

TABLE I

ABSORPTION SPECTRA DATA OF SOME CHALCONE DERIVATIVES (IN HEXANE SOLUTION)

Compound	Molar concn. $\times 10^3$	Maxima		Minima	
		$\lambda_{\text{A.}}$	$\epsilon \times 10^{-3}$	$\lambda_{\text{A.}}$	$\epsilon \times 10^{-3}$
(IA) m. p. 120-121°	12.50	2510	15.90	2310	6.59
		3150	0.19		
(IB) m. p. 71-72°	11.15	2590	17.91	2320	6.46
		3300	0.21		
50% (IA) + 50% (IB)	10.10	2555	16.25
1-Benzyl-2-phenyl-3-benzoyl-ethylenimine	10.81	2430	12.62	2300	9.56
		3250	0.16		
Benzyl- <i>p</i> -methylacetophenone	11.90	2485	16.01	2250	3.93
Benzal- <i>p</i> -methylacetophenone	9.13	2990	26.86	2440	4.00
Benzylacetophenone	23.81	2380	12.40	2600	1.10
		2800	1.50		
Benzalacetophenone	14.50	2260	12.10	2410	4.85
		2990	23.90		

TABLE II

ABSORPTION SPECTRA DATA OF SOME CHALCONE DERIVATIVES (IN 95% ALCOHOL SOLUTION)

Compound	Molar concn. $\times 10^3$	Maxima		Minima	
		$\lambda_{\text{A.}}$	$\epsilon \times 10^{-3}$	$\lambda_{\text{A.}}$	$\epsilon \times 10^{-3}$
(IA) m. p. 120-121°	6.07	2595	17.0	2320	4.71
(IB) m. p. 71-72°	0.477	2620	18.3	2310	5.30
(IB) (crude) m. p. 71-74°	0.621	2620	18.3	2320	5.25
Benzyl- <i>p</i> -methylacetophenone	1.14	2540	15.2	2350	2.61
Benzal- <i>p</i> -methylacetophenone	1.08	3100	27.8	2480	3.39

Effect of Time and Light Exposure on the Absorption Spectra of *cis* and *trans* Ethylene Imine Ketones (IB) and (IA).—A 0.000117 to 0.000100 molar solution in hexane of each of the highly purified samples of (IA) and (IB) was prepared. These solutions were stored in new, volumetric flasks which had been bathed in concentrated sulfuric acid for several days, and then rinsed with distilled

water and dried. These solutions were stored in the dark. The ultraviolet spectra were examined periodically and little or no change observed. After two days the solutions were each divided into two portions, one portion of each being exposed to direct sunlight for about forty-eight hours. The remaining portions were again stored in the dark. No significant changes in the spectra of (IA) were observed with either portion. With (IB) the portion again stored in the dark showed no change, but that exposed to sunlight displayed approximately a 100 Å. shift in the wave length of the maximum absorption band and a general broadening of the band.

TABLE III

EFFECT OF LIGHT ON LOW MELTING 1-BENZYL-2-PHENYL-3-*p*-TOLUYLETHYLENE IMINE (IB)

Storage time	λ_{max} Å.					
	0	24	48	96	2500	2600
Dark storage	0	24	48	96	48	48
Light storage	0	0	0	0	48	48
Total hours	0	24	48	96	96	96
$\epsilon_{\text{max}} \times 10^{-3}$	18.08	17.91	17.92	17.74	17.57	16.30

TABLE IV

EFFECT OF LIGHT ON HIGH MELTING 1-BENZYL-2-PHENYL-3-*p*-TOLUYLETHYLENE IMINE (IA)

Storage time	λ_{max} Å.				
	0	24	48	96	48
Dark storage	0	24	48	96	48
Light storage	0	0	0	0	48
Total hours	0	24	48	96	96
$\epsilon_{\text{max}} \times 10^{-3}$	15.24	15.27	15.27	15.25	15.15

In Table I and Fig. 3 are given the results of a study made with a freshly prepared 50-50 mixture of (IA) and (IB) in hexane solutions. These studies were made within two hours of the time the solution was prepared.

