

excess of benzene, approximately two moles of hydrogen chloride was evolved. Since the apparent reaction was of the Friedel-Crafts type, the following experiment was carried out:

A solution of 35 g. of DDT (m. p. 107-108°) in 200 ml. of dry benzene was stirred vigorously at room temperature while 13 g. of anhydrous aluminum chloride was added during the course of twenty-five minutes. Rapid evolution of hydrogen chloride occurred while the first part of the aluminum chloride was being added, but little or no gas evolution was noted during addition of the last third. There was no appreciable increase in the temperature of the reaction mixture. Stirring was continued for one hour. The black reaction mass was diluted with ice water and then transferred to a separatory funnel. The reddish-orange benzene solution was shaken with water until the washings were neutral to congo red. The benzene solution was allowed to stand in the ice box, and the prisms that separated were recrystallized from benzene to a constant melting point of 210-212°.

Anal. Calcd. for C₂₆H₂₂: C, 93.37; H, 6.63. Found: C, 93.65; H, 6.79.³

No depression in melting point could be observed when this material was mixed with *sym*-tetraphenylethane.⁴ Both samples gave a faint yellow color when tested with tetranitromethane.

The benzene mother liquor was concentrated to a volume of about 100 ml. and a second crop of *sym*-tetraphenylethane was obtained. The filtrate was steam-distilled, and the distillate was separated from the water and fractionated. After the benzene had distilled, 1.1 g. of chlorobenzene distilled at 128-130°, *n*_D²⁰ 1.5238.

The mother liquor from a second run was concentrated to about 30 ml. after the *sym*-tetraphenylethane had been removed. After it had stood in the ice box for several months, large diamond-shaped crystals were obtained. These crystals were removed mechanically from the brick-red residue and recrystallized from *n*-pentane to a constant melting point of 87-88°. No depression in melting point could be observed when this product was mixed with 1,1-dichloro-2,2-bis-(*p*-chlorophenyl)-ethylene.⁵

Approximately the same per cent. yield of *sym*-tetraphenylethane was obtained when the experiment was repeated with 3.5 g. of DDT (m. p. 108-109°) obtained by three recrystallizations from alcohol.

In order to determine whether the *sym*-tetraphenylethane was a reaction product of DDT or an impurity, several compounds related to DDT were treated as above, 0.01 mole being used in each case.

1,1-Dichloro-2,2-bis-(*p*-chlorophenyl)-ethane gave a red solution when aluminum chloride was added. With the addition of water this color faded, and the resulting colorless solution yielded *sym*-tetraphenylethane.

1-Trichloro-2,2-diphenylethane and 1-trichloro-2-(*p*-chlorophenyl)-2-(*o*-chlorophenyl)-ethane yielded *sym*-tetraphenylethane.

1,1-Dichloro-2,2-bis-(*p*-chlorophenyl)-ethylene did not yield *sym*-tetraphenylethane.

Where *sym*-tetraphenylethane was isolated, the yield was about 10% of the theoretical in all cases except in that of 1,1-dichloro-2,2-bis-(*p*-chlorophenyl)-ethane, when a 25% yield resulted.

When chlorobenzene was substituted for benzene in the reaction, no *sym*-tetraphenylethane could be isolated.

It is therefore evident that the use of benzene and aluminum chloride gives rise to a number of competing reactions. Besides the dehydrohalogenation reaction a dechlorination or "halogen migration"⁶ occurs. These reactions are accompanied by formation of unidentified colored material.

(3) Analysis by W. F. Barthel.

(4) Norris, Thomas and Brown, *Ber.*, **43**, 2940 (1910).

(5) Zeidler, *ibid.*, **7**, 1181 (1874).

(6) Thomas, "Anhydrous Aluminum Chloride in Organic Chemistry," Reinhold Publishing Corp., New York, N. Y., 1941, p. 692.

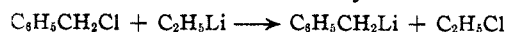
The catalytic elimination of hydrogen chloride is much more difficult from 1,1-dichloro-2,2-bis-(*p*-chlorophenyl)-ethane than from the corresponding trichloromethyl derivative.³ This may account for the high yield of *sym*-tetraphenylethane in this case.

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Ethynyllithium Compounds by Halogen-Metal Interconversions

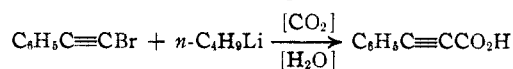
BY HENRY GILMAN AND A. H. HAUBEIN

It was shown recently,¹ incidental to the development of an improved procedure for the quantitative analysis of alkyl lithium compounds, that benzyl chloride underwent a halogen-metal interconversion reaction with ethyllithium.



