

The Isomerization and Epimerization of Some Derivatives of Aziridines. X¹

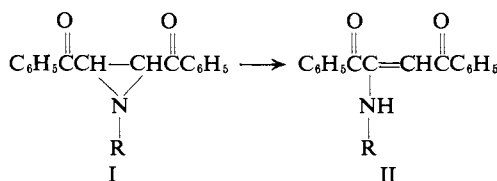
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The isomerization of *cis*- and *trans*-1-benzyl-, -1-cyclohexyl-, and -1-methyl-2,3-dibenzoylaziridines into 1-benzylamino-, 1-cyclohexylamino-, and 1-methylamino-1,2-dibenzoylethenes occurs by treatment of the aziridines with glacial acetic acid at mild temperatures. The epimerization of the above *trans*-aziridines as well as *trans*-1-benzyl- and *trans*-1-cyclohexyl-2-phenyl-3-benzoylaziridines and *trans*-1-cyclohexyl-2-phenyl-3-*p*-toluylaziridine is easily accomplished by means of alcoholic sodium ethoxide. The synthesis of 7-benzyl-2,5-diphenyl-3,4,7-triaza-2,4-norcaradiene is also described.

Introduction

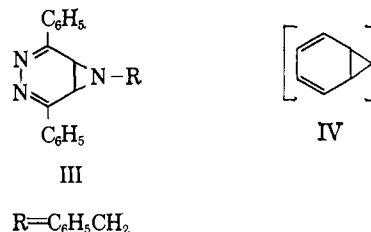
The rearrangement of 1-alkyl-2,3-dibenzoylaziridines (I) into the isomeric enamine system, 1-alkylamino-1,2-dibenzoylethenes (II), has not been reported hitherto although both types of compounds have been known for some time.³ A number of such isomerizations involving the *cis* and *trans* isomers of 1-benzyl-, 1-cyclohexyl-, and 1-methyl-2,3-dibenzoylaziridines are described in this paper.



Epimerization of *cis* and *trans* isomers of aziridines has seldom been observed. Cromwell had noted that *trans*-1-benzyl-2-phenyl-3-*p*-toluylaziridine (m.p. 74–76°), dissolved in petroleum ether and exposed to direct sunlight^{4a} or dissolved in dry acetone–ether containing a small quantity of hydrogen chloride,^{4b} isomerized slightly (<10%) to the higher melting (120–124°) *cis* isomer.^{4c} The present communication reports the epimerizations in good yields of various *trans*-1-substituted 2,3-dibenzoylaziridines and *trans*-1-substituted 2-phenyl-3-arylaziridines into the corresponding *cis* isomers.

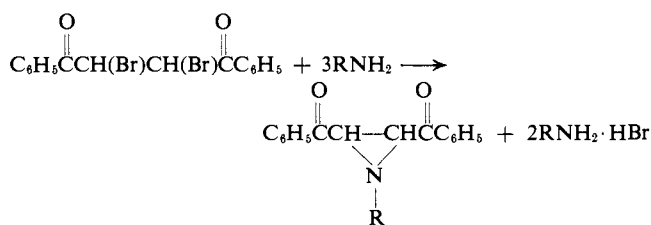
The synthesis of 7-benzyl-2,5-diphenyl-3,4,7-triaza-2,4-norcaradiene (III) is also delineated. III, in con-

trast to the elusive norcaradiene (IV), is isolable and stable at room temperature.



Results

Reaction of either *meso*- or *dl*-2,3-dibromo-1,4-diphenyl-1,4-butanedione with benzylamine formed the identical 1-benzyl-2,3-dibenzoylaziridine. Lutz had previously observed the same result using methylamine.³ As will be shown subsequently these aziridines have the *trans* configuration and are designated in this



paper as the “B” series.

If the 1-benzyl-, 1-methyl-, or 1-cyclohexyl-2,3-dibenzoylaziridines obtained in this manner are treated briefly with hot sodium ethoxide solutions, they are converted to isomeric aziridines. That the products were indeed isomeric aziridines was shown by their elementary analysis, infrared spectra, ultraviolet spectra, and p.m.r. spectra. Chemical evidence confirming the close structural similarity of the two forms lies in the conversion of both isomers to the identical enamine (II). These aziridines are designated the “A” series and are *cis*.