Summary

cis and *trans* racemates of 1-benzyl-2-phenyl-3-*p*-toluylethylenimine have been isolated from the reaction of benzylamine with α,β -dibromobenzyl-*p*-methylacetophenone. The physical properties, absorption spectra and behavior with hydrogen chloride are consistent with the configurations that have been assigned. The interconvertibility of these geometrical isomers has been studied.

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[CONTRIBUTION FROM AVERY LABORATORY OF THE UNIVERSITY OF NEBRASKA]

Ethylene Imine Ketones. V.¹ Reaction with Hydrogen Chloride²

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Previous investigations of the reactions of ethylene imine ketones with hydrogen halides have shown that the ethylene imine ring cleaves in the two directions under various conditions.^{1,4}

It was of interest to re-investigate the reaction

(1) For paper IV see, Cromwell and Hoeksema, *THIS JOURNAL*, **71**, 708 (1949).

(2) Presented before a session of the Division of Organic Chemistry, 113th Meeting of the American Chemical Society, Chicago, Illinois, April 20, 1948.

(3) Abstracted from the Ph.D. thesis (1949); du Pont Fellow, 1947-1948.

(4) Cromwell and Caughlan, *THIS JOURNAL*, **67**, 2235 (1945).

of benzylamine with α,β -dibromobenzylacetophenone⁵ in an attempt to account for a larger portion of the starting materials. A further aim of this investigation was a quantitative product study of the reaction of ethylene imine ketones with minimum amounts of hydrogen chloride.

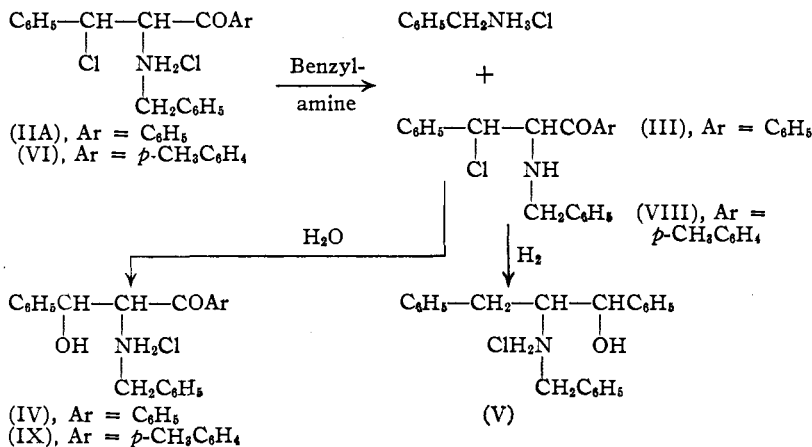
We were unable to isolate a lower-melting, more soluble form of 1-benzyl-2-phenyl-3-benzoyl-ethylenimine. However, when the filtrate from the isolation of the higher-melting, less soluble form of this compound (I) (m. p. 108°)⁵ was treated with

(5) Cromwell, Babson and Harris, *ibid.*, **65**, 312 (1943).

excess dry hydrogen chloride, most of the remaining starting materials were accounted for. A mixed dichloride product ($C_{22}H_{21}NOCl_2$) resulted which was separated by recrystallization into nearly equal amounts of β -chloro- α -benzylamino-benzylacetophenone hydrochloride (IIA) and α -chloro- β -benzylaminobenzylacetophenone hydrochloride (IIB). The isomer (IIA) had been obtained in a previous investigation of the reaction of ethylene imine ketone (I) with excess hydrogen chloride, and assigned this structure.⁶

The dichloride (IIB) reacted with dry, acidified acetone solutions of potassium iodide to release nearly one equivalent of iodine, while (IIA) gave almost no reaction under the same conditions.⁶ Neither of these products showed any tendency to rearrange to the other on standing in either methyl alcohol or benzene saturated with dry hydrogen chloride.

