[Contribution from the Chemical Laboratory of Northwestern University]

THE USE OF GRIGNARD REAGENTS IN ATTEMPTED SYNTHESES OF ASYMMETRIC ALLENE BASES

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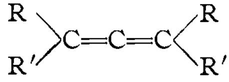
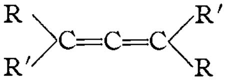
Nearly fifty years ago, van't Hoff ventured the prediction of optical isomerism in certain types of allenes. This speculation was based on the concept of molecular asymmetry rather than atomic asymmetry. Molecules of the types  $\genfrac{}{}{0pt}{}{R}{R'}\!\!>\!C{=}C{=}C\!<\!\genfrac{}{}{0pt}{}{R}{R'}$ and  $\genfrac{}{}{0pt}{}{R}{R'}\!\!>\!C{=}C{=}C\!<\!\genfrac{}{}{0pt}{}{R'}{R}$ were regarded as isomeric, inasmuch as the spatial models of these two forms could not be superimposed. This prediction has never been verified by experiment and as yet, because of the difficulties encountered, no decisive experiment has been recorded.

For purposes of optical resolution, there should be either an acidic or a basic group in the allene molecule to provide for salt formation with an optically active base or an optically active acid. It is reasonable to infer that such salts could be resolved into their *dextro* and *levo* parts by the usual methods of fractional crystallization. The difficulties which attend the preparation of such allenes, however, have been so great that no compound has yet been prepared which unquestionably possesses such a structure.

Dimroth and Feuchter,[1] in an attempt to study this problem, were unable to prepare their starting material, 1-phenyl-3-naphthyl-allene-1-carboxylic acid. Lapworth and Wechsler[2] were somewhat more successful in that they claim to have isolated the allene acid which was desired, namely, 1,3-diphenyl-1-α-naphthyl-allene-3-carboxylic acid. However, their work with this allene acid was effectually blocked, inasmuch as they were unable to obtain any crystalline compounds in the reaction of this compound with optically active bases.

The other allene acids which are reported in the literature have little or no proof to support their structure, and no basic allenes have been reported whatsoever. During the course of the present investigation, mention was made[3] of an unsuccessful attempt to prepare 1,3-di-(*p*-dimethylaminophenyl)-1,3-diphenyl-allene by the dry distillation of the barium salt of *p*-dimethylaminodiphenylacetic acid.

Ziegler[4] has developed a method for the preparation of allenes which consists essentially in the dehydration of a tetrasubstituted allyl alcohol; $Ar_2C{=}CH{-}CAr_2OH \longrightarrow Ar_2C{=}C{=}CAr_2 + H_2O$. Thermal decompo-

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[1] Dimroth and Feuchter, *Ber.*, **36**, 2238 (1903).

[2] Lapworth and Wechsler, *J. Chem. Soc.*, **97**, 38 (1910).

[3] Singh, *ibid.*, **127**, 2445 (1925).

[4] (a) Ziegler, *Ber.*, **55**, 2257 (1922); (b) **57**, 1983 (1924); (c) *Ann.*, **434**, 34 (1923).

sition of these tertiary alcohols produces very effective dehydration in some cases, whereas in others better results are produced with dehydrating agents. Because of the reported simplicity in the conversion of these tertiary alcohols to allenes, and because such alcohols are seemingly prepared with ease from a diarylvinylmagnesium bromide, $Ar_2C{=}CHMgBr$, and a ketone, it was inferred that the use of basic ketones might permit an extension of this method to form an asymmetric allene molecule which would contain a tertiary amino nitrogen atom.

Grignard Reagents from Diarylvinyl Bromides

A study of the reaction of magnesium with disubstituted vinyl bromides revealed the fact that whereas diphenylbromo-ethylene reacted vigorously and gave about 70% yield of the Grignard reagent,[5] no vinyl bromide with two dissimilar substituent groups was found that behaved at all satisfactorily in this respect. The best yield from phenyl-*p*-anisylbromo-ethylene was 33%, and from phenylmethyl bromo-ethylene, 17%; side reactions were very prominent, chief of which, perhaps, was a modified Wurtz reaction giving butadienes. Diphenyl-di-*p*-anisyl butadiene and diphenyl-di-*p*-tolyl butadiene were discovered in this manner. Phenyl-*p*-tolylbromo-ethylene, hitherto undescribed, was prepared in the hope that its similarity to diphenylbromo-ethylene would extend to the formation of its Grignard reagent, but only 4–6% yields were obtained. The most satisfactory bromo-ethylene was phenyl-α-naphthylbromo-ethylene, in spite of the fact that the formation of its Grignard reagent was a matter of days instead of hours. Following a suggestion of Professor Henry Gilman, it was found that turnings from a commercial magnesium-copper alloy reacted much more readily than did magnesium. With phenylnaphthylbromo-ethylene, the time of reaction was reduced from half a week to half a day. Another argument in its favor comes from the fact that it changed the yield of Grignard reagent with phenyl-*p*-tolylbromo-ethylene from 5 to 51%.

Ketone Bases

Two ketone bases, *p*-dimethylaminobenzophenone and β-pyridylmethyl ketone, were used in this study. The latter compound is new. Efforts to prepare large amounts of another ketone base, *p*-dimethylamino-acetophenone, were fruitless. However, enough of it was prepared to discover that the boiling point of 108–110°, at 12 mm., as reported by Staudinger and Kon,[6] is in error; the true value is 172–175°, at 11 mm.

Behavior of Ketone Bases with Grignard Reagents

In consideration of the low yield of Grignard reagents and the presence of by-products with phenylmethylbromo-ethylene and with phenylanisyl bromo-ethylene, little hope was entertained that they would prove fruitful

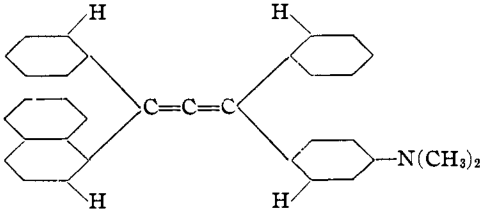
[5] See Experimental Part, below; also Ref. 4 c, p. 75.

