nesium in 150 ml. of ether was added to 45.31 g. (0.25 mole) of ethyl 2-cyano-3,4-dimethyl-2-pentenoate[24] and 0.5 g. of cuprous chloride in 100 ml. of ether. After the addition was completed, the solution was heated under reflux for 2 hr. After product isolation in the usual manner, distillation afforded 45.22 g. (75%) of a pale yellow, viscous oil, homogeneous by vapor phase chromatography, b.p. 140–143° (1.25 mm.). A forerun, 8.04 g., of biphenyl and recovered cyano ester was obtained. Upon standing at room temperature for 2 days, most of the material from the Grignard reaction solidified. The solid was removed from the liquid and was recrystallized from ether–hexane to give the analytical sample, m.p. 65–66°.

Anal. Calcd. for $C_{16}H_{21}NO_2$: C, 74.10; H, 8.16; N, 5.40. Found: C, 74.28; H, 8.16; N, 5.38.

3,4-Dimethyl-3-phenylpentanoic Acid.—A vigorously stirred mixture of 25.93 g. (0.10 mole) of the saturated cyano ester, 50 g. of potassium hydroxide, and 200 ml. of diethylene glycol was heated at 180–195° under 1 atm. of nitrogen for 23 hr. The solution was cooled, poured over ice, and extracted with ether. The solution was acidified with hydrochloric acid and extracted with five 100-ml. portions of ether. The ethereal solution was washed well with water, dried, filtered, treated with decolorizing carbon, and filtered again. Removal of the ether left an oil which crystallized on standing. After one recrystallization from ether–hexane, 17.15 g. (83%) of acid, m.p. 73–76°, was obtained. The analytical sample, after recrystallization from the same solvent pair, melted at 75.5–77°.

Anal. Calcd. for $C_{13}H_{18}O_2$: C, 75.69; H, 8.80. Found: C, 75.92; H, 8.85.

3-Methyl-3-isopropyl-1-indanone.—A mixture of 10.00 g. (48.5 mmoles) of the pentanoic acid and 100 g. of polyphosphoric acid was heated on the steam bath until homogeneous. The viscous solution was allowed to cool and then stirred occasionally for 9 hr. at room temperature. After isolating the neutral product in the usual manner, 9.73 g. of clear oil was obtained. Distillation afforded 8.42 g. (92%) of clear, colorless oil, b.p. 89–91° (0.8 mm.), infrared maximum 5.86 μ (carbonyl), $n^{24}D$ 1.5374. The 2,4-dinitrophenylhydrazone, m.p. 173–174°, was obtained from ethanol–ethyl acetate, λ_{max} 384 mμ (log ϵ 4.50).

Anal. Calcd. for $C_{19}H_{20}N_4O_4$: C, 61.94; H, 5.47; N, 15.21. Found: C, 62.11; H, 5.65; N, 15.46.

Acknowledgment.—We would like to thank Dr. A. K. Bose, Stevens Institute of Technology, Dr. Werner Herz, Florida State University, and Dr. Leon Mandell, Emory University, for their assistance in carrying out and interpreting several of the n.m.r. spectra reported in this paper. We would also like to thank Professor R. B. Woodward for his guidance and direction during that portion of the work carried out at Harvard University.

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[24] A. Brandstrom, *Acta. Chem. Scand.*, **13**, 963 (1959).

Amino Ketone Rearrangements. III. The Rearrangement of α-Hydroxy N-Phenylimines[1,2]

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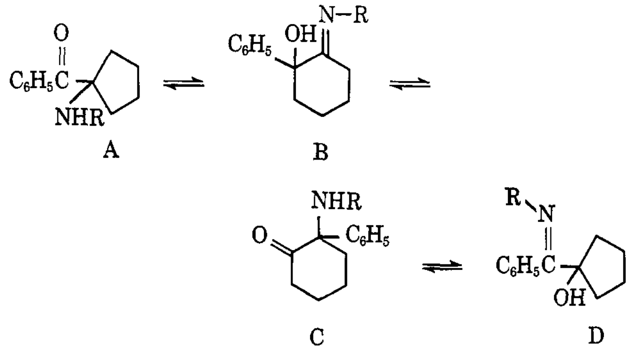
Seven C-phenyl- and N-phenyl-substituted 1-(α-phenyliminobenzyl)cyclopentanols were prepared and subjected to thermal rearrangement to their respective 2-phenyl-2-phenylaminocyclohexanones. Isomeric C-phenyl- and N-phenyl-substituted hydroxy imines were seen to have identical first-order rearrangement rate constants, and a reaction constant, ρ, of -0.32 was obtained for the series. The reaction mechanism is discussed.