When (IIA) was warmed with a benzene solution of benzylamine the base (III), α -benzylamino- β -chlorobenzylacetophenone, resulted. Compound (III) was readily hydrolyzed by warm aqueous alcohol to α -benzylamino- β -hydroxybenzylacetophenone hydrochloride (IV). Catalytic hydrogenation converted (III) into the known⁷ 2-benzylamino-1,3-diphenylpropanol-1 hydrochloride (V) (and picrate). This latter experiment seems to afford unequivocal proof for the structure assigned to (IIA).

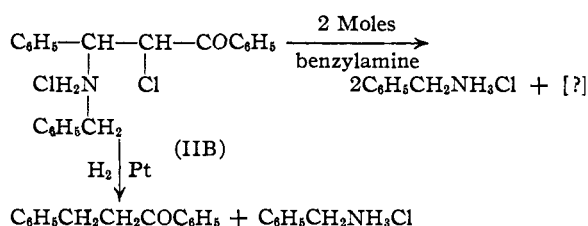


When the dichloride (IIB) was treated with a warm benzene solution of benzylamine, two equivalents of benzylamine hydrochloride were formed. This indicated that the chlorine attached to carbon was more readily removed here than in (IIA). Catalytic hydrogenation of (IIB) gave a good yield of benzylacetophenone. The intermediate product in this latter reaction may have been β -benzylaminobenzylacetophenone. It has been reported previously, from this laboratory, that such β -amino ketones readily undergo beta elimination during catalytic hydrogenation.⁸

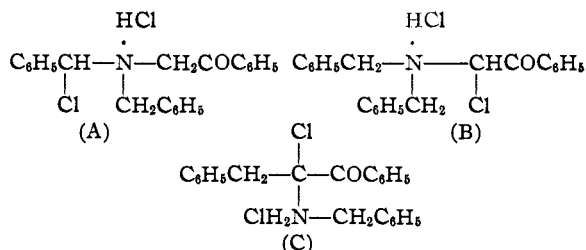
(6) Cromwell and Wankel, *THIS JOURNAL*, **70**, 1321 (1948).

(7) Wilson and Sun, *J. Chinese Chem. Soc.*, **2**, 243 (1935).

(8) Cromwell, Wiles and Schroeder, *THIS JOURNAL*, **64**, 2432 (1942).



We believe the structure of (IIB) has been definitely established. Other structures, such as (A), (B) and (C), for these products (IIA) and (IIB), seem to have been eliminated. Moreover, it is not possible for (IIA) and (IIB) to be related as racemates of the same position isomer, (IIA) or (IIB).



The isomeric dichlorides (IIA) and (IIB) were also obtained from a quantitative experiment with pure 1-benzyl-2-phenyl-3-benzoyl ethylenimine (m. p. 108°) (I). When minimum amounts of dry hydrogen chloride were employed, the α -chloro ketone (IIB) was the major (73.5%) product, while (IIA) was formed in lesser amounts (26.5%). Addition of one equivalent of dry hydrogen chloride to a cold acetone-ether solution of (I) resulted in the primary precipitation of quite pure (IIB). From the filtrate of (IIB) some unchanged ethylene imine ketone (I) was isolated. Addition of a second calculated amount of dry hydrogen chloride to the filtrate of (I) caused the formation of a mixed dichloride.

This latter product was separated into the two isomers, (IIA) and (IIB), by taking advantage of the expected differences in the basic strengths of the free bases of these two dichlorides.

Iodine release data showed the above dichloride to be approximately a 50-50 mixture of (IIA) and (IIB). This product was treated with one equivalent of benzylamine and the precipitated benzylamine hydrochloride filtered off. One-half of an equivalent of hydrogen chloride was added to precipitate (IIB), the hydrochloride of the stronger base. A second one-half equivalent of the same reagent then precipitated (IIA).

