and Manske,[2] has recently been modified by Schumann and Boissonnas,[3,4] who replaced the hydrazine of the original procedure with phenylhydrazine.

The work of the latter authors has shown that the reaction products with phthalylglycine and phenylhydrazine, using tri-*n*-butylamine as a catalyst, are glycine and N-phenylphthalhydrazide. The alternative reaction, which would result in the formation of phthalhydrazide and N-phenylglycine, does not appear to occur to any significant degree.

The use of four additional substituted hydrazines has now been studied. Of three which are derivatives of phenylhydrazine, neither 2,4-dinitrophenylhydrazine nor hydrazobenzene underwent the reaction under the usual conditions. Only 2,5-dichlorophenylhydrazine attacked phthalylglycine and gave the expected N-(2,5-dichlorophenyl)-phthalhydrazide in moderate yield.

The other compound studied, methylhydrazine, was found to enter the reaction readily to give an excellent yield of N-methylphthalhydrazide. Thus, the course of the reaction brought about by this alkylhydrazine was the same as that effected by the arylhydrazines so far reported. Unlike hydrazine itself, however, none of its derivatives appear to react at an appreciable rate in the absence of the catalyst. Whether this is due to steric or other factors has not yet been investigated.

N - (2,5 - dichlorophenyl)phthalhydrazide was found to be inactive against *M. tuberculosis* in concentrations up to 100 γ per ml. *in vitro*.

EXPERIMENTAL[5,6]

N-(2,5-Dichlorophenyl)phthalhydrazide. A solution of 1.8 g. (0.010 mole) of 2,5-dichlorophenylhydrazine, 1.03 g. (0.00500 mole) of phthalylglycine,[7] and 0.93 g. (0.005 mole) of tri-*n*-butylamine in 5 ml. of 95% ethanol was refluxed on a steam bath for 12 hr. Fifteen ml. of acetone was then added and the mixture refluxed for 15 min. more. The precipitated glycine was filtered off and the filtrate evaporated *in vacuo*, leaving a clear golden oil as residue. This was dissolved in 15 ml. of ether and treated with dry hydrogen chloride for one min. The ether was evaporated and the orange solid which remained was ground with water, filtered, and thoroughly washed with water. The dry solid weighed 1.2 g. (40%). After two recrystallizations from 95% ethanol it was faintly yellow, m.p. 204–205°.

Anal. Calc'd for $C_{14}H_8Cl_2N_2O_2$: N, 9.02; Cl, 23.09. Found: N, 8.88; Cl, 22.74, 23.03.

N-Methylphthalhydrazide. 1.03 g. (0.00500 mole) of phthalylglycine and 1.85 g. of tri-*n*-butylamine (0.0100 mole) were dissolved in 30 ml. of 95% ethanol. To this was added a solution of methylhydrazine prepared by distilling 1.44 g. (0.0100 mole) of methylhydrazine sulfate with excess alcoholic potassium hydroxide. The mixture was heated under reflux for 20 hours, after which it was evaporated to one-third its volume and 40 ml. of 2-butanone added. The mixture was refluxed for 15 min., cooled, and the glycine filtered off and washed with ether. It weighed 346 mg. (92%) and gave a benzoyl derivative, m.p. 188–190°, unchanged on mixing with authentic hippuric acid.

The filtrate and washings were evaporated to give a clear yellow oil. Forty ml. of ether and 100 ml. of pentane were added and the mixture allowed to stand overnight. The faintly yellow precipitate of N-methylphthalhydrazide was separated by filtration. It weighed 770 mg. (88%) and was insoluble in cold water, ether, and dilute hydrochloric acid, but soluble in dilute aqueous potassium hydroxide. Recrystallization from 95% ethanol gave white granular crystals, m.p. 238.5–239.5° after some sublimation above 180°. (Reported[8] m.p. 239°.) Refluxing 30 min. with acetic anhydride, followed by addition of water and sodium carbonate, gave a white crystalline precipitate, m.p. 139.5–140.5° (reported[8] for N-acetyl-N′-methylphthalhydrazide, 140°).

Acknowledgments: The author wishes to express thanks to Dr. I. M. Hunsberger for his helpful interest in this work and to Dr. M. G. Van Campen, Jr., of the Wm. S. Merrell Co., for the bacteriological tests.