The thermal rearrangement of α-amino ketones is a general phenomenon.[5] The rearrangement of α-amino ketones with accompanying alkyl *di*substitution on the α-carbon atom bearing the amino group is unique with double carbon skeletal rearrangement being encountered. The thermal rearrangement of a specific α-amino ketone is envisioned as involving an equilibrium between four isomeric partners. For example, A–D would be the compounds involved in thermal equilibration of a 1-aminocyclopentyl phenyl ketone. Thus, proceeding from A through C one encounters alkyl migration, phenyl migration, and alkyl migration in that order, and, indeed, with other specific but analogous compounds, thermal rearrangement from all four isomer types has been observed. In conjunction with our study of this phenomonon, we desired to isolate one equilibrium reaction of the three for an initial kinetic analysis. The conversion C to D was chosen for two reasons: first, the C ⇄ D equilibrium constant is very small in most systems so that the rearrangement of D to C could, for practical purposes, be treated as an irreversible reaction; second, α-hydroxy imines of type D (R = C_6H_5) were readily available from the reaction of epoxy ethers with substituted anilines.[6] The cyclopentyl phenyl ketone carbon skeleton was chosen because its rearrangement reactions were the cleanest and of the highest yield of those systems studied. Further, all compounds involved were crystalline and easily characterized. It was hoped that ring-size stability effects, while cer-



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(1) Presented in part at the 144th National Meeting of the American Chemical Society, Los Angeles, Calif., April 1963; Abstracts, p. 14M.

(2) Paper II of this series: C. L. Stevens, R. D. Elliott, and B. L. Winch, *J. Am. Chem. Soc.*, **85**, 1464 (1963).

(3) NATO Fellow, 1961–1962.

(4) National Science Foundation Predoctoral Fellow, 1963–1964. This paper was abstracted in part from the Ph.D. Dissertation of F. A. Daniher, Wayne State University, 1964.

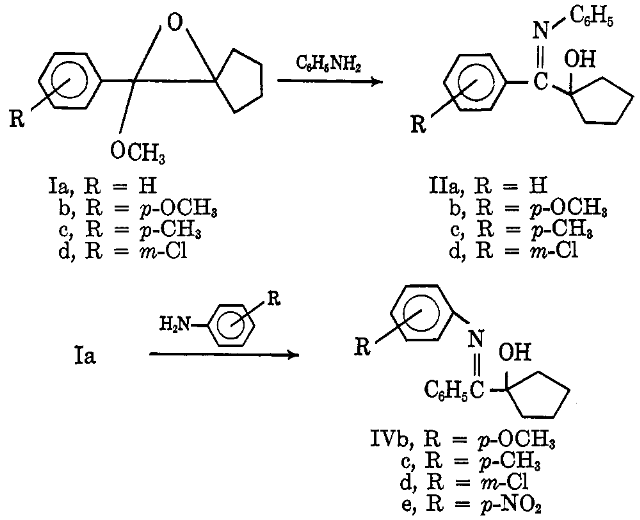
(5) K. L. Nelson, J. C. Robertson, and J. J. Duvall, *J. Am. Chem. Soc.*, **86**, 684 (1964), and included references.

(6) For synthesis of α-hydroxy imines of general type D with R = alkyl, *cf.* C. L. Stevens, P. Blumbergs, and M. Munk, *J. Org. Chem.*, **28**, 331 (1963).

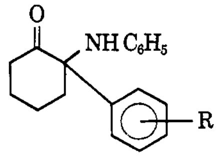
tainly not absent, would not be overriding for the case of expansion from five to six membered rings.[7]

Synthesis.—The α-hydroxy imines II and IV were prepared by heating 1–4 equiv. of the appropriate aniline with the appropriate epoxy ether I at temperatures from 110 to 135° (Scheme I). Reaction times of 0.5 hr. were optimum. The formation of hydroxy imines in these reactions indicates an opening of the oxirane ring in the direction that is observed for acid-catalyzed reactions.[8] Aliphatic amines[9a] including N-methylaniline[9b] open epoxy ethers by attack at the alcohol carbon and yield α-amino ketones as major products. The direction of epoxy ether opening with primary anilines was not entirely unexpected since 3,4,6-tri-O-acetyl-1,2-anhydro-β-D-glucopyranose (Brigl's anhydride) affords a β-glucosylamine on reaction with p-toluidine.[10] Elucidation of the mechanistic fine points of the duality of amine–epoxy ether reactions requires further study.