[6] Staudinger and Kon, *Ann.*, **384,** 110 (1911).

in the allene syntheses. However, the anisyl compound was treated with β-pyridylmethyl ketone. There was evidence of the formation of the anticipated tetrasubstituted allyl alcohol in the isolation of a small quantity of a thick oil with basic properties. Concentrated hydrochloric acid dissolved this oil, producing a red color which rapidly faded; sulfuric acid gave a red solution. However, no satisfactory method, out of several tried, was found to purify this material.

The Grignard reagent from phenyl-*p*-tolylbromo-ethylene and magnesium-copper alloy consistently refused to react with pyridylmethyl ketone. No reason for this was apparent. To test whether or not this Grignard reagent would react with ketones, a solution of acetophenone in ether was added to it; the mixture boiled, which certainly was an indication of some chemical reaction. To test whether or not β-pyridylmethyl ketone would react with Grignard reagents, a solution of it was added to a large excess of phenylmagnesium bromide. There was a heavy precipitation; from the reaction mixture there was isolated a 42% yield of a low-melting solid which was shown to be phenylpyridylethylene, $C_6H_5(C_5H_4N)C{=}CH_2$.

The Grignard reagent from phenyl-α-naphthyl bromo-ethylene displayed considerable sluggishness towards *p*-dimethylaminobenzophenone. The tars which were produced proved very difficult to purify, but finally a solid was isolated which possessed analytical values for the desired allene, but which instead, was probably a cyclic isomer of it related to indene (Formula II). Two seemingly unavoidable details in its purification, namely, high temperature[7] and contact with acetic acid, induce this type of isomerization with aromatic allenes. Reaction with ozone furnished evidence that the allene had been isomerized. Hydrolysis of the allene-ozonide should have yielded phenylnaphthyl ketone, carbon dioxide and *p*-dimethylaminobenzophenone, the latter two of which were definitely shown to be absent. It would be relatively simple to predict the structure of the compound from the ozonide of the allene isomer, were its structure known. However, each of the four nuclear hydrogens, so marked in Formula I, seems equally capable of wandering to the middle carbon of the allene chain. Four different cyclic isomers would result, each possessing Nucleus II. Each would give a different aldehyde-ketone, III, by the ozone treatment.



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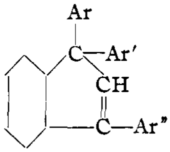
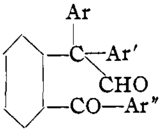


II



III

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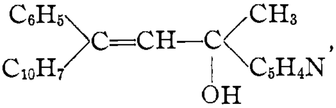
[7] Vorländer and co-workers, *Ber.*, **39**, 1024 (1906); **56**, 1122, 1136 (1923). Ref. 4c.

Therefore, no positive attempts were made to identify the dark brown solid from the ozone reaction other than to prove the absence of dimethylaminobenzophenone.

The Grignard reagent from phenylnaphthylbromo-ethylene was also treated with β-pyridylmethyl ketone. A vigorous reaction ensued, and the tetrasubstituted allyl alcohol,  $(C_6H_5)(C_{10}H_7)C{=}CH{-}C(OH)(CH_3)(C_5H_4N)$, was isolated in fair yields. The attempts to dehydrate this compound proved to be less fortunate. Dark colored solids or tars were formed which were quite intractable. The allene, or an isomer of it, may have been formed, but since the purest product obtainable melted over a 10° range, it is not surprising that the analytical data on this material failed to conform to any possible compound.

Experimental Part

Preparation of the Disubstituted Ethylenes.—Phenyl-α-naphthylethylene,[8] phenylmethylethylene[9a] and diphenylethylene[9b] were all prepared by literature methods. Yields in the literature, however, were never stated, and the quantities employed were small. In our work, in which nearly equivalent quantities of the reacting materials were taken, the yields in 100–500 g. lots were 51, 53 and 58%, respectively. Furthermore, the directions were vague relative to the dehydration of the intermediate tertiary alcohols to the desired ethylene by distillation. We found that phenylnaphthylmethyl carbinol was effectively dehydrated in a single distillation, phenyldimethyl carbinol in four distillations and diphenylmethyl carbinol in three.

Phenyl-*p*-anisylethylene.—This compound was prepared by an analogous, but hitherto unreported, method. The reagents used were bromobenzene (165 g.), magnesium (26 g.), *p*-methoxy-acetophenone (148 g.) and ether (400 cc.). After solution of the magnesium and addition of the ketone, the mixture was refluxed for three hours and then set aside overnight. One distillation of the phenylanisylmethyl carbinol at 2 mm., 155–170°, yielded 170 g. of the ethylene, or 81%. This crude material melted at 65–73°. One recrystallization from alcohol changed this melting point to 75°, the value given by Stoermer and Simon,[10] who prepared it from methylmagnesium iodide and *p*-methoxybenzophenone.

For a pure product, our method seems somewhat preferable to Stoermer and Simon's if the *p*-methoxy-acetophenone is to be synthesized by the Friedel and Crafts reaction from anisole.[11] The melting point of the ketone prepared by this method is 61–62° (we confirmed this), whereas 67–68° is its melting point when prepared by a method[12] which excludes any *ortho* isomer as an impurity.

Phenyl-*p*-tolylethylene.—*p*-Bromotoluene, magnesium and acetophenone, taken in molecular proportions, were found to react in a similar manner. Three distillations were essential in the dehydration of the intermediate tertiary alcohol. Phenyl-*p*-tolyl-

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[8] Stoermer and Simon, *Ber.*, **37**, 4167 (1904).

