

EXPERIMENTAL

Melting points are corrected.

Synthesis gas (a mixture of hydrogen and carbon monoxide) was manufactured and compressed by the Bureau of Mines at Bruceton, Pa. Dicobalt octacarbonyl¹³ and 2-ethylthiophene¹⁶ were prepared by methods described in the literature. 2-Acetylthiophene was obtained from commercial sources. Thiophene, 2-methylthiophene, and 2,5-dimethylthiophene were gifts of the Socony-Vacuum Oil Co. 2-Thenyl alcohol was prepared in 85% yield by the lithium aluminum hydride reduction of 2-thiophenecarboxaldehyde in refluxing ethyl ether.

Each experiment was conducted at 180–190° with an initial pressure of 3500–4000 p.s.i. of 2:1 synthesis gas (2H₂:1CO) at room temperature, using benzene as solvent and dicobalt octacarbonyl, or a mixture of dicobalt octacarbonyl and cobaltous carbonate, as catalyst in a 500-ml., type 347 stainless steel, rocking autoclave purchased from the American Instrument Co. A 2-foot Heligrad Podbielniak column was used for precision fractional distillations.

The results are shown in Table I. A detailed description of the reduction of 2-acetylthiophene is given as an example.

Reduction of 2-acetylthiophene. In the 500-ml. autoclave were placed 90.0 g. (0.72 mole) of 2-acetylthiophene, 3.0 g. of cobaltous carbonate, and 20 ml. of a benzene solution containing 1.3 g. of dicobalt octacarbonyl. The autoclave was pressured to 3500 p.s.i. with 2:1 synthesis gas at room temperature and heated at about 185°. After the pressure had dropped to 3000 p.s.i. in 4 hr., the autoclave was cooled to room temperature and repressured from 1700 to 3500 p.s.i. It was then heated at about 185° for an additional 5 hr. The final pressure at room temperature was 3100 p.s.i. A total of 2.6 moles of gas had been absorbed. Fractional distillation of the reaction mixture gave 41.7 g. (52%) of 2-ethylthiophene, b.p. 133–135°, and 21.7 g. (26%) of 2-ethylthiolane, b.p. 154–158°. After purification by chromatographic absorption through silica gel, followed by azeotropic distillation with Cellosolve, the 2-ethylthiolane had the following physical constants: b.p. 156° at 736 mm., n_D^{25} 1.4870, d_4^{20} 0.9405.

Anal. Calcd. for C₆H₁₂S: C, 62.00; H, 10.41. Found: C, 62.08; H, 10.42.

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(16) W. J. King and F. F. Nord, *J. Org. Chem.*, **14**, 638 (1949).

(17) E. V. Whitehead, R. A. Dean, and F. A. Fidler, *J. Am. Chem. Soc.*, **73**, 3632 (1951).

An Anomalous Reaction of Michler's Ketone with Grignard Reagents

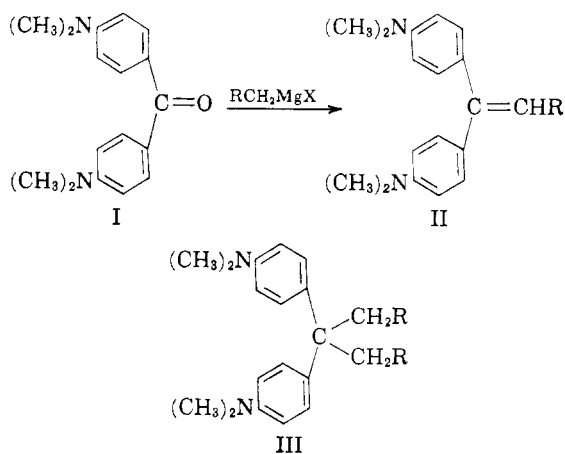
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The reaction of Michler's ketone (I) with Grignard reagents to give the corresponding di- or triphenylmethane dyes is the basis for a very sensi-

tive color test for Grignard reagents.¹ As a preparative tool, however, this reaction is often unsatisfactory and wide variations in yields of the corresponding 1,1-bis(*p*-dimethylaminophenyl)ethylenes have been reported.²

Roleff^{2f} reported quantitative yields of II (R=H) when Michler's ketone was heated with four moles of methylmagnesium bromide in benzene. Repetition of his procedure furnished 40–50% of 2,2-bis(*p*-dimethylaminophenyl)propane (III, R=H) in addition to II. Under similar conditions, benzylmagnesium chloride and I gave an 80% yield of III (R=C₆H₅ or the *o*-tolyl isomer) and no detectable II (R=C₆H₅).

