

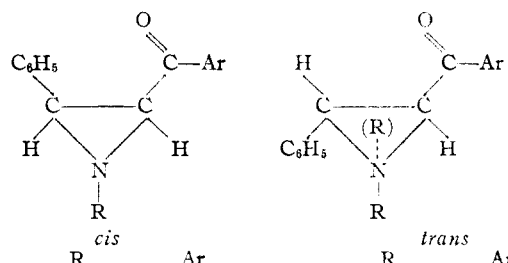
[CONTRIBUTION FROM AVERY LABORATORY, UNIVERSITY OF NEBRASKA]

Ethylene Imine Ketones. VII.<sup>1</sup> Stereochemical Configurations, Absorption Spectra and Reactions with Phenylhydrazine<sup>2</sup>BY NORMAN H. CROMWELL, NORVAL G. BARKER, RONALD A. WANKEL,<sup>3</sup> PHILLIP J. VANDERHORST, FRANK W. OLSON AND J. HILL ANGLIN, JR.

The objective of the present investigation was to obtain more examples of geometrical isomerism in this 1,2,3-trisubstituted ethylene imine series and to develop methods of assigning the most probable configurations to such isomers. Seven new ethylene imine ketones have been prepared by the previously described method. The ultraviolet and infrared absorption spectra of these and several known ethylene imine ketones have been determined. A detailed study of the diagnostic reactions of phenylhydrazine with the *cis-trans* isomeric pairs of the ethylene imine ketones has been made. Theoretical arguments are offered for using these spectral and chemical differences as a basis for assigning new geometrical configurations to the ethylene imine ketones. It has been concluded that the geometrical isomer which has its characteristic carbonyl absorption band at the lower frequency in both the ultraviolet and infrared ranges of the spectrum, and which reacts the most readily with phenylhydrazine to produce a 4-aminopyrazoline is the *trans* isomer. The *cis* isomers produce the corresponding pyrazole in the phenylhydrazine reaction. This appears to be the first reported attempt to apply absorption spectral methods to the elucidation of structures of cyclic geometrical isomers.

The absolute assignment of geometrical configurations to *cis* and *trans* isomers in cyclic series of organic compounds has often been a formidable problem. Since the molecules of the ethylene imine ketones being studied in these investigations contain no elements of symmetry the assignment of geometrical configurations from X-ray studies would be a relatively complicated undertaking. Although such studies will probably be made eventually it is now possible to present a demanding combination of absorption spectral and chemical evidence for the configurations now assigned to these isomeric ethylene imine ketones. The present paper is concerned with a reinterpretation of the phenylhydrazine reactions of these compounds and the presentation of a considerable amount of new evidence and argument to substantiate the new structural assignments.

Using the method of preparation developed previously,<sup>4</sup> four different pairs of *cis-trans* ethylene imine ketones have now been obtained from the corresponding  $\alpha,\beta$ -dibromoketones and separated for the present studies; see IA and IB, IIA and IIB, IIIA and IIIB, and IVA and IVB. The purity of the isomers is indicated by the sharpness of the characteristic carbonyl band in the infrared, near  $6\mu$ ; see Figs. 7-12.



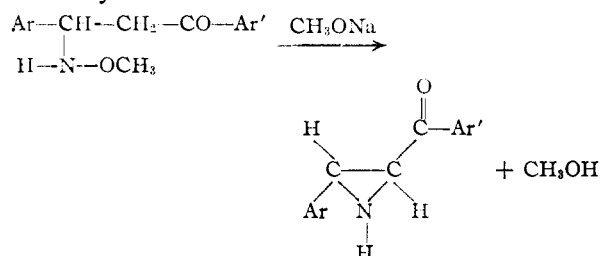
	R	Ar		R	Ar
IA	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub>	C <sub>6</sub> H <sub>5</sub>	IB	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub>	C <sub>6</sub> H <sub>5</sub>
IIA	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub>	C <sub>6</sub> H <sub>4</sub> CH <sub>3</sub> - <i>p</i>	IIB	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub>	C <sub>6</sub> H <sub>4</sub> CH <sub>3</sub> - <i>p</i>
IIIA	C <sub>6</sub> H <sub>11</sub>	C <sub>6</sub> H <sub>5</sub>	IIIB	C <sub>6</sub> H <sub>11</sub>	C <sub>6</sub> H <sub>5</sub>
IVB	C <sub>6</sub> H <sub>11</sub>	C <sub>6</sub> H <sub>4</sub> CH <sub>3</sub> - <i>p</i>	IVB	C <sub>6</sub> H <sub>11</sub>	C <sub>6</sub> H <sub>4</sub> CH <sub>3</sub> - <i>p</i>
			V	CH <sub>3</sub>	C <sub>6</sub> H <sub>4</sub> CH <sub>3</sub> - <i>p</i>
			VI	H	C <sub>6</sub> H <sub>4</sub> CH <sub>3</sub> - <i>p</i>

A consideration of the mechanism of the reaction of  $\alpha,\beta$ -dibromoketones with amines<sup>5</sup> suggests that when R is a large group, having nearly the same steric requirements as the phenyl group, the *cis* and *trans* forms of the ethylene imine ketones might both be expected to be formed in considerable amounts. This was found to be true for the preparation of these four isomeric pairs I-IV.

The R group on nitrogen would be expected to lie on the opposite side of the plane of the three-ring with respect to the phenyl and aroyl groups in the *cis* structure. In the *trans* structure the R group might be located on either side of the plane of the three-ring. This point is discussed more fully in the following paper in this series.

When R is a small group such as methyl, the ring closure step of this reaction series might be expected to favor somewhat the formation of the *trans* isomer. Apparently V was formed in over 50% yields and the spectral and chemical evidence indicates it to be the *trans* form. Unfortunately the *cis* form of V could not be isolated as a solid but chemical evidence for its presence in the reaction mixture was obtained.

2-Phenyl-3-*p*-toluylethylenimine VI was prepared in a 61% yield using the reaction previously offered by Blatt<sup>6</sup> for the preparation of  $\alpha$ -amino- $\alpha,\beta$ -unsaturated ketones. That this compound VI has an ethylene imine ketone structure is now apparent from the spectral and chemical properties. This carefully developed reaction series of Blatt<sup>6</sup> constitutes the only good method of preparing this type of ethylene imine ketone. It is important to observe that only one product is formed here in this reaction series in excellent yields. It is obvious that one should expect to obtain mainly the least sterically crowded *trans* structure in this series



(1) For the previous paper in this series see Cromwell and Hoeksema, THIS JOURNAL, 71, 716 (1949).

