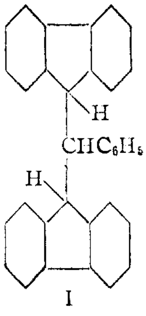
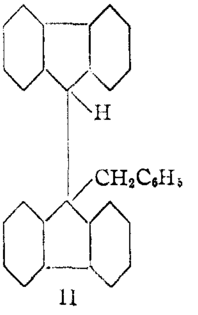
(I) was prepared by the method of Pinck and Hilbert,[2] (II) by the action of benzylmagnesium chloride on dibiphenylene-ethylene.[6] An attempt to prepare (I) from 2 moles of fluorenyllithium and 1 mole of benzal chloride did not lead to any identifiable product.



I



II

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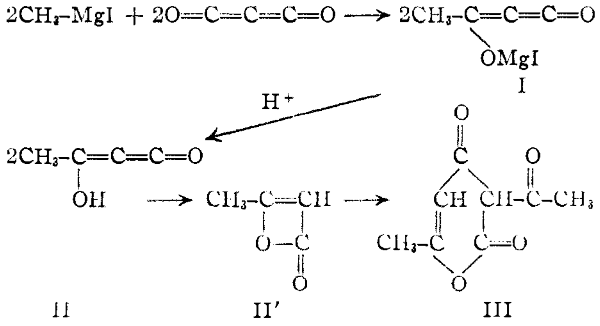
The Reactions of Carbon Suboxide with Grignard Reagents

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

RECEIVED NOVEMBER 30, 1951

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).

DEPARTMENTS OF CHEMISTRY
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2-Methoxycyclohexylmercury Mandelate

BY ROBERT E. BUCKLES AND ROBERT J. SMITH

RECEIVED DECEMBER 17, 1951

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).

mercury bromide obtained from the addition with mercuric *dl*-mandelate. Thus, no effective synthesis of the optically active bromide was accomplished.

Experimental

Mercuric *dl*-Mandelate.—A solution of 30.4 g. (0.2 mole) of *dl*-mandelic acid in 250 ml. of water was mixed with a solution of 31.9 g. (0.1 mole) of mercuric acetate in 150 ml. of water. The precipitated product was removed by filtration, washed with water, and allowed to stand under 100 ml. of 95% ethanol for 24 hours. A yield of 45.6 g. (91%) of mercuric *dl*-mandelate, m.p. 182–183°, was obtained. The m.p. checks that listed by Hart and Andersen.[2]

Mercuric (+)-Mandelate.—A solution of 6.09 g. (0.04 mole) of (+)-mandelic acid,[3] m.p. 130–131°, $[\alpha]^{25}$D 152.5° (2% solution in water), in 100 ml. of water was mixed with a solution of 6.37 g. (0.02 mole) of mercuric acetate in 50 ml. of water. The procedure of product isolation used for the *dl*-salt yielded 9.6 g. (95%) of mercuric (+)-mandelate, m.p. 172–174°, $[\alpha]^{25}$D 102.5° (2% solution in 5% aqueous acetic acid).

Anal. Calcd. for $C_{16}H_{14}O_6Hg$: Hg, 39.9. Found: Hg, 39.5.

2-Methoxycyclohexylmercury *dl*-Mandelate.—To a suspension of 10.1 g. (0.020 mole) of mercuric *dl*-mandelate in 50 ml. of methanol was added 2.05 g. (0.025 mole) of cyclohexene. The reaction mixture was allowed to stand for 24 hours. The solid product which precipitated was recrystallized from a hexane fraction (60–70°) to give 3.6 g. (39%) of 2-methoxycyclohexylmercury *dl*-mandelate, m.p. 130–131°.

Anal. Calcd. for $C_{15}H_{20}O_4Hg$: Hg, 43.1. Found: Hg, 42.8.

Treatment of 1.0 g. of the mandelate in methanol with 5% aqueous potassium bromide yielded 0.70 g. (83%) of α-2-methoxycyclohexylmercury bromide, m.p. 112–113°. There was no lowering of the m.p. when this compound was mixed with the bromide prepared from the corresponding acetate.[1]

2-Methoxycyclohexylmercury (+)-Mandelate.—The reaction of 5.0 g. (0.010 mole) of mercuric (+)-mandelate with 1.0 g. (0.012 mole) of cyclohexene in 25 ml. of methanol for 48 hours yielded a clear solution. The solution was neutralized with base and concentrated under reduced pressure. The residue was crystallized from hexane (60–70°) to yield 2.5 g. (54%) of a mixture, m.p. 84–85°.

Anal. Calcd. for $C_{15}H_{20}O_4Hg$: Hg, 43.1. Found: Hg, 42.7.

Fractional crystallization of the mixture from acetone yielded two fractions: m.p.'s 112–115° and 96–99°. Each product when treated with 5% potassium bromide as described for the *dl*-mandelate yielded the α-bromide, m.p. 112–114°, which was optically inactive.