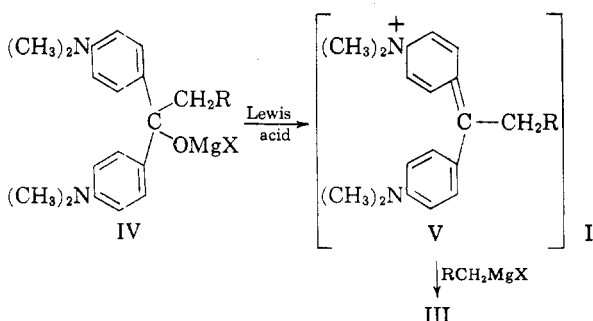


Although this anomalous reaction of Grignard reagents with Michler's ketone to form the corresponding dialkyl compounds has not been described, several examples of similar reactions of Grignard reagents with carbonyl compounds have been reported.³ In all examples, an amino nitrogen is adjacent to or conjugated with the carbonyl group. This suggests that the reaction proceeds through a resonance-stabilized carbonium ion. Thus, the intermediate IV may be converted to V by a process in which a molecule of Grignard reagent, or the magnesium halide in equilibrium with the Grignard reagent, functions as a Lewis acid. The ion V then reacts with more Grignard to give the product III.

(1) H. Gilman and F. Schulze, *J. Am. Chem. Soc.*, **47**, 2002 (1925).

(2) (a) H. Fecht, *Ber.*, **40**, 3902 (1907); (b) G. Busignies, *Compt. rend.*, **149**, 349 (1909); (c) M. Freund and F. Mayer, *Ber.*, **39**, 1117 (1906); (d) P. Pfeiffer and R. Wizinger, *Ann.*, **461**, 132 (1928); (e) D. S. Tarbell and E. G. Lindstrom, *J. Am. Chem. Soc.*, **68**, 1930 (1946); (f) Roleff, *Chem. Ztg.*, **67**, 81 (1943); *Chem. Abstr.*, **38**, 5207.

(3) (a) F. Sachs and W. Weigert, *Ber.*, **40**, 4361 (1907); W. L. Semon and D. Craig, *J. Am. Chem. Soc.*, **58**, 1278 (1936); R. Lukes and O. Frossman, *Collection Czechoslov. Chem. Commun.*, **8**, 533 (1936).



A very similar mechanism has been proposed by Conover and Tarbell⁴ for the hydrogenolysis of some amino- and alkoxy-substituted aromatic acids and carbonyl compounds by lithium aluminum hydride. The reaction was only observed with those compounds which are capable of forming a carbonium ion highly stabilized by resonance.

In agreement with this hypothesis, the reaction of *p*-dimethylaminobenzophenone with a large excess of methylmagnesium bromide in boiling benzene did not afford a detectable quantity of anomalous product corresponding to III.

EXPERIMENTAL

Reaction of Michler's ketone with methylmagnesium bromide.

A suspension of 2.0 moles of methylmagnesium bromide in 500 ml. of benzene under nitrogen was treated with 128 g. (0.48 mole) of Michler's ketone, m.p. 173–176°, dissolved in 1.5 liters of hot benzene. After heating under reflux for 3 hr., the mixture was chilled and treated with saturated ammonium chloride solution. The crude product (119 g.), m.p. 60–110°, was fractionally crystallized from ethanol to give 59 g. (46.5%) of II, R=H, m.p. 122–124° (lit. m.p. 124°). The balance of the material was obtained as crude III, R=H, m.p. 60–75°. Repeated recrystallization of the latter from aqueous alcohol afforded material melting at 78.5–81°.