It has been reported¹ that excess amounts of

dry hydrogen chloride reacted with *trans*-1-benzyl-2-phenyl-3-*p*-toluyl-ethylenimine to give β -chloro- α -benzylaminobenzyl-*p*-methylacetophenone hydrochloride (VI). The *cis* isomer gave a mixed dichloride which was indicated to contain approximately 54% of (VI) and 46% of α -chloro- β -benzylaminobenzyl-*p*-methylacetophenone hydrochloride (VII).

Quantitative experiments using minimum amounts of dry hydrogen chloride, as with the ethylene imine ketone (I), have been carried out with these *cis* and *trans* isomers mentioned above. The *trans* isomer gave 78% of the α -chloro ketone (VII) and 22% of the β -chloro ketone (VI). The *cis* isomer gave 54% of (VII) and 46% of (VI). These relative percentage yields were approximated from iodine release studies with the chloride products. Figure 1 compares the rate of iodine release by relatively pure α -chloro ketone (VII) with that of a pure sample of (IIB).

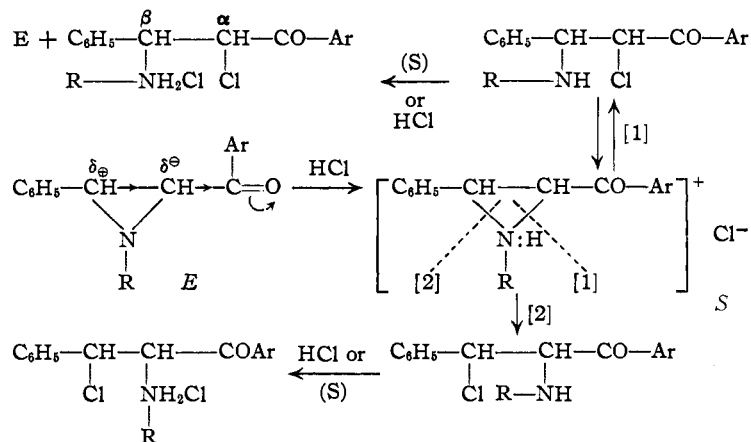
From both of these hydrogen chloride cleavage experiments some ethylene imine ketone was recovered. It is significant that, from the experiment starting with the *cis* isomer, we isolated the *trans* ethylene imine ketone. This indicates that the rearrangement of the *cis* isomer to the *trans* isomer may be catalyzed by acid as well as by light.¹

β -Chloro- α -benzylaminobenzyl-*p*-methylacetophenone hydrochloride (VI) reacted with a warm benzene solution of excess benzylamine to lose only one equivalent of hydrogen chloride, and form the base (VIII). Warm, aqueous alcohol converted (VIII) to β -hydroxy- α -benzylaminobenzyl-*p*-methylacetophenone hydrochloride (IX). Configuration studies of these dichlorides, including ring closure to the ethylene imine ketones by the α -chloro products, are being undertaken.

Discussion of Hydrogen Chloride Reaction Mechanisms.—It seems evident that the first product from the reaction of an ethylene imine ketone with hydrogen chloride is the simple salt (S). A hydrochloride of type (S) was isolated in a previous investigation.⁵ The direction of the cleavage of the ethylene imine ring in the salt (S) is determined by the conditions of the experiment and the configuration of the original ethylene imine ketone. The results obtained from the quantitative dry hydrogen chloride experiments suggest several possible mechanisms that serve as a working hypothesis for the kinetic studies that are in progress.

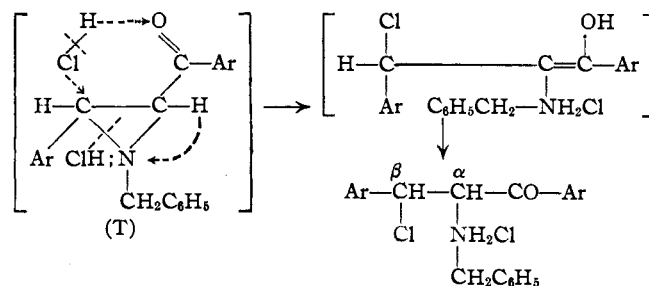
S_N1 and/or S_N2 Ring Cleavage Mechanism