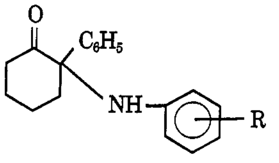
SCHEME I



The synthesis of the 2-anilino-2-phenylcyclohexanones III and V could be effected by heating the necessary epoxy ether and aniline (in excess) at 180° for several hours in decalin solvent. Cleaner products and higher rearrangement yields resulted, however, when the pure hydroxy imines II and IV were heated in decalin solvent. When following this latter procedure, the product amino ketones generally crystallized when the reaction solution was cooled. Rearrangements of related hydroxy imines have been reported[2,11] and have been found synthetically useful in the steroid area.[11c]



IIIa, R = H
b, R = p-OCH3
c, R = p-CH3
d, R = m-Cl



Vb, R = p-OCH3
c, R = p-CH3
d, R = m-Cl
e, R = p-NO2

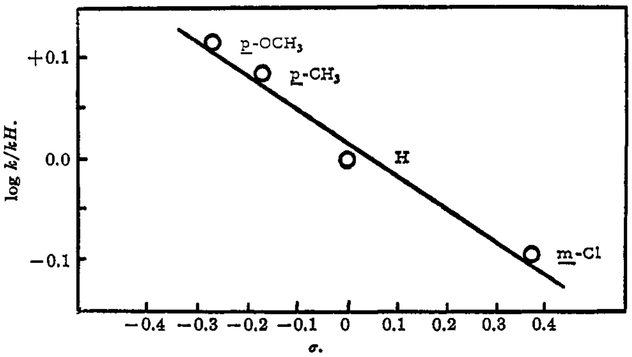


Figure 1.—Correlation of log k/k_H and σ for the rearrangement of α-hydroxy imines at 208°; σ^+ value of p-OCH_3 is −0.78, for p-CH_3, −0.31.

Rate and Basicity Studies.—Decalin solutions containing 6% (w./v.) of the hydroxy imine under study were heated in an oil bath maintained at 208 ± 2°. At intervals, individual reactions were cooled, evacuated to remove the solvent, and made up to the appropriate volume in chloroform, whereupon the infrared spectrum was recorded. Comparison of the carbonyl band intensity (at ∽5.83 μ) with that of a prepared calibration curve revealed the concentration of the resulting aminocyclohexanone. The reactions, with one exception, followed clean first-order kinetics and their rate constants are recorded in Table I. The p-nitro imine IVe appeared to be decomposed by a somewhat slower competing route. Thus, while its initial rate of rearrangement was indeed slower ($k \backsimeq 3 \times 10^5$ sec.$^{-1}$) than that of IVd, it exhibited drifting rate constants and thus was excluded from the calculation of ρ. The relative rates are correlated with σ-substituent constants[12] in Figure 1. The resultant reaction constant, ρ, has the value of −0.32. A similar plot

TABLE I

FIRST-ORDER RATE CONSTANTS FOR THE REARRANGEMENT OF α-HYDROXY IMINES IN DECALIN AT 208°

Compd.	$k_{av} \times 10^5$ sec.$^{-1a}$	Relative rate
IIa	4.8	1
b	6.2	1.3
c	5.7	1.2
d	4.0	0.83
IVb	6.2	1.3
c	5.7	1.2
d	3.9	0.81

[a] Average of at least five values calculated from the expression $k = 1/t \log [a/(a-x)]$ where a = initial concentration of hydroxy imine, x = concentration of ketone formed. The k_{av} values of duplicate runs were identical; maximum deviation from the average was ±10%.

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[7] E. L. Eliel, "Stereochemistry of Carbon Compounds," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, Chapters 7, 8, and 9.

[8] See, for example, C. L. Stevens, R. L. McLean, and A. J. Weinheimer, *J. Am. Chem. Soc.*, **80**, 2276 (1958).