The p.m.r. spectra of the aziridines of the A and B series show complex absorption in the vicinity of τ 1.9 and 2.4 characteristic of benzoyl groups and, at room temperature, singlets at τ 6.5–6.8 in the A series and τ 5.9–6.1 in the B series assignable to the aziridine ring protons. The chemical shifts of the aziridine ring protons and of the protons of methyl or methylene groups attached to the nitrogen atom are listed in Table I. The cyclohexyl derivatives show broad, poorly resolved complex absorption τ 7.5–9.1 attributed to the cyclohexyl groups. The integrals obtained are consistent with these assignments. At low temperature the signals for the aziridine ring protons of the A series are shifted slightly and broadened to a half-width of about 1.5 c.p.s. at -58° . The signals

(1) Aziridines. IX: H. W. Heine and F. Scholer, *Tetrahedron Letters*, No. 48, 3667 (1964).

(2) (a) Bucknell University; we wish to thank the Smith, Kline and French Laboratories and the Petroleum Research Fund for financial aid; (b) General Electric Company.

(3) R. E. Lutz, T. Amacker, S. M. King, and N. H. Shearer, *J. Org. Chem.*, 15, 181 (1950).

(4) (a) N. H. Cromwell and H. Hoeksema, *J. Am. Chem. Soc.*, 71, 708 (1949); (b) N. H. Cromwell and R. Wankel, *ibid.*, 71, 711 (1949); (c) The higher melting form of 1-benzyl-2-phenyl-3-*p*-toluylaziridine has been assigned the *cis* configuration: N. H. Cromwell, N. G. Barker, R. A. Wankel, P. J. Vanderhorst, F. W. Olson, and J. H. Anglin, Jr., *ibid.*, 73, 1044 (1951).

Table I. P.m.r. Parameters for 1-Substituted 2,3-Dibenzoylaziridines^a

R	27° ^b				-58° ^b					
	Series "A"		Series "B"		Series "A"		Series "B"		S _A - S _B ^f	J _{AB} ^f
	Ring	R	Ring	R	Ring	R	Ring	R		
Methyl	6.75	7.25 ^c	6.08	7.38 ^c	6.65	7.25 ^c	6.04	7.40 ^c	7.4	2.6
Benzyl	6.62	6.10 ^d	5.90	6.05	6.50	6.05 ^d	5.86	6.08 ^d	8.2	2.3
Cyclohexyl	6.62	...	5.93	...	6.55	...	5.92	...	6.8	2.5

^a All p.m.r. spectra were taken at 60 Mc.p.s. on a Varian A-60 spectrometer. Above -30° the samples were 10% solutions in deuteriochloroform. Below -30° saturated solutions were employed. Coupling constants and chemical shifts downfield from internal tetramethylsilane are reported in c.p.s. ^b ±2°. ^c N-Methyl protons. ^d Methylene protons. ^e ±0.2 c.p.s. ^f ±0.1 c.p.s.

Table II. Ultraviolet Absorption Spectral Maxima for 1-Substituted 2,3-Dibenzoylaziridines and Related Compounds in Absolute Ethanol

Compound	M.p., °C.	Maxima	
		λ, mμ	ε × 10 ⁻³
1-Benzyl-2,3-dibenzoylaziridine (1A)	152-154	251	21.6
1-Benzyl-2,3-dibenzoylaziridine (1B)	134-136	254	24.4
1-Cyclohexyl-2,3-dibenzoylaziridine (2A)	148-150	251	21.5
1-Cyclohexyl-2,3-dibenzoylaziridine (2B)	138-140	253.5	28.0
1-Methyl-2,3-dibenzoylaziridine (3A)	125-126	250.5	23.7
1-Methyl-2,3-dibenzoylaziridine (3B)	88-88.5	252	26.2
<i>cis</i> -1-Benzyl-2-phenyl-3-benzoylaziridine ^a	108	243	12.62
<i>trans</i> -1-Benzyl-2-phenyl-3-benzoylaziridine ^a	59-62	248	14.41
<i>cis</i> -1-Cyclohexyl-2-phenyl-3-benzoylaziridine ^a	107-109	244	9.84
<i>trans</i> -1-Cyclohexyl-2-phenyl-3-benzoylaziridine ^a	99-101	246	14.92
<i>cis</i> -Chalcone oxide ^b	96-97	248	12.9
<i>trans</i> -Chalcone oxide ^b	89-90	250.5	17.2
<i>cis</i> -1,2-Dibenzoylcyclopropane ^c	123-124	243 ^d	2.67 ^d
<i>trans</i> -1,2-Dibenzoylcyclopropane ^c	103-104	245 ^d	3.13 ^d

^a Reference 4c. ^b H. H. Wasserman and N. E. Aubrey, *J. Am. Chem. Soc.*, **77**, 590 (1955). ^c G. W. Griffin, E. J. O'Connell, and H. A. Hammond, *ibid.*, **85**, 1001 (1963). ^d Observed in cyclohexane. Two other maxima are not listed here.

of the aziridine ring protons of the B series at first broaden with decreasing temperature and ultimately split into AB quartets. This behavior is illustrated in Figure 1 for the methyl derivatives. The coupling constants and chemical shifts obtained from conventional analyses of AB patterns⁵ are compiled in Table I.