(2) The material in this article was a part of a paper presented in the Symposium on the Chemistry of Small Ring Compounds at the 117th Meeting of the American Chemical Society, Philadelphia, Pa., April 11, 1950.

(3) du Pont Fellow, 1947-1948.

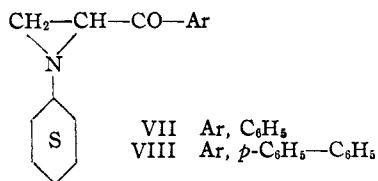
(4) See Cromwell and Hoeksema, THIS JOURNAL, 71, 708 (1949).

(5) Cromwell, Chem. Revs., 38, 118 (1946).

(6) Blatt, THIS JOURNAL, 61, 3494 (1939).

although the mechanism of ring closure here is somewhat obscure. It was of considerable importance to find that VI had the chemical and spectral characteristics to be expected of the *trans* configuration.

Two examples, VII and VIII, of a new type of ethylene imine ketone were prepared from the corresponding  $\alpha,\beta$ -dibromoketones. Excellent



yields of single products were obtained. The possibility of stereoisomerism at nitrogen might be expected to allow these compounds to exist in two geometrical forms, but the likelihood of ring closure taking place in such a manner as to have the aroyl and nitrogen R-group turn up on the same side of the plane of the three-ring seems improbable.

**Absorption Spectra and Configuration.**—An inspection of the ultraviolet absorption spectra curves, Figs. 1–4, indicates that the ethylene imine ketones I–VII have one strong band between 240 and 260 m $\mu$ . This is essentially associ-

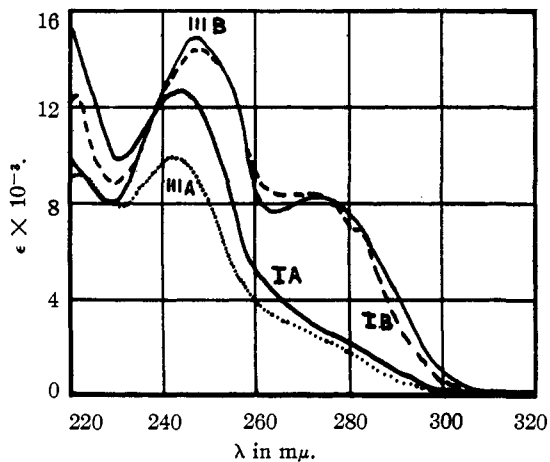


Fig. 1.—Ultraviolet absorption spectra of IA, IB, IIIA and IIIB in heptane.

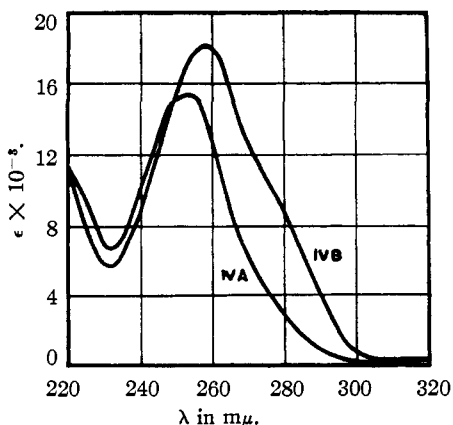


Fig. 2.—Ultraviolet absorption spectra of IVA and IVB in heptane.

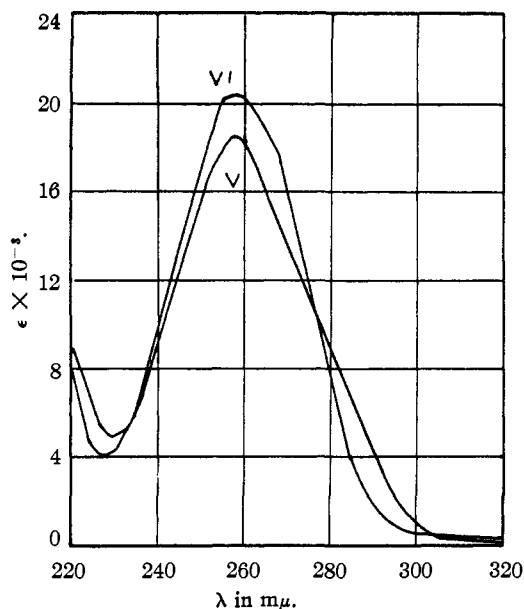


Fig. 3.—Ultraviolet absorption spectra of V and VI in heptane.

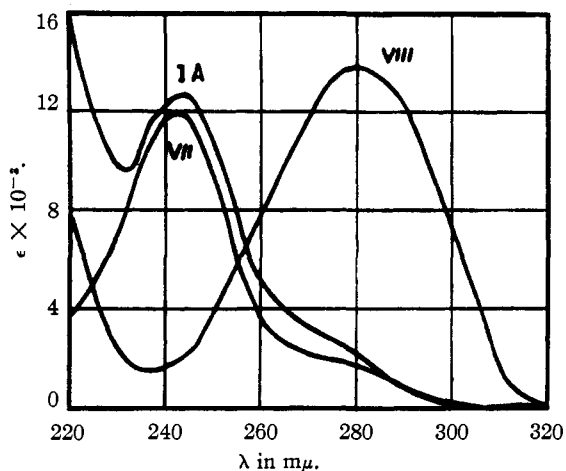


Fig. 4.—Ultraviolet absorption spectra of IA, VII and VIII in heptane.

ated with electronic vibrations within the aroyl grouping, which has a small but definite interaction with the  $\pi$ -electrons (unshared electrons on nitrogen) of the three-ring. In the case of the isomeric pairs I–IV it is possible to divide these into an A and a B-series where members of the B-series are those which absorb at slightly longer wave lengths with somewhat greater intensities in the 240–260 m $\mu$  region; see Table I. This would indicate a greater electron mobility and a longer conjugated unsaturated system in the B-series. Previous ultraviolet absorption spectra studies<sup>4,7</sup> have shown the considerable differences between the spectra of the ethylene imine ketones in general and the related  $\alpha$ -amino- and  $\beta$ -amino- $\alpha,\beta$ -unsaturated ketones.