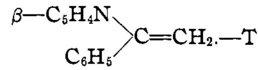
[9] Tiffeneau, *Ann. chim. phys.*, [8] **10**, (a) 153, (b) 359 (1907).

[10] Ref. 8, p. 4166.

[11] Gattermann, *Ber.*, **23**, 1204 (1890).

[12] Ramart-Lucas, *Ann. chim. phys.*, [8] **30**, 397 (1913).

ethylene was collected between 278–294°; yield, 48–60%. Tiffeneau[13] has prepared this compound, without stating the yield, from phenylmagnesium bromide and *p*-methylacetophenone.

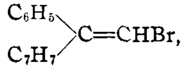
Phenyl-β-pyridylethylene,  $\begin{matrix}\beta\text{—}C_5H_4N\\ C_6H_5\end{matrix}\!\!>C{=}CH_2$.—Twenty-five g. (0.16 mole) of bromobenzene was converted to phenylmagnesium bromide with 4 g. of magnesium. To this was added a solution of 4 g. (0.033 mole) of β-pyridylmethyl ketone in ether (for preparation, see below). A heavy precipitate formed. This mixture was hydrolyzed in the usual way, thereby producing a small amount of dark, strong-smelling tar, which was discarded. Benzene and diphenyl were removed by ether extraction. The aqueous solution was then made alkaline and the product was extracted with ether. After evaporation of the solvent, an oil remained which solidified after a little stirring. This material was quite soluble in most organic solvents save petroleum ether, and no method of recrystallization was found. It was soluble in acids and was reprecipitated by bases. It reduced permanganate in acetone solution, and absorbed bromine in carbon disulfide solution.

Distillation of this material at 22 mm. gave 2.5 g. of the ethylene (42% yield, based on the ketone), which was collected at 200–215°; m. p., 55–77°. Another similar distillation gave a product which boiled at 204–210°, at 23 mm.; the melting point, however, was not improved. This was analyzed. Some of the crude oil, which had not been stirred to induce solidification, was set aside for two weeks. A few crystals separated; these were collected upon a filter and were washed with methanol; m. p., 78–82°.

Anal. Subs., 0.2861: N_2, 18.95 cc. (22°, 745 mm., over 50% KOH). Calcd. for $C_{13}H_{11}N$: N, 7.7. Found: 7.4.

Preparation of Disubstituted Bromo-ethylenes

The syntheses of phenyl-α-naphthylbromo-ethylene,[14] phenylmethylbromo-ethylene,[15] phenylanisylbromo-ethylene[14] and diphenylbromo-ethylene[16] followed the general directions of the literature; yields, 87, 61, 52 and 87%, respectively. In no case was reference made to the yields by the earlier investigators. Instead of collecting phenylanisylbromo-ethylene at 16 mm., we used a higher vacuum and collected it between 175°, at 3 mm., and 184°, at 1 mm.

Phenyl-*p*-tolylbromo-ethylene,  $\begin{matrix}C_6H_5\\ C_7H_7\end{matrix}\!\!>C{=}CHBr$, was prepared from 84 g. of phenyl-*p*-tolylethylene, 350 g. of carbon disulfide and 70 g. of bromine. External cooling was supplied during the half-hour that bromine was added. Heat was then applied for eight hours; hydrogen bromide started to evolve at 30°. After removal of the solvent, phenyl-*p*-tolylbromo-ethylene was collected at 192–210°, at 20 mm. Redistillation gave 63 g. (53%) of material; b. p., 195–202°, at 20 mm. This compound was a light yellow liquid, somewhat more viscid than water. A sample of middle distillate was taken for analysis. The low result is explicable, due to the presence of ditolyl. Ditolyl was undoubtedly formed simultaneously with the formation of the Grignard

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[13] Ref. 9, p. 360.

[14] Ref. 8, p. 4166.

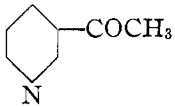
[15] Ref. 9 a, p. 168.

[16] Lipp, *Ber.*, **56**, 569 (1923).

reagent. Since it boils at 295°, at 750 mm., it would not be completely removed either in the distillation of the ethylene or of the bromide.

Anal. Subs., 0.3350: AgBr, 0.2243. Calcd. for $C_{15}H_{13}Br$: Br, 29.3. Found: 28.5.

Preparation of Basic Ketones



β-Pyridylmethyl Ketone, —This ketone has been prepared only by Engler.[17] His method, that of distillation of a mixture of calcium acetate and calcium nicotinate, gave a poor yield. He found that the ketone boiled at 220°, its phenylhydrazone melting at 137° and its oxime at 112°.

We prepared this ketone in 60% yields by hydrolysis of the β-ketonic ester, ethyl nicotino-acetate. Pinner[18] has prepared the α- and γ-pyridylmethyl ketones by an analogous process. He did not describe the preparation of the beta isomer, although he did condense ethyl nicotinate with ethyl acetate, and precipitated the resulting compound as the potassium salt.

Ethyl Nicotino-acetate, $C_5H_4N—CO—CH_2—CO_2C_2H_5$, and its Hydrolysis to β-Pyridylmethyl Ketone.—To a mixture of 117 g. (0.77 mole) of ethyl nicotinate and 90 g. (1.02 moles) of ethyl acetate, free from alcohol, contained in a half-liter flask, 80 g. (1.17 moles) of dry, powdered sodium ethylate was gradually added. The mixture was then set aside for an hour, after which it was heated on the water-bath for one and one-half hours. It was then set aside for three days.

The solid mass was taken up in 550 cc. of distilled water, and was freed from ethyl acetate and ethyl nicotinate by extraction with ether. The solution was then diluted with 1 liter of water and made neutral with 60 cc. of concd. hydrochloric acid. An oil, presumably ethyl nicotino-acetate, appeared at this stage; it was disregarded and redissolved by an additional 240 cc. of hydrochloric acid. For four hours the solution was refluxed; carbon dioxide was evolved. The solution was then made alkaline with potassium carbonate and the β-pyridylmethyl ketone was removed by exhaustive extraction with ether. The ether solution was dried with potassium carbonate. After removal of the ether the residue was distilled; 66 g. (70% yield) was collected between 217° and 221°. The phenylhydrazone, after one recrystallization from alcohol, melted at 134° and 137°.