[9] (a) C. L. Stevens, M. E. Munk, C. H. Chang, K. G. Taylor, and A. L. Schy, *J. Org. Chem.*, **29**, 3146 (1964). (b) C. L. Stevens and C. H. Chang, *ibid.*, **27**, 4392 (1962). Perhaps significantly, the isolated yield of α-amino ketone from N-methylaniline is low, 39%.

[10] Y. Inoue, K. Onodera, and I. Karaswada, *J. Agr. Chem. Soc. Japan*, **28**, 193 (1954); *Chem. Abstr.*, **49**, 6839*h* (1955).

[11] (a) I. Elphimoff-Felkin, *Bull. soc. chim. France*, 653 (1962). (b) C. L. Stevens, R. D. Elliott, B. L. Winch, and I. L. Klundt, *J. Am. Chem. Soc.*, **84**, 2272 (1962). (c) D. F. Morrow, M. E. Brokke, G. W. Moersch, M. E. Butler, C. F. Klein, W. A. Neuklis, and E. C. Y. Huang, *J. Org. Chem.*, **30**, 212 (1965). (d) A report on additional synthetic aspects of the amino ketone rearrangement is in preparation.

[12] J. Hine, "Physical Organic Chemistry," 2nd Ed., McGraw-Hill Book Co., Inc., New York, N. Y., 1962, Chapter 4.

using σ^+-substituent constants[12,13] resulted in a poorer straight-line fit.

For the purpose of correlating basicity with rate of rearrangement, an attempt was made to determine the pK_a values of the hydroxy imines. This was impossible in solvents containing water owing to the extremely rapid rate of hydrolysis of the imines. Titration in nonaqueous media proved satisfactory, however, with the method of Fritz[14] being applicable. Thus, the hydroxy imines were titrated potentiometrically in acetonitrile with perchloric acid in dioxane as titrant. The potential at half-neutralization (HNP) was obtained from a graph of the titration curve. Further, a plot of the HNP values *vs.* pK_a values[15] of three substituted anilines gave a perfectly straight line. Using this graph, the pK_a values of the hydroxy imines were estimated. All of these data are listed in Table II.

TABLE II

HALF-NEUTRALIZATION POTENTIALS OF α-HYDROXY IMINES

Compd.	HNP[a]	p$K_a{}'$[b]
IIa	360	4.58
IIb	330	4.88
IIc	340	4.78
IId	424	3.94
IVb	305	5.15
IVc	325	4.93
IVd	450	3.69
Aniline	360	4.58[c]
m-Chloroaniline	470	3.49[c]
p-Toluidine	315	5.02[c]

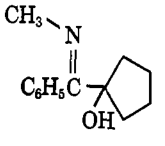
[a] In millivolts. [b] Estimated from a plot of HNP *vs.* p$K_a{}'$ of substituted anilines. [c] Determined in 50% methanol–water (v./v.).

Discussion

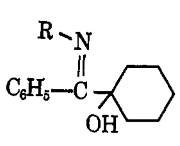
While the experimental first-order rate constants were obtained with a relatively low precision,[16] it is clearly evident that a reaction constant with a small negative value (−0.32) is obtained. It is further evident that the data are correlated better by the use of σ rather than σ^+ constants. Within the experimental error, isomeric α-hydroxy imines undergo rearrangement at the same rate. In view of the relatively low experimental precision, this last fact does not appear, at first to hold significant meaning. However, its relevance becomes apparent on examination of the basicity study results.

The half-neutralization potentials obtained were converted, for purposes of familiarity, to p$K_a{}'$ values. Their relation to p$K_a{}'$ values in aqueous systems is not clear, but their internal consistency is apparent. Thus, as would be expected, the N-phenyl-substituted imines of series IV are more sensitive to substituent change than are those of the C-phenyl-substituted series II. Therefore, we have isomeric α-hydroxy imines differing in "pK_a'" by as much as 0.27 units. Were the rearrangement rate dependent on imine basicity alone, one would expect, *a priori*, that a Hammett analysis would provide log k (relative) *vs.* σ graphs with a more negative ρ for series IV than for series II, with the lines intersecting at hydrogen. However, the rate and basicity data provide us with the curious revelation that, while IIa and IIb, with a ΔpK_a of 0.3, rearrange at measurably different rates, the rearrangement rates of isomers IIb and IVb, ΔpK_a = 0.27, are indistinguishable. Clearly then, in any mechanistic consideration, one must implicate the availability of not only the unshared nitrogen electron pair, but also the availability of those of the π system encompassed by the benzyl N-phenylimine structural unit.

