state in the conifers as was demonstrated by comparative studies on the native, and the enzymatically liberated lignins of white Scots pine. Should this condition prevail for the hardwoods studied then it must be concluded that the high methoxyl contents of the "Klason lignins" obtained from the woods are artifacts resulting from the vigorous action of the reagents applied during the isolation.

A study of the lignin liberated by means of fungal decay of native lignin-free hardwood should reveal which one of the above two possibilities actually prevails. If the lignin so liberated possesses a characteristically high methoxyl content and contains syringyl as well as guaiacyl nuclei, the first condition should represent the true state of the lignin. If, on the other hand, the enzymatically liberated lignin resembles the native lignin portion and contains only guaiacyl groups, then the conclusion must be drawn that there exists no essential difference between these hardwood lignins and softwood lignin.

Such enzymatic studies are at present in progress.

Acknowledgment.—This work was carried out with the aid of a grant from the Office of Naval Research.

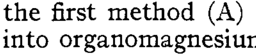
NEW YORK 58, N. Y. RECEIVED JUNE 19, 1950

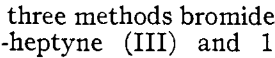
[CONTRIBUTION NO. 768 FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF PITTSBURGH]

The Propargylic Rearrangement. II. The Dehalogenation of Propargylic Bromides

BY JOHN H. WOTIZ

Propargylic bromides were dehalogenated in three different ways: by treating their Grignard reagent with water, by means of the zinc–copper alcohol reagent, or by the action of lithium aluminum hydride. The product was always a mixture of acetylenic and allenic hydrocarbons. Possible reaction mechanisms are discussed.

In a recent paper[1] it was shown that primary propargylic bromides, $\mathrm{R{-}C{\equiv}C{-}CH_2Br}$, can be converted in high yields *via* nitriles or by the malonic ester synthesis into acetylenic acids. However, the same bromides when converted into Grignard reagents on carbonation[2] yielded a mixture of acetylenic and allenic acids. The present study was undertaken to determine whether the formation of an organometallic compound is necessary for the formation of rearranged (allenic) products. Such a possible explanation was suggested by Hennion and Sheehan[3] who dehalogenated *n*-propylethynylcarbinyl chloride, $\mathrm{C_3H_7{-}CHCl{-}C{\equiv}CH}$, and obtained 1,2-hexadiene in 71% yields. A small amount of the isomeric 1-hexyne was found. The authors pictured the reaction mechanism as going through an intermediate organozinc compound,  $\mathrm{C_3H_7{-}\underset{\displaystyle ZnCl}{\underset{|}{C}H}{-}C{\equiv}CH}$, which in the presence of alcohol yielded the allenic product.

Two isomeric propargylic bromides, 1-bromo-2-heptyne (I), $\mathrm{C_4H_9{-}C{\equiv}C{-}CH_2Br}$, and 3-bromo-1-heptyne (II),  $\mathrm{C_4H_9{-}\underset{\displaystyle Br}{\underset{|}{C}H}{-}C{\equiv}CH}$, were dehalogenated by three different methods to yield mixtures of acetylenic and allenic hydrocarbons. In the first method (A) the bromides were converted into organomagnesium bromides[2] which were then hydrolyzed. In the second method (B) the zinc–copper–alcohol reagent described by Hennion[3] was used. In the third method (C) the halogen was removed by the action of lithium aluminum hydride.[4] In all three methods bromide I produced a mixture of 2-heptyne (III) and 1,2-heptadiene (IV), and bromide II, a mixture of 1-heptyne (V) and 1,2-heptadiene (IV). The yields were found to depend on the method of preparation. The findings of Hennion[3] that 3-halo-1-alkynes yield mainly 1,2-dienes when dehalogenated with zinc–copper–alcohol were substantiated. However, the isomeric 1-halo-2-alkyne with the reagent yielded only one half as much allenic as acetylenic product. Individual experiments are listed in Table I, and the yields are calculated from the amount of hydrocarbons distilling over the listed boiling range. Despite the use of high efficiency fractionating columns, imperfect separation took place. This was apparent from the refractive index and infrared spectrum determinations of individual distillate fractions. The product ratios III to IV and V to IV in Table I are estimated from the refractive index and infrared spectral data. The tabulation of constants of possible products is given in Table II. In Fig. 1 are given the infrared spectra of two fractions of reaction products in the dehalogenation of II by method B, to illustrate how the products were qualitatively and quantitatively analyzed. A linear variation in refractive indices of mixtures of isomeric hydrocarbons was assumed in order to obtain a semi-quantitative estimation of composition. The semi-quantitative analysis on the basis of the infrared spectrum utilized the extinction coefficient for pure IV, which was estimated for the typical allenic band near 1950 cm.$^{-1}$. This value allows an estimation of this compound in mixtures by the use of Beer's law. Usually the minor component was determined spectroscopically and the other one by difference. Thus the fractions in Fig. 1 boiling at 97 and 103°, contain 10 and 0% of V, on the basis of absorption, and 20 and 1%, respectively, on the basis of mixed refractive indices.