***p*-Dimethylaminobenzophenone** was prepared in 71–77% yield by a method which will be published in *Organic Syntheses*, volume 7.

***p*-Dimethylamino-acetophenone.**—The existing methods[19] for the preparation of this ketone are very poor. In a search for a better method, we tried the following, all of which failed. (1) The reaction of dimethylaniline, acetanilide and phosphorus oxychloride, with or without benzene or toluene as diluents; only intractable tars were obtained. (2) A Friedel

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[17] Engler and Kiby, *Ber.*, **22**, 597 (1889).

[18] Pinner, *Ber.*, **33**, 1230 (1900); **34**, 4234 (1901).

[19] (a) Weil, *Monatsh.*, **29**, 905 (1908). (b) Ref. 6.

and Crafts method, with dimethylaniline, carbon disulfide, acetic anhydride and aluminum chloride. (3) The oxidation of *p*-dimethylaminophenylmethyl carbinol hydrochloride with potassium permanganate.

A few grams of the ketone was prepared by Staudinger and Kon's method, which had the correct melting point, and which gave a phenylhydrazone with the melting point given by Weil. However, the boiling point was observed to be 172–175°, at 11 mm., instead of 108–110°, at 12 mm., the value reported by Staudinger and Kon. Analysis confirmed the fact that our compound was *p*-dimethylamino-acetophenone.

Anal. Subs., 0.2120, 0.2971: N_2, 17.2 cc. (26°, 751 mm.), 24.0 cc. (25°, 740 mm.) (over 50% KOH). Calcd. for $C_{10}H_{13}ON$: N, 8.6. Found: 8.99, 8.93.

***p*-Dimethylaminophenylmethyl Carbinol,** mentioned above, was prepared in 85% yield (crude) from magnesium *p*-bromodimethylaniline and an excess of acetaldehyde. This has been made heretofore,[20] only by the action of methylmagnesium iodide on *p*-dimethylaminobenzaldehyde.

Preparation of Grignard Reagents from Disubstituted Bromo-ethylenes, and Their Reaction with Basic Ketones

1. With Phenyl-α-naphthylbromo-ethylene, Magnesium and *p*-Dimethylaminobenzophenone.—The magnesium dissolved with great reluctance. Baeyer's "activated magnesium" was even less satisfactory, and practically no reaction was observed in a sealed-tube experiment with ordinary magnesium turnings maintained at 95° for two days.

A mixture of 32 g. of phenyl-α-naphthylbromo-ethylene, 3 g. of magnesium turnings (Eastman), a little iodine and butyl bromide was placed in 100 cc. of dry ether. This was refluxed for three days. A fairly large amount of magnesium disappeared and a small quantity of a brown precipitate, probably *diphenyldinaphthyl butadiene,* was noticed. This Grignard solution was poured into a warm solution of 14 g. of dimethylaminobenzophenone (60% of the calculated amount) in 300 cc. of dry ether. A yellow precipitate formed. The mixture was stirred and refluxed for two hours. Then 150 g. of dry benzene was added,[21] the ether was distilled from the mixture and the benzene solution refluxed for several hours. The mixture was hydrolyzed, extracted with ether, and the ether dried and evaporated. A sticky, purple tar was obtained which resisted all attempts at crystallization; it dissolved in acetic acid to give a purple solution.

Finally, the plan of vacuum distillation (at 5 mm., bath temp., 280°) was adopted. The distillate, which weighed about 10 g., proved to be a mixture of phenylnaphthylethylene, phenylnaphthyl bromo-ethylene and dimethylaminobenzophenone. The residue weighed 18 g. and no longer gave a purple color in acetic acid solution, but instead developed a brown color. Since neither the ethylene derivative, the bromide nor

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[20] Sachs and Sachs, *Ber.*, **38**, 512 (1905).

[21] When ether was retained as solvent, the yields were much smaller, and the product seemed almost incapable of purification. Similar treatment to that which is described for the benzene procedure yielded a light brown solid which gave a poor melting point, between 90° and 100°. Analytical values were as follows: C, 90.5, 89.5, 89.9; H, 5.6, 5.5, 5.5; N, 1.3, 1.2%; mol. wt., 521. These values seem to fit no possible compound.

the ketone produce purple solutions in acetic acid, it is evident that some change occurred.

An Isomer of 1,3-Diphenyl-1-α-naphthyl-3-*p*-dimethylaminophenyl-allene, $C_{10}H_7—C(C_6H_5)=C=C(C_6H_5)—C_6H_4N(CH_3)_2$.—The 18 g. of solid was dissolved in hot acetic acid, the solution filtered and the solute precipitated by water. It was then collected on a filter. When dry, it was refluxed for a few hours with a mixture of 350 g. of acetyl chloride and 350 g. of acetic anhydride. The solute was again precipitated by water and was purified by the acetic acid method. When dried in a vacuum desiccator, there was obtained 10 g. of a light brown solid. This was suspended in 250 cc. of warm, dry ether for ten minutes and the solution was filtered. The ether was allowed to evaporate, the final portion being taken off in a vacuum desiccator. The material puffed up in the desiccator and formed beautiful, bronze-colored leaves which were really broken bubbles; 6.5 g. of this solid was obtained. The melting point was difficult to determine, but it seemed between 94° and 105°.

Anal. Subs., 0.3145, 0.3426: N_2, 9.0 cc. (25°, 745 mm.), 9.6 cc. (25°, 746 mm.) (over 50% KOH). Calcd. for $C_{33}H_{27}N$: N, 3.2. Found: 3.16, 3.1.

