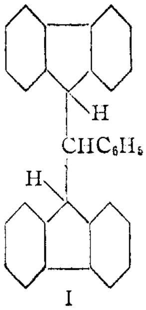
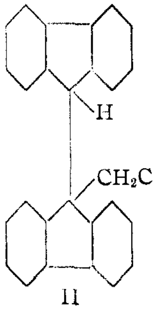
(I) was prepared by the method of Pinck and Hilbert,[2] (II) by the action of benzylmagnesium chloride on dibiphenylene-ethylene.[6] An attempt to prepare (I) from 2 moles of fluorenyllithium and 1 mole of benzal chloride did not lead to any identifiable product.



I



II

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The Reactions of Carbon Suboxide with Grignard Reagents

BY JOHN H. BILLMAN[1] AND CARL M. SMITH

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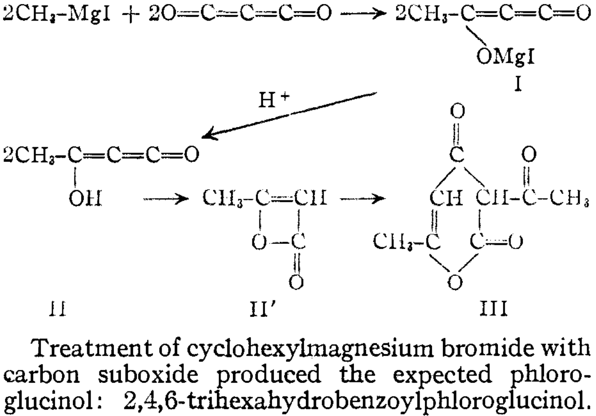
In an earlier publication[2] it was reported that methylmagnesium iodide reacts with carbon suboxide to produce 2,4,6-triacetylphloroglucinol in a 24% yield. In some subsequent experiments this phenol was obtained in yields as high as 39%.

Further examination of the reaction mixture has revealed the presence of another condensation product which upon identification proved to be dehydroacetic acid (III). The formation of this compound may be accounted for by the condensation of two molecules of acetylketene (II) which could be formed by the hydrolysis of the Grignard addition product (I) in which only one molecule of the Grignard reagent has been added to the carbon suboxide.[2]



$$2CH_3\text{-}MgI + 2O{=}C{=}C{=}C{=}O \longrightarrow 2CH_3\text{-}\underset{\displaystyle OMgI}{C}{=}C{=}C{=}O$$

Treatment of cyclohexylmagnesium bromide with carbon suboxide produced the expected phloroglucinol: 2,4,6-trihexahydrobenzoylphloroglucinol. Proof of the structure of the latter compound was obtained by analysis and by mixed melting points with a sample of 2,4,6-trihexahydrobenzoylphloroglucinol prepared by the Fries rearrangement of the trihexahydrobenzoate of phloroglucinol in the same way that the 2,4,6-triacetylphloroglucinol was synthesized.[2]

Since lithium methyl and methylmagnesium halides frequently undergo similar reactions, it seemed of interest to see if lithium methyl would react with carbon suboxide to produce 2,4,6-triacetylphloroglucinol. When this reaction was tried using identical conditions,[2] none of the expected product could be isolated from the reaction mixture.

Experimental

Dehydroacetic Acid.—A solution of 10.7 g. of carbon suboxide dissolved in 292 ml. of dry ether was added to a solution of methylmagnesium iodide, prepared from 28 g. of methyl iodide and 4.7 g. of magnesium, in a monomer similar to the procedure previously described.[2] After hydrolysis and extraction of the reaction mixture with ether, the ether solution was evaporated to a mush. This residue was treated with an excess of a saturated sodium bicarbonate solution and filtered. The residue yielded 3.4 g. of 2,4,6-triacetylphloroglucinol.

On adding dilute sulfuric acid to the bicarbonate extract, 1.5 g. of a yellow solid was obtained. A high boiling petroleum ether extract of the solid yielded 0.68 g. of dehydroacetic acid melting at 108–110°. A mixed melting point with some authentic dehydroacetic acid showed no depression. Its monoanilide, prepared according to the method of Oppenheim and Precht,[3] melted at 119–120° and did not depress the m.p. of an authentic sample. The identity of dehydroacetic acid was also confirmed by its solubility and its neutral equivalent.

2,4,6-Trihexahydrobenzoylphloroglucinol.—To an ether solution of cyclohexylmagnesium bromide, prepared from 85 ml. of cyclohexyl bromide, 10 g. of magnesium and 170 ml. of ether, was added 183 ml. of an ether solution containing 15 g. of carbon suboxide. The reaction was carried out as previously described.[2]

The reaction mixture was hydrolyzed with dilute sulfuric acid and extracted with ether. After extracting the ether layer with 3 × 50-ml. portions of a saturated bicarbonate solution, the ether layer was dried with anhydrous sodium sulfate and then evaporated to a paste. Extraction of the paste with 100 ml. of low boiling petroleum ether left a residue of 12.41 g. of crystals which when recrystallized from benzene melted at 195–196°, and did not depress the melting point of an authentic sample of 2,4,6-trihexahydrobenzoylphloroglucinol prepared from phloroglucinol by means of the Fries rearrangement.

Anal. Calcd. for $C_{27}H_{36}O_6$: C, 71.54; H, 7.96. Found: C, 71.01; H, 7.96.

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[1] Indiana University, Bloomington, Indiana.

[2] J. H. Billman and C. M. Smith, THIS JOURNAL, **61**, 457 (1939).

[3] A. Oppenheim and H. Precht, *Ber.*, **9**, 1100 (1876).

2-Methoxycyclohexylmercury Mandelate

BY ROBERT E. BUCKLES AND ROBERT J. SMITH

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Mercuric *dl*-mandelate reacted with cyclohexene in methanol to form 2-methoxycyclohexylmercury *dl*-mandelate. This compound was converted by the action of potassium bromide to the α-2-methoxycyclohexylmercury bromide described by Romeyn and Wright.[1] By this means the mandelate was shown to have the same configuration as the corresponding acetate and lactate prepared[1] before.

The use of mercuric (+)-mandelate in the addition reaction with cyclohexene gave rise to a mixture which was separated into two crude fractions. Each of these fractions reacted with potassium bromide to give the same α-2-methoxycyclohexyl-

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[1] J. Romeyn and G. F. Wright, THIS JOURNAL, **69**, 697 (1947).