Discussion of Results

The infrared spectrograms of samples in each individual experiment listed in Table I, show con-

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[1] Newman and Wotiz, THIS JOURNAL, **71**, 1292 (1949).

[2] Wotiz, *ibid.*, **72**, 1639 (1950).

[3] Hennion and Sheehan, *ibid.*, **71**, 1964 (1949).

[4] Trevoy and Brown, *ibid.*, **71**, 1675 (1949).

TABLE I

ANALYSIS OF PRODUCTS

	Halide		Reagent		Product					
									Ratio	
Expt.		Quant., mole	Method[d]	Quant., mole	Total yield, %	B.p. range, °C.	$n^{25}D$	$C_5H_{11}C{\equiv}CH$	$C_4H_9CH{=}C{=}CH_2$	$C_4H_9C{\equiv}CCH_3$
1	$C_4H_9C{\equiv}CCH_2Br$	0.6	A	[a]	76	103–110	1.4315–1.4190	...	1.1	1.0
2	$C_4H_9C{\equiv}CCH_2Br$	.3	B	[a]	81	103–110	1.4280–1.4208	...	1.0	2.0
3	$C_4H_9C{\equiv}CCH_2Br$	.3	C	0.4	94[b]	103–110	1.4156–1.4192[b]	...	1.0	15.0[b]
4	$C_4H_9C{\equiv}CCH_2Br$	.4	C	0.125	47	103–110	1.4182–1.4188	...	[c]	[c]
5	$C_4H_9\underset{Br}{CH}{-}C{\equiv}CH$	.2	A	[a]	50	95–103	1.4153–1.4326	1.0	2.6	...
6	$C_4H_9\underset{Br}{CH}{-}C{\equiv}CH$	.3	B	[a]	77	95–103	1.4203–1.4330	1.0	22.0	...
7	$C_4H_9\underset{Br}{CH}{-}C{\equiv}CH$	.15	C	0.2	48	95–103	1.4150–1.4330	1.0	9.0	...

[a] Excess. [b] Contained ether; ratio not as accurately estimated as in the rest of cases. [c] Not analyzed by infrared spectrum; 43% of halide recovered. [d] A, magnesium followed by water; B, zinc–copper–alcohol; C, lithium aluminum hydride.

