$$CH_2{=}CHBr + RLi \longrightarrow CH[Li]{=}CHBr \longrightarrow CH{\equiv}CH \xrightarrow{[RLi]} LiC{\equiv}CLi \xrightarrow[[H_2O]]{[CO_2]} HO_2CC{\equiv}CCO_2H$$

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 vinyllithium 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 Courtot[5]). 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 phenylpropiolic 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 Bourguel and Truchet[6]). 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 phenylpropiolic acid. In order to reduce the possibility that the phenylpropiolic 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 acid[7]; then this was converted to 1-phenyl-1,2,2-trichloroethane,[7] which with alcoholic potassium hydroxide[8] gave the desired chloride. The yield of phenylpropiolic 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 phenylpropiolic 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-workers[9]) 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 propiolic acid. In this reaction, the mixture turned white as before, but only after two hours.

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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] Bourguel and Truchet, *Compt. rend.*, **190**, 753 (1930).

[7] Biltz, *Ann.*, **296**, 266 (1897).

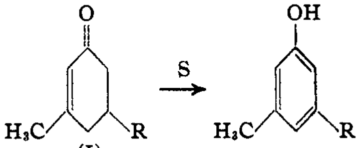
[8] Nef, *ibid.*, **308**, 316 (1899).

[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



(I)

methyl, ethyl and isopropyl. This conversion has been accomplished previously in several instances[1] 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-one[2] 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. 58–60°.

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° (reported[3] 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° (reported[4] m. p. 55°).

The **phenylurethan** was obtained from benzene–ligroin, m. p. 147–148° (reported[4] 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° (reported[5] m. p. 54°).

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

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[1] Knoevenagel, *Ann.*, **281**, 25 (1894); **288**, 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).

Anal. Calcd. for $C_{17}H_{19}O_2N$: C, 75.80; H, 7.11. Found: C, 75.77; H, 7.01.

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Isolation of Betaine from Guayule[1]

BY C. W. MURRAY AND E. D. WALTER

In the processing of guayule, *Parthenium argentatum* Gray, for the isolation of natural rubber, a large amount of residual plant material is discarded. It is important to determine whether useful products can be found in and recovered from such residues. Also, since guayule is a satisfactory natural rubber for incorporation with synthetic rubber in building tires, knowledge of the composition of the non-rubber constituents of guayule is of great interest. It is possible that these constituents affect the quality of the rubber.

From the water soluble fraction of the leaves and from the defoliated shrub, betaine was isolated as the hydrochloride.[2]

We have isolated betaine from the acetone and benzene insoluble fraction of guayule rubber, thus proving the presence of betaine in the crude pebble-milled rubber. Betaine was also obtained from the product of each step in the extraction of the rubber, such as the dispersion prepared by cutting or comminuting the shrub in water and used for separation of rubber as latex, the solution obtained in parboiling of shrub to remove leaves, and the pebble mill slurry.

Isolation.—The dry, defoliated guayule shrub (2586 g.) was cut in a Ball and Jewell mill, a 1/4-inch screen being used. The material was placed in an 8-gallon container, and four gallons of cold distilled water was added. The mixture was mechanically stirred for about an hour and drained through a coarse filter paper. A second extraction was made with cold distilled water by allowing the mixture to stand overnight. The product was filtered as before, and the filtrate was added to the first. The combined extract was concentrated by passing steam through copper coils immersed in the liquor. After the extract was transferred to a 2-liter beaker, about 100 ml. of concentrated hydrochloric acid was added. A precipitate consisting of organic material and calcium sulfate formed was filtered off. The filtrate was further concentrated, and again precipitated inorganic salts and some humin-like material were filtered off. The residue was washed with warm methanol, the washings being added to the filtrate. The filtrate was clarified several times with Nuchar and was further concentrated until betaine hydrochloride began to crystallize. The mixture was cooled, and the betaine hydrochloride was filtered off, washed with cold absolute ethanol, and recrystallized from 95% ethanol: yield, 12 g. or about 0.4% of betaine hydrochloride.

The above experiment was repeated on 2893 g. (dry wt.) of defoliated shrub with hot instead of cold water; yield, 14 g. or about 0.5% of betaine hydrochloride.

A similar experiment with 1415 g. of dry, cut leaves yielded 13 g. or about 0.9% of betaine hydrochloride.

Optical Properties.—The betaine hydrochloride, crystallized from 95% ethanol, consisted of monoclinic prisms, tabular forms and triangular fragments. The refractive indices (determined in daylight by immersion in organic liquids) were: $n_\alpha = 1.515$, $n_\beta = 1.535$, $n_\gamma = 1.594$, all ± 0.003. In parallel polarized light (crossed nicols) many crystals did not show complete extinction on rotating the stage. These showed the emergence of a well centered optic axis interference figure by conoscopic observation in convergent polarized light (crossed nicols). The optic sign was positive. The double refraction was strong ($n_\gamma - n_\alpha = 0.079$). The extinction was usually parallel or symmetrical, and an occasional section had positive elongation with an extinction angle of about 35°: $2V = 62° 16'$ calcd.; $r > v$ weak. The optical properties of an authentic sample of synthetic betaine hydrochloride agreed in all respects with those of the material isolated from guayule. This comparison served to positively identify the isolated substance.

Anal.[3] Calcd. for $C_5H_{11}O_2N \cdot HCl$: C, 39.09; H, 7.87; N, 9.12; mol. wt., 153.6. Found: C, 39.0; H, 8.24; N, 8.94; equiv. wt. (when titrated with NaOH to phenolphthalein), 155.6.

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(1) Not copyrighted.

(2) A. J. Haagen-Smit and co-workers, at the California Institute of Technology, previously stated, in a private communication, that they obtained betaine as the hydrochloride from alcohol extracts of guayule shrub.

(3) The authors are indebted to Norman L. Kaufman of this Laboratory for analytical results reported.

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Dielectric Constants of Ethylene Dichloride–Benzene Mixtures

BY ARTHUR A. VERNON, JEFFRIES WYMAN[1] AND ROBERT A. AVERY[2]

The dielectric constants of ethylene dichloride and of benzene are well known and the dielectric constants of *dilute* solutions of ethylene dichloride in benzene have been measured by Williams,[3] Gross,[4] and Muller.[5] In the course of some recent experimental work it was necessary to determine the dielectric constants of these solutions over the complete range and the results are given below.

Experimental

The benzene, C. P. thiophene-free, was stored for several days over anhydrous calcium chloride and then distilled from anhydrous aluminum oxide. The first fifth and last

TABLE I

DIELECTRIC CONSTANT OF BENZENE–ETHYLENE DICHLORIDE MIXTURES AT 25°

Mole fraction of benzene	Wave length in meters	Dielectric constant	$\frac{E-1}{E+2}$
1.000	6.800	2.274	0.29815
0.887	7.533	2.791	.3748
.789	8.215	3.318	.4359
.658	8.8825	3.879	.4897
.554	9.786	4.707	.5527
.395	10.969	5.914	.6209
.281	11.881	6.940	.6644
.143	13.115	8.455	.7131
.000	14.522	10.365	.7574

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(1) Department of Biology, Harvard University.

(2) United States Public Health Service, St. Louis, Missouri.

(3) Williams, *Z. physik. Chem.*, **A138**, 75 (1928).

(4) Gross, *Physik. Z.*, **32**, 587 (1931).

(5) Muller, *ibid.*, **34**, 689 (1933).