Method C.—The procedure was that used in A except that 7.6 g. (0.2 mole) of lithium aluminum hydride was used. The 1-phenylpropylamine boiled at 84–85° (10 mm.), $n^{25}\text{D}$ 1.5182, weight 19.5 g. (62%). The crude imine boiled at 100–150° (2.8 mm.), weight 3.2 g. (10%).

2-Amino-1-phenylbutane.—The procedure was that used in method A for 1-phenylpropylamine except that benzylmagnesium chloride prepared from 38 g. (0.3 mole) of benzyl chloride, 19 g. (0.8 mole) of magnesium and 300 ml. of ether was used in place of phenylmagnesium bromide. The product boiled at 96–97° (9.5 mm.), $n^{25}\text{D}$ 1.5130, weight 26.2 g. (71%).

1-Amino-2-phenylbutane is reported[6] to boil at 106° (15 mm.), $n^{20}\text{D}$ 1.5142.

1-Phenylhexylamine.—The procedure was that used in method A for 1-phenylpropylamine except that 24.3 g. (0.25 mole) of *n*-capronitrile was substituted for the propionitrile. The product boiled at 82–83° (0.90 mm.), $n^{25}\text{D}$ 1.5070, weight 23.6 g. (54%).

Anal. Calcd. for $C_{12}H_{19}N$: N, 7.90. Found: N, 7.76.

3-Aminopentane.—The procedure was essentially that used in method A for 1-phenylpropylamine. Ethylmagnesium bromide was prepared from 32.7 g. (0.30 mole) of ethyl bromide, 7.2 g. (0.3 mole) of magnesium and 300 ml. of ether. After the reaction mixture was decomposed with water and base, the organic phase was added to 200 ml. of dilute hydrochloric acid and concentrated *in vacuo* to 75 ml. The amine was liberated with 50% sodium hydroxide and dried in ether solution over magnesium sulfate. The product boiled at 87° at ordinary pressure, $n^{25}\text{D}$ 1.4030, weight 4.8 g. (23%). The hydrochloride was prepared in ether and recrystallized twice from methanol–ethyl acetate, m.p. 215–216°, weight 4.8 g.

The amine is reported[7] to boil at 90° and its hydrochloride[8] to melt at 215–216°.

4-Diethylamino-1-phenylbutylamine.—The procedure was that used in method B for 1-phenylpropylamine except that 28 g. (0.20 mole) of 4-diethylaminobutyronitrile was used in place of propionitrile. The product boiled at 115–116° (0.80 mm.), $n^{25}\text{D}$ 1.5081, weight 27.5 g. (62%).

Anal. Calcd. for $C_{14}H_{24}N_2$: N, 12.71. Found: N, 12.95.

The amine is reported[9] to boil at 116–118° (1 mm.).

N-(1-Phenylpropyl)-1-phenylpropylidenimine.—A reaction mixture containing 26.8 g. (0.2 mole) of propiophenone, 26.8 g. (0.2 mole) of 1-phenylpropylamine, 4.8 g. (0.2 mole) of sodium hydride and 150 ml. of benzene was refluxed overnight without the formation of water in the water separator. No imine was isolated by distillation. Another run using 6 ml. of triethylamine was unsuccessful.

1-Phenylpropylideniminomagnesium bromide was prepared as described in method A. Then 33.8 g. (0.25 mole) of 1-phenylpropylamine was added dropwise. The reaction mixture was refluxed with stirring for three hours and then decomposed by addition of 4 ml. of water, 3 ml. of 20% sodium hydroxide and finally 24 ml. of water. After stirring for two hours at room temperature, the ether solution was decanted and dried over magnesium sulfate. The product distilled at 125–126° (0.60 mm.), $n^{25}\text{D}$ 1.5552, weight 46.0 g. (74%).

Hydrolysis of N-(1-Phenylpropyl)-1-phenylpropylidenimine.—A reaction mixture containing 7.0 g. of the imine in 100 ml. of dilute hydrochloric acid was refluxed for one hour. The insoluble oil was dissolved in ether. The ether was distilled and the 2,4-dinitrophenylhydrazone of the residual oil was prepared. After three recrystallizations from ethyl acetate, the product melted at 188–189°, weight 2.0 g. There was no depression in the mixed melting point with an authentic sample of propiophenone 2,4-dinitrophenylhydrazone.[10] The acid aqueous phase was concentrated to dryness *in vacuo* and the 1-phenylpropylamine hydrochloride[11] recrystallized from methanol–ethyl acetate solution, m.p. 193–194°, weight 3.6 g.