TABLE II

PHYSICAL PROPERTIES OF POSSIBLE PRODUCTS

S Strong M Medium W Weak Intensities of Bands

			Characteristic absorption bands, cm.$^{-1}$						
Compound	B.p., °C.	n_D (°C.)	$C{\equiv}C{-}H$	$C{\equiv}C$	$C{=}C{=}CH_2$	$CH{=}CH_2$	$-\overset{H}{C}{=}\overset{H}{C}-$	$-\overset{H}{C}{=}\underset{H}{C}-$	$C{=}C{-}C{=}C$
$C_5H_{11}CH{=}CH_2$[a]	93	1.3999 (20)				910, 990 S			
$C_4H_9\overset{H}{C}{=}\underset{H}{C}{-}CH_3$[b]	97–99	1.4056 (24)						967 S	
$C_4H_9\overset{H}{C}{=}\overset{H}{C}{-}CH_3$[a]	99	1.4052 (25)					1600–1650 W		
$CH_3(CH_2)_5CH_3$[c]	98	1.3877 (20)							
$C_5H_{11}C{\equiv}C{-}H$[d]	97	1.4038 (25)	3270 S	2100–2140 M					
$C_4H_9CH{=}C{=}CH_2$[e]	105	1.4322 (18)			1900–2000 S				
$C_4H_9CH{=}C{=}CH_2$[f]	103	1.4330 (25)			1950 S				
$C_3H_7C{\equiv}C{-}C_2H_5$[d]	104	1.4165 (25)		2190–2260[h] W					
$C_2H_5CH{=}CH{-}CH{=}CHCH_3$[g]	107	1.4534 (20)							1580–1610 M
$C_4H_9C{\equiv}C{-}CH_3$[d]	109	1.4199 (25)		2190–2260[h]					

[a] Egloff, "Physical Constants of Hydrocarbons," ACS Monograph No. 78, Reinhold Publishing Corporation, New York, 1939, p. 200. [b] Egloff, *ibid.*, p. 201. [c] Egloff, *ibid.*, p. 40. [d] Wotiz and Miller, THIS JOURNAL, **71**, 3441 (1949). [e] Egloff, ref. *a*, p. 311. [f] This paper. [g] Egloff, ref. *a*, p. 312. [h] Did not appear in the authentic specimen; see reference *d*.

clusively that the only product of dehalogenation of I was a mixture of III and IV, and that II yielded only IV and V.[5] It is now apparent that the ratio of products differs significantly with the dehalogenating reagent.

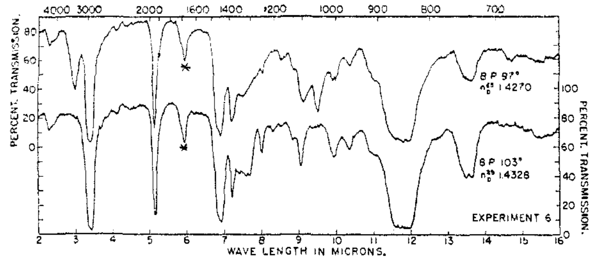
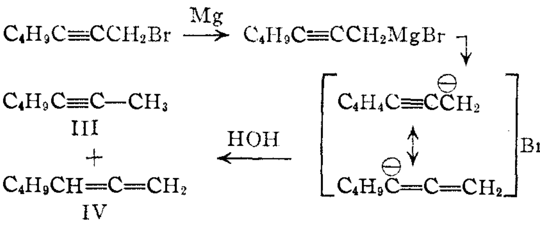


Fig. 1.—Asterisk signifies overtone of the strong band near 848 cm.$^{-1}$.

Method A.—Using the cyclic reactor for the preparation of Grignard reagents from very active halides,[6] the formation of organomagnesium intermediate compound was substantiated by carbonation to acids.[2] The rearrangement could have proceeded according to the equation



$$C_4H_9C{\equiv}CCH_2Br \xrightarrow{Mg} C_4H_9C{\equiv}CCH_2MgBr \rightarrow \left[\begin{array}{c} C_4H_4C{\equiv}C\overset{\ominus}{C}H_2 \\ \updownarrow \\ C_4H_9\overset{\ominus}{C}{=}C{=}CH_2 \end{array}\right] BrMg^{+} \xrightarrow{HOH} \underset{III}{C_4H_9C{\equiv}C{-}CH_3} + \underset{IV}{C_4H_9CH{=}C{=}CH_2} \quad (1)$$

A similar equation can be written for II to yield IV and V.

Method B.—One possible mechanism for this method was proposed by Hennion and Sheehan.[3] A possible alternate route is suggested in equation 1. However, there is no experimental justification for

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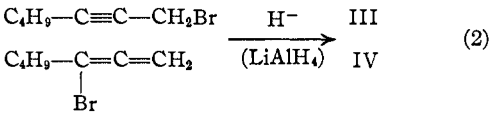
(5) The author wishes to express his gratitude to Dr. Foil A. Miller of the Mellon Institute for the determination and interpretation of spectrograms. With the exception of Fig. 1, these spectrograms are not included, to conserve space; however, they can be obtained on request from the author.