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The Preparation of Aliphatic Propynylcarbinols[1]

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Received Aug. 20, 1956

In connection with a research program in these laboratories, it was necessary to prepare 1-propynylcyclohexanol(I) and 1-propynylcyclopentanol(II). Propynylcarbinols of the general type RR′C(OH)C≡C—CH_3 have been prepared by Iotsitch and coworkers[2] by the reaction of propynylmagnesium bromide with various ketones. Zakharova[3] has recently reported the preparation of several of these compounds by the reaction between methylacetylene and aliphatic ketones, using KOH as a condens-

(1) Paper I from the Acetylene Research Program, St. Edward's University; based in part on the B.S. thesis of James E. Kmiecik.

(2) (a) G. I. Iotsitch, *et al.*, *J. Russ. Phys. Chem. Soc.*, **39**, 652 (1907); *Bull. Soc. chim.*, **6**, 98 (1909). (b) G. I. Iotsitch, *et al.*, *J. Russ. Phys. Chem. Soc.*, **41**, 529, 540 (1909); *Bull. Soc. chim.*, **8**, 889, 890 (1910).

(3) (a) A. I. Zakharova, *J. Gen. Chem.* (*U.S.S.R.*), **17**, 686 (1947); *Chem. Abstr.*, **42**, 1871 (1948). (b) A. I. Zakharova, *J. Gen. Chem.* (*U.S.S.R.*), **19**, 83 (1949); *Chem. Abstr.*, **43**, 6153 (1949). (c) A. I. Zakharova and K. N. Dobromyslova, *J. Gen. Chem.* (*U.S.S.R.*), **20**, 2029 (1950); *Chem. Abstr.*, **45**, 5607 (1951).

TABLE I

$RR'C(OH)C{\equiv}C{-}CH_3$

R	R'	% Yield Li; NH_3	% Yield Grignard	KOH	B.P. °C.	B.P. mm.	n_D^t	t (°C.)
CH_3	CH_3	39[a]	47[b]	55[c]	133.5–134.5	750	1.4402	25
CH_3	C_2H_5	46		80[c]	149–150	750	1.4449	27
CH_3	$(CH_3)_2CH$	51			69–70	18	1.4485	25
	$-(CH_2)_4-$	0	81		99–100	30	1.4837	25
	$-(CH_2)_5-$	41[d]	41[d]		106–110	30	[e]	[e]

[a] The highest yield for several runs; the other yields determined in these experiments are for single runs. [b] Various yields have been reported by other workers; *cf.* references 2a and 3a. The indicated yield was obtained by Brother William Fitch, C.S.C., in these laboratories. [c] Reference 3. [d] Yield based on recrystallized product; the other yields are based on weight of crude distillate. [e] M.p. 48–50°.

ing agent, and McLamore and coworkers[4] report the preparation of methylvinylpropynylcarbinol in 33% yield by the reaction of lithium methylacetylide and methyl vinyl ketone in liquid ammonia.

Although ethynylcyclohexanol can be prepared conveniently and in good yield by the reaction between sodium acetylide and cyclohexanone in liquid ammonia,[5] we were unable to prepare the propynyl homolog (I) by the analogous procedure, using sodium methylacetylide. When lithium was used instead of sodium, 1-propynylcyclohexanol was obtained in 41% yield.

Attempts to prepare II by the reaction between lithium methylacetylide and cyclopentanone were unsuccessful. It is well known[6] that sodium acetylide reacts with cyclopentanone much less readily than with cyclohexanone. Compound II was subsequently prepared in good yield by the reaction of propynylmagnesium bromide with cyclopentanone.

Since methylacetylene is now commercially available,[7] considerable interest attaches to the preparation of propynylcarbinols. A brief investigation of the scope of the lithium methylacetylide reaction was undertaken, using a series of simple aliphatic ketones. The results are shown in Table I.

In most cases, the yields of propynylcarbinols by the lithium methylacetylide reaction were less than those obtained or reported by other procedures. The failure of the lithium methylacetylide procedure to yield isolable amounts of II seems indicative of the limited scope of the reaction. A single run with isobutyraldehyde also gave negative results by this method, although Iotsitch[2b] has reported the successful preparation of the corresponding propynylcarbinol by the Grignard method.

