# Ketimines. V. Alkyl 1,1-Diphenylethyl Ketimines

BY P. L. PICKARD AND E. F. ENGLES

Ketimines have been prepared by the action of 2,2-diphenylpropanenitrile on one aryl and six alkyl Grignard reagents. One of the alkyl ketimines and the aryl ketimine failed to reduce to the amine catalytically at atmospheric pressure. The aryl ketimine was not hydrolyzed in 6 N hydrochloric acid. The other compounds hydrogenated and hydrolyzed readily.

The study of ketimines in this Laboratory has led to the production of several types,[1,2] but none of the compounds previously prepared has contained an aralkyl group. It was desired to determine whether the relatively slow rates of hydrolysis noted for certain of the aryl ketimines would change when the aromatic nucleus is not in conjugation with the imino group. In order that there might be no possibility of stabilization through tautomerism of the ketimine and conjugation of the resulting eneamine structure with the aromatic nucleus

Ar—C(R)H—C(=NH)—R $\rightleftarrows$ Ar—C(R)=C(NH₂)—R
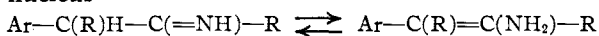
2,2-diphenylpropanenitrile was chosen. It has also been shown to be remarkably resistant to hydrolysis.

With Grignard reagents from the normal alkyl halides, methyl through amyl, the ketimines were obtained without difficulty. With isopropyl, isobutyl and s-butyl Grignard reagents, however, the product was a mixture of basic material from which no constant-boiling fraction could be obtained. Isoamylmagnesium bromide reacted normally, as did o-tolylmagnesium bromide.

ratio of Grignard reagent to nitrile. All the imines hydrolyzed rapidly in 6 N hydrochloric acid except o-tolyl 1,1-diphenylethylketimine, from which no ketone could be obtained. It was previously reported that the aryl ketimines, under the same conditions, were only partially hydrolyzed.[1] Catalytic reduction was successful with all compounds except the o-tolyl and isoamyl 1,1-diphenylethylketimines, which could not be reduced over Adams catalyst at atmospheric pressure.

Under the conditions employed, hydrolysis rates were so rapid as to make rate measurements impractical. Relative reduction rates based on the least readily reduced compound, n-butyl 1,1-diphenylethylketimine, as 1.00, are n-amyl, 1.03; ethyl, 1.84; methyl, 3.43; propyl, 3.61.

Experimental

2,2-Diphenylpropanenitrile.—This nitrile was prepared by the previously reported method[3] from diphenylacetonitrile and methyl iodide. From 5 g. of the nitrile refluxed for 168 hours with saturated alcoholic potassium hydroxide was obtained 4 g. of the amide and only a trace of the acid.

Ketimines.—All preparations were by the method previously described.[1] The compounds derived and analyses are given in Table I.

TABLE I

NH
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KETIMINES C—C(C₆H₅)₂—C —R

R	B.p., °C.	Mm.	d^{20}_4	n^{20}_D	Nitrogen, % Calcd.	Found	M.p., °C.	Picrate Nitrogen, % Calcd.	Found
CH₃	138–139	0.5	1.0550	1.5866	6.27	5.14	143	10.60	12.32
C₂H₅	144–145	0.5	1.0447	1.5808	5.90	5.84	139	11.96	12.07
C₃H₇	142–144	1.0	1.0328	1.5731	5.57	5.82	200[a]	4.87[a]	5.12[a]
C₄H₉	150–152	0.5	1.0213	1.5661	5.28	5.46	168	11.33	11.38
n-C₅H₁₁	165–166	1.0	1.0053	1.5591	5.01	4.74	142	11.02	10.90
i-C₅H₁₁	152–154	1.0	1.0069	1.5568	5.01	4.99	174	11.02	10.81
o-Tolyl	172–175 M.p. 100	0.5	....	....	4.68	4.94	262 d.	10.60	10.44

[a] Hydrochloride.

TABLE II

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KETONES C—C(C₆H₅)₂—C—R

R	B.p. °C.	Mm.	d^{20}_4	n^{20}_D	Carbon, % Calcd.	Found	Hydrogen, % Calcd.	Found	M.p., °C.	Semicarbazone Nitrogen, % Calcd.	Found
CH₃	130–131	0.5	1.0685	1.5793	85.67	85.83	7.19	6.91	182	14.94	15.13
C₂H₅	135–136	.5	1.0575	1.5720	85.67	85.87	7.61	7.37	206	14.23	13.98
C₃H₇	145–146	.5	1.0429	1.5714	85.67	85.42	7.99	7.83	212	13.58	13.75
C₄H₉	144–145	.5	1.0285	1.5592	85.68	85.84	8.33	8.27	185	12.99	13.27
n-C₅H₁₁	152–153	.5	1.0169	1.5509	85.68	85.58	8.63	8.46	194	12.45	12.52
i-C₅H₁₁	150–151	1.0	1.0139	1.5495	85.68	85.37	8.63	8.30	180	12.45	12.61

The yields were about 40% in all preparations and were not changed appreciably by a change in

Ketones.—Each of the ketimines was refluxed with 6 N hydrochloric acid for three hours, ether extracted, dried and distilled. Physical data, derivatives and analyses of

(1) P. L. Pickard, et al., THIS JOURNAL, 72, 876 (1950).
(2) Ibid., 72, 5017 (1950); 73, 42 (1950); 74, 4607 (1952).
(3) Ibid., 73, 864 (1951).

