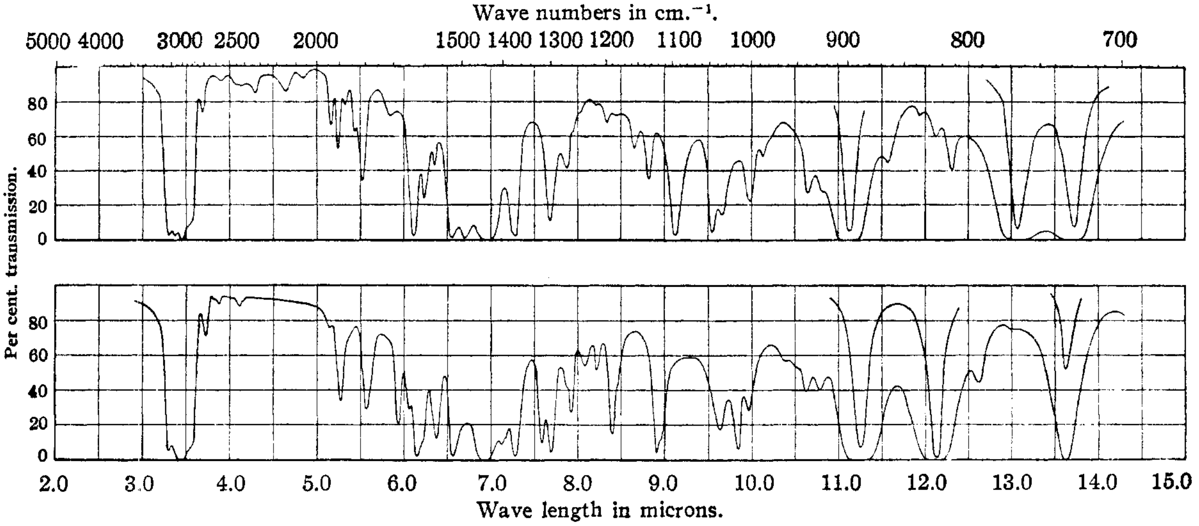

Fig. 2.—Infrared spectra of 1-methyl-2-isopropenylbenzene (upper curve) and 1-methyl-4-isopropenylbenzene (lower curve). Cell lengths, 0.1 mm. and 0.01 mm. in each case.

## Experimental

Ultraviolet absorption measurements were made with a Beckman Spectrophotometer, model DU with ultraviolet accessories. Iso-octane, purified by passage through a column of silica gel, was used as solvent. The infrared spectra were obtained on a recording spectrophotometer made by the Gaertner Scientific Corp., very similar, optically, to the instrument described by McAlister.[4]

The 1-methyl-4-isopropenylbenzene boiled at 83° at 18.5 mm.

The 1-methyl-2-isopropenylbenzene boiled at 172–173° at 760 mm. This olefin was reduced by hydrogen at 40 atmospheres at 25° in a rotating autoclave in the presence of UOP nickel on kieselguhr.

**Acknowledgment.**—Samples of the hydrocarbons were furnished by Dr. Herman Pines of this Laboratory. His cooperation is hereby gratefully acknowledged.

## Summary

The ultraviolet absorption spectrum of *p*-methylisopropenylbenzene resembles that of styrene while the spectrum of the ortho isomer does not have the expected maximum near 250 mμ. This difference can be accounted for on the basis that in the ortho compound there is steric interference with the resonance between the benzene ring and the olefinic group in the side chain. A similar conclusion is reached by comparison of the infrared spectra of the two compounds.

RIVERSIDE, ILLINOIS RECEIVED JUNE 21, 1948

(4) McAlister, Matheson and Sweeney, *Rev. Sci. Instruments*, **12**, 314 (1941).

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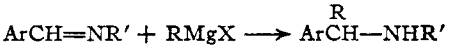
[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF NOTRE DAME]

# The Reaction of Grignard Reagents with Schiff Bases[1]

BY KENNETH N. CAMPBELL, C. H. HELBING,[2] M. PATRICIA FLORKOWSKI[3] AND BARBARA K. CAMPBELL[4]

Some years ago we became interested in preparing amines of the type ArCH(R)–NHR′. Compounds of this type are not readily available by the conventional methods for making secondary amines. The Leuckart reaction with substituted formamides can be used, but the yields are low.[5] The reaction of 1-aryl-1-halo-alkanes with primary amines can also be used, but here also the yields are frequently low, as halides of this type tend to form olefins in the presence of basic reagents. The most feasible synthesis of amines of this type seemed to be the reaction of a Grignard reagent with the Schiff base formed from an aromatic aldehyde and an aliphatic primary amine


$$\mathrm{ArCH{=}NR' + RMgX \longrightarrow Ar\overset{R}{C}H{-}NHR'}$$

At the time this work was started, very little information had been published on this reaction. Busch and Leefheim[6] had synthesized a few amines in this way, and Grammaticakis[7] had also used the reaction to some extent.