If the mechanism is of an S_N1 type then the ring would be expected to open, mainly according



to scheme [1] if the α -carbon has the greater electron density. For an S_N2 type of ring cleavage, scheme [2] would be the major reaction course if the β -carbon is the more electrophilic. It is to be recalled that the *trans* ethylene imine ketones gave, mainly, the α -chloro ketones with minimum amounts of hydrogen chloride. The *cis* form studied reacted much more rapidly to give only slightly more α -chloro ketone than β -chloro ketone, under these conditions. Excess chloride ion concentration should favor the S_N2 mechanism and course [2].

Carbonyl Directed 1-4 Ring Cleavage Mechanism



Under the influence of excess hydrogen chloride the salt (S) might also be expected to undergo ring cleavage by way of a carbonyl directed 1,4-attack, as indicated above. An inspection of scale models indicates that with the *trans* structures transition complex (T) could form readily. In the *cis* form the aryl group on the β -carbon would be expected to repel the chlorine atom of the hydrogen chloride molecule to such an extent that a transition complex (T) would seem unlikely. It is to be recalled that excess dry hydrogen chloride converted the *trans* ethylene imine ketones almost entirely into β -chloro ketones. A similar experiment with the *cis* compound gave only slightly less α -chloro ketone than β -chloro ketone.

Acknowledgment.—The senior author appreciates a grant from the Research Council of the University of Nebraska which aided in the completion of this investigation.

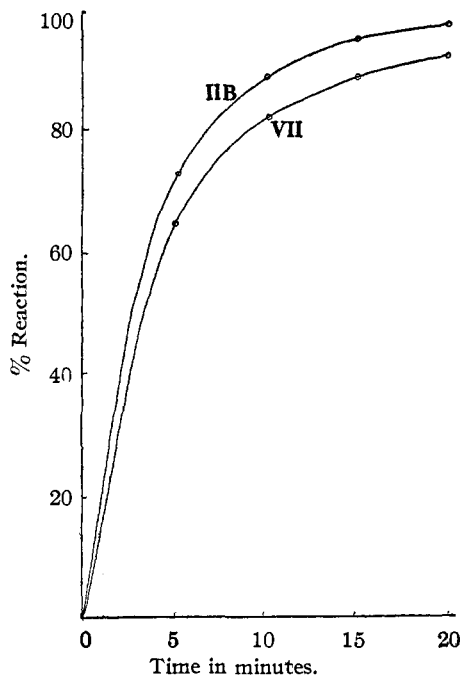


Fig. 1.—Rates of iodine release by α -chloro- β -amino ketones (IIB) and (VII) in a dry acetone-alcohol acidic solution of potassium iodide at 66°.

Experimental

Reaction of α,β -Dibromobenzylacetophenone with Benzylamine. Quantitative Studies.—Following the directions outlined previously¹ for the preparation of 1-benzyl-2-phenyl-3-*p*-toluylethylenimine, a 46% yield of 1-benzyl-2-phenyl-3-benzoylethylenimine, m. p. 108° was obtained from α,β -dibromobenzylacetophenone. It was not possible to isolate a solid, low-melting isomer in this case. The reaction mixture filtrate was treated with an excess of an absolute alcohol solution of dry hydrogen chloride, to give as a first crop, colorless crystals, 24% yield, m. p. 159–164°. Two recrystallizations of this product from methyl alcohol and dry ether gave a 20% yield of (IIA), m. p. 164–166°. Iodine release⁶ at 66° in thirty minutes was 6.4% for this product.

Anal. Calcd. for $C_{22}H_{21}NOCl_2$: Cl, 18.36. Found: Cl, 18.30.

The filtrate from (IIA) was treated with several times its volume of dry ether and cooled for two days to give a second crop of colorless crystals (20% yield), m. p. 149–150°, of (IIB); recrystallized from methyl alcohol and dry ether, m. p. 151–152°. (IIB) released 95.4% of one equivalent of iodine at 66° in fifteen minutes. See also Figure 1.

