obtained after dilution of the mother liquor with water. After two recrystallizations from glacial acetic acid the product melted at 231–232° (lit. m.p. 230–231°).[6]

**Chlorination of 4-Methyl-*o*-phenylenedibenzenesulfonamide: 4-Methyl-3,5,6-trichloro-*o*-phenylenedibenzenesulfonamide.**—Into a solution of 10 g. of 4-methyl-*o*-phenylenedibenzenesulfonamide in 40 ml. of dimethylformamide, chlorine was passed until the reaction mixture had gained 9.5 g. in weight, keeping the temperature below 50°. The mixture was worked up as described for the methyl-free product. The yield was 7.8 g. (62%). A sample was recrystallized for analysis from glacial acetic acid; white microcrystalline powder, m.p. 237–238°.

*Anal.* Calcd. for $C_{19}H_{15}Cl_3N_2O_4S_2$: C, 45.12; H, 2.95; N, 5.54. Found: C, 45.36; H, 3.20; N, 5.53.

**Acknowledgment.**—The authors are indebted to Miss Emily Davis, Mrs. Jean Fortney and Mrs. Katherine Pih for the microanalyses and to Miss Helen Miklas and Miss Elizabeth Petersen for the infrared spectra determinations.

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(6) R. Adams and C. N. Winnick, THIS JOURNAL, **73**, 5687 (1951).

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## Preparation and Hydrolysis of Optically Active 2-Butyl Acetal

BY ELLIOT R. ALEXANDER,[1] HIRSH M. BUSCH[2] AND GEORGE L. WEBSTER

RECEIVED FEBRUARY 11, 1952

O'Gorman and Lucas[3] have recently shown that hydrolysis with 5% aqueous phosphoric acid of D-(+)-2-octyl acetal leads to totally unracemized D-(+)-2-octanol. They concluded that the reaction does not proceed through a secondary octyl carbonium ion.

We have confirmed their conclusions using D-(+)-2-butyl acetal from D-(+)-2-butyl orthoformate.[4] The hydrolysis of this acetal to D-(+)-2-butanol gives alcohol of the same specific rotation as that used initially. It is, therefore, probable that none of the reactions employed in this cycle involves cleavage of the oxygen–butyl bond and that no secondary butyl carbonium intermediate is involved.

### Experimental[5]

**D-(+)-2-Butanol.**—2-Butanol, Eastman Kodak Company White Label, was resolved by the method of Pickard and Kenyon[6] according to the modification of Sprung and Wallis[7] and had an observed rotation of +7.98 ± 0.02° in a one-decimeter tube at 25°.

**D-(+)-2-Butyl Orthoformate.**—The preparation of D-(+)-2-butyl orthoformate, $[\alpha]^{25}$D +27.07 ± 0.02° (*l* 1, no solvent), was carried out as described by Alexander and Busch.[4]

**D-(+)-2-Butyl Acetal.**—To 24.0 g. (0.103 mole) of D-(+)-2-butyl orthoformate, 2.0 g. (0.025 mole) of granulated ammonium nitrate and 6.0 ml. of D-(+)-2-butanol was added 15.0 g. (0.34 mole) of freshly prepared acetaldehyde. After the mixture was refluxed for 90 minutes, 150 ml. of ether was added to the cooled solution. It was then washed with aqueous ammonium hydroxide (1:1) and distilled water. The ether solution was dried over anhydrous potassium carbonate. The ether was removed and the solution was distilled under vacuum through a five-inch column packed with glass helices. Active *s*-butyl acetal (11.5 g., 64.5%) was obtained as a colorless liquid, b.p. 66–68° (16 mm.); $n^{20}$D 1.4050; $d^{20}_4$ 0.8279, $[\alpha]^{25}$D +25.40 ± 0.02° (*l* 1, no solvent).

*Anal.* Calcd. for $C_{10}H_{22}O_2$: C, 68.91; H, 12.73; *MR*, 51.68. Found: C, 68.62; H, 12.95; *MR*, 51.59.

**Hydrolysis of Acetal.**—A mixture of 11.5 g. (0.066 mole) of D-(+)-2-butyl acetal and 100 ml. of 5% phosphoric acid was refluxed for 1 hour. The cooled solution was saturated with potassium carbonate and extracted with ether. After drying over anhydrous potassium carbonate, the ether solution was distilled. Alcohol, (6.7 g., 71%) b.p. 97–98° with $[\alpha]^{25}$D +8.00 ± 0.02° (*l* 1), was obtained.

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(1) Deceased.

(2) University of Illinois, College of Dentistry, Chicago, Illinois.

(3) J. M. O'Gorman and H. J. Lucas, THIS JOURNAL, **72**, 5489 (1950).