In cases where the yields are comparable, the speed and convenience of the lithium methylacetylide reaction makes it preferable to the Grignard procedure.

EXPERIMENTAL

1-Propynylcyclohexanol (I). A one-liter, 3-necked r.b. flask fitted with a mechanical stirrer and an acetylene inlet tube was charged with 750 ml. of a commercial grade of anhydrous liquid ammonia. Methylacetylene[7] was allowed to bubble through the rapidly stirring solution, while 4.9 g. (0.7 g. atom) of lithium wire[8] was added over a period of 30 min. Methylacetylene addition was continued for 15 minutes after all of the lithium had been added. A solution of 49.1 g. (0.5 mole) of cyclohexanone in 75 ml. of anhydrous ether was added during 10 min., with good stirring. The ammonia was allowed to evaporate for 6 hr., after which a solution of 40 g. of NH_4Cl in 150 ml. of water was added with stirring. One hundred ml. of ether was added, and the aqueous layer was separated and extracted with 125 ml. of ether in two portions. The combined ethereal layers were washed with two 50 ml. portions of 10% HCl saturated with brine, followed by two 75 ml. portions of brine. The solution was dried over $MgSO_4$, the ether was removed, and the product was distilled. There was a considerable forerun (*ca.* 15 g.) of cyclohexanone. The product boiling at 106–110°/30 mm. was collected. It solidified upon cooling and was recrystallized from petroleum ether; 28.5 g. (41%); m.p. 47–49°. A sample which had been recrystallized twice from petroleum ether melted 48–50°.

Anal.[9] Calc'd for $C_9H_{14}O$: C, 78.21; H, 10.21. Found: C, 77.95; H, 10.23.

The other yields listed in column 3 of Table I were obtained by a similar procedure.

1-Propynylcyclopentanol (II). A solution of ethylmagnesium bromide (from 0.65 g. atom of magnesium and 0.65 mole of ethyl bromide) in *ca.* 350 ml. of ether was saturated with methylacetylene at room temperature, during a period of 30 min. The reaction mixture was cooled in an ice bath and stirred for 15 min. while additional methylacetylene was bubbled through it. It was allowed to warm up to room temperature slowly during 12 hours and then saturated with methylacetylene as before. After standing at room temperature for 4 hr., the solution was heated under gentle reflux for 30 min. A solution of 42 g. (0.5 mole) of cyclopentanone (Arapahoe Chemicals, Inc.) in 60 ml. of anhydrous ether was added dropwise to the reaction mixture.

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(5) J. H. Saunders, *Org. Syntheses*, Coll. Vol. 3, 416 (1955).

(6) G. W. Stacy and R. A. Mikulec, *J. Am. Chem. Soc.*, 76, 525 (1954).

(7) The methylacetylene used in these experiments was obtained as a gift from the Air Reduction Company, New York.

(8) When sodium was used instead of lithium, a white solid precipitated from solution. K. N. Campbell and B. K. Campbell [*Proc. Indiana Acad. Sci.*, 50, 123 (1940); *C. A.*, 35, 5457 (1941)] have described the use of lithium acetylide, and observed that it is more soluble than sodium acetylide in liquid ammonia.

(9) The carbon and hydrogen analyses were performed by Micro-Tech Laboratories, Skokie, Illinois.

When addition was complete (1 hr.), the reaction mixture was allowed to stand at room temperature for 4 hr., and then poured into 500 ml. of ice water containing 50 g. of NH_4Cl. The aqueous layer was separated and extracted with 60 ml. of ether. The combined ethereal layers were washed with two 100 ml. portions of 20% NH_4Cl and then with brine. After drying over $MgSO_4$, the ether was removed and the product was distilled through an 8 cm. helix-packed column. The fraction boiling 99–100°/30 mm. was collected; 50.5 g. (81%). A sample which had been redistilled twice through a 20 cm. Widmer column had the following physical properties: b.p. 99–100°/30 mm., 85–85.5°/15 mm.; n_D^{25} 1.4837; d^{25} 0.9669. The I.R. spectrum in CCl_4 solution showed strong absorption at 2.95 μ and weak absorption at 4.5 μ.