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(1) This paper was presented before the Medicinal Division at the Chicago A. C. S. meeting, April, 1948.

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(5) Goodson, Weigand and Splitter, THIS JOURNAL, **68**, 2174 (1946).

(6) Busch and Leefheim, *J. prakt. Chem.*, **77**, 20 (1908).

(7) Grammaticakis, *Compt. rend.*, **207**, 1224 (1938).

Recently, Moffett and Hoehn[8] have prepared a large series of amines by this reaction. The present work was completed before the appearance of Moffett and Hoehn's paper, but to a considerable extent it supplements their work. They used but one Grignard reagent, benzylmagnesium chloride, on the aldimines from a wide variety of substituted benzaldehydes; most of their work was done on methyl and ethylimines. We have used several Grignard reagents on the imines from benzaldehyde and methyl, ethyl, propyl, butyl and benzylamines.

TABLE I

EFFECT OF STRUCTURE ON YIELDS OF AMINES

Equimolar Quantities of Aldimine and Grignard Reagent

| Aldimine | Grignard | Yield, % |
|---|---|---|
| $C_6H_5CH{=}N{-}Me$ | Et | 75 |
| | *n*-Pr | 66 |
| | *i*-Pr | 60 |
| $C_6H_5CH{=}N{-}Et$ | Et | 39 |
| | *n*-Pr | 40 |
| | *n*-Bu | 37 |
| | Benzyl | 74 |
| $C_6H_5CH{=}N{-}Pr$ | Et | 27 |
| | Phenyl | 25 |
| $C_6H_5{-}CH{=}N{-}Bu$ | Et | 30 |
| | Phenyl | 27 |

TABLE II

PHYSICAL CONSTANTS OF ALDIMINES, $C_6H_5CH{=}NR$

| R | B. p. °C. | Mm. | $n^{20}_D$ | $d^{20}_4$ | $MR_D$ obs. | $MR_D$ calcd. | Reference |
|---|---|---|---|---|---|---|---|
| Me | 68–69 | 20 | 1.5519 | 0.9617 | 39.6 | 38.5 | *a* |
| Et | 98–99 | 28 | 1.5397 | .9365 | 44.6 | 43.2 | *b* |
| *n*-Pr | 101–102 | 18 | 1.5302 | .9183 | 49.5 | 47.8 | *a* |
| *n*-Bu | 128–131 | 25 | 1.5249 | .9021 | 54.8 | 52.4 | *c* |
| Benzyl | 158 | 6 | 1.5955 | 1.0382 | 63.9 | 62.7 | *d* |

[a] Zaunschirm, *Ann.*, **245**, 281 (1888); [b] Auwers and Ottens, *Ber.*, **57**, 446 (1924); [c] Stein and Day, THIS JOURNAL, **64**, 2569 (1942); [d] Auwers and Wunderling, *Ber.*, **65**, 70 (1932); Mignonac, *Ann. chim.*, [11] **2**, 225 (1934).

Our results, together with those of Moffett and Hoehn, show that the reaction is capable of wide application; it can be used with hydroxy and alkoxy substituted benzaldehydes and with many Grignard reagents and primary aliphatic amines. Busch and Leefheim[6] used the Grignard reagent and aldimine in equimolar amounts; we have found that this is satisfactory only with the most reactive Grignard reagents (*e. g.*, methylmagnesium bromide) and the simplest Schiff base, benzylidene methylamine. With higher Grignard reagents, and especially with larger alkyl groups on the nitrogen atom, it is necessary to use an excess of the Grignard reagent in order to obtain satisfactory yields of the amine. The influence of structure on the yields of amine, where equimolar quantities of reactants were used, are shown in Table I.

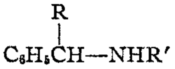
We had hoped to prepare a series of acetylenic amines by this reaction, using the Grignard reagents derived from mono-alkylacetylenes. The acetylenic Grignard reagents are not very reactive, however, and we were unable to obtain any addition to the carbon–nitrogen double bond. The only product that could be isolated analyzed for a dimer of the original aldimine. At present we can offer no explanation for this dimerization, or any structure for the product, except that it appears to be a diamine which forms a stable dihydrochloride.