(6) Greenlee, Boord and Rowlands, Abstracts of the Organic Division, 117 National A. C. S. Meeting, Philadelphia, April, 1950.

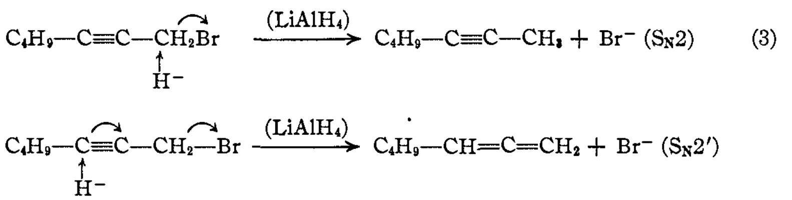
the formation of an intermediate organozinc compound in such a reaction.

Method C.—The mechanism of reaction of lithium aluminum hydride with alkyl halides was studied by Trevoy and Brown.[4] They concluded that it involves a direct nucleophilic attack on carbon by the hydride ion with inversion of configuration. If their findings also apply to our case, the formation of acetylenic and allenic hydrocarbons could be explained on the presence of individual acetylenic and allenic halides.



$$\left.\begin{array}{l} C_4H_9-C\equiv C-CH_2Br \\ C_4H_9-\underset{\underset{\displaystyle Br}{|}}{C}=C=CH_2\end{array}\right. \xrightarrow[(LiAlH_4)]{H^-} \begin{array}{l}III\\IV\end{array} \qquad (2)$$

An alternate mechanism[7] is pictured in equation 3.

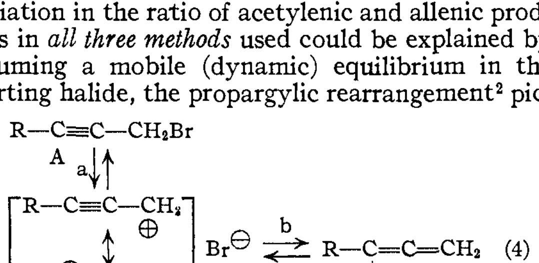


$$C_4H_9-C\equiv C-\underset{\underset{\displaystyle H^-}{\uparrow}}{\overset{\curvearrowright}{CH_2}}Br \xrightarrow{(LiAlH_4)} C_4H_9-C\equiv C-CH_3 + Br^-\ (S_N2) \qquad (3)$$

$$C_4H_9-\underset{\underset{\displaystyle H^-}{\uparrow}}{\overset{\curvearrowright}{C}}\equiv C-\overset{\curvearrowright}{CH_2}-Br \xrightarrow{(LiAlH_4)} C_4H_9-CH=C=CH_2 + Br^-\ (S_N2')$$

The significantly lower yield in experiment 7 can be explained considering the formation of an organometallic compound from the terminal hydrogen, $\equiv C-H$,[8] followed by coupling with the unreacted halide. In experiment 4 the ratio of I to lithium aluminum hydride was 3.3 to 1, (theory is 4 to 1). The yield of combined hydrocarbons was 47 and 43% of the starting bromide was recovered (identified by boiling point and refractive index). The composition of products was about the same as in experiment 3 where using a great excess (1 to 1.3) of lithium aluminum hydride, the yield was 94%.[9]

Results of experiments using method C, show that an organometallic intermediate is not necessary for the formation of allenic products. The variation in the ratio of acetylenic and allenic products in *all three methods* used could be explained by assuming a mobile (dynamic) equilibrium in the starting halide, the propargylic rearrangement[2] pictured in equation 4.



