium *t*-butoxide in olefin free petroleum ether was slowly added with stirring 55.6 g. (0.22 mole) of bromoform. The products were isolated by a procedure similar to isolation of IV. The solid material which resulted was recrystallized from ether and yielded 12.5 g. (25.6%) of V, m.p. 123°.

Anal. Calcd. for $C_{10}H_{14}Br_4O$: C, 25.68; H, 3.24; Br, 67.80. Found: C, 25.67; H, 2.99; Br, 67.93.

Bis(2-chloro-2-phenyl-3,3-dimethylcyclopropyl) ether (VI). To 6.3 g. (0.05 mole) of diisobutenyl ether, 3 g. of *t*-butyl alcohol, and 2.4 g. (0.1 mole) of sodium hydride in hexane was added slowly and with stirring 16.1 g. (0.1 mole) of benzal dichloride. The product was isolated by a procedure similar to that used in isolation of IV. The remaining solid was recrystallized from petroleum ether and yielded 5.0 g. (26.6%) of VI, m.p. 144–145° dec.

Anal. Calcd. for $C_{22}H_{24}Cl_2O$: C, 70.40; H, 6.45; Cl, 18.89. Found: C, 70.20; H, 6.60; Cl, 18.87.

Department of Chemistry
Duquesne University
Pittsburgh 19, Pa.

---

[5] Melting points and boiling points are uncorrected. Spectra were determined on a Perkin-Elmer Model 137 double beam infrared spectrophotometer. Analyses were carried out by Drs. Weiler and Strauss, Oxford, England, and Alfred Bernhardt, Mulheim, Germany.

[6] The authors wish to acknowledge gifts of generous quantities of divinyl ether from Merck & Co., Chemical Division, Rahway, N. J.

(7) Prepared according to the procedure given in ref. 3.

Some Organolithium Compounds Containing Silicon

Henry Gilman and Richard D. Gorsich

Received August 18, 1961

As an approach to the synthesis of high molecular weight, unsymmetrical molecules, we have briefly examined the synthetic utility of R_3SiCH_2Li reagents where two of the R groups are different. Previously, trimethylsilylmethyllithium was pre-