

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

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

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 m μ . 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

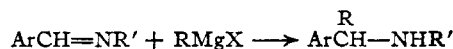
[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF NOTRE DAME]

The Reaction of Grignard Reagents with Schiff Bases¹

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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



At the time this work was started, very little information had been published on this reaction. Busch and Leeheim⁶ had synthesized a few amines in this way, and Grammaticakis⁷ had also used the reaction to some extent.

(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 Leeheim, *J. prakt. Chem.*, **77**, 20 (1908).

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

Recently, Moffett and Hoehn⁸ 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

application; it can be used with hydroxy and alkoxy substituted benzaldehydes and with many Grignard reagents and primary aliphatic amines. Busch and Leefheim⁶ 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 I

EFFECT OF STRUCTURE ON YIELDS OF AMINES		
Equimolar Quantities of Aldimine and Grignard Reagent	Grignard	Yield, %
C ₆ H ₅ CH=N—Me	Et	75
	<i>n</i> -Pr	66
	<i>i</i> -Pr	60
C ₆ H ₅ CH=N—Et	Et	39
	<i>n</i> -Pr	40
	<i>n</i> -Bu	37
	Benzyl	74
C ₆ H ₅ CH=N—Pr	Et	27
	Phenyl	25
C ₆ H ₅ —CH=N—Bu	Et	30
	Phenyl	27

TABLE II

PHYSICAL CONSTANTS OF ALDIMINES, C ₆ H ₅ CH=NR							
R	B. p. °C.	Mm.	<i>n</i> _D ²⁰	<i>d</i> ₄ ²⁰	MR _D obs.	MR _D calcd.	Reference
Me	68–69	20	1.5519	0.9617	39.6	38.5	<i>a</i>
Et	98–99	28	1.5397	.9365	44.6	43.2	<i>b</i>
<i>n</i> -Pr	101–102	18	1.5302	.9183	49.5	47.8	<i>a</i>
<i>n</i> -Bu	128–131	25	1.5249	.9021	54.8	52.4	<i>c</i>
Benzyl	158	6	1.5955	1.0382	63.9	62.7	<i>d</i>

^a Zauschirm, *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).

TABLE III

PHYSICAL CONSTANTS OF AMINES C ₆ H ₅ CH—NHR'									
R	R'	B. p. °C.	Mm.	<i>n</i> _D ²⁰	<i>d</i> ₄ ²⁰	MR _D obs.	MR _D calcd.	Nitrogen, %	
								Found	Calcd.
<i>n</i> -Pr	Me	100–102	15	1.5030	0.9076	53.18	53.34	8.62	8.58
<i>i</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		
<i>n</i> -Pr	Et	75–76	6	1.4966	.8894	57.94	57.96	7.90	7.90
<i>n</i> -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	<i>n</i> -Pr	108–109	15	1.5013	.8948	58.40	57.96	7.83	7.90
C ₆ H ₅	<i>n</i> -Pr	144–146	3	1.5616				6.33	6.22
Et	<i>n</i> -Bu	137–139	28	1.4944	.8926	62.44	62.58	7.28	7.32
C ₆ H ₅	<i>n</i> -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

methyl and ethylimines. We have used several Grignard reagents on the imines from benzaldehyde and methyl, ethyl, propyl, butyl and benzylimines.

Our results, together with those of Moffett and Hoehn, show that the reaction is capable of wide

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

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

TABLE IV

AMINE HYDROCHLORIDES, $C_6H_5-\overset{R}{\underset{ }{\text{C}}}-\text{NHR}'\cdot\text{HCl}$			Chlorine, %	
R	R'	M. p., °C.	Found	Calcd.
<i>n</i> -Pr	Me	150 (dec.)	18.0	17.8
<i>i</i> -Pr	Me	164-165 (dec.)	17.8	17.8
<i>n</i> -Pr	Et	180 (dec.)	16.7	16.6
<i>n</i> -Bu	Et	170 (dec.)	15.7	15.6
Benzyl	Et	235-236 (dec.)	14.2	13.6
Et	<i>n</i> -Pr	184 (dec.)	16.8	16.6
Phenyl	<i>n</i> -Pr	233-234 (dec.)	13.4	13.6
Et	<i>n</i> -Bu	198-199 (dec.)	16.1	15.6
Phenyl	<i>n</i> -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 etha-

nol-ether mixtures. They were colorless, crystalline, non-hygroscopic 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 $C_{15}H_{21}NCl$: 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

[CONTRIBUTION FROM HERCULES EXPERIMENT STATION, HERCULES POWDER COMPANY]

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

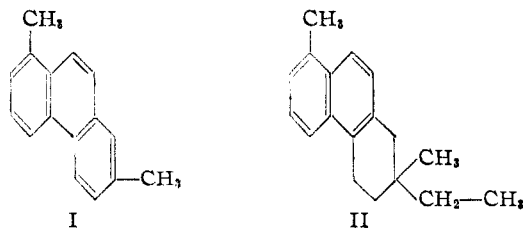
BY GEORGE C. HARRIS AND THOMAS F. SANDERSON

Recently Sørensen and Bruun² 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 $C_{21}H_{30}ON_3$, 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 Sørensen 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

methylenecyclohexane 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 pimaranthrene (I) was isolated in fairly good yield. As in the case of the pimaric-type acids³ the trialkylated naphthalene hydrocarbon (II) was also isolated from the dehydrogenation mixture. The



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,

(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. Sørensen 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).