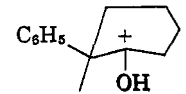
Evidence supporting this twofold involvement can be seen from two other rearrangement examples. Thus, the more basic hydroxy imine VI,[11b] p$K_a{}'$ = 6.65, rearranges at a rate calculated[17] to be roughly four times faster than IIb. But in the series VII, hydroxy imine VIIb with the longer π system undergoes smooth rearrangement at 185° with ring expansion, while the more basic VIIa fails to rearrange at that temperature.[18] The small magnitude of the observed ρ obviously precludes conclusive statements concerning change development in the transition state. However, the data do appear to be more consistent with the development of partial positive charge at the imine carbon and nitrogen atoms in the transition state and argue against the formation of charge-separated intermediate species such as VIII, the formation of which should be accompanied by a positive ρ value.



VI



VIIa, R = CH_3
b, R = C_6H_5



VIII

Since, as the rearrangement proceeds, the imine carbon undergoes an $sp^2 \rightarrow sp^3$ hydridization change, stabilization by direct resonance interaction between the reaction center and *para* substituents is not likely. This borne out by the substantially poorer Hammett correlation when σ^+-substituent constants are employed. The rearrangement, as the first-order kinetics would indicate, is almost certainly completely intramolecular and is expected to have thermodynamic values similar to those found for the rearrangement of VI (ΔH^* 26.2 kcal., ΔS^* −11 e.u.). Thus, the following reaction path is proposed and is envisioned as proceeding in a concerted manner (Scheme II).[19] Before a complete answer is known additional studies encompassing solvent effects, ring-size effects, catalysis

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[13] H. C. Brown and Y. Okamota, *J. Am. Chem. Soc.*, **80**, 4979 (1958).

[14] J. A. Fritz, *Anal. Chem.*, **25**, 407 (1953), and references cited therein.

[15] Obtained on the automatic, semimicro, recording titrimeter described by A. M. Wilson and M. E. Munk, *ibid.*, **34**, 443 (1962).

[16] The standard deviation (s = 0.27) and correlation coefficient (r = 0.77) of the recorded k_{av} values are not impressive but are acceptable for our purposes: H. H. Jaffe, *Chem. Rev.*, **53**, 191 (1953).

[17] The authors thank Mr. H. T. Hanson for providing rate data at T = 166 and 184° from which this calculation was made.

[18] The authors wish to thank Drs. D. R. K. Murty and I. L. Klundt for these data.

[19] The hydroxy imines II and IV exhibit hydrogen-bonded hydroxyl protons, with broad absorption at 3340 cm.$^{-1}$ indicating a *probable syn* ground-state arrangement for the phenyl groups as shown in Scheme II.

TABLE III

α-BROMOCYCLOPENTYL PHENYL KETONES

α-Bromocyclopenty ketone	% yield	M.p., (b.p.,) °C.	C, % Calcd.	C, % Found	H, % Calcd.	H, % Found	O, % Calcd.	O, % Found
p-Methoxyphenyl	85	36–36.5	55.13	55.24	5.34	5.46	11.30	11.40
p-Tolyphenyl	68	(114)[a]	58.44	58.73	5.66	5.82	5.99	6.22
m-Chlorophenyl	90	53–54	50.11	50.32	4.21	4.41	5.56	5.73

[a] At 0.01 mm., n^{25}_D 1.5724.

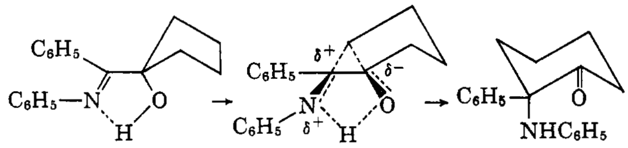
TABLE IV

PHENYL-SUBSTITUTED EPOXY ETHERS

1-Oxaspiro[2.4]heptanes	% yield	B.p., °C. (mm.)	C, % Calcd.	C, % Found	H, % Calcd.	H, % Found	O, % Calcd.	O, % Found
2-Methoxy-2-*p*-methoxyphenyl- (Ib)	72[a]	45–48[b]	71.75	71.54	7.75	7.82	20.49	20.26
2-Methoxy-2-*p*-tolyl- (Ic)	82	82 (0.3)[c]	77.03	76.93	8.31	8.26	14.66	14.83
2-Methoxy-2-*m*-chlorophenyl- (Id)	70	76 (0.007)[d]	65.40	65.64	6.33	6.39	14.85	15.02

[a] Yield from α-chloro ketone. [b] Melting point after distillation at 87° (0.07 mm.). [c] n^{25}_D 1.5140. [d] n^{25}_D 1.5261.