This reaction was significant as decisive experimental evidence for the formation of an RLi compound from an alkyl chloride by the interconversion reaction.² However, because of the extremely small yield of benzyl lithium in this reaction, it was desirable to get confirmatory evidence with an RCl compound like phenylethynyl chloride.

We first showed that phenylethynyl bromide underwent a smooth interconversion with *n*-butyllithium to give, subsequent to carbonation, an 87% yield of phenylpropionic acid.



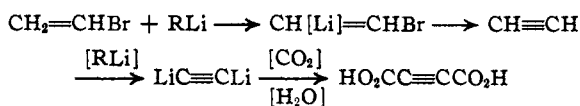
From phenylethynyl chloride the yield of phenylpropionic acid was 20%. The reaction, of course, is not intended for synthetic purposes inasmuch as phenylethynyllithium is most readily prepared from phenylacetylene.

Vinyl lithium would be a highly useful tool for the introduction of the vinyl group, particularly in studies concerned with pharmacologically active compounds derived from nitrogen heterocycles like pyridine and quinoline. It was shown earlier³ that β -bromostyrene and *n*-butyllithium, when allowed to react in petroleum ether and then carbonated, gave a 23% yield of *trans*-cinnamic acid. This suggested the possibility of preparing vinyl lithium by a corresponding reaction with vinyl bromide. However, acetylenedicarboxylic acid was formed. One of the mechanisms for this reaction may be like that suggested for the formation of phenylpropionic acid when β -bromostyrene is treated with *n*-butyllithium³ or phenyllithium,² in diethyl ether: namely, a lateral metalation followed by the loss of lithium bromide.

(1) Gilman and Haubein, *THIS JOURNAL*, **66**, 1515 (1944).

(2) Wittig and Witt, *Ber.*, **74**, 1474 (1941). This article describes a series of interesting experiments on the reaction of phenyllithium with carbon tetrachloride, benzotrichloride, benzyl chloride, benzohydril chloride, triphenylmethyl chloride, and β -chlorostyrene.

(3) Gilman, Langham and Moore, *THIS JOURNAL*, **62**, 2327 (1940).



In the reaction of vinyl bromide with an RLi compound we may be dealing with two competitive reactions: metalation and halogen-metal interconversion. The rates of such reactions are markedly influenced by the nature of the RLi compound and by the solvent.⁴ It may be possible to find a suitable combination to effect the formation of vinyl lithium from vinyl bromide.

Experimental

Phenylethynyl Bromide and *n*-Butyllithium.—To 0.05 mole of *n*-butyllithium in 200 cc. of ether cooled to 0° was added 7.6 g. (0.042 mole) of phenylethynyl bromide (prepared in accordance with the directions of Grignard and Courtot⁵). The solution turned yellow immediately. After five minutes, one-half of the solution was carbonated, and forty minutes later the other half was carbonated. The first part carbonated gave 2.8 g. (90%) of phenylpropionic acid; the other portion gave 2.6 g. (85%). The combined neutral fractions yielded 1.2 g. (21%) of *n*-butyl bromide.

Phenylethynyl Chloride and *n*-Butyllithium.—To 200 cc. of ether containing 0.02 mole of *n*-butyllithium was added 1.05 g. (0.0077 mole) of phenylethynyl chloride (prepared from phenylethynylsodium and benzenesulfonyl chloride by the procedure of Bourguet and Truchet⁶). The solution, which became yellow as in the preceding reaction, was refluxed for two and a half hours and then carbonated to yield 0.24 g. (20%) of phenylpropionic acid. In order to reduce the possibility that the phenylpropionic acid was not formed by the metalation of phenylacetylene which may have been contained in the phenylethynyl chloride, this chloride was prepared by another sequence of reactions. First, β -chlorostyrene was prepared from cinnamic acid⁷; then this was converted to 1-phenyl-1,2,2-trichloroethane,⁷ which with alcoholic potassium hydroxide⁸ gave the desired chloride. The yield of phenylpropionic acid from this chloride and *n*-butyllithium was 15%. This reaction with the chloride proceeds rather rapidly, for carbonation of an aliquot after a one-half hour period of reaction gave a 23% yield of phenylpropionic acid. It is probable that this interconversion reaction will also take place with RMgX compounds.

Vinyl Bromide and *n*-Butyllithium.—A solution of 5.4 g. (0.05 mole) of vinyl bromide (prepared in accordance with the directions of Kharasch and co-workers⁹) dissolved in 50 cc. of ether cooled to 0° was added to 0.05 mole of *n*-butyllithium in 100 cc. of ether at 0°. After stirring for fifteen minutes, the milky white mixture was carbonated by Dry Ice to yield 2 g. (34%) of acetylenedicarboxylic acid.