The infrared absorption spectra studies also indicated it was possible to place the isomeric ethylene imine ketones into an A and B-series;

(7) Cromwell and Watson, *J. Org. Chem.*, **14**, 411 (1949).

TABLE I  
ULTRAVIOLET ABSORPTION SPECTRA MAXIMA FOR ETHYLENE  
IMINE KETONES AND DERIVATIVES

Compound	No.	Molar concn. $\times 10^4$	Maxima $\lambda_{m\mu}$ $\epsilon \times 10^{-3}$	
Ethylene imine				
1-Benzyl-2-phenyl-3-benzoyl	IA	1.081	243	12.62 <sup>a</sup>
	IB	0.880	248	14.41
1-Benzyl-2-phenyl-3- <i>p</i> -toluyl	IIA	1.250	251	15.90 <sup>a</sup>
	IIB	1.115	259	17.91 <sup>a</sup>
1-Cyclohexyl-2-phenyl-3-benzoyl	IIIA	1.107	244	9.84
	IIIB	0.962	246	14.92
1-Cyclohexyl-2-phenyl-3- <i>p</i> -toluyl	IVA	0.972	253	15.40
	IVB	1.071	258	18.16
1-Methyl-2-phenyl-3- <i>p</i> -toluyl	V	1.020	258	18.56
2-Phenyl-3- <i>p</i> -toluyl	VI	1.010	256	20.52
1-Cyclohexyl-2-benzoyl	VII	1.623	243	11.89
1-Cyclohexyl-2- <i>p</i> -phenyl-benzoyl	VIII	1.030	280	14.41
Benzylacetophenone		2.38	238	12.4 <sup>a</sup>
Benzyl- <i>p</i> -methylacetophenone		1.19	248	16.0 <sup>a</sup>
Pyrazoline			359	23.40
1,5-Diphenyl-3- <i>p</i> -toluyl-4-cyclohexylamino	X	0.686	313	7.52
			244	17.47
4-N-Acetylcyclohexylamino	XI	.787	362	21.42
			310	6.77
			246	19.28
4-Methylamino	XV	.836	360	21.20
			244	18.55
4-Amino	XVI	.973	355	17.89
			244	15.69
1,3,5-Triphenyl-4-benzylamino <sup>b</sup>	XIII	.361	360	19.36
			310	6.96
			242	16.67
4-Cyclohexylamino	XIV	1.086	355	18.98
			242	15.27
Acetylphenylhydrazone of IVA <sup>b</sup>	IX	0.962	330	14.05
			299	13.23
			244	22.90

<sup>a</sup> Cromwell and Hoeksema, *THIS JOURNAL*, 71, 711 (1949).  
<sup>b</sup> In 95% ethanol solution.

see Table II. The B-compounds are the isomers having their characteristic absorption bands, associated with the carbonyl bond stretching vibrations, at the longer wave lengths (lower frequencies). These studies were done with two different instruments and in solution as well as in solid suspension to be sure of the reality and consistency of these differences. Again it is clearly indicated that the ethylene imine ketones of the B-series contain a more polarized and/or polarizable carbonyl group (the carbon-oxygen bond has more single bond character) than that of the A-series members. The only structural differences possible here which could account for these spectral differences in both the ultraviolet and infrared ranges of the spectrum are those which would provide for greater interaction between the carbonyl bond electrons and other unsaturated centers in the molecule to aid in lowering the energy level of the excited state. This extra interaction must be with the three-ring  $\pi$ -electrons. The C=O band is found at 1685  $\text{cm}^{-1}$  for acetophenone and propiophenone but at 1655  $\text{cm}^{-1}$  for benzophenone.<sup>8</sup>

(8) Thompson and Torkington, *J. Chem. Soc.*, 640 (1945).

TABLE II  
INFRARED ABSORPTION SPECTRA OF ETHYLENE IMINE  
KETONES

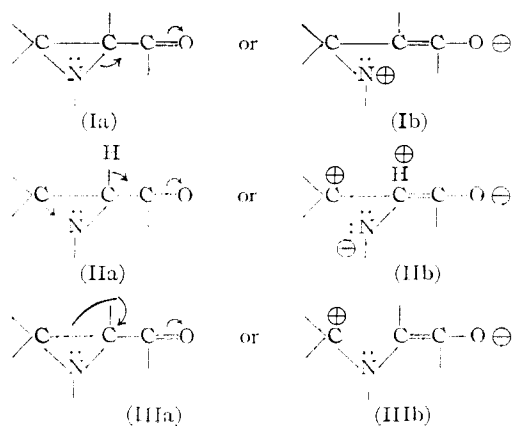
Compound	No.	Carbonyl frequency, $\text{cm}^{-1}$		
		Run 1 <sup>a</sup>	Run 2 <sup>b</sup>	Run 3 <sup>c</sup>
Ethylene imine				
1-Benzyl-2-phenyl-3-benzoyl	IA	1685	1684	1685
	IB	1668	1666	1670
3- <i>p</i> -Toluyl	IIA	1675	1678 <sup>d</sup>	..
	IIB	1655	1651 <sup>d</sup>	..
1-Cyclohexyl-2-phenyl-3-benzoyl	IIIA	1686	..	..
	IIIB	1658	..	..
3- <i>p</i> -Toluyl	IVA	1684	1682	1685
	IVB	1652	1653	1666
1-Methyl-2-phenyl-3- <i>p</i> -toluyl	V	1658	1655	1668
2-Phenyl-3- <i>p</i> -toluyl	VI	1662	1665	1666
1-Cyclohexyl-2-benzoyl	VII	1679	1674	1683
Benzyl- <i>p</i> -methylacetophenone		1670	..	..

<sup>a</sup> Nujol mulls—Baird I. R. spectrophotometer. <sup>b</sup> Nujol mulls—Perkin-Elmer I. R. spectrophotometer. <sup>c</sup>  $\text{CHCl}_3$  Solution—Perkin-Elmer I. R. spectrophotometer. <sup>d</sup> Cromwell, Miller, Johnson, Frank and Wallace, *THIS JOURNAL*, 71, 3337 (1949).