Subs., 0.2027, 0.2217: CO_2, 0.6672, 0.7242; H_2O, 0.1137, 0.1229. Calcd. for $C_{33}H_{27}N$: C, 90.6; H, 6.4. Found: C, 89.8, 89.1; H, 6.23, 6.16.

Mol. wt. Subs., 0.4248, in 20 cc. of C_6H_6: Δt, 0.279°. Calcd. for $C_{33}H_{27}N$: mol. wt., 437. Found: 445.

The analysis, molecular weight, reactions and method of preparation indicate that the allene, or more probably its isomer, was obtained in a slightly impure form. This compound shows no halochromism as aromatic allenes do. It will be recalled that before the vacuum distillation, halochromism seemed to be shown. Isomerization seems to have occurred when the oils were distilled from the solids. At this time, the temperature of the bath was 280°. Furthermore, there are two other places where isomerization could have taken place, namely, the contact with hot acetic acid or with acetyl chloride.

Reaction with Ozone.[22]—About 2 g. of the substance was dissolved in carbon tetrachloride, and oxygen containing about 8% of ozone was passed through the solution for about eight hours. Yellow crystals formed which were not removed. The solvent was evaporated in a vacuum, and a brown solid remained. Part of it was hydrolyzed by placing it in a distilling flask with 30 cc. of water, and then distilling off all of the water. The escaping gases were forced through lime water, but no turbidity was noticed, therefore carbon dioxide was absent.

The rest of the ozonide was boiled with 50 cc. of water until only about 15 cc. remained. The dark brown product was then extracted with 2 *N* hydrochloric acid for 12 hours. After filtration, the filtrate was made alkaline. No precipitate formed, nor did the solution contain any material which could be extracted with ether, therefore dimethylaminobenzophenone was absent.

The product from this hydrolysis was a dark brown solid; m. p., 70–90°. No effort was made to identify it further.

To **ascertain how much Grignard reagent** might be anticipated in the reaction of magnesium with phenyl-α-naphthylbromo-ethylene, the contents of a similar run from 10 g. of the latter, 1 g. of magnesium and 50 cc. of dry ether (three and one-half days' refluxing) were analyzed by the method recommended by Gilman.[23] The principle of the method is the titration

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[22] The ozonides were prepared by Mr. L. U. Spence in the Research Laboratory of the Westinghouse Electric and Manufacturing Co., East Pittsburgh, Pa. We gratefully acknowledge this assistance.

[23] Gilman and others, THIS JOURNAL, **45**, 150 (1923).

of the basic magnesium halide formed in the hydrolysis of the Grignard solution; the results are reported to come uniformly high. It was found impracticable to siphon it as Gilman advised; furthermore, the consistency of this mixture would not allow ordinary filtration without undue exposure to the air.

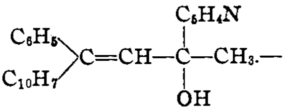
The solution was diluted to 100 cc. with dry ether and 25cc. portions were pipetted into a mixture of 50 cc. of water and 50 cc. of 0.5749 *N* acid. The solutions were warmed at 60° until clear, and the excess of acid was titrated with standard alkali, using methyl orange as the indicator; the end-point was poor. The three samples required, respectively, 10.43, 9.21 and 10.58 cc. of standard acid, an average of 71% of Grignard reagent. It will be noticed that the checks are poor, the error being over one part in ten. Very probably, 71% is far in excess of the true amount of Grignard reagent present in the solution. The discrepancy is easily explained by the fact that the precipitates probably contained basic magnesium compounds, and perhaps even metallic magnesium.

2. With Phenyl-α-naphthylbromo-ethylene, Magnesium-Copper Turnings and β-Pyridylmethyl Ketone.—A commercial alloy of magnesium and copper (12.75% of copper) was dissolved much more quickly than magnesium itself. Instead of taking half a week, the reaction was complete in a few hours.

Run 1.—The Grignard reagent in this case was prepared from 3 g. of the alloy turnings, 35 g. of phenylnaphthylbromo-ethylene and 60 g. of dry ether, together with a little iodine and ethyl bromide as catalysts. It was treated with 7.5 g. of ketone in 35 g. of ether. The mixture became nearly solid, but it was refluxed for two hours; the ether was then distilled away and 130 g. of dry benzene was added. Refluxing was resumed for five hours more, and the solution was then set aside overnight. A gummy solid precipitated on hydrolysis. Nothing remained in the water or the benzene layers. The solid could not be crystallized, so it was dissolved in 100 cc. of acetic anhydride and heated for two hours at 95°. The solution was filtered hot, diluted with water and made alkaline. The solid precipitate was collected upon a filter and, when dry, was dissolved in absolute ether. This solution was filtered from some dark, insoluble material, and then evaporated. Four g. of a dark colored, low-melting solid was obtained, which was dissolved in carbon tetrachloride and ozonized for eight hours. This ozonide was treated like the other; no β-pyridylmethyl ketone was found in the products of hydrolysis, which indicated that the allene, as such, was absent in the low-melting solid.

Run 2.—A Grignard solution was similarly made from 45 g. of the bromide. To it was added 11 g. of the ketone (63% of the equivalent amount). Again the mixture nearly solidified. Refluxing was continued for five hours, and benzene was not added as it was in Run 1. The mixture was allowed to stand overnight and was hydrolyzed with ice, water and hydrochloric acid. A slight amount of gummy solid formed which was discarded. When the ether and the aqueous layers were shaken together, a brownish-yellow precipitate resulted. It was filtered and washed with dilute alkali, the color becoming lighter; yield, 9.5 g., or 30%, based on the ketone.

Phenyl-1-α-naphthyl-1-β-pyridyl-3-butene-1-ol-3,



$$(C_6H_5)(C_{10}H_7)C{=}CH{-}C(C_6H_4N)(OH){-}CH_3.—$$

This solid seemed nearly pure since it melted sharply at 159–161°. Attempts to purify it further by crystallization, precipitation or evaporation of solutions were ineffectual.