$$\begin{array}{c} R-C\equiv C-CH_2Br \\ \text{A}\ \ {\scriptstyle a}\downarrow\uparrow \\ \left[\begin{array}{c} R-C\equiv C-\overset{\oplus}{CH_2} \\ \updownarrow \\ R-\overset{\oplus}{C}=C=CH_2\end{array}\right] Br^{\ominus} \overset{b}{\rightleftharpoons} R-\underset{\underset{\displaystyle Br}{|}}{C}=C=CH_2 \\ \text{B} \qquad\qquad\qquad \text{C}\end{array} \qquad (4)$$

Such a proposal is made to point out the great similarity of propargylic bromides to allylic bromides whose rearrangement has been exhaustively studied by W. G. Young and his collaborators.[10] The form B in equation 4 was proposed Pauling, *et al.*,[11] to explain the surprisingly long carbon–halogen bond length in propargyl (R equals H) chloride, bromide and iodide. It could also offer an explanation for the presence of the "new" band in the infrared spectrum[12] for which the conventional formulas offer no explanation. Whether step b in equation 4 takes place in the "pure" bromide or only in the presence of solvents or reagents cannot be determined on the basis of the presented experimental facts.

It is interesting to compare the results of this study with related reactions in the literature, especially with the use of propargylic bromides in the Reformatsky reaction which is known to proceed through an organozinc intermediate.[13] The products were invariably identified as β-hydroxyacetylenes.[14] The yields were always high, reaching 90% in the case of condensation of I with benzaldehyde.[14b] The absence of allenic products can be explained by assuming insufficient analysis, or that the equilibrium in the intermediate organozinc compound (Eq. 1) favored the formation of acetylenic products in the reaction with aldehydes or ketones.

On the basis of the present findings, one should carefully scrutinize the reaction products of propargylic halides. Often what was thought to be a pure acetylenic product may have contained appreciable amounts of the allenic isomer, and *vice versa.* This is especially likely in cases where the boiling points of isomers are very close.

Experimental

1-Bromo-2-heptyne (I) was prepared as previously described.[1,2] Its infrared spectrum was recently published.[15]

***n*-Butylethynylcarbinol**, $C_4H_9CH(OH)-C\equiv CH$, **Method A.**—Following the procedure of Truchet[16] 192 g. (2 moles) of 1-heptyne[17] and 111 g. (1 mole) of selenium dioxide were refluxed for 10 hours in 300 cc. of absolute alcohol. The yield of the acetylenic alcohol was 60 g. (27%) b.p. 55 to 60° at 5 mm. This product was identical with the one in method B.

Method B.—*n*-Valeraldehyde (295 g., 3.4 mole) in 300 cc. of dry ether was allowed to react with sodium acetylide (from 92 g., 4 mole of sodium) in liquid ammonia.[17,18] The yield of the carbinol was 140 g. (37%), b.p. 69° at 18 mm., $n^{25}\mathrm{D}$ 1.4360. Its infrared spectrum was recently published.[12]

3-Bromo-1-heptyne (II).—The procedure used for the preparation of I was employed. *n*-Butylethynylcarbinol (194 g., 1.73 moles) and 162 g. (0.6 mole) of phosphorus tribromide yielded 120 g. (40%) of II; b.p. 63–65° at 20 mm., $n^{25}\mathrm{D}$ 1.4700. On redistillation, the fraction boiling at 64° at 20 mm., $n^{25}\mathrm{D}$ 1.4695, was analyzed.[19] Calcd. for $C_7H_{11}Br$: C, 48.0; H, 6.3; Br, 45.6. Found: C, 48.2; H, 6.2; Br, 45.6. Its infrared spectrum was recently published.[12]

Dehalogenation: Method A.—The cyclic reactor previously described[6] was used. The bromide in 200 to 300 cc. of dry ether was passed through the reaction tube filled with amalgamated magnesium for from 5 to 7 hours. To the ice-cooled solution of the Grignard reagent in 600 to 700 cc. of ether was added an excess of a saturated solution of am-

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[7] The author wishes to thank Referee I for this suggestion.

[8] Compare this with the case of fluorine in ref. 4.

[9] These results are in agreement with the recent findings of Johnson, Blizzard and Carhart, THIS JOURNAL, **70**, 3664 (1948), that not all four hydrogens in $LiAlH_4$ show the same reactivity toward alky halides.