Anal. Calcd. for $C_{22}H_{21}NOCl_2$: Cl, 18.36. Found: Cl, 18.32. A 50-50 mixture of (IIA) and (IIB) showed a m. p. 150–159° and gave an iodine release value of 51% in either fifteen or thirty minutes.

In this experiment, 90% of the original α,β -dibromobenzylacetophenone was accounted for. Neither (IIA) nor (IIB) underwent any appreciable change on standing at room temperature in dry methyl alcohol solution for four days.

α -Benzylamino- β -chlorobenzylacetophenone (III).—A 5.0 g. (0.013 mole) sample of the hydrochloride (IIA) was mixed with 50 ml. of benzene and 1.39 g. (0.013 mole) of benzylamine, heated on the steam-bath for ten minutes, and then allowed to stand at room temperature for three hours. Dry ether was added and the colorless precipitate of benzylamine hydrochloride filtered off, wt. 1.85 g. (99% of one equivalent). The filtrate was evaporated under

reduced pressure and petroleum ether added. Colorless crystals formed and were filtered off, wt. 3.0 g. (0.0086 mole, 66% yield), m. p. 92–93°; iodine release at 66° in thirty minutes was 3.0%.

Anal. Calcd. for $C_{22}H_{20}NOCl$: C, 75.52; H, 5.76. Found: C, 75.88; H, 5.84.

Compound (III) decomposed after standing at room temperature for twenty-four hours in a vacuum desiccator.

When the hydrochloride (IIB) was placed in benzene and treated with benzylamine, two equivalents of benzylamine hydrochloride were formed immediately. Evaporation of the benzene left an oil which solidified at –15° but which could not be resolved to a solid product at room temperature. This possibly was a low melting form of 1-benzyl-2-phenyl-3-benzoylethylenimine.

α -Benzylamino- β -hydroxybenzylacetophenone Hydrochloride (IV).—An attempted recrystallization of this product (III) from hot aqueous alcohol resulted in a hydrolysis, and precipitated a product no longer soluble in ether or acetone, m. p. 210° (IV).

Anal. Calcd. for $C_{22}H_{22}NO_2Cl$: C, 71.82; H, 6.03; N, 3.81. Found: C, 71.54; H, 6.20; N, 3.93.

A more extensive decomposition accompanied this hydrolysis as indicated by the presence of benzaldehyde.

Hydrogenation of (III).—A 2.0-g. sample of (III) was dissolved in 20 ml. of methanol and 0.5 g. of 10% palladium-on-charcoal catalyst added. This mixture was shaken for two hours with hydrogen at room temperature under a pressure of 38 lb. per sq. inch. The catalyst was filtered off and the methanol evaporated under reduced pressure. Addition of dry ether gave mixed hydrochlorides, wt. 1.0 g., m. p. 205–210°. This product was dissolved in water and the solution treated with dilute sodium hydroxide to give an oily precipitate which was extracted with ether. On passing dry hydrogen chloride into the dried ether solution, a colorless precipitate formed, m. p. 223–225°; recrystallized from alcohol and ether, m. p. 228–229°; wt. 0.7 g. (V).

Anal. Calcd. for $C_{22}H_{24}NOCl$: C, 74.66; H, 6.84; N, 3.96. Found: C, 74.36; H, 6.96; N, 3.78.