## Experimental

**Preparation of Aldimines.**—These were prepared by adding one mole of the primary amine to one mole of redistilled aldehyde, with shaking and cooling in an ice-bath. The mixture was allowed to stand for one to two hours, ether was added and the water layer removed. The ether solution was dried over magnesium sulfate and distilled in vacuum. The yields were usually 80–90%. All of the aldimines used in this work have been prepared before, but not all of the physical constants have been reported. These are summarized in Table II.

TABLE III

PHYSICAL CONSTANTS OF AMINES



$C_6H_5CH(R){-}NHR'$

| R | R' | B. p. °C. | Mm. | $n^{20}_D$ | $d^{20}_4$ | $MR_D$ obs. | $MR_D$ calcd. | Nitrogen, % Found | Nitrogen, % Calcd. |
|---|---|---|---|---|---|---|---|---|---|
| *n*-Pr | Me | 100–102 | 15 | 1.5030 | 0.9076 | 53.18 | 53.34 | 8.62 | 8.58 |
| *i*-Pr | Me | 108–109 | 28 | 1.5048 | .9168 | 52.8 | 53.34 | 8.43 | 8.58 |
| Et | Et[a] | 98–100 | 17 | 1.4996 | .9024 | 53.17 | 53.34 | | |
| *n*-Pr | Et | 75–76 | 6 | 1.4966 | .8894 | 57.94 | 57.96 | 7.90 | 7.90 |
| *n*-Bu | Et | 106–108 | 9 | 1.4940 | .8914 | 62.48 | 62.58 | 7.20 | 7.32 |
| Benzyl | Et | 143–144 | 3 | 1.5559 | .9895 | 73.18 | 72.83 | 6.30 | 6.22 |
| Et | *n*-Pr | 108–109 | 15 | 1.5013 | .8948 | 58.40 | 57.96 | 7.83 | 7.90 |
| $C_6H_5$ | *n*-Pr | 144–146 | 3 | 1.5616 | | | | 6.33 | 6.22 |
| Et | *n*-Bu | 137–139 | 28 | 1.4944 | .8926 | 62.44 | 62.58 | 7.28 | 7.32 |
| $C_6H_5$ | *n*-Bu | 151–155 | 3 | 1.5537 | | | | 5.97 | 5.85 |
| Et | Benzyl[b] | 153–154 | 6 | 1.5531 | .9918 | 72.71 | 72.83 | 6.28 | 6.22 |

[a] Previously reported by Busch and Leefheim.[6] [b] Previously reported by Grammaticakis.[7]

**Preparation of Amines.**—A typical procedure is as follows: To one mole of *n*-propylmagnesium bromide in 250 ml. of dry ether was added a solution of 66.5 g. (0.5 mole) of benzylidene ethylamine in 50 ml. of dry ether, over a period of one and one-half to two hours; the reaction mixture was refluxed for several hours and allowed to stand overnight. It was hydrolyzed by pouring onto ice and hydrochloric acid, the ether layer was separated and the aqueous layer extracted with ether. These ether solutions

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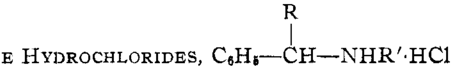
(8) Moffett and Hoehn, THIS JOURNAL, **69**, 1792 (1947).

TABLE IV

AMINE HYDROCHLORIDES, 

$C_6H_5—CH(R)—NHR'\cdot HCl$

| R | R' | M. p., °C. | Chlorine, % Found | Chlorine, % Calcd. |
|---|---|---|---|---|
| *n*-Pr | Me | 150 (dec.) | 18.0 | 17.8 |
| *i*-Pr | Me | 164–165 (dec.) | 17.8 | 17.8 |
| *n*-Pr | Et | 180 (dec.) | 16.7 | 16.6 |
| *n*-Bu | Et | 170 (dec.) | 15.7 | 15.6 |
| Benzyl | Et | 235–236 (dec.) | 14.2 | 13.6 |
| Et | *n*-Pr | 184 (dec.) | 16.8 | 16.6 |
| Phenyl | *n*-Pr | 233–234 (dec.) | 13.4 | 13.6 |
| Et | *n*-Bu | 198–199 (dec.) | 16.1 | 15.6 |
| Phenyl | *n*-Bu | 195–197 (dec.) | 11.2 | 10.9 |
| Et | Benzyl | 172–173 | 13.7 | 13.6 |

were discarded. Sometimes the amine hydrochloride precipitated at this point and could be removed by filtration; otherwise the bright green aqueous layer was made strongly basic with sodium hydroxide (the green color disappeared at this point) and extracted three times with ether. The extracts were dried over potassium hydroxide and distilled. When two moles of Grignard reagent were used per mole of aldimine the yields were excellent (60–90%), but when the reactions were carried out with equimolar amounts, the yields varied with the Grignard reagent, and especially with the alkyl group of the aldimine, as shown in Table I.