The assignment of *cis* and *trans* structures is based in part on ultraviolet spectroscopy. In Table II are presented the ultraviolet absorption spectral maxima of the A and B series, the related known *cis*- and *trans*-1-substituted 2-phenyl-3-benzoylaziridines, *cis*- and *trans*-chalcone oxides and *cis*- and *trans*-1,2-dibenzoylcyclopropanes.

Structural assignments on the 1-benzyl-2,3-dibenzoylaziridines of the A and B series were further strengthened by dipole moment measurements. The B isomer had a μ-value of 2.62 D. and the A isomer had a μ-value of 4.74 D. Because of the limited solubility of the compounds in nonpolar solvents it was necessary to measure the dipole moments in 1,4-dioxane.

1-Benzyl-2,3-dibenzoylaziridine of the A series reacted rapidly with hydrazine in alcohol to form III. The corresponding aziridine of the B series did not react at all with hydrazine under the same experimental conditions.

The structure of III was assigned on the basis of elementary analysis, infrared spectrum, and p.m.r. spectrum. The p.m.r. spectrum of III shows the benzyl protons as a sharp singlet at τ 6.17 and the aziridine protons as a sharp singlet at τ 7.31. In addition

to these two singlets of approximately the same intensity were the aromatic protons of the benzyl group at τ 2.87 and the multiplets in the aromatic

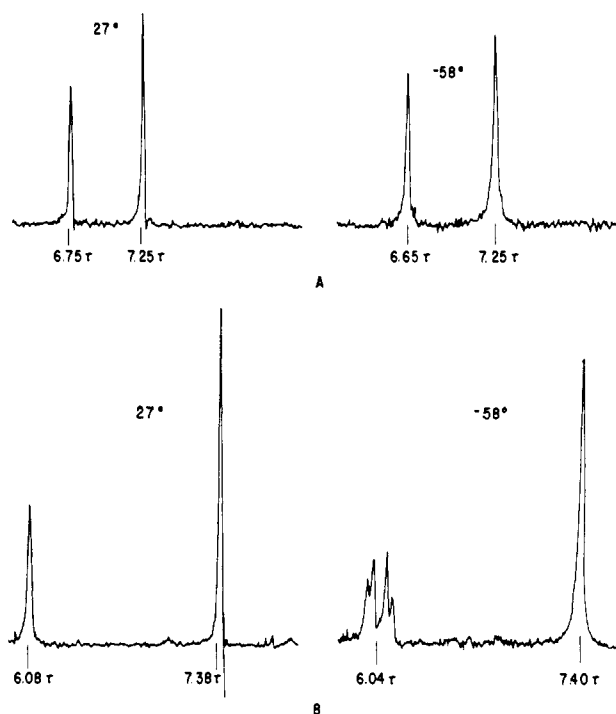


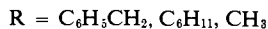
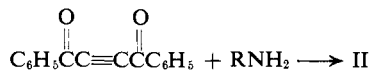
Figure 1. Temperature dependence of the p.m.r. spectra of 1-methyl-2,3-dibenzoylaziridines: (A) *cis*, (B) *trans*.

region τ 2.62 for aromatic protons *meta* and *para* to C=N and τ 2.10-2.20 for aromatic protons *ortho*

(5) P. L. Corio, *Chem. Rev.*, **60**, 363 (1960).

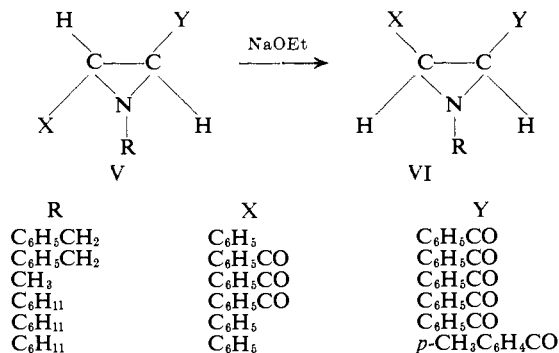
to C=N. The infrared spectrum of III is also consistent with the triazanorcaradiene ring system. There is a C=N double bond band at 6.5 μ and no NH band.