[10] For a recent review of the allylic rearrangement see W. G. Young, *J. Chem. Ed.*, **27**, 357 (1950).

[11] Pauling, Gordy and Saylor, THIS JOURNAL, **64**, 1753 (1942).

[12] Wotiz, Miller and Palchak, *ibid.*, **72**, 5055 (1950).

[13] Dain, *J. Russ. Phys.-Chem. Soc.*, **28**, 593 (1896).

[14] (a) Zeile and Meyer, *Ber.*, **75**, 356 (1942); (b) Henbest, Jones and Walls, *J. Chem. Soc.*, 2696 (1949); (c) Golse and Le-Van-Thoi, *Compt. rend.*, **230**, 210 (1950).

[15] Wotiz and Miller, THIS JOURNAL, **71**, 3441 (1949).

[16] Truchet, *Compt. rend.*, **196**, 706 (1933). The reported yield was 27%; b.p. 67° at 18 mm., $n^{20}\mathrm{D}$ 1.443.

[17] Henne and Greenlee, THIS JOURNAL, **64**, 545 (1945).

[18] Campbell, Campbell and Eby, *ibid.*, **60**, 2882 (1938).

[19] Microanalysis by G. L. Stragand at the Microchemical Analytical Laboratory of the University of Pittsburgh.

monium chloride. The organic layer was separated and washed with dilute hydrochloric acid, sodium carbonate and water, then dried over calcium chloride. The major portion of ether was rapidly distilled off through a small column.

Method B.—The directions described by Hennion[3] were closely followed.

Method C.—To a solution of the halide in 100 cc. of dry ether was added an ether solution of lithium aluminum hydride (1.6 molar) at a rate to maintain refluxing. The clear solution was stirred under reflux for an additional 2 hours, and hydrolyzed with a concentrated solution of ammonium chloride at the reflux temperature of ether. The ether solution was decanted, washed with dilute hydrochloric acid, and dried over calcium chloride. Most of the ether was removed by a rapid distillation through a small column. The residue was fractionally distilled.

Fractional Distillation and Analysis.—A two-foot column packed with nickel saddles (column 1) or a one-foot semimicro column (column 2)[20] was used. There was a little difference in the efficiency of these two columns as evident from the infrared spectrum analysis. Cumene was used as a "chaser." The boiling point of collected fractions is listed in Table I. Fractions boiling below the listed boiling range consisted almost entirely of ether (methods A and C) or of alcohol (method B). There was a steep rise in temperature after the product exceeded the upper limit of the listed boiling range. Although boiling points showed a very good separation of isomers refractive indices and the intensities of bands in the infrared spectrum, showed a constant variation in composition. With the exception of experiment 3, refractive indices of individual fractions showed a gradual variation within the values of pure acetylenic and allenic products. The infrared analyses were usually performed within 48 hours after distillation. The refractive index of the lower boiling fraction in experiment 3, was outside the limit of the pure hydrocarbons. This was due to incomplete removal of ether (column 1 was used), found in rather high molar concentration by the infrared analysis. No other unexpected absorption bands were found in any experiment or fraction.

PITTSBURGH, PA. RECEIVED APRIL 11, 1950

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[20] Manufactured by the Glass Engineering Laboratories of Belmont, Cal. Claimed efficiency by 75 theoretical plates. The author wishes to thank Drs. Orchin and Wender of the U. S. Bureau of Mines, Bruceton, Pa., for the use of this column.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF DE PAUL UNIVERSITY]

Preparation of Some 2-Picolyl Ketones Using Phenyllithium

BY ROBERT P. ZELINSKI AND MARY BENILDA[1]

2-Picoline has been acylated in the presence of phenyllithium with ethyl benzoate, ethyl 2-furancarboxylate and ethyl 2-thiophenecarboxylate to yield the corresponding 2-picolyl ketones. These have been characterized and then reduced by Wolff–Kishner reduction to give substituted 2-pyridylethanes.