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[2] M. C. Hart and H. P. Andersen, *ibid.*, **57**, 1059 (1935).

[3] L. Gatterman and H. Wieland, "Laboratory Methods of Organic Chemistry," The Macmillan Company, New York, N. Y., 1937, p. 228.

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4-Pyridylacetone

BY ALFRED BURGER, JAMES R. RECTOR AND
A. CHANDLER SCHMALZ

RECEIVED OCTOBER 24, 1951

4-Pyridylacetone has been obtained by decarboxylative acylation[1] of 4-pyridylacetic acid with acetic anhydride in analogy to the preparation of the 3-isomer reported by Burger and Walter.[2] 4-Picolylthiomorpholide[3] used as an intermediate in the synthesis of 4-pyridylacetic acid could be desulfurized by the method of Kornfeld[4] to 1-(4-pyridyl)-2-morpholinoethane.

Experimental[5]

4-Pyridylacetone.—A mixture of 40 g. (0.23 mole) of 4-pyridylacetic acid hydrochloride, 31.4 g. (3.8 moles) of anhydrous sodium acetate and 56.4 g. (0.52 mole) of acetic anhydride was refluxed for 18 hours, the dark reaction mixture was hydrolyzed with 100 ml. of water, cleared with Darco, and concentrated under reduced pressure. It was then made carbonate alkaline and extracted exhaustively with ether. The oily pale yellow ketone boiled at 76.5–78° (0.5 mm.) and weighed 15.6 g. (50%).

Anal. Calcd. for C_8H_9NO: C, 71.09; H, 6.71. Found: C, 70.83; H, 6.55.

The **semicarbazone** crystallized from water, m.p. 188–189°.

Anal. Calcd. for $C_9H_{12}N_4O$: N, 29.15. Found; N, 29.20.

Methyl 4-Pyridylacetate.—This ester was prepared from 4-pyridylacetic acid hydrochloride with diazomethane in ether–methanol solution. The colorless oily product boiled at 103–105° (2–3 mm.).

4-Pyridylacetamide.—This amide was obtained in 97% yield from ethyl or methyl pyridylacetate by the procedure described for 3-pyridylacetamide,[2] and recrystallization from dioxane. The colorless crystals melted at 143.5–145°.

Anal. Calcd. for $C_7H_8N_2O$: N, 20.58. Found: N, 20.73.

1-(4-Pyridyl)-2-morpholinoethane.—A solution of 10 g. of 4-picolylthiomorpholide in 200 ml. of absolute ethanol was added to 70 g. of alcohol-moist Raney nickel, and the mixture was refluxed under an atmosphere of nitrogen for three hours. The nickel was filtered, most of the solvent removed under reduced pressure, the residue was treated with alkali and extracted with ether. The amine from the ether extracts boiled at 128–130° (0.7 mm.) and weighed 3.6 g. (41%). The free base was not stable enough to be analyzed.

The dihydrochloride melted at 215.5–217° after recrystallization from methanol–ethyl acetate.

Anal. Calcd. for $C_{11}H_{18}Cl_2N_2O$: N, 10.58. Found: N, 10.82.

The yellow dipicrate crystallized from water, m.p. 190–192°.

Anal. Calcd. for $C_{23}H_{22}N_8O_{15}$: N, 17.23. Found: N, 17.37.

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[1] J. A. King and F. H. McMillan, THIS JOURNAL, **73**, 4911 (1951).

[2] A. Burger and C. R. Walter, Jr., *ibid.*, **72**, 1988 (1950); H. S. Mosher and J. E. Tessieri [*ibid.*, **73**, 4925 (1951)] working with 3-pyridylacetonitrile have stated that "none of the isomeric pyridylacetonitriles has previously been reported." The 3-isomer had served us as an intermediate in an alternative synthesis of 3-pyridylacetone.

[3] R. L. Malan and P. M. Dean, *ibid.*, **69**, 1797 (1947).

[4] E. C. Kornfeld, *J. Org. Chem.*, **16**, 131 (1951).

[5] All melting points are corrected.

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The Preparation of 1,5-Anhydro-D-mannitol (Styracitol) from D-Mannitol

BY HEWITT G. FLETCHER, JR., AND HARRY W. DIEHL

RECEIVED FEBRUARY 25, 1952

1,5-Anhydro-D-mannitol, originally discovered by Asahina[1] in the husks of the fruit of *Styrax obassia* and named styracitol, was first synthesized by Zervas[2] through the catalytic reduction of tetraacetyl-2-hydroxy-D-glucal. A recent communication[3] from this Laboratory described a more convenient synthesis based on the reduction of tetraacetyl-α-D-mannopyranosyl bromide with lithium

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[1] Y. Asahina, *Arch. Pharm.*, **245**, 325 (1907); **247**, 157 (1909).

[2] L. Zervas, *Ber.*, **63**, 1689 (1930).

[3] R. K. Ness, H. G. Fletcher, Jr., and C. S. Hudson, THIS JOURNAL, **72**, 4547 (1950).