Although the approach to coplanarity of the carbonyl group with the three-ring and the  $\beta$ -phenyl group (through electron interaction) is somewhat difficult to conceive of in either case, this should be less sterically restricted in the case of the *trans* structure. The *trans* structures might be expected to have a somewhat greater endocyclic carbon-nitrogen bond strain when the R group on nitrogen is larger than H. This should also contribute to bond deformation and interaction between the  $\pi$ -electrons of the three-ring and those of the carbonyl bond.

1-Cyclohexyl-2-benzoyl ethyleneimine (VII) shows a carbonyl frequency in the infrared which indicates only a small interaction between the electrons of its three-ring and those of the carbonyl group. This result would seem to demonstrate the importance of the presence of the phenyl group on the  $\beta$ -carbon atom which aids (through resonance interaction) in carrying the partial positive charge in this portion of the *trans* molecules of IB, IIB, IIIB, IVB, V and VI. Furthermore in VII we would not expect as much endocyclic carbon-nitrogen bond strain as in IB, IIB, IIIB, IVB and V.

It is difficult to describe clearly by structural formulas the nature of the electron interaction between the three-ring and the carbonyl group.



By formulas (Ia) to (IIIb) we intend to imply a kind of hyperconjugation or no-bond resonance in which the unshared electrons on the nitrogen participate in a manner similar to that suggested by Rogers<sup>9</sup> for the epoxy compounds. Other structures showing the distribution in the aromatic ring of the  $\beta$ -carbon atom positive charges of (IIb) and (IIIb) are to be considered when a phenyl group is attached to this position.

It is now proposed that on the basis of the above considerations the ethylene imine ketones of the B-series of I-IV as well as V and VI be assigned a *trans* configuration. The members of the A-series are the corresponding *cis* isomers. These assignments are consistent with the logical conclusions to be drawn from the chemical studies which are included in this paper and in the following one in the series.

**Reactions with Phenylhydrazine.**—The previous<sup>1</sup> paper in this series reported a study of the reactions of the ethylene imine ketones IIA and IIB with phenylhydrazine. One of the isomeric compounds was found to produce the triarylpyrazole while the other gave the corresponding 4-aminotriarylpyrazoline. Having assumed the incorrect configurations for these ethylene imine ketones at the outset, the conclusion was drawn that the *cis* structure produced the stable 4-aminopyrazoline while the *trans* structure was thought to form an unstable 4-aminopyrazoline which lost the amine by an improbable *cis* elimination to give the pyrazole.

In view of the many instances reported in the literature of preferred *trans* elimination of water<sup>10</sup> and amines<sup>11</sup> from cyclic compounds, it now seems much more probable that it is in truth the *trans* ethylene imine ketones, such as IB, IIB, IIIB, IVB, V and VI, which should produce the more stable 4-amino-1,3,5-triarylpyrazolines in which the amino group and the hydrogen on the adjacent carbon atom are *cis* to each other. The ultraviolet absorption spectra given in Figs. 5 and 6 and in Table I establish the common general structures of the 4-aminopyrazolines. The *cis* ethylene imine ketones IA, IIA, IIIA, IVA and the 1-cyclohexyl-2-benzoyl ethylenimine (VII), all give the expected pyrazole.

A series of competitive reactions with phenylhydrazine showed that in all cases the *trans* ethylene imine ketone successfully competes for the reagent and often the *cis* compound may be recovered unchanged from the reaction mixture. If electrical factors predominate (as they probably do, see the following paper) then one would actually expect the *cis* isomer to react the most rapidly with phenylhydrazine to form the intermediate phenylhydrazone hydrate. It cannot be decided *a priori* whether the *cis* or the *trans* isomer phenylhydrazone should have the more favorable equilibrium constant of formation. No phenylhydrazones have been isolated as yet. Be this as it may, the de-

(9) Rogers, THIS JOURNAL, **69**, 2544 (1947).

(10) (a) Vavon, Bull. soc. chim., [4] **49**, 567 (1931); (b) Price and Karabinos, THIS JOURNAL, **62**, 1159 (1940).

(11) (a) Vavon and Chilouet, Compt. rend., **203**, 1526 (1936); *ibid.*, **204**, 53 (1937); (b) Dhar, Hughes, Ingold, et al., J. Chem. Soc., 2117 (1948).

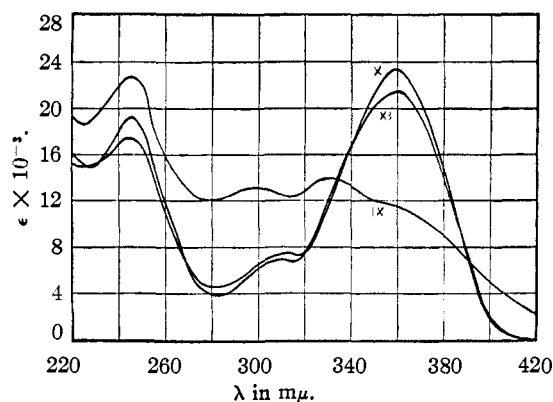


Fig. 5.—Ultraviolet absorption spectra of IX in ethanol and X and XI in heptane.

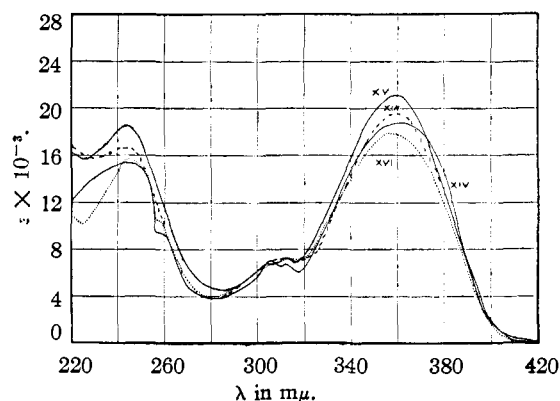
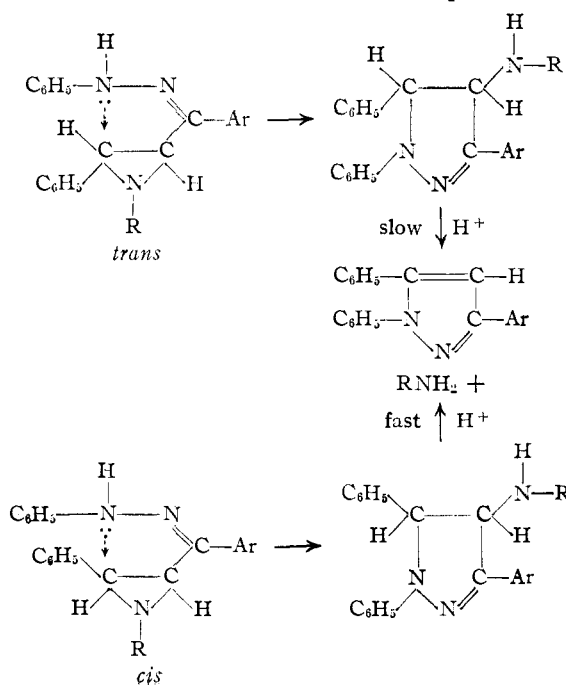