Therefore, for analysis, a portion of it was dissolved in warm absolute ether and filtered from any foreign matter. This solution was evaporated in a vacuum.

The solid was quite soluble in methyl, ethyl and butyl alcohols and in ethyl acetate, very soluble in pyridine, less soluble in pure acetone than in ordinary acetone, slightly soluble in xylene and ether, and insoluble in petroleum ether, carbon tetrachloride and water. It dissolved in acetic anhydride and was reprecipitated by alkalies. It gave a wine-colored solution with sulfuric acid, changing to brown as it was warmed.

Anal. Subs., 0.1925, 0.1555: CO_2, 0.6030, 0.4881; H_2O, 0.1132, 0.0882. Calcd. for $C_{25}H_{21}ON$: C, 85.42; H, 6.03. Found: C, 85.43, 85.62; H, 6.53, 6.30.

Attempted Dehydration to the Allene.—Attempts to prepare the allene by heating this "vinyl carbinol" to 160–170° gave a dark mass that could not be purified. Acetic anhydride, however, gave a more promising product.

Three and one-half g. of the solid was dissolved in 100 cc. of acetic anhydride. This solution was kept at 98° for one hour and then was filtered hot. Distilled water was added and the solution made alkaline; a dark solid separated on cooling. This was washed with water and dried; m. p., 55–75°. It dissolved easily in methyl, ethyl, *n*-butyl- and *tert.*-butyl alcohols, in acetic acid, ethyl acetate, ether, benzene and xylene, but was insoluble in petroleum ether and water. No purification could be effected by crystallization, or by partial precipitation from solution.

For analysis, 2.2 g. of material was dissolved in absolute ether and the solution filtered from a dark, insoluble portion. A light colored solid, which decolorized an acetone solution of potassium permanganate to some extent, remained when the ether was evaporated.

Anal. Subs., 0.2193, 0.2105: CO_2, 0.6817, 0.6537; H_2O, 0.1276, 0.1180. Found: C, 84.76, 84.69; H, 6.46, 6.23.

These values did not fit any possible compound. An attempt at further purification was made. The solid was dissolved in acetic acid, filtered and precipitated with alkali. This solid was filtered off and was then placed in a liter of distilled water for a day. It was collected on a filter, dried, dissolved in ether, filtered and again left as a residue by evaporation of the ether in a vacuum. Very light colored flakes were obtained; m. p., 45–55°. Obviously, this was still a mixture, but analyses were made which, as before, did not fit any possible compound.

Anal. Subs., 0.1746, 0.2005: CO_2, 0.5466, 0.6266; H_2O, 0.1015, 0.1147. Found: C, 85.38, 85.23; H, 6.46, 6.36.

Mol. wt. Subs., 0.3645, in 20 cc. of C_6H_6: Δt, 0.287°. Found: mol. wt., 372.

Anal. Subs., 0.4120 (recovered from mol. wt. detn.): N_2, 17.65 cc. (26°, 747 mm., over 50% KOH). Found: N, 4.74.

In Table I are given the calculated values for analyses and molecular weights of the allene or of possible addition products.

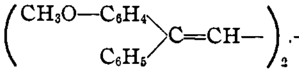
TABLE I

CALCULATED ANALYSES AND MOLECULAR WEIGHTS

	C, %	H, %	N, %	Mol. wt.
Allene, or isomer	90.09	5.71	4.20	333
Allene + H_2O	85.42	6.03	4.00	351
Allene + CH_3CO_2H	82.44	5.85	3.53	391
Allene + ether	85.50	7.13	3.44	407

3. With Phenyl-*p*-anisylbromo-ethylene, Magnesium and β-Pyridylmethyl Ketone.—Three g. of magnesium, 29 g. of the bromide, 70 g. of ether and the usual catalysts were refluxed for one hour. The mixture was cooled and filtered[24] into standard acid and analyzed for the Grignard reagent by Gilman's method. The fairly large amount of solid was placed in another portion of standard acid. The ether was evaporated, and each solution heated until clear. Then each was back-titrated with standard alkali. A total of 58.00 cc. of 0.5754 *N* acid was required, which indicated a 33.3% yield of Grignard reagent. When the Grignard solution was prepared by three hours' refluxing, the yield dropped to 7.6%.

1,4-Diphenyl-1,4-di-*p*-anisyl Butadiene-1,3,



$$\left(\begin{array}{l}CH_3O-C_6H_4\\ C_6H_5\end{array}>C{=}CH-\right)_2$$

.—About 5% of the phenyl-*p*-anisylbromo-ethylene, and as much as 9.5% in other runs, underwent a modified Wurtz reaction to form diphenyldianisyl butadiene, a new substance. It was present in the portion that was insoluble in ether, and it remained as a yellow solid after treatment with water. It was filtered off and washed with ether; weight, 1 g. This was recrystallized from 150 cc. of ethyl acetate; about 0.6 g. of crystals resulted; m. p., 215–217°. Another crystallization yielded a small sample of light yellow needles; m. p., 218.5–219.5° (uncorr.). The 215–217° material was analyzed. It was found to be insoluble in ether, petroleum ether, cold ethyl acetate and hot or cold alcohol. The solubility in ethyl acetate was found to be immensely augmented by the presence of impurities.

Mol. wt. Subs., 0.1335, in 20 cc. of C_6H_6: Δt, 0.093°. Calcd. for $C_{30}H_{26}O_2$: mol. wt., 418. Found: 420.

Anal. Subs., 0.1712, 0.1982: CO_2, 0.5442, 0.6260; H_2O, 0.0985, 0.1119. Calcd. for $C_{30}H_{26}O_2$: C, 86.1; H, 6.2. Found: C, 86.7, 86.2; H, 6.4, 6.2.