SCHEME II



effects, and others are necessary. The results of such studies on the amino ketone rearrangement will be reported in subsequent communications.

Experimental

Melting points are uncorrected and were obtained on a Thomas–Hoover capillary melting point apparatus. Elemental analyses were done by Midwest Microlab, Inc.

2-Methoxy-2-phenyl-1-oxaspiro[2.4]heptane (Ia)[2] and **cyclopentyl *p*-methoxyphenyl ketone**[20] have been described previously.

Cyclopentyl *p*-tolyl ketone was prepared in 43% yield from *p*-toluonitrile and cyclopentylmagnesium bromide following the general procedure of Curtin and Schmukler[20]: b.p. 80° (0.08 mm.), n^{25}_D 1.5417.

Anal. Calcd. for $C_{13}H_{16}O$: C, 82.92; H, 8.57. Found: C, 82.62; H, 8.58.

2,4-Dinitrophenylhydrazone had m.p. 119–120°.

Anal. Calcd. for $C_{19}H_{20}N_4O_4$: C, 61.95; H, 5.47; N, 17.37. Found: C, 62.01; H, 5.69; N, 17.25.

***m*-Chlorophenyl cyclopentyl ketone** was prepared in 50% yield from *m*-chlorobenzonitrile and cyclopentylmagnesium bromide following the general procedure of Curtin and Schmukler[20]: b.p. 108° (0.5 mm.), n^{25}_D 1.5529.

Anal. Calcd. for $C_{12}H_{13}ClO$: C, 69.06; H, 6.28. Found: C, 69.28; H, 6.53.

α-Bromo ketones from which epoxy ethers were prepared were readily obtained by bromination at room temperature of the corresponding ketone in chloroform or carbon tetrachloride solvents. Occasionally it was necessary to initiate the uptake of bromine by heating or by the addition of small amounts of hydrobromic acid. The pertinent details are listed in Table III. The bromination of cyclopentyl *p*-methoxyphenyl ketone, however, was best effected at 0°. At temperatures above ambient, the aromatic ring was brominated.

Epoxy ethers are listed in Table IV and were prepared by the method of Stevens and Farkas[21] with the single modification that the reactions were performed at ambient temperature. Epoxy ether Ib was prepared in better yield by the following procedure. A solution of 22.0 g. of α-chlorocyclopentyl *p*-methoxyphenyl ketone in 100 ml. of anhydrous ether was added slowly with vigorous stirring to a suspension of dry powdered sodium methoxide (prepared by the reaction of 2.1 g. of sodium metal with excess anhydrous methanol) in 200 ml. of anhydrous ether. After the addition was complete, the reaction mixture was heated at reflux with vigorous stirring for 24 hr. The reaction mixture was filtered and the filtrate was concentrated *in vacuo* to yield an oil. The oil was flash distilled at 100° (0.1 mm.). The flash distillate was fractionated to yield Ib.

α-Chlorocyclopentyl *p*-Methoxyphenyl Ketone.—Chlorine gas was slowly bubbled into a solution of 10.0 g. of *p*-methoxyphenyl cyclopentyl ketone in 50 ml. of carbon tetrachloride. The addition of chlorine was continued until solution became a permanent light green in color. When the color could no longer be discharged by warming the solution to about 45°, the solvent was removed at aspirator pressure to yield a viscous colorless oil. The oil was taken up in dry hexane and crystallization was induced by cooling in a Dry Ice–acetone bath and scratching. The material was filtered and recrystallized once more from hexane to give 9.5 g. (82%) of product, m.p. 36–37°.

Anal. Calcd. for $C_{13}H_{15}ClO_2$: C, 65.40; H, 6.33; O, 13.40. Found: C, 65.65; H, 6.61; O, 13.42.