Fig. 6.—Ultraviolet absorption spectra of XIII in ethanol and XIV, XV and XVI in heptane.

cisive factor in the competitive reaction series is undoubtedly the non-reversible opening of the three-ring by either the hydrazone or its hydrate to form the five-membered ring by a backside attack at the  $\beta$ -carbon atom.

With the *trans* isomer, this would produce the



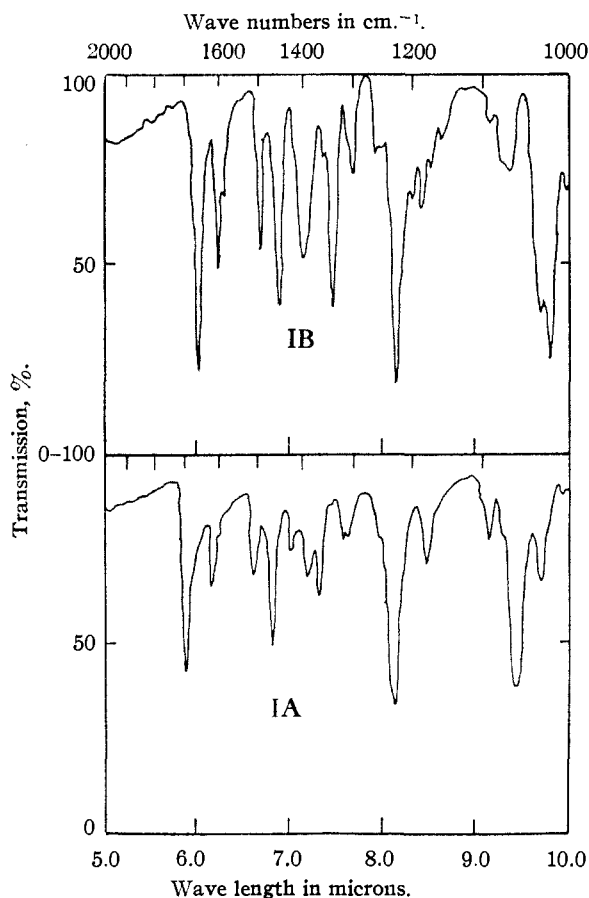


Fig. 7.—Infrared spectra of IA and IB; all curves are traced from the complete traces 2–16  $\mu$  as determined with a Baird I. R. recording spectrophotometer.

4-aminopyrazoline in which the hydrogen on the adjacent carbon is in the relatively stable *cis* position to the 4-amino group. The backside attack to open the three-ring in the *cis* ethylene imine ketone would be sterically hindered by the  $\beta$ -phenyl group.

It was important to find that 2-phenyl-3-*p*-toluylethylenimine (VI), which because of its method of preparation would be expected to have the *trans* structure, also produced a 4-amino-1,3,5-triarylpyrazoline on treatment with phenylhydrazine. All of these 4-amino-1,3,5-triarylpyrazolines are readily converted to the 1,3,5-triarylpyrazoles after sufficient heating in acid solution. These 4-aminopyrazolines react with acetic anhydride to give the *N*-acetyl derivatives such as XI and XII and not a diacetyl derivative as previously reported.<sup>1</sup> The spectrum of XI is included in Fig. 5. Both XI and XII give the corresponding 1,3,5-triarylpyrazole on heating with acids.

In glacial acetic acid the *cis* ethylene imine ke-

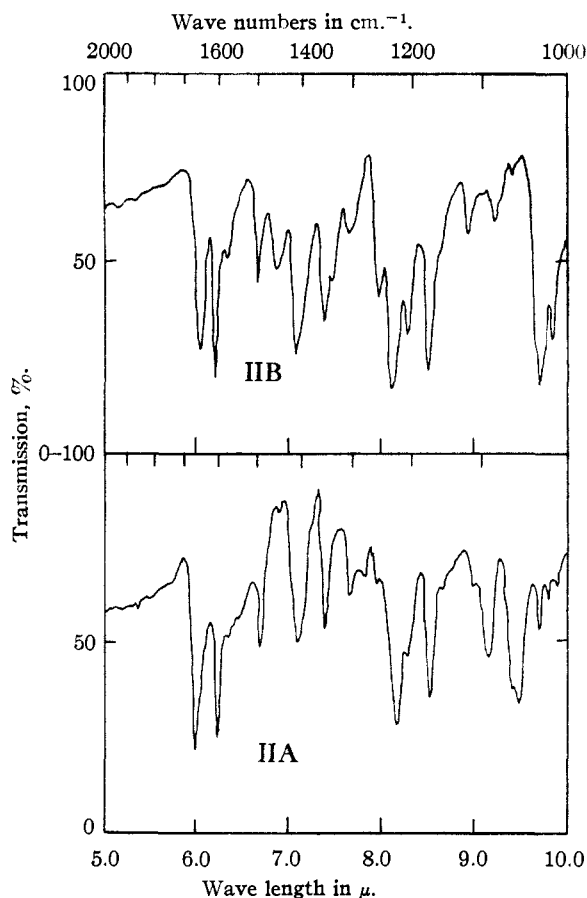
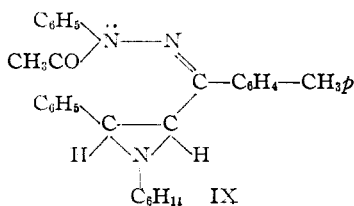


Fig. 8.—Infrared spectra of IIA and IIB.

tones react with phenylhydrazine to produce, besides the pyrazole, yellow compounds which analyses, absorption spectra studies (Fig. 5) and acid hydrolysis indicate to be acetyl phenylhydrazones of the ethylene imine ketones. Compounds of this type such as IX would be expected to be quite stable and to be slow to undergo the three-ring opening, five-ring closure to give the pyrazole.<sup>1</sup>

It was interesting to learn that  $\beta$ -benzylamino-benzalacetophenone, isomeric with IA and IB, does not react readily with phenylhydrazine.