Hydrogenation of N-(1-Phenylpropyl)-1-phenylpropylidenimine.—The imine, 10.0 g. (0.04 mole), was reduced in 200 ml. of ethanol using 200 mg. of platinum oxide catalyst. The reduction required 0.04 mole of hydrogen. The catalyst was collected on a filter and the filtrate concentrated *in vacuo*. The residual oil was dissolved in ether and the hydrochloride prepared using anhydrous hydrogen chloride. Two optical forms of di-(1-phenylpropyl)-amine hydrochloride were separated by fractional crystallization from methanol–ethyl acetate. The α-form, after five recrystallizations, melted at 252–253°, weight 0.8 g.

Anal. Calcd. for $C_{18}H_{23}N{\cdot}HCl$: C, 74.58; H, 8.36; N, 4.83; Cl, 12.23. Found: C, 74.70; H, 8.47; N, 5.05; Cl, 12.41.

The more soluble β-form, after five recrystallizations, melted at 242–243°, weight 2.7 g. A mixed melting point was 215–217°.

Anal. Calcd. for $C_{18}H_{23}N{\cdot}HCl$: C, 74.58; H, 8.36; N, 4.83; Cl, 12.23. Found: C, 74.23; H, 8.49; N, 5.09; Cl, 12.40.

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[6] N. Kornblum and D. C. Iffland, This Journal, **71**, 2137 (1949).

[7] M. A. Mailhe, *Bull. soc. chim., France*, [4] **15**, 327 (1914).

[8] W. A. Noyes, *Am. Chem. J.*, **15**, 539 (1893).

[9] W. J. Humphlett, M. J. Weiss and C. R. Hauser, This Journal, **70**, 4020 (1948).

[10] T. Thomson and T. S. Stevens, *J. Chem. Soc.*, 2607 (1932).

[11] P. Billon, *Ann. chim.*, **7**, 314 (1927).

[Contribution from the Department of Chemistry, University of Oklahoma]

Ketimines. VI. *o*-Tolyl Alkyl Ketimines[1]

By P. L. Pickard and S. H. Jenkins, Jr.

Received July 6, 1953

Seven ketimines have been prepared by the action of Grignard reagents on *o*-tolunitrile. Each imine was hydrolyzed to the corresponding ketone. With the exception of *s*-butyl *o*-tolyl ketimine, the imines reduced readily to the corresponding primary amines. Polarographic half wave potentials of the imines and ketones in absolute alcohol were obtained.

Most of the work reported in earlier papers[2–6] of this series has been devoted to the determination of factors which contribute to the stability of a ketimine toward hydrolysis. It was noted that *o*-tolyl *t*-butyl ketimine is stable while the *o*-tolyl isopropyl ketimine hydrolyzes readily.[2] In later papers isopropyl 1-methyl-3-isopropyl-cyclopentyl ketimine[5] and *o*-tolyl 1,1-diphenylethyl ketimine[6] were shown to be stable. These findings have prompted further interest in the *o*-tolyl ketimines and the alkyl series was prepared to determine the reactivity compared to the *o*-tolyl isopropyl and *t*-butyl ketimines which have been reported.

It was found that the time needed for the addition of Grignard reagent to nitrile is considerably less than previously considered necessary. In the synthesis of the isoamyl ketimine, for example, 44-hour refluxing gave a yield of 55% while a

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[1] From a thesis submitted in partial fulfillment of the requirements for the Ph.D. at the University of Oklahoma.

[2] P. L. Pickard, *et al.*, This Journal, **72**, 876 (1950).

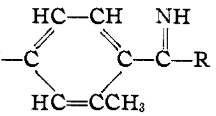
[3] *Ibid.*, **72**, 5017 (1950).

[4] *Ibid.*, **73**, 42 (1951).

[5] *Ibid.*, **74**, 4607 (1952).

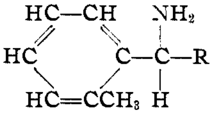
[6] *Ibid.*, **75**, 2148 (1953).