Anal. Calc'd for $C_8H_{12}O$: C, 77.37; H, 9.74. Found: C, 77.52; H, 9.80.

The other yields listed in column 4 of Table I were obtained by a similar procedure.

Acknowledgment. We are indebted to the Research Corporation for financial assistance during this investigation.

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Preparation of Alkyl Vinyl Ketones

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Received Aug. 20, 1956

In connection with another problem the need arose for some alkyl vinyl ketones. The procedure devised by McMahon *et al*[1] is unsuitable for larger scale work due to the violence of the dehydrohalogenation. Woodward[2] recommended that several small scale experiments (39 g.) be run to obtain sizable amounts of ethyl vinyl ketone.

We have found that the dehydrohalogenation of 1-chloro-3-pentanone proceeds smoothly when an intimate mixture of the haloketone and anhydrous sodium benzoate is stirred and heated. In this way it is possible to obtain the desired unsaturated ketone in 78% crude yield on mole scale runs. The two disadvantages of the method, namely, the poorer yields that resulted in the preparation of higher homologs and the mechanical difficulties in handling the cooled cement-like residues, were overcome by employing Dowtherm as a diluent in the reaction. In this way the yield of butyl vinyl ketone was increased from 30% to 58%, and the nonvolatile material remained fluid throughout.

In our preferred method we found it expedient to use the crude undistilled chloroketone. The over-all yield based on the acid chloride was at least as good as that obtained when distilled ketone was used. It was possible to obtain the higher alkyl vinyl ketones in approximately 30% over-all yield with a minimum of manipulation.

EXPERIMENTAL[3]

Ethyl vinyl ketone. A 500-ml. three-necked flask was equipped with a Hershberg stirrer and a still-head connected to a condenser set for downward distillation. The receiver, containing 0.1 g. of hydroquinone, was immersed in ice. A mixture of 90 g. of 1-chloro-3-pentanone and 0.5 g. of hydroquinone was placed in the flask and the stirrer was started. Anhydrous sodium benzoate (120 g.) was added portionwise over a 10-min. period. A second 90-g. portion of the chloroketone was added followed by a second 120-g. portion of sodium benzoate.

After the reagents were thoroughly mixed the flask was heated by means of a heating mantle. After a few minutes the contents solidified but after about 10 minutes the whole liquefied, allowing the stirrer to function. Within the next hr. and one-half the entire distillate, b.p. 100–135°, was collected.

The apparatus was dismantled while still hot and the residue immediately was emptied into a stone crock (hood). The distillate was separated from a small amount of water and dried. The crude ethyl vinyl ketone weighed 99 g. (78%).

TABLE I

ALKYL VINYL KETONES $RC(=O)CH{=}CH_2$

R	Yield[a]	B.P., °C. (mm.)	Formula	Analyses: Carbon Calc'd	Carbon Found	Hydrogen Calc'd	Hydrogen Found
n-Propyl	27	25–26 (11)	$C_6H_{10}O$	73.43	73.28	10.27	10.52
n-Butyl	34	44–45 (11)	$C_7H_{12}O$	74.95	74.50	10.79	10.66
n-Amyl	26	58–61 (11)	$C_8H_{14}O$	76.14	76.00	11.18	11.60

[a] Yield based on the acid chloride used to prepare the β-chloroketone. In the case of propyl vinyl ketone distilled 1-chloro-3-hexanone furnished the desired product in 82% yield. However there was no gain in over-all yield.

A small portion reacted with aniline to furnish 1-phenylamino-3-pentanone, m.p. 56.2–57.2° after two crystallizations from absolute ethanol. McMahon[1] reported m.p. 56.5–57°.

General method for the preparation of the alkyl vinyl ketones. One and one-half moles of the acid chloride was treated with ethylene in chloroform as described by Woodward.[2] The crude chloroketone was obtained after removal of the solvent and was weighed and used directly in the next step.

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(2) R. B. Woodward, F. Sondheimer, D. Taub, K. Heusler and W. M. McLamore, *J. Am. Chem. Soc.*, **74**, 4223 (1952).

(3) Analyses were carried out by Mr. K. D. Fleischer and his staff of this Institute.