### Experimental<sup>12</sup>

**Preparation of Ethylene Imine Ketones. 1-Benzyl-2-phenyl-3-benzoylethylenimines, IA and IB.**—The residual oil from the isolation of IA, m.p. 108°,<sup>13</sup> was induced to crystallize from methanol by cooling in a Dry Ice-acetone-bath. The solid product was twice recrystallized from methanol to give a 35% yield, based on the starting  $\alpha,\beta$ -dibromobenzylacetophenone, of colorless, fluffy needles, IB, m.p. 59–62°.

**Anal.** Calcd. for  $\text{C}_{22}\text{H}_{19}\text{NO}$ : mol. wt., 313; C, 84.31; H, 6.11. Found for IB: mol. wt., 331; C, 84.36; H, 6.08.

**1-Benzyl-2-phenyl-3-*p*-toluylethylenimines, IIA and IIB.**—The previously described directions<sup>4</sup> were followed to give a 34% yield of IIA, m.p. 116–118° and a 40% yield of IIB, m.p. 74–76° (average yields from four runs). Both products were recrystallized from ethanol-water mixtures.

**1-Cyclohexyl-2-phenyl-3-benzoylethylenimines, IIIA and IIIB.**—Using cyclohexylamine and  $\alpha,\beta$ -dibromobenzylaceto-

(12) Many of the micro analyses for carbon and hydrogen are by the Clark Microanalytical Laboratory, Urbana, Illinois, arranged for through the courtesy of the Smith, Kline and French Laboratories, Philadelphia, Pa.

(13) Cromwell and Wankel, *THIS JOURNAL*, **71**, 711 (1949).

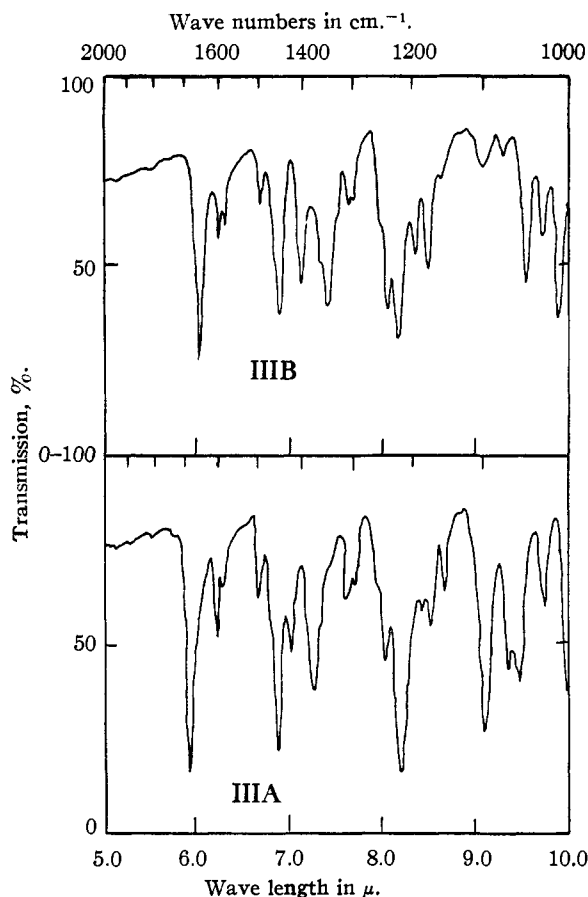


Fig. 9.—Infrared spectra of IIIA and IIIB.

phenone and the directions previously described<sup>4</sup> for the preparation of IIA and IIB, these isomers IIIA, m.p. 107–109°,<sup>14</sup> and IIIB, m.p. 99–101°, were obtained in yields of 40 and 38%, respectively. Both products were recrystallized from methanol.

*Anal.* Calcd. for  $C_{21}H_{23}NO$ : C, 82.62; H, 7.54; N, 4.59. Found for IIIB: C, 82.27; H, 7.31; N, 4.68.

**1-Cyclohexyl-2-phenyl-3-*p*-toluylethylenimines, IVA and IVB.**—From cyclohexylamine and  $\alpha,\beta$ -dibromobenzyl-*p*-methylacetophenone, IVA, m.p. 111–112° and IVB, m.p. 89–90° were obtained in yields of 41 and 36% respectively. The isomer IVB was readily extracted from IVA with petroleum ether, b.p. 60–70°. Both colorless products were recrystallized from 95% ethanol.

*Anal.* Calcd. for  $C_{22}H_{25}NO$ : mol. wt., 319; C, 82.72; H, 7.89; N, 4.39. Found for IVA: mol. wt., 320; C, 82.38; H, 7.74; N, 4.43. Found for IVB: mol. wt., 313; C, 82.58; H, 7.98; N, 4.41.

The isomeric ethylene imine ketones IVA and IVB were also obtained in 45 and 40% yields, respectively, from the reaction of  $\alpha$ -bromobenzal-*p*-methylacetophenone with two molar equivalents of cyclohexylamine in dry ether solution.

**1-Methyl-2-phenyl-3-*p*-toluylethylenimine (V).**—Reaction of  $\alpha,\beta$ -dibromobenzyl-*p*-methylacetophenone with an ether solution of methylamine at room temperature for 24 hours gave a 46% yield of colorless crystals, V, m.p. 76–78°, recrystallized from 95% ethanol.

*Anal.* Calcd. for  $C_{17}H_{17}NO$ : C, 81.27; H, 6.77. Found for V: C, 81.61; H, 6.77.

Evaporation of the residual reaction mixture from the isolation of V left a yellow oil which could not be induced to crystallize. Treatment of this oil with phenylhydrazine and acetic acid in absolute ethanol<sup>1</sup> gave a 29% yield of 1,5-diphenyl-3-*p*-tolylpyrazole, m.p. 129–130°,<sup>1</sup> and an 8% yield of 1,5-diphenyl-3-*p*-tolyl-4-methylaminopyrazoline

(14) Cromwell, Babson and Harris, *THIS JOURNAL*, **65**, 312 (1943).