TABLE I

KETIMINES 

R	B.p. °C.	B.p. Mm.	d^{20}_4	n^{20}_D	Yield, %	Nitrogen, % Calcd.	Nitrogen, % Found	Hydrochloride M.p., °C.	Hydrochloride Nitrogen, % Calcd.	Hydrochloride Nitrogen, % Found	Acetyl derivative M.p., °C.	Acetyl derivative Nitrogen, % Calcd.	Acetyl derivative Nitrogen, % Found
Methyl	58–61	1.5	0.9754	1.5390	40	10.52	10.18	161	8.26	8.36	Oil	..	..
Ethyl	73–74	3	.9263	1.5342	75	9.52	9.33	185	7.63	7.56	Oil	..	..
n-Propyl	77–78	3	.9486	1.5252	58	8.63	8.49	144	7.09	7.16	126	6.89	6.63
n-Butyl	84–86	1	.9384	1.5215	68	7.99	7.69	123	6.62	6.57	136	6.45	6.28
i-Butyl	85–87	2	.9350	1.5175	86	7.99	7.97	186	6.62	6.77	154	6.45	6.44
s-Butyl	82–83	4	.9446	1.5235	77	7.99	7.89	144	6.62	6.62	Oil	..	..
i-Amyl	105–106	3	.9235	1.5155	68	7.40	7.17	142	6.21	6.05	107.5	6.45	6.35

TABLE II

AMINES 

R	B.p. °C.	B.p. Mm.	d^{20}_4	n^{20}_D	Nitrogen, % Calcd.	Nitrogen, % Found	Hydrochloride M.p., °C.	Hydrochloride Nitrogen, % Calcd.	Hydrochloride Nitrogen, % Found	Acetyl derivative M.p., °C.	Acetyl derivative Nitrogen, % Calcd.	Acetyl derivative Nitrogen, % Found
Methyl[a]	55–57	1	0.9739	1.5313	..	..	175	8.11	7.93	92	7.90	7.62
Ethyl	68–69	4	.9452	1.5242	9.39	9.24	208	7.54	7.40	69	..	..
n-Propyl	79–80	3	.9336	1.5178	8.58	8.35	223	..	..	90	6.82	7.05
n-Butyl	83–85	3	.9256	1.5184	7.90	7.45	225	..	..	89	6.39	6.52
i-Butyl	89–90	2	.9206	1.5115	7.90	7.83	262	6.55	6.45	122	6.39	6.51
i-Amyl	99–100	3	.9143	1.5085	7.32	7.29	...	..	..	124	6.00	5.90

[a] "Beilstein," 4th Ed., Vol. XII, Suppl. II, p. 625, lists b.p. 89–91° (14 mm.) and hydrochloride, m.p. 173°.

reflux period of only 14 hours resulted in a yield of 69%.

All these imines hydrolyzed in 6 *N* hydrochloric acid in 6 hours or less to give an average of 90% recovery of ketone. The ketimines were reduced catalytically with the exception of the *o*-tolyl *s*-butyl which absorbed hydrogen at a near-negligible rate. Relative reduction rates were calculated with the rate of *s*-butyl *o*-tolyl ketimine being taken as unity.

Polarographic half wave potentials were determined for the ketimines and ketones. The reduction potentials of the ketones are all in the range of −1.68 to −1.76 v. The potentials of the imines, however, range from −1.67 to −2.02 v., paralleling the relative catalytic reduction rates.

Experimental

Ketimines.—All preparations were by the method earlier described[2] but the maximum reaction time was usually about 12 hours. *o*-Tolunitrile and an alkyl Grignard reagent were used in each case. Hydrochlorides were prepared by bubbling HCl gas into an anhydrous ether solution of the imine. Recrystallization was effected from chloroform–ether or chloroform–hexane. The recrystallized salts were dried before analysis in a vacuum desiccator at room temperature since elevated temperatures cause decomposition.

The acetyl derivatives were prepared by adding one gram of the imine and two drops of pyridine to ten ml. of acetic anhydride. After 5 minutes refluxing the mixture was cooled, poured into 25 ml. of cold water and neutralized with sodium carbonate. The solid derivatives separated and were recrystallized from alcohol–water. Data on the imines are contained in Table I.