A sample of 2-benzylamino-1,3-diphenylpropanol-1 hydrochloride was prepared and found to have a m. p. of 228–229° instead of m. p. 220° as previously reported.⁷ Several careful mixed m. p. and mixed freezing point experiments indicated this compound to be identical with (V). The picrate of the free base of (V) was prepared, m. p. 149–150°, and found to be identical with the authentic picrate of 2-benzylamino-1,3-diphenylpropanol-1.⁷

Hydrogenation of (IIB).—A 0.6 g. (0.00155 mole) sample of the hydrochloride (IIB) was dissolved in 20 ml. of absolute alcohol and 0.1 g. of platinum oxide catalyst added. The mixture was shaken for thirty minutes with hydrogen at room temperature under a pressure of 45 lb. per sq. inch. The catalyst was filtered off and the solvent evaporated under reduced pressure. Addition of dry ether gave 0.15 g. (0.00104 mole) of benzylamine hydrochloride. Evaporation of the ether filtrate gave 0.2 g. (0.00095 mole, 61% yield) of a colorless, crystalline product, m. p. 70°, identical with benzylacetophenone.

Treatment of 1-Benzyl-2-phenyl-3-benzoylethylenimine with Minimum Amounts of Hydrogen Chloride.—A 3.0-g. (0.00959 mole) sample of 1-benzyl-2-phenyl-3-benzoylethylenimine (m. p. 108°) was dissolved in 25 ml. of dry acetone and cooled in an ice-bath to 5°. A 25.1-ml. quantity of a 0.383 molar dry, hydrogen chloride-in-ether solution (0.0096 mole of HCl) was added slowly with stirring. A large amount of white precipitate formed immediately and remained for several hours (the ethylene imine ketone hydrochloride).⁸ After standing at room temperature for one day, the solution had developed a pale-yellow color, the original precipitate had disappeared and a lesser amount of larger, colorless crystals appeared which were filtered off, m. p. 149°, wt. 1.0 g. (0.00259 mole, 27% yield). This product was identical in all respects with (IIB), giving an iodine release of 93.2% in fifteen minutes at 66°.

Anal. Calcd. for $C_{22}H_{21}NOCl_2$: C, 68.39; H, 5.48; N, 3.63. Found: C, 68.17; H, 5.71; N, 3.42.

Evaporation of the filtrate from (IIB) left a semi-solid residue which was recrystallized from a benzene-petroleum ether mixture to give 0.60 g. (0.00192 mole) of the starting ethylene imine ketone, m. p. 103–106°, identified by a mixed m. p. experiment and by its behavior in direct sunlight (turned pink).

Assuming that about 0.0044 mole of the chlorobenzylaminobenzylacetophenones remained in the filtrate from the recovery of the ethylene imine ketone, 11.5 ml. of the 0.383 molar dry, ether-hydrogen chloride solution (0.0044 mole of HCl) were added and the solution cooled in an ice-bath to give an immediate precipitation of a colorless product which was filtered off; wt. 1.5 g. (0.00389 mole); m. p. 141–145°; iodine release, 49.4% in fifteen minutes at 66°.

A separation of this mixed product melting at 141–145° was effected by a method based upon the differences in the basic strengths of α -chloro- β -benzylaminobenzylacetophenone and α -benzylamino- β -chlorobenzylacetophenone. A 0.70 g. (0.00182 mole) sample was mixed with 25 ml. of dry ether and treated with 0.20 g. (0.00187 mole) of benzylamine. After standing for fifteen hours in the ice chest the precipitated benzylamine hydrochloride was filtered off. The ether filtrate was then treated with 0.0009 mole of hydrogen chloride. After cooling at 0° for one day, a colorless product was filtered off, wt. 0.34 g. (0.00088 mole), m. p. 148–150°; iodine release at 66° in fifteen minutes was 77%. This was fairly pure (IIB). To the filtrate was now added a second 0.0009 molar quantity of hydrogen chloride. After standing for twenty-four hours, a second product was obtained, m. p. 161–162°, wt. 0.27 g. (0.0007 mole); iodine release at 66° in thirty minutes was 2.3%. This was fairly pure (IIA).

This entire experiment was repeated with the same results at each step, within 5–10%.

The chloride (IIA) was identical in all respects with the chloride obtained previously from the reaction of excess dry or aqueous hydrogen chloride and 1-benzyl-2-phenyl-3-benzoylethylenimine, and was assigned the structure β -chloro- α -benzylaminobenzylacetophenone hydrochloride.^{4,6} Both (IIA) and (IIB) remained unchanged after standing for several days in a mixture of dry benzene and dry ether saturated with dry hydrogen chloride.