Acylations of 2-picoline and similar methyl ammono ketones by means of basic reagents and acid halides, anhydrides and esters have been briefly reviewed elsewhere.[2]

The present investigation describes the preparation of three 2-picolyl ketones by acylation of 2-picoline in the presence of phenyllithium with ethyl benzoate, ethyl 2-furancarboxylate[3] and ethyl 2-thiophenecarboxylate. In agreement with the results reported for the acylation of 2-picoline by alkali amide and ethyl benzoate,[2] it has been found that altering the mole ratio of phenyllithium to 2-picoline materially changed the yield of ketone. 2-Picolyl phenyl ketone (2-phenacylpyridine) decomposed slowly on standing, but 2-picolyl 2-furyl ketone and 2-picolyl 2-thienyl ketone were stable.

In agreement with a recent report,[2] these 2-picolyl ketones have been found to manifest ketonic reactions. Treatment with 2,4-dinitrophenylhydrazine gave good yields of the hydrazones. However, while reaction with 2-picolyl 2-furyl ketone was successful in the presence of acetic acid, hydrochloric acid catalyzed the formation of a distinctly different product. Presumably, this was furyldinitropyridylindole formed in a particularly rapid indole synthesis.[4,5]

Reduction of the 2-picolyl ketones by a Wolff–Kishner reaction gave the expected hydrocarbons, all of which rapidly resinified at room temperature. However, the picrates of these were stable. With excess picric acid the dipicrates appear to form, but these are converted to monopicrates by recrystallization.

Experimental[6]

2-Picolyl Phenyl Ketone.—A solution of 0.63 mole of ethyl benzoate in 100 ml. of anhydrous ether was rapidly added with stirring to 200 ml. of an ethereal solution of 2-picolyllithium prepared from 1.4 g. atoms of lithium sand, 0.71 mole of bromobenzene and 1.4 moles of 2-picoline. After the initial vigorous reaction the mixture was stirred under reflux for 1 hour. It was then poured onto 200 g. of ice and water, and the aqueous layer was saturated with salt and extracted with ether. After having been dried over anhydrous sodium sulfate, the combined ether solution was distilled through a heated column, 1.2 × 20 cm., packed with glass helices. The 2-picolyl phenyl ketone, b.p. 158–170° (1 mm.), weighed 34 g. (27% yield, 87% based on ester not recovered). Recrystallization from petroleum ether (b.p. 30–60°, Skellysolve F) gave yellow needles, m.p. 52.5–54°, literature[7] 54°. When the mole ratio of ethyl benzoate 2-picoline and phenyllithium was 1:1:1, the yield was 20% based on the total amount of ester employed.

Anal. Calcd. for $C_{13}H_{11}NO$: N, 7.11. Found: N, 7.51.

The **picrate**[8] melted at 180–181° after recrystallization from 95% alcohol. It darkened on exposure to light.

Anal. Calcd. for $C_{19}H_{14}N_4O_4$: N, 13.14. Found: N, 13.35.

The **2,4-dinitrophenylhydrazone**[9] of 2-picolyl phenyl ketone was obtained in 63% yield after recrystallization from alcohol, m.p. 193–194°.

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[1] Abstracted from the thesis submitted by Sr. Mary Benilda Nadzieja, Fel., O.S.F., in partial fulfillment of the requirements for the degree of Master of Science.

[2] Weiss and Hauser, THIS JOURNAL, **71**, 2023 (1949).

[3] This ester has been previously used for the acylation of 2-quinaldine with alkali amide as the basic reagent: Bergstrom and Moffat, THIS JOURNAL, **59**, 1494 (1937).

[4] Fischer, *Ber.*, **19**, 1563 (1886).

[5] Robinson and Robinson, *J. Chem. Soc.*, **113**, 639 (1918).

[6] All analyses are by the Micro-Tech Laboratories, Skokie, Illinois.

[7] Kloppenburg and Wibaut, *Rec. trav. chim.*, **65**, 393 (1946).

[8] Shriner and Fuson, "The Systematic Identification of Organic Compounds," 3rd ed., John Wiley and Sons, Inc., New York, N. Y., 1948, p. 180.

[9] *Ibid.*, p. 171.