Amines.—All the ketimines were hydrogenated to the corresponding amines over prereduced platinum in absolute ethanol except the *s*-butyl. Hydrogenation at atmospheric pressure using a gas buret was employed for determination of relative reduction rates. To obtain a sample of amine for characterization the imine was hydrogenated at 30 pounds pressure. Both methods gave yields of 80–95% amine recovered by vacuum distillation.

s-Butyl *o*-tolyl ketimine did not add hydrogen in either system. An attempt was made to reduce 0.03 mole of this imine with 0.01 mole of lithium aluminum hydride in 100 ml. of absolute ether; however, the imine failed to reduce and was recovered quantitatively.

Data on the amines and their derivatives are included in Table II. The derivatives were prepared in the same manner described for the imines. The acetyl derivatives were also prepared from the hydrochlorides by the addition of an amount of sodium acetate equivalent to the hydrochloride before heating with acetic anhydride.

Ketones.—The imines were refluxed 3–6 hours with 6 *N* hydrochloric acid and ether extracted. The extracts were washed with water, dried over anhydrous magnesium sulfate and the ketones distilled in vacuum after evaporation of the ether. A yield of 85–95% was obtained in all cases. The 2,4-dinitrophenylhydrazones were dissolved in hot hexane and the solutions filtered. In each case the solvent was evaporated and the residue recrystallized from 95% alcohol. The semicarbazones were prepared by refluxing a mixture of 1 g. of the ketone, 1 g. of semicarbazide hydrochloride, 1 ml. of pyridine and 10 ml. of 95% ethanol for a half hour. The solution was then concentrated to 5 ml. and cooled in an ice-bath, 5 ml. of water was added, and the solution was stirred in an ice-bath until the derivative crystallized. The semicarbazones were thoroughly washed with water and recrystallized to constant melting point from ethanol–water mixtures followed by chloroform–hexane mixtures. Data are in Table III.

Analyses.—Micro Kjeldahl procedures were used on all samples. For ketimines, amines and derivatives of each the method of Clark[7] was followed. The ketone derivatives were analyzed using the prereductive treatment of Fish[8] or Friedrich,[9] the former proving preferable due to its relative simplicity.

Polarography.—The instrument used was a Heyrovsky Polarograph, Type X, photographic recording, made in

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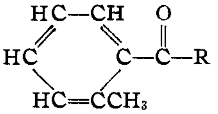
[7] E. Clark, "Semimicro Quantitative Organic Analysis," Academic Press, Inc., New York, N. Y., 1943, p. 40.

[8] V. Fish, *Anal. Chem.*, **24**, 760 (1952).

[9] F. Pregl, "Quantitative Organic Microanalysis," J. and A. Churchill, Ltd., London, England, 1945, 4th ed., p. 82.

TABLE III

KETONES



R	B.p. °C.	Mm.	d^{20}_4	n^{20}D	2,4-DNP[f] M.p., °C.	2,4-DNP[f] Nitrogen, % Calcd.	2,4-DNP[f] Nitrogen, % Found	Semicarbazone M.p., °C.	Semicarbazone Nitrogen, % Calcd.	Semicarbazone Nitrogen, % Found
Methyl[a]	59–60	1.5	1.0114	1.5325	161–162	...	...	205–206	...	...
Ethyl[b]	72–73	1.5	0.9967	1.5250	106–107	17.07	16.78	172–173	...	...
n-Propyl[c]	84–85	2	.9774	1.5181	92–93	16.37	15.74	185–186	19.16	19.18
n-Butyl	97–98	2	.9645	1.5141	76–78	15.72	15.43	151–152	18.01	18.04
i-Butyl[d]	85–86	3	.9578	1.5104	91–92	15.72	15.57	171.5–172	18.01	18.06
s-Butyl[e]	79–80	4	.9639	1.5115	73–74.5	15.72	15.66	....	...	...
i-Amyl	108–109.5	2.5	.9544	1.5090	105–106	15.13	14.94	143–144	16.99	16.84

[a] E. Huntress and S. Mulliken, "Identification of Pure Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1941, p. 390, gives d^{20}_4 1.014; n^{20}D 1.5320; 2,4-DNP, m.p. 159°; semicarbazone, m.p. 206°. [b] J. Senderens, *Ann. chim.*, **28**, 332 (1913), reports semicarbazone, m.p. 169°. [c] *Ibid.*, **28**, 332 (1913), reports semicarbazone, m.p. 176°. [d] *Ibid.*, **28**, 333 (1913), reports semicarbazone, m.p. 166°. [e] *Anal.* Calcd. for ketone: C, 81.77; H, 9.15 Found: C, 81.79; H, 9.39. [f] 2,4-Dinitrophenylhydrazone.