Reaction of *cis* and *trans* 1-Benzyl-2-phenyl-3-*p*-toluylethylenimines with Minimum Amounts of Hydrogen Chloride.—Following the procedure as outlined above for 1-benzyl-2-phenyl-3-benzoylethylenimine, the following results were obtained with these *cis* and *trans* isomeric ethylene imine ketones.¹

From 1.8 g. (0.0055 mole) of this *trans* isomer, the first hydrochloride product (VII) weighed 0.5 g. (0.00125 mole), m. p. 155–161°; iodine release in fifteen minutes at 66° was 88.7% (see also Fig. 1). When recrystallized from methanol and ether, the melting point increased to 163–167°; but the iodine release value was practically unchanged. This sample (VII) was almost pure α -chloro- β -benzylaminobenzyl-*p*-methylacetophenone hydrochloride.

Also obtained in the second step was 0.9 g. (0.00225 mole) of mixed hydrochlorides, m. p. 159–162°, which gave an iodine release of 65.4%. Evaporation of the residual mixture gave 0.35 g. (0.00107 mole) of unreacted ethylene imine ketone.

From 2.0 g. (0.00612 mole) of the *cis* isomer, the first hydrochloride product weighed 0.57 g. (0.00142 mole), m. p. 156–159°; iodine release for this product at 66° in fifteen minutes was 53.8%. Evaporation of the filtrate from this product gave 0.2 g. (0.00061 mole) of the *trans* instead of the *cis* ethylene imine ketone, as shown by a mixed m. p. and its light sensitivity. Treatment of the residual solution with more dry hydrogen chloride gave a second hydrochloride product, wt. 1.08 g. (0.0027 mole), m. p. 150–155°. Iodine release for this product in fifteen minutes at 66° was 54.2%.

Continuous fractional recrystallizations from ethanol and dry ether separated both of these products into nearly equal amounts of (VII) and β -chloro- α -benzylaminobenzyl-*p*-methylacetophenone hydrochloride (VI).

β -Chloro- α -benzylaminobenzyl-*p*-methylacetophenone (VIII).—Repeating the procedure outlined above for the preparation of (III), 2.0 g. of the hydrochloride (VI) gave 0.714 g. of benzylamine hydrochloride and 1.0 g. of (VIII); recrystallized from an ether-petroleum ether mixture, m. p. 105° (decomposed then resolidified).

Anal. Calcd. for $C_{23}H_{22}NOCl$: C, 75.93; H, 6.09; N, 3.85. Found: C, 76.11; H, 6.07; N, 4.10.

β -Hydroxy- α -benzylaminobenzyl-*p*-methylacetophenone Hydrochloride (IX).—Following the procedure outlined for the preparation of (IV), 0.4 g. of (VIII) gave 0.23 g. of (IX), recrystallized from methanol and ether, m. p. 208–210°.

Anal. Calcd. for $C_{23}H_{24}NO_2Cl$: C, 72.33; H, 6.34; N, 3.67. Found: C, 72.09; H, 6.52; N, 3.71.

Summary

1. Excess amounts of dry hydrogen chloride react with the *trans* forms of ethylene imine ketones to give mainly the β -chloro- α -aminoketone hydrochlorides. Minimum amounts of this reagent convert these *trans* forms largely into the isomeric α -chloro- β -aminoketone hydrochlorides.

2. The *cis* form of 1-benzyl-2-phenyl-3-*p*-toluylethylenimine reacts very rapidly with excess or minimum amounts of dry hydrogen chloride to give nearly equal amounts of the α -chloro and β -chloro ketones.

3. Structure proofs for the closely related α -chloro- β -aminoketones and β -chloro- α -aminoketones have been devised. Possible mechanisms to account for these different ring cleavages have been discussed.

LINCOLN, NEBRASKA

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