Anal. Calcd. for C₁₉H₂₆N₂: C, 80.80; H, 9.28; N, 9.92. Found: C, 80.49; 80.60; H, 9.58, 9.62; N, 10.06, 9.90.

An authentic sample of III, R=H, m.p. 80–83.5°, mixed m.p. 78.5–82°, was prepared by the reaction of dimethylaniline hydrochloride with acetone.⁵ The infrared spectra of the two samples were identical.

Reaction of Michler's ketone with benzylmagnesium chloride. A suspension of 0.8 mole of benzylmagnesium chloride⁶ in 150 ml. of benzene under nitrogen was treated with 52.5 g. (0.20 mole) of Michler's ketone dissolved in 400 ml. of boiling benzene. The mixture was heated under reflux for 5 hr., then chilled and treated with saturated ammonium chloride. The crude product was washed twice with warm ethanol to give 70 g. (80.5%) of white solid, m.p. 165–173°. This dissolved readily in dilute hydrochloric acid to give a colorless solution, showing the absence of II (R=C₆H₅) or the corresponding carbinol. Both of these compounds would give intense blue or green colors with dilute acids. An analytical sample, m.p. 169–173°, was prepared by recrystallization from ligroin (Skellysolve B).

Anal. Calcd. for C₃₁H₃₄N₂: C, 85.67; H, 7.89; N, 6.45. Found: C, 85.73, 85.97; H, 8.03, 7.92; N, 6.83, 6.72.

(4) L. H. Conover and D. S. Tarbell, *J. Am. Chem. Soc.*, **72**, 3586 (1950).

(5) J. von Braun, *Ann.*, **472**, 1 (1929).

(6) H. Gilman and W. E. Catlin, *Org. Syntheses*, **Coll. Vol. I**, 471 (1941).

Heating of the material at 60° for several days caused a progressive lowering of the melting point, apparently due to rearrangement since the composition was unchanged. The reaction product of benzylmagnesium chloride with 1,2,3,4-tetra-phenylfulvene undergoes a similar depression of the melting point on standing.⁷

An attempt to prepare III (R=C₆H₅) by the reaction of dimethylaniline hydrochloride with dibenzyl ketone at 170° resulted in nearly complete recovery of starting materials.

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(7) A. G. Bonagura, M. B. Meyers, J. J. Storer, and E. I. Becker, *J. Am. Chem. Soc.*, **76**, 6122 (1954).

Reaction of 1-Bromo-2,3-epoxybutane and 3-Bromo-1,2-epoxybutane with Phenol¹

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The reaction between epichlorohydrin and phenol in basic solution has been reported by Boyd and Marle² as producing 3-phenoxy-1,2-epoxypropane. This result leads to some interesting speculations as to the mechanism of the reaction. Because of the structure of the epichlorohydrin, it is impossible to state beyond peradventure whether the phenoxide ion reacted by a simple replacement of the chloride ion from the epichlorohydrin, or whether the phenoxide ion first attacked the terminal epoxide carbon to form an intermediate secondary alkoxide ion which became stabilized by loss of the chloride ion and formation of a new oxirane ring. The final product in either case would be the same. An interesting point of conjecture is the lack of reaction between the phenoxide ion and the central carbon of the epichlorohydrin. From considerations of the electronic structure of the molecule one would expect this central carbon atom to be the most highly electrophilic,³ hence in the absence of other influences predominate reaction should be at this carbon.

To obviate the difficulty inherent in the structure of epichlorohydrin in studying this reaction mechanism, two isomeric haloepoxides were used which are similar in structure to epichlorohydrin. These compounds were 3-bromo-1,2-epoxybutane, I, and

(1) This paper was presented before the Organic Division of the American Chemical Society at its 125th meeting in Kansas City, Mo., March 23 to April 1, 1954.

(2) D. R. Boyd and E. R. Marle, *J. Chem. Soc.*, **93**, 838 (1908).

(3) The chloromethyl group tends to withdraw electrons in one direction from this carbon and the oxygen atom in the other. See A. E. Remick, *Electronic Interpretations of Organic Chemistry*, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 59.