The amines were converted to the hydrochlorides in ether solution, and the salts were recrystallized from ethanol-ether mixtures. They were colorless, crystalline, nonhygroscopic solids. The data on the amines and their salts are summarized in Tables III and IV.

**Reaction of Butylethynylmagnesium Bromide with Benzylidene Ethylamine.**—Butylethynylmagnesium bromide was prepared by the addition of 82 g. (1 mole) of *n*-butylacetylene to a solution of 1 mole of ethylmagnesium bromide in 170 ml. of dry ether. A solution of 55 g. (0.41 mole) of benzylidene ethylamine in 50 ml. of dry ether was added dropwise and the mixture was refluxed for twenty-six hours. Hydrolysis was accomplished in the usual way. Distillation of the dried ether extract gave 32 g. of a viscous oil, b. p. 133–164° (0.5 mm.), which solidified. This product could be recrystallized from alcohol, high-boiling petroleum ether or acetone, and the purified material melted at 87–88°. It was fairly soluble in most organic solvents.

*Anal.* Calcd. for $C_{15}H_{21}N$: N, 6.5; mol. wt., 215. Calcd. for $C_{18}H_{24}N_2$: N, 10.4; mol. wt., 268. Found: N, 10.7, 10.5; mol. wt., 266. The substance formed a stable hydrochloride which melted at 246° with decomposition. *Anal.* Calcd. for $C_{15}N_{22}NCl$: Cl, 14.09. Calcd. for $C_{18}H_{26}N_2Cl_2$: Cl, 20.8. Found: Cl, 21.34.

## Summary

1. Several new amines have been prepared by the action of Grignard reagents on Schiff bases.

2. The effect of structure of the aldimine and of the Grignard reagent on the yield of amine has been determined.

NOTRE DAME, INDIANA RECEIVED JULY 20, 1948

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[CONTRIBUTION FROM HERCULES EXPERIMENT STATION, HERCULES POWDER COMPANY]

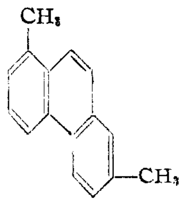
# Resin Acids. VII. Isolation and Structure of Isodextropimarinal,[1] a Possible Resin Acid Precursor

BY GEORGE C. HARRIS AND THOMAS F. SANDERSON

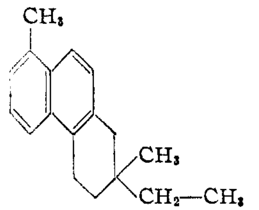
Recently Sörensen and Bruun[2] reported the isolation of a tricyclic "diterpene-ketone" ("diterpene-camphor"), with melting point 50–52°, from Scots Fir (*Pinus sylvestris L.*) and termed it cryptopinone. Its purified semicarbazone melted at 223–224° and analyzed for $C_{21}H_{33}ON_3$ corresponding to a carbonyl compound with empirical formula $C_{20}H_{30}O$.

We have recently isolated what appears to be the same substance with melting point 50–52° from the neutral fraction of commercial wood and gum rosins whose source is the longleaf (*Pinus palustris*) and slash (*Pinus caribaea*) pines. Its semicarbazone melted at 223–225° in agreement with that obtained by Sörensen and Bruun from cryptopinone. Its 2,4-dinitrophenylhydrazone was also prepared, melted at 192–194°, and analyzed for a carbonyl compound with empirical formula $C_{20}H_{30}O$. A positive silver mirror test indicated the compound to be an aldehyde. The presence of two double bonds was shown by hydrogenation with palladium–carbon catalyst in methylcyclohexane and platinum oxide catalyst in acetic acid; one double bond was more resistant to hydrogenation.

The structure of the new aldehyde was determined as follows. It was shown to possess a hydrophenanthrene nucleus related to the pimaric-type acids since on dehydrogenation pimanthrene (I) was isolated in fairly good yield. As in the case of the pimaric-type acids[3] the trialkylated naphthalene hydrocarbon (II) was also isolated from the dehydrogenation mixture. The



I



II

separation of the two hydrocarbons was readily accomplished by passing a hexane solution of the dehydrogenation mixture of hydrocarbons through a column of silica gel and separating two fractions,

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[1] The aldehyde of isodextropimaric acid has been termed isodextropimarinal. The acid was described by the authors in "Resin Acids. III," THIS JOURNAL, **70**, 2079 (1948).

[2] N. A. Sörensen and T. Bruun, *Acta Chem. Scand.*, **1** [1], 112 (1947).

[3] G. C. Harris and T. F. Sanderson, "Resin Acids. IV," THIS JOURNAL, **70**, 2081 (1948).