TABLE IV

CATALYTIC REDUCTION RATES AND POLAROGRAPHIC HALF-WAVE POTENTIAL

R	K^a	Relative rate	Half-wave potential Ketimine	Half-wave potential Ketone
Methyl	1.67	5.97	−1.67	−1.68
Ethyl	0.93	3.32	−1.72	−1.71
n-Propyl	.74	2.64	−1.90	−1.71
n-Butyl	.66	2.36	−1.91	−1.70
i-Butyl	.43	1.54	−1.91	−1.68
i-Amyl	.41	1.47	−1.94	−1.73
s-Butyl	.28	1.00	−2.02	−1.76

[a] K = milliliters of hydrogen per minute per gram imine.

Germany. Tetramethylammonium chloride was used as supporting electrolyte in a concentration of 0.15 M in ethanol. The organic compounds were freshly distilled and samples were dissolved in the 0.15 M tetramethylammonium chloride to produce solutions 5 × 10^{-3} M in the compound being run. A large constant area mercury pool was used as the reference electrode. The drop time of the dropping mercury electrode was 2.5 seconds. All solutions were degassed prior to determining the polarogram. Nitrogen was bubbled through alkaline pyrogallol to remove oxygen, through absolute alcohol to saturate it with alcohol vapor and minimize solvent loss from the sample, and then through the sample. It was found that ten minutes bubbling was sufficient to remove dissolved oxygen from the sample. Each wave exhibited a maximum except the *o*-tolyl *s*-butyl ketimine. These maxima could not be eliminated by addition of gelatin or methyl red, by changing galvanometer sensitivity or by varying concentration of electrolyte or test compound. Half-wave potentials are listed in Table IV.

NORMAN, OKLAHOMA

[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

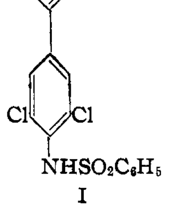
Quinone Imides. XXXI. 3,3-Dimethoxydiphenoquinonedibenzenesulfonimide and its Reaction Products

BY ROGER ADAMS, RICHARD R. HOLMES AND JOHN W. WAY[1]

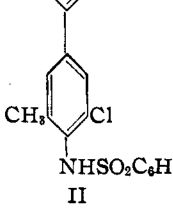
RECEIVED JUNE 17, 1953

The diimide obtained by the oxidation of the dibenzenesulfonyl derivative of *o*-dianisidine was subjected to hydrogen chloride addition. Oxidation of the resulting monochlorodiamide and addition of hydrogen chloride to the diimide thus formed gives N,N′-dibenzenesulfonyl-5,5′-dichloro-3,3′-dimethoxybenzidine. The structure was established by showing its non-identity to the other two symmetrical isomeric dichloro-3,3′-dimethoxybenzidines and by the similarity of the infrared absorption spectrum to that of N-benzenesulfonyl-2-chloro-6-methoxyaniline.

The addition of hydrogen chloride to the diphenoquinonedibenzenesulfonimides formed by lead tetraacetate oxidation of the N,N′-dibenzenesulfonyl derivatives of benzidine and tolidine has been described in previous papers.[2] The process involves 1,8-addition. The products derived from benzidine and tolidine on repeated oxidation and addition of hydrogen chloride were established as 3,3′,5,5′-tetrachlorodiphenoquinonedibenzenesulfonamide (I) and 3,3′-dichloro-5,5′-dimethyldiphenoquinonedibenzenesulfonamide (II).



I



II

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[1] An abstract of a thesis submitted by John W. Way to the Graduate College of the University of Illinois, 1953, in partial fulfillment of the requirements for the Degree of Doctor of Philosophy. Minnesota Mining and Manufacturing Company Fellow, 1951–1952; Allied Chemical and Dye Corporation Fellow, 1952–1953.

[2] R. Adams and R. R. Holmes, THIS JOURNAL, **74**, 3033 (1952); **74**, 3038 (1952).