A solution of this butadiene in carbon disulfide decolorized a solution of bromine in the same solvent. Further proof of its structure was obtained by oxidizing it to phenyl-*p*-anisyl ketone. This was accomplished by heating 0.5 g. of it in 100 cc. of glacial acetic acid with 0.5 g. of chromic anhydride for 30 minutes. Water was added and the acid neutralized. The solution was then extracted with ether. On evaporation of the ether, a small amount of oil was obtained which formed a phenylhydrazone, m. p. 165–171°, and a *p*-nitrophenylhydrazone. The latter, after recrystallization from methanol, melted at 184–192°. The *p*-nitrophenylhydrazone of a known sample of phenyl-*p*-anisyl ketone was prepared and was found to melt at 187–192°.

Reaction of Phenyl-*p*-anisylvinylmagnesium Bromide with the Ketone Base.—For this experiment, the Grignard solution was prepared from 6 g. of magnesium and 50 g. of the bromide. The cooled solution was filtered from undissolved solid, largely diphenyldianisyl butadiene, through a pinhole into an ether solution which contained 5 g. (20% of the calculated amount) of β-pyridylmethyl ketone. A yellow solid separated. The mixture was stirred and refluxed for two hours, and then was set aside overnight. It was hydrolyzed with dilute acid and ice, and was repeatedly extracted with ether to free it from some unused bromo-ethylene, some of the butadiene and about 1.5 g. of phenylanisylethylene.

The acidic solution (aqueous) was made alkaline and the basic compounds therein were extracted with ether. About 3 g. of a light colored oil was obtained in this manner. Color reactions with acids indicated the presence of the desired allene or of its parent vinyl carbinol, but no effective means of purification was found. This oil dissolved in concd. hydrochloric acid with formation of a reddish-brown color which rapidly changed to brown. Dil. hydrochloric acid formed a slightly milky solution; concd. sulfuric acid formed a red solution and acetic acid a green solution.

4. With Phenyl-*p*-tolylbromo-ethylene, Magnesium-Copper Turnings and β-

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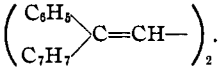
[24] For purposes of rapid filtration, a pinhole was made in the paper.

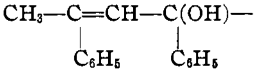
Pyridylmethyl Ketone.—A mixture of 20.5 g. of the bromide, 2.5 g. of the turnings, a little iodine and ethyl bromide and 40 g. of absolute ether was heated for one hour. Analysis of a duplicate run, after pinhole filtration, revealed a 51.7% yield, since 67.43 cc. of 0.5754 *N* acid was neutralized.

Three attempts were made to cause this solution to react with β-pyridylmethyl ketone. No precipitate was formed in any case. In the first case, the mixture was refluxed for some time, allowed to stand overnight and was hydrolyzed. In the second and third cases, after refluxing the ether solution, the ether was distilled off, dry benzene was added and refluxing was resumed for some time. In none of these cases could any reaction product be isolated.

1,4-Diphenyl-1,4-di-*p*-tolyl Butadiene-1,3,  $\left(\begin{matrix}C_6H_5\\C_7H_7\end{matrix}\!>\!C{=}CH\text{—}\right)_2$.—When magnesium turnings were used instead of the magnesium-copper alloy, only a 4–6% yield of Grignard reagent was obtainable, and there was observed a small amount of yellow solid, insoluble in the ether. This was not observed in the run with the alloy. Because of its similarity to the other butadienes which have been mentioned, this substance was also regarded as a member of that series. This was confirmed by a molecular-weight determination. The material was recrystallized from ethyl acetate; weight, less than 0.1 g.; m. p., 207–210°. The percentage of carbon and hydrogen was not determined because of an accident to the combustion furnace while the analysis was in progress.

Mol. wt. Subs., 0.0792, in 20 cc. of C_6H_6: Δt, 0.060°. Calcd. for $C_{30}H_{26}$: mol. wt., 386. Found: 387.

5. The Grignard Reagent from Phenylmethylbromo-ethylene.—When a mixture of 8 g. of magnesium, 31 g. of the bromide, 30 g. of dry ether and a few crystals of iodine was warmed, a brisk reaction soon started. When this subsided, the solution was refluxed for one hour. Two similar runs were refluxed for two hours and for 20 hours. A white precipitate of diphenyldimethyl butadiene, m. p. 134–136°, which had formed (1.5 g.) was removed by filtration. Analysis of the mixture was performed by hydrolysis and fractional distillation of the products of the reaction. The yields of Grignard reagent in the three cases, based on the amount of phenylmethylethylene collected, were 17, 14 and 11%, respectively. Simultaneously there were produced 5, 8 and 11% of phenyl-1-propene-1; 11, 8 and 11% of phenylmethylacetylene; and 49, 47 and 53% of solids. These solids were shown to consist very largely of the butadiene.

This bromide was absolutely unsatisfactory for our purposes, so was abandoned. Evidence of a similar nature was furnished in the attempted preparation of *diphenyl-2,4-pentene-3-ol-2*,  $CH_3\text{—}\underset{C_6H_5}{C}{=}CH\text{—}\underset{C_6H_5}{C}(OH)\text{—}CH_3$, by the interaction of the reaction product of magnesium and phenylmethylbromo-ethylene with an equivalent part of acetophenone. Dimethyldiphenyl butadiene was the only crystalline compound found. Three fractionations (to 230°) of the liquid reaction products in a vacuum of 1 mm. gave no material that distilled constantly.

6. The Grignard Reagent from Diphenylbromo-ethylene.—In the first of the two runs that were performed, a mixture of 15.5 g. of diphenylbromo-ethylene, 2.5 g. of magnesium, a little iodine and ethyl bromide was refluxed in ether for 75 minutes. Reaction started without heating, and the reaction was almost as vigorous as with bromobenzene. A very little white precipitate of the butadiene was formed. A Gilman analysis used 76.87 cc. of 0.5754 *N* acid, which indicated a 73.9% yield of Grignard reagent. As a little loss of solution occurred before back-titration with base, the test was repeated. With 20.5 g. of bromide, 3.5 g. of magnesium and the usual catalysts, the analysis required 93.60 cc. of 0.5754 *N* acid. This represented a 68% yield of Grignard reagent.