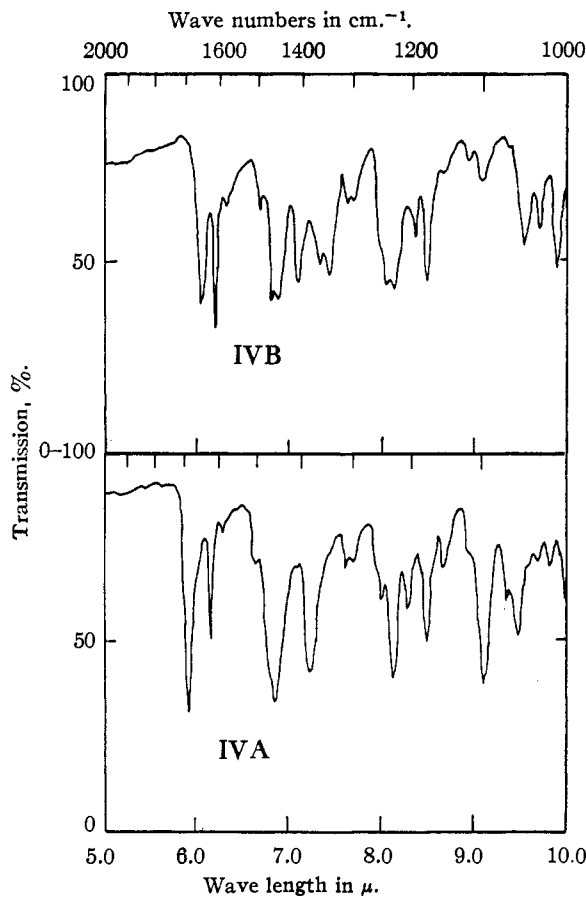


Fig. 10.—Infrared spectra of IVA and IVB.

(XV), m.p. 157–158°, described below. This would indicate that the reaction of methylamine with the dibromide produced at least a 54% yield of V.

**2-Phenyl-3-*p*-toluylethylenimine (VI).**—This compound, m.p. 89–92°, was obtained in a 61% yield using the directions given by Blatt<sup>6</sup> for the supposed preparation of  $\alpha$ -aminobenzal-*p*-methylacetophenone.

**1-Cyclohexyl-2-benzoylethylenimine (VII).**— $\alpha,\beta$ -Dibromopropiophenone<sup>15</sup> (10.0 g., 0.0343 mole) was allowed to react with 10.19 g. (0.1029 mole) of cyclohexylamine in dry ether at 15° for a period of 4 hours. A colorless crystalline product, wt. 6.23 g. (80% yield), m.p. 61–62° (recrystallized from ethanol and water) resulted.

*Anal.* Calcd. for  $C_{15}H_{19}NO$ : C, 78.56; H, 8.35; N, 6.11. Found for VII: C, 78.55; H, 8.25; N, 6.02.

**1-Cyclohexyl-2-*p*-phenylbenzoylethylenimine (VIII).**—The  $\alpha,\beta$ -dibromo-*p*-phenylpropiophenone required for this preparation was obtained in a 92% yield, m.p. 85–86° (recrystallized from hot 95% ethanol). The directions of Davis<sup>15</sup> and Kohler<sup>16</sup> as given for  $\alpha,\beta$ -dibromopropiophenone were followed using  $\alpha,\beta$ -dibromopropionyl chloride and diphenyl.

*Anal.* Calcd. for  $C_{18}H_{19}Br_2O$ : C, 48.94; H, 3.29. Found: C, 48.70; H, 3.51.

Using the procedure described for VII, this ethylene imine ketone VIII was obtained in an 80% yield, m.p. 88–89° (recrystallized from petroleum ether and from ethanol and water).

*Anal.* Calcd. for  $C_{21}H_{25}NO$ : C, 82.04; H, 8.20; N, 4.56. Found: C, 82.18; H, 8.16; N, 4.64.

#### Reactions of Ethylene Imine Ketones with Phenylhydrazine

In general the ethylene imine ketone was dissolved in the minimum amount of absolute ethanol and treated with one molar equivalent of pure phenylhydrazine and two equiva-

(15) Davis, *ibid.*, **63**, 1677 (1941).

(16) Kohler, *Am. Chem. J.*, **42**, 398 (1909).

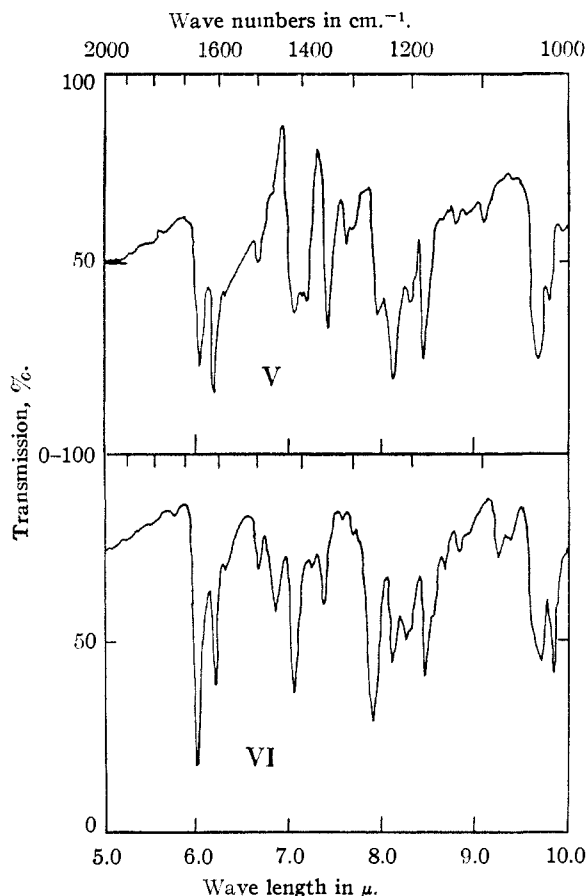
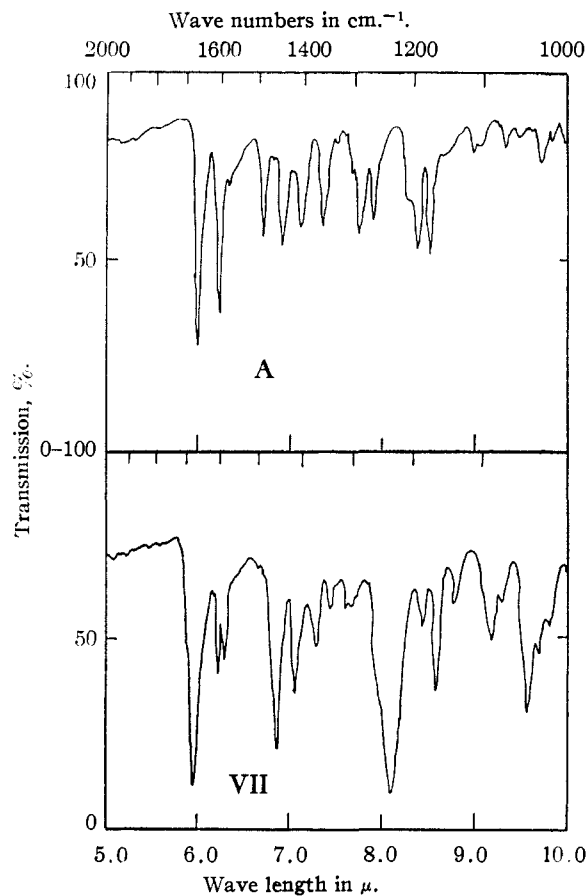