From a corresponding reaction in which petroleum ether instead of diethyl ether was used as the solvent, and where the reaction was run for ten hours at 14°, there was isolated 1.5 g. (26%) of acetylenedicarboxylic acid together with a small quantity of propionic acid. In this reaction, the mixture turned white as before, but only after two hours.

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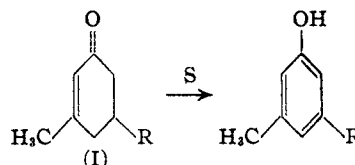
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- (4) Gilman, Moore and Baine, *THIS JOURNAL*, **63**, 2479 (1941).
- (5) Grignard and Courtot, *Bull. soc. chim.*, [4] **17**, 228 (1915).
- (6) Bourguet and Truchet, *Compt. rend.*, **190**, 753 (1930).
- (7) Biltz, *Ann.*, **296**, 266 (1897).
- (8) Nef, *ibid.*, **308**, 316 (1899).
- (9) Kharasch, McNab and Mayo, *THIS JOURNAL*, **55**, 2521 (1933).

Sulfur Dehydrogenation of Alkylcyclohexenones

BY E. C. HORNING

In the course of examining certain reactions of 3-methyl-5-alkyl-2-cyclohexen-1-ones, aromatization to the corresponding phenols by means of sulfur dehydrogenation has been carried out for cyclohexenones (I) in which the alkyl group was



methyl, ethyl and isopropyl. This conversion has been accomplished previously in several instances¹ by addition of one molecule of bromine, followed by dehydrohalogenation. The sulfur dehydrogenation of these cyclohexenones proceeded readily; the yield of phenol was 26–29%.

Experimental

3,5-Dimethylphenol.—A mixture of 62 g. (0.50 mole) of 3,5-dimethyl-2-cyclohexen-1-one² and 16.0 g. (0.50 mole) of sulfur was heated under gentle reflux for one hour. The hydrogen sulfide, which was evolved rapidly at first, was absorbed in a sodium hydroxide trap. The reaction mixture was distilled *in vacuo*, collecting to 130° (12 mm.). The distillate was dissolved in ether, and the phenol extracted with dilute sodium hydroxide solution. The ether solution yielded 14.5 g. of unchanged ketone, b. p. 205–207°. The aqueous alkaline solution was saturated with carbon dioxide, and the precipitated phenol removed by filtration. The aqueous solution was extracted once with benzene. The filtered yield of crude phenol was 15.0 g.; this was combined with the benzene extract. Distillation at atmospheric pressure from a small amount of copper bronze yielded 12.4 g. (26% based on unrecovered ketone) of 3,5-dimethylphenol, b. p. 214–216°, m. p. 53–60°.

Recrystallization from ligroin (60–75°)–petroleum ether (30–40°) yielded fine, colorless needles, m. p. 62–63°.

The phenylurethan was prepared by warming equivalent amounts of the phenol and phenyl isocyanate, with a drop of pyridine, on a steam-bath for fifteen minutes. Several crystallizations from benzene–ligroin gave colorless needles, m. p. 150–151° (reported³ m. p. 148–149°).

3-Methyl-5-ethylphenol.—3-Methyl-5-ethyl-2-cyclohexen-1-one (69 g., 0.50 mole) heated with one equivalent of sulfur yielded 14.7 g. of unchanged ketone and 14.8 g. (28% based on unrecovered ketone) of 3-methyl-5-ethylphenol, b. p. 118–121° (13 mm.); m. p. 40–43°. Recrystallization from ligroin–petroleum ether yielded colorless needles; m. p. 51–52° (reported⁴ m. p. 55°).

The phenylurethan was obtained from benzene–ligroin, m. p. 147–148° (reported⁴ m. p. 152°).

3-Methyl-5-isopropylphenol.—3-Methyl-5-isopropyl-2-cyclohexen-1-one (76 g., 0.50 mole) heated with one equivalent of sulfur yielded 16.5 g. of unchanged ketone and 16.5 g. (29% based on unrecovered ketone) of 3-methyl-5-isopropylphenol, b. p. 125–127° (14 mm.), m. p. 45–47°. Recrystallization from ligroin–petroleum ether yielded colorless needles, m. p. 48–49° (reported⁵ m. p. 54°).

The phenylurethan was obtained from benzene–ligroin as colorless needles, m. p. 112–113°.

- (1) Knoevenagel, *Ann.*, **261**, 25 (1894); **268**, 321 (1895); *Ber.*, **26**, 1951 (1893); **27**, 2347 (1894).
- (2) Horning, Denekas and Field, *J. Org. Chem.*, **9**, 547 (1944).
- (3) Carlinfanti and Germain, *Atti accad. Lincei*, [5] **19**, II, 234 (1910).
- (4) Kruber and Schmitt, *Ber.*, **64**, 2270 (1931).
- (5) Knoevenagel, *ibid.*, **27**, 2347 (1894).