Summary

A systematic attempt has been made to synthesize certain asymmetric allenes containing a basic nitrogen atom in the molecule. Ultimately in the synthesis, the plan was to dehydrate a tetrasubstituted allyl alcohol, $RR'C{=}CH{-}C(OH)RR'$, in which one R group contained a basic nitrogen atom.

Satisfactory preparations are indicated for the ethylenes of the general formula $RR'C{=}CH_2$, and for the corresponding bromo-ethylenes, $RR'C{=}CHBr$, where "RR'" represents phenyl-α-naphthyl, phenylmethyl, phenyl-*p*-anisyl, phenyl-*p*-tolyl, phenyl-β-pyridyl and biphenyl. In general, the ethylenes were prepared by the thermal decomposition of the corresponding tertiary alcohols, and the bromo-ethylenes by the thermal decomposition of the corresponding dibromides. The methods for the preparation of phenylanisyl- and of phenyltolylethylene are new; phenyl-β-pyridylethylene and phenyl-*p*-tolylbromo-ethylene are new compounds.

A study was made of the reactions of these vinyl bromides with magnesium. Except with diphenylbromo-ethylene, the yields of the Grignard reagents were low. An important competing reaction was a modified Wurtz synthesis giving butadienes. Diphenyl-di-*p*-anisyl butadiene and diphenyl-di-*p*-tolyl butadiene were discovered in this way. Decidedly better yields of the Grignard reagent were obtained when a magnesium-copper alloy was used in place of magnesium.

p-Dimethylaminobenzophenone and β-pyridylmethyl ketone were employed as intermediates. The latter compound is new; it was synthesized in 70% yield from ethyl nicotinate. A good method of preparation for *p*-dimethylamino-acetophenone was not found, but it was discovered that its boiling point is about 65° higher than the value given in the literature by Staudinger and Kon.

Reactions of the diarylvinylmagnesium bromide solutions with the ketone bases gave tarry products that were exceedingly uninviting. No allenes were isolated in a state of purity, but an isomer of diphenyl-α-naphthyl-dimethylaminophenyl-allene was obtained. The structure of this isomer is discussed. The pure, tetrasubstituted allyl alcohol, from which phenylnaphthylmethylpyridyl-allene would be derived, was isolated, but it could not be satisfactorily dehydrated to the allene. The reaction product from phenylanisyl bromo-ethylene, magnesium and pyridylmethyl ketone was an oil which exhibited halochromism. This oil may have been the desired allene, or its parent vinyl carbinol, but it could not be purified.

For some reason the Grignard solution from phenyl-*p*-tolylbromo-ethylene and magnesium-copper turnings failed to react with β-pyridylmethyl ketone, although it apparently reacted with acetophenone. Due to many side reactions in the formation of its Grignard reagent, phenylmethylbromo-ethylene was found to be useless as an intermediate in allene syntheses.

EVANSTON, ILLINOIS

[CONTRIBUTION FROM THE LABORATORY OF ORGANIC CHEMISTRY OF THE STATE UNIVERSITY OF IOWA]

ACETYLBENZOYL DERIVATIVES OF 2-AMINO-7-HYDROXYNAPHTHALENE

BY L. CHAS. RAIFORD AND WILLIAM F. TALBOT

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In studies designed to test the configuration of naphthalene and diphenyl, Kaufler[1] and collaborators found that the behavior of certain naphthalene derivatives indicates that Positions 2,6 and 2,7 are more closely related than the plane-surface formula suggests. Thus, the conversion of 2,7-naphthalene-disulfonic acid completely into the 2,6 acid by long heating was interpreted to mean that these substituents render each other labile and that the effect indicates that radicals in Position 2,7 are more closely related than in the 2,6 isomer. Kaufler and Karrer[2] found that when 2,7-diaminonaphthalene reacts with chlorodinitro- and chlorotrinitrobenzene, respectively, but one amino radical is involved. They were able to diazotize only one amino radical,[3] and argued that these results, taken in connection with the formation of a monophthalylnaphthalenediamine could best be explained by a formula which requires the two rings of naphthalene to lie in different planes. Although the rate of hydrolysis of 2-carboxy-7-cyanonaphthalene[4] indicated that these positions are comparable with the *meta* relationship in a benzene derivative, which might suggest in advance that the migration of acyl between nitrogen and oxygen, which is characteristic of acetylbenzoyl derivatives of *o*-aminophenols, would not occur here, it was a matter of interest to us to examine the behavior of such a compound obtained from 2,7-aminonaphthol, because of the rearrangement observed by Raiford and Clark[5] when 8-acetylamino-1-naphthol was benzoylated. The argument of Huggins[6] to the effect that acenaphthene and naphthalic

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[1] Kaufler, *Ber.*, **40**, 3250 (1907); *Ann.*, **351**, 151 (1907).

[2] Kaufler and Karrer, *Ber.*, **40**, 3262 (1907).

[3] This failure to diazotize the second group was probably due to experimental conditions rather than to steric hindrance, in that the reaction may occur in two stages, producing an intermediate aminodiazonium salt that is insoluble in the medium used. Morgan and Micklethwait [*J. Chem. Soc.*, **97**, 2558 (1910)] carried out the experiment in a medium different from that used by Kaufler and Karrer and succeeded in obtaining a bisdiazonium salt.

[4] Kaufler and Thien, *Ber.*, **40**, 3257 (1907).

[5] Raiford and Clark, THIS JOURNAL, **48**, 483 (1926).

[6] Huggins, *ibid.*, **44**, 1615 (1922).