TABLE III

NH$_2$

AMINES C—C(C$_6$H$_5$)$_2$—CH—R

R	B.p. °C.	Mm.	d^{20}_4	n^{20}D	Nitrogen, % Calcd.	Found	M.p., °C.	Picrate Nitrogen, % Calcd.	Found
CH$_3$	133–134	0.5	1.0464	1.5847	6.22	6.00	210	12.38	12.17
C$_2$H$_5$	141–142	.5	1.0382	1.5797	5.85	5.93	174	12.01	12.08
C$_3$H$_7$	142–143	.5	1.0276	1.5715	5.53	5.26	163	11.61	11.42
C$_4$H$_9$	151–152	.5	1.0104	1.5643	5.24	5.17	172	11.28	11.01
n-C$_5$N$_{11}$	164–165	.5	1.0029	1.5594	4.98	4.95	132	10.98	11.11

the ketones are given in Table II. o-Tolyl-1-diphenylethyl ketimine was refluxed for 48 hours, but no ketone was obtained.

Amines.—A weighed sample of ketimine was added to methanol containing prereduced Adams catalyst and reduced at room temperature and atmospheric pressure. When no more hydrogen was taken up, the total volume required was read from the buret, and the milliliters of hydrogen absorbed per minute per gram of sample was calculated. For the methyl through amyl compounds, in order of in-

creasing molecular weight, these values are 0.222, 0.119, 0.234, 0.065 and 0.066, respectively. Relative rates of reduction, based on these figures are 3.43, 1.84, 3.61, 1.00 and 1.03. The o-tolyl- and isoamylketimines absorbed no hydrogen under these conditions even after repurification, cleaning the system used, and preparing fresh catalyst.

The amines were separated from the reduction mixture by filtration of the catalyst and distillation. Physical data derivatives and analyses are given in Table III.

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The Reactions of Some p-Aminotriphenylmethyl Ions with Methanol and Methylate Ion

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It had been observed that the molecular extinction coefficients of the bands of N-dimethyl-p-aminotriphenylmethyl ion are markedly less in methanol than in acetic acid.[1] In this paper this phenomenon has been attributed to the formation of a colorless benzenoidal ion, (CH$_3$)$_2$$\overset{+}{N}HC_6H_4$C-(C$_6H_5$)$_2OCH_3$, in a reversible reaction between the quinoidal ion and methanol. That the phenomenon has not been observed with the related ions N-methyl-N-phenyl-p-aminotriphenylmethyl ion, N-phenyl-p-aminotriphenylmethyl ion and N-diphenyl-p-aminotriphenylmethyl ion has been attributed to the stabilization of the quinoidal ions by the resonance interaction of the extra phenyl groups in these conjugate systems.

Confirmation of this theory has been found in the restoration of the color by reducing the activity of the methanol with perchloric acid.

An estimate has been made of the molecular extinction coefficient of the pure quinoidal ion. This has been used to calculate the quinoidal fraction of the ion under different conditions.

The reactions of methylate ion with the four aminotriphenylmethyl ions already mentioned have been given as the equilibrium constants of the reverse reactions, the neutralizations of the methyl ethers to form the quinoidal ions. These base strengths were found to decrease with the degree of phenylation, the dimethyl compound being the strongest and the diphenyl one the weakest base. This order of base strengths is the same as that of the parent aromatic amines (dimethylaniline, diphenylamine and triphenylamine). The decrease

in basicity with the number of phenyl groups of the color base is much less than that of the parent amine. These relationships have been taken as showing that the resonance interactions of the extra phenyl groups in the quinoidal ions are less than those of the same groups in the aromatic amines, but that they are strong enough to almost entirely repress the benzenoidal ions.

The base strength of 3-carbazyldiphenylmethyl methyl ether to form a quinoidal ion was also measured. It proved to be the weakest of the bases.

Reaction with Methanol

Table I shows the molecular extinction coefficients at the peaks of the bands in the spectra of four closely related ions. The measurements are given for solutions in methanol, acetic acid and chloroform. For each ion the positions of the bands in acetic acid and methanol are the same. In chloroform the positions of the bands are shifted a little toward the red. The data are taken from a previous paper by the authors.[1]

The related ions all have the general formula

$$\mathrm{{R \atop R'}\!\!>\!\overset{+}{N}\!=\!\!\left\langle\!\!\!=\!\!\!\right\rangle\!\!=\!C(C_6H_5)_2}$$
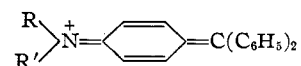
For I, R = CH$_3$, R' = CH$_3$; for II, R = CH$_3$, R' = C$_6$H$_5$; for III, R = H, R' = C$_6$H$_5$; for IV, R = C$_6$H$_5$, R' = C$_6$H$_5$. In general we shall use these Roman numerals instead of the names. It is simplest to name them from the formulas of another phase in the resonance. For instance I may be called dimethyl-p-aminotriphenylmethyl ion.

Table I shows that the molecular extinction coef-

(1) H. Walba and G. Branch, THIS JOURNAL, 73, 3341 (1951).