Fig. 11.—Infrared spectra of V and VI.

Fig. 12.—Infrared spectra of VII and A (benzyl-*p*-methylacetophenone).

lents of glacial acetic acid at room temperature. The mixtures stood for 4 to 8 hours. The products were isolated and recrystallized from either 95% or absolute ethanol. All reaction mixtures producing the 4-aminopyrazolines developed a blue fluorescence within 5 minutes after admixture. The 4-aminopyrazolines all gave positive Knorr<sup>17</sup> tests.

The competitive reaction experiments were carried out in a similar manner with equal amounts of the isomeric pairs of ethylene imine ketones by adding only enough phenylhydrazine and glacial acetic acid to give complete reaction with one of the isomers. These reaction mixtures stood at room temperature for 24 hours. In some cases the unreacted isomer could be isolated.

**Reactions with IVA and IVB.**—The isomer IVA gave a 60% yield of 1,5-diphenyl-3-*p*-tolylpyrazole, m.p. 128–130°,<sup>1</sup> in ethanol solution. When this reaction was carried out in glacial acetic acid as described previously<sup>1</sup> for IIA, a 65% yield of the pyrazole resulted along with a 11% yield of a yellow solid IX, m.p. 156–157° (recrystallized from absolute ethanol).

*Anal.* Calcd. for C<sub>20</sub>H<sub>23</sub>N<sub>3</sub>O: C, 79.78; H, 7.37; N, 9.31. Found for IX: C, 79.39; H, 7.62; N, 9.46.

In absolute ethanol the isomer IVB gave a 60% yield of 1,5-diphenyl-3-*p*-tolyl-4-cyclohexylaminopyrazoline (X), m.p. 127–128° and a 15% yield of 1,5-diphenyl-3-*p*-tolylpyrazole.

*Anal.* Calcd. for C<sub>28</sub>H<sub>31</sub>N<sub>3</sub>: C, 82.11; H, 7.63; N, 10.26. Found for X: C, 82.11; H, 7.55; N, 10.38.

The aminopyrazoline X was converted to 1,5-diphenyl-3-*p*-tolylpyrazole in 60% yield by warming with glacial acetic acid on the steam-bath for 2 hours. When X was refluxed for 2 hours with acetic anhydride the *N*-acetyl derivative XI, m.p. 177–178°, was produced in 85% yield. This compound also showed a blue fluorescence and gave a positive Knorr test.<sup>17</sup> On heating with dilute sulfuric

(17) Knorr, *Ann.*, **238**, 200 (1887).

acid it produced 1,5-diphenyl-3-*p*-tolylpyrazole in 85% yield.

*Anal.* Calcd. for C<sub>30</sub>H<sub>33</sub>N<sub>3</sub>O: mol. wt., 451; C, 79.78; H, 7.37; N, 9.31. Found for XI: mol. wt., 424; C, 79.78; H, 7.25; N, 9.50.

The acetylation of 1,5-diphenyl-3-*p*-tolyl-4-benzylaminopyrazoline previously reported<sup>1</sup> to yield 1,5-diphenyl-3-*p*-tolyl-4-acetobenzylamino-4-acetopyrazoline was repeated. Again a product melting over the range of 91–96° was obtained. Inspection of this yellow product under a strong glass showed the presence of a small amount of colorless material, m.p. 96–98°, which could be separated mechanically. Recrystallization of the remaining yellow crystals from petroleum ether gave the pure 1,5-diphenyl-3-*p*-tolyl-4-acetobenzylaminopyrazoline (XII), m.p. 135–137°, in 65% yield.

*Anal.* Calcd. for C<sub>31</sub>H<sub>29</sub>N<sub>3</sub>O: C, 81.01; H, 6.36; N, 9.14. Found for XII: C, 80.85; H, 6.05; N, 9.33.

This compound XII produced the 1,5-diphenyl-3-*p*-tolylpyrazole in 63% yield on heating with dil. sulfuric acid on the steam-bath for 4 hours.

The competitive reaction of IVA and IVB produced a 75% yield of the aminopyrazoline X. About 30% of the starting IVA was recovered.

**1,3,5-Triphenyl-4-benzylaminopyrazoline (XIII).**—This aminopyrazoline was obtained from IB by reaction in absolute ethanol, in a 78% yield, m.p. 109–110°; recrystallized from hot 95% ethanol.

*Anal.* Calcd. for C<sub>28</sub>H<sub>25</sub>N<sub>3</sub>: C, 83.34; H, 6.25. Found for XIII: C, 83.03; H, 6.23.

The aminopyrazoline XIII on treatment with dry hydrogen chloride in ether solution gave 1,3,5-triphenylpyrazole.<sup>18</sup>

An attempt to produce XIII, or some other product, by reaction of phenylhydrazine with  $\beta$ -benzylaminobenzalacetophenone,<sup>14</sup> isomeric with IA and IB, gave no reaction, and the starting material was recovered unchanged.

(18) Wislicenus, *et al.*, *Ann.*, **308**, 253 (1899).