α-Hydroxy imines are listed in Table V and were prepared by the procedure outlined below for imine IVc.

1-(α-*p*-Tolyliminobenzyl)cyclopentanol (IVc).—A mixture of 1.0 g. of epoxy ether Ia and 600 mg. of *p*-toluidine was heated in an oil bath. The bath temperature was raised from room temperature to 110° over a period of 45 min. and then maintained at 110° for 30 min. The methanol formed during the reaction was removed with the aid of a partial vacuum (100 mm.). The reaction mixture was cooled to room temperature, taken up in hot pentane, clarified with charcoal, and filtered. Upon cooling, 600 mg. of material, m.p. 83–88°, crystallized. A further recrystallization from pentane yielded 500 mg. of IVc.

The preparation of α-hydroxy imine IIb by this procedure was successful when the cooled reaction mixture was immediately subjected to an evaporatory distillation at 0.01 mm. With the bath temperature at 70° a mixture of 1-(*p*-methoxybenzoyl)-cyclopentanol (a hydrolysis product) and α-hydroxy imine slowly distilled. After 12 hr. the bath temperature was raised to 130° whereupon α-hydroxy imine IIb distilled as a heavy oil, solidifying on standing.

2-Phenyl-2-phenylaminocyclohexanones are recorded in Table VI. The following illustrates the superior method A.

2-Phenyl-2-*p*-tolyaminocyclohexanone (Vc).—A solution of 1.6 g. of α-hydroxy imine IVc in 25 ml. of dry decalin was heated at reflux for 5 hr. Upon cooling, 1.4 g. of a light tan solid separated. The material was clarified with Norit and recrystallized from ethanol to give 1.3 g. of Vc. A further recrystallization from ethanol failed to change the melting point.

The following is illustrative of method B.

2-*m*-chlorophenyl-2-phenylaminocyclohexanone (IIId).—A solution of 1.5 g. of epoxy ether Id and 0.7 g. aniline in 10 ml. of decalin was refluxed 4 hr. The amino ketone crystallized on cooling affording 500 mg. with m.p. 100°. Two recrystallizations from ethanol gave IIId.

Kinetic Studies. A.—The decalin used was purified by the following procedure. Technical grade decalin (500 g.) was stirred vigorously overnight at steam-bath temperature with an equal weight of concentrated sulfuric acid. The decalin layer was separated and washed with 100-ml. portions of concentrated sulfuric acid until the acid washes were colorless. The

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[20] D. Y. Curtin and S. Schmukler, *J. Am. Chem. Soc.*, **77**, 1105 (1955).

[21] C. L. Stevens and E. Farkas, *ibid.*, **74**, 618 (1952).

TABLE V

PROPERTIES OF α-HYDROXY IMINES

Compd.	% yield	M.p., °C.	Recryst.[a] solvent	C, %		H, %		N, %	
				Calcd.	Found	Calcd.	Found	Calcd.	Found
Ketone N-phenylimine									
1-Hydroxycyclopentyl phenyl (IIa)	82	100–101	A	81.46	81.39	7.22	7.49	5.28	5.04
1-Hydroxycyclopentyl *p*-methoxyphenyl (IIb)	50	68–69	C	77.26	77.04	7.17	7.42	4.74	4.50
1-Hydroxycyclopentyl *p*-tolyl (IIc)	54	72–73	B	81.68	81.40	7.57	7.68	5.01	4.94
1-Hydroxycyclopentyl *m*-chlorophenyl (IId)	68	95–96	A	72.11	72.36	6.06	6.21	4.67	4.77
Cyclopentanol									
1-(α-*p*-Methoxyphenyliminobenzyl)- (IVb)	68	80–81	A	77.26	77.31	7.17	7.39	4.74	4.72
1-(α-*p*-Tolyliminobenzyl)- (IVc)	44	90–91	B	81.68	81.77	7.57	7.59	5.01	5.00
1-(α-*m*-Chlorophenyliminobenzyl)- IVd	73	107–108	A	72.11	72.13	6.06	5.83	4.67	4.70
1-(α-*p*-Nitrophenyliminobenzyl- (IVe)	53	137–138	A	69.66	69.50	5.85	5.85	9.03	9.00

[a] A, hexane; B, pentane; C, petroleum ether (b.p. 30–60°).