(4) E. R. Alexander and H. M. Busch, *ibid.*, **74**, 554 (1952).

(5) All boiling points are uncorrected.

(6) R. Pickard and J. Kenyon, *J. Chem. Soc.*, **103**, 1937 (1913).

(7) M. Sprung and E. Wallis, THIS JOURNAL, **56**, 1717 (1934).

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## The Addition of Fluorene to, and the Fine Structure of, Benzylidenefluorene

BY ERNST D. BERGMANN AND DAVID LAVIE

RECEIVED OCTOBER 29, 1951

Like all fulvenes,[1] benzylidenefluorene has a polar semicyclic double bond; the moment of the latter is directed toward the five-membered ring. It is, therefore, correct to regard the addition of fluorene to benzylidenefluorene, which has been observed by Pinck and Hilbert,[2] as a special case of the Michael condensation; the latter occurs only with polar unsaturated systems.[3]

The direction of the dipole moment in benzylidenefluorene demands that in the addition of fluorene the proton derived from the 9-hydrogen atom of fluorene combines with the 9-carbon atom of the benzylidene compound and the fluorenyl anion with the phenylated carbon atom, thus giving di-(9-fluorenyl)-phenylmethane (I), in analogy to the addition of lithium aluminum hydride in which the negative hydrogen ion[4] combines with the phenylated carbon atom, the $(LiAlH_3)^+$ ion with the central carbon atom of benzylidenefluorene.[5]

Pinck and Hilbert[2] have not decided whether their condensation product of m.p. 240° was (I) or the isomeric 9-benzyl-9,9′-difluorenyl (II), which would have resulted from the inverse addition of fluorene to benzylidenefluorene. (II)[6] has, moreover, the same melting point as Pinck and Hilbert's hydrocarbon.

It has now been shown that this hydrocarbon is not identical with (II); a mixture of the two compounds gives a strong melting point depression.[7] It is, therefore, concluded that formula (I) is correct. The Michael condensation of fluorene and benzylidenefluorene (I), is, thus, an additional proof for the direction of the moment in the latter which has been predicted by the theory.

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(1) A. Pullman, G. Berthier and B. Pullman, *Bull. soc. chim. France*, 1097 (1950), and previous publications; G. W. Wheland and D. F. Mann, *J. Chem. Phys.*, **17**, 264 (1949); H. Lumbroso, A. Pacault and B. Pullman, *Bull. soc. chim. France*, 34 (1950); E. D. Bergmann and E. Fischer, *ibid.*, 1084 (1950).

(2) L. A. Pinck and G. E. Hilbert, THIS JOURNAL, **68**, 2014 (1946).

(3) E. D. Bergmann, D. Ginsburg and R. Pappo, in preparation.

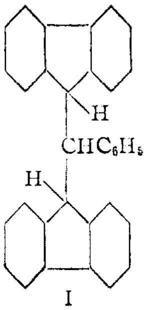
(4) L. W. Trevoy and W. G. Brown, THIS JOURNAL, **71**, 1675 (1949).

(5) D. Lavie and E. D. Bergmann, *Bull. soc. chim. France*, 250 (1951).

(6) R. C. Fuson and H. D. Porter, THIS JOURNAL, **70**, 895 (1948).

(7) The referee kindly informed the authors that he has made the same observation with the two original samples obtained by Pinck and Hilbert and by Fuson and Porter, respectively.

(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.



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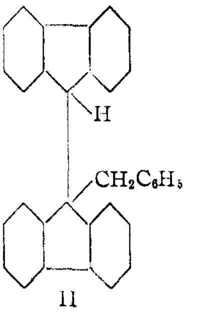

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## The Reactions of Carbon Suboxide with Grignard Reagents

By John H. Billman[1] and Carl M. Smith

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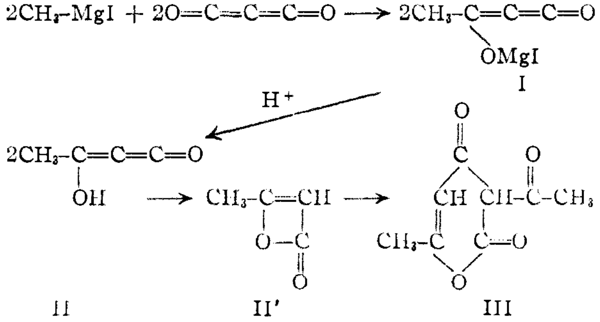
In an earlier publication[2] it was reported that methylmagnesium iodide reacts with carbon suboxide to produce 2,4,6-triacetylphloroglucinol in a 24% yield. In some subsequent experiments this phenol was obtained in yields as high as 39%.

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]



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).

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## 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).