TABLE VI

2-PHENYL-2-PHENYLAMINOCYCLOHEXANONES

Cyclohexanone	% yield	M.p., °C.	Recrystn.[a] solvent	C, %		H, %		N, %	
				Calcd.	Found	Calcd.	Found	Calcd.	Found
2-Phenyl-2-phenylamino- (IIIa)	82	157–158	A	81.46	81.65	7.22	7.17	5.28	5.26
2-*p*-Methoxyphenyl-2-phenylamino- (IIb)	77	135–136	B	77.26	77.15	7.17	7.36	4.47	4.75
2-*p*-Tolyl-2-phenylamino- (IIIc)	15[b]	154–156	B	81.68	81.86	7.57	7.62	5.01	5.11
2-*m*-Chlorophenyl-2-phenylamino- (IIId)	20[b]	167–168	A	72.11	72.20	6.06	6.09	4.67	4.73
2-Phenyl-2-*p*-methoxyphenylamino- (Vb)	89[c]	111–112	A	77.26	77.44	7.17	7.38	4.47	4.78
2-Phenyl-2-*p*-tolyamino- (Vc)	80	162–163	A	81.68	81.57	7.57	7.77	5.01	5.01
2-Phenyl-2-*m*-chlorophenylamino- (Vd)	77	135–136	A	72.11	72.24	6.06	6.17	4.67	4.68
2-Phenyl-2-*p*-nitrophenylamino- (Ve)	38s	196–197	C	69.66	69.53	5.85	5.90	9.03	9.14

[a] Solvent A, ethanol; B, methanol; C, chloroform–hexane. [b] Prepared by method B. [c] 70% when method B was used.

decalin was then washed with saturated sodium bicarbonate solution and water and dried over calcium chloride. The decalin was distilled from sodium through a 30-cm. Vigreux column and the fraction boiling 188–190° was collected (about 200 g.)

B.—In an 8-ml. round-bottom flask was placed 60 mg. of the imino alcohol to be studied. The material was then dissolved in exactly 1 ml. of decalin, and the flask was sealed and immersed in an oil bath whose temperature was maintained at 208 ± 2°. After the flask had been immersed for the desired length of time, it was removed and immediately cooled in an ice bath. The decalin was removed *in vacuo* and the residue was dissolved in exactly 1 ml. of reagent grade chloroform. The infrared spectrum of this material was then recorded in the region of 5.0–6.5 μ. The height of the carbonyl peak was measured and the concentration of ketone was determined with the aid of a calibration curve, prepared from the infrared spectra of α-hydroxy imine–amino ketone synthetic mixtures.

The precision of the method was considered to be ±10% since most of the rate constants obtained varied by less than 10% from the average rate constant, although some discrepancies of as much as 20% from the average were observed. These latter values were discarded in the calculation of the average rate constant. However, it was noted that those determinations which varied by greater than 10% from the average rate constant occurred in the initial determination. This may be due to the fact that the error in determining the amount of ketone formed at this interval would be expected to be the largest since the concentration of ketone is least at this interval.

Basicity Studies. A. Apparatus.—The following equipment was used: Beckman Model G potentiometer, Leeds and Northrope STD. 1199-31 calomel reference electrode, and Beckman 41262 glass electrode.

B. **Materials.**—The anilines used were commercially available and were purified either by distillation or recrystallization prior to use. The dioxane was purified by distillation from lithium aluminum hydride and then stored over sodium wire. The acetonitrile was purified by distillation from phosphorus pentoxide. The perchloric acid was Baker Analyzed reagent grade, assay 70–72%.

C. **General Procedure.**—A sample of the hydroxy imine, approximately 0.7 mequiv., was dissolved in 20 ml. of dry acetonitrile and titrated potentiometrically with standard perchloric acid in dioxane. The titrant was added in 0.5-ml. increments and the potential drop was recorded after each addition. The readings were plotted on a curve of milliliter of titrant *vs.* potential. The potential at half-neutralization (HNP) was read from the graph.

The titrant was prepared and standardized following the procedure of Fritz.[14] The average value obtained from three standardizations was 0.0789 *N*.

In order to show that the hydroxy imines did not hydrolyze under titration conditions, an equimolar mixture of substituted hydroxy ketone, which would arise from the hydrolysis of the hydroxy imine under study, and aniline was titrated under the same conditions. The HNP of this mixture was found to be the same as that obtained when pure aniline itself was titrated.

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