The *cis* and *trans* isomers of 1-benzyl-, 1-cyclohexyl-, and 1-methyl-2,3-dibenzoylaziridines (I) rearrange in glacial acetic acid at room temperature into the corresponding 1-alkylamino-1,2-dibenzoylethenes (II). The structure of II was confirmed by an alternate synthesis involving addition of benzylamine or cyclohexylamine to dibenzoylacetylene. The enamine, 1-



methylamino-1,2-dibenzoylene, had been characterized previously.³

Finally, conversion of the known *trans*-1-benzyl- and *trans*-1-cyclohexyl-2-phenyl-3-benzoylaziridines^{4c} and *trans*-1-cyclohexyl-2-phenyl-3-*p*-toluylaziridine^{4c} to the corresponding *cis* isomers (VI) occurs by mild treatment of the *trans*-aziridines (V) with alcoholic sodium ethoxide. The procedure is quite analogous to the epimerization of the *trans*-2,3-dibenzoylaziridines described earlier.



Discussion

On the basis of ultraviolet spectra, p.m.r. spectra, dipole moment measurements, and reaction with hydrazine, the A series of the 1-substituted 2,3-dibenzoylaziridines can be assigned the *cis* configuration and the B series the *trans* configuration.

The temperature dependence of the p.m.r. spectra of the B series of aziridines and the insensitivity of the p.m.r. spectra of the A series of aziridines to temperature changes clearly establish that the A series consists of the *cis* isomers and the B series of the *trans* isomers. The temperature dependence of the p.m.r. spectra of a number of 1-substituted aziridines has been previously demonstrated.⁶⁻⁹ The interpretation has been offered that at sufficiently low temperatures the lifetime with respect to inversion of the two configurations of the groups bonded to the nitrogen atom is long enough that separate signals may be obtained from the ring protons *cis* and *trans* to the substituent on nitrogen. While one *cis-trans* isomer pair was examined previously,⁷ no account of the difference in behavior of *cis* and *trans* isomers has been published.

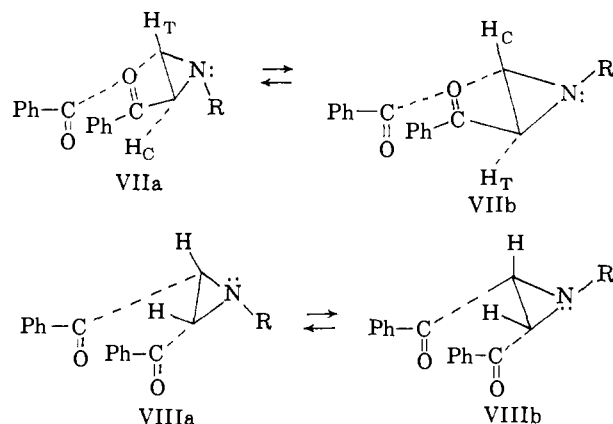
(6) A. T. Bottini and J. D. Roberts, *J. Am. Chem. Soc.*, **78**, 5126 (1956).

(7) A. T. Bottini and J. D. Roberts, *ibid.*, **80**, 5203 (1958).

(8) H. S. Gutowsky, *Ann. N. Y. Acad. Sci.*, **70**, 786 (1958).

(9) A. Loewenstein, J. F. Neumer, and J. D. Roberts, *J. Am. Chem. Soc.*, **82**, 3599 (1960).

Recently the spectra of *trans*-2,3-dimethyl-N-nitrosoaziridine and of *trans*-2,3-dimethylaziridine at -22° have been interpreted in terms of spin coupling of the *trans* ring protons.¹⁰ The configurations of the *trans* compounds may be represented by VIIa,b and those of the *cis* compounds by VIIIa,b. In neither VIIa nor



VIIb are the ring protons magnetically equivalent. Thus the ring protons of the *trans* compound should give two signals of equal intensity which should be further split by spin-spin coupling, at temperatures at which the inversion rate is comparable to or less than $2\pi(\delta_c - \delta_t)$. The results for the B series of aziridines are in accord with these predictions. In the two configurations of the *cis* compounds, the ring protons are equivalent to one another, but the magnetic environment of the ring protons of VIIIa is not the same as that of the ring protons of VIIIb. Thus two singlets of relative intensity determined by the position of the equilibrium between VIIIa and VIIIb are to be expected at sufficiently low temperatures. The results for the A series of aziridines can be reconciled with these predictions if the concentration of VIIIa or VIIIb is very small. It seems probable that the equilibrium between VIIIa and VIIIb, particularly at lower temperatures, should favor VIIIb. Bottini and Roberts⁷ reached a similar conclusion in interpreting the temperature insensitivity of the spectrum of 1-methyl-*cis*-2,3-dimethylaziridine. The small but real downfield shift of the signals from the ring protons of the A series with respect both to tetramethylsilane and to the signals of the methyl or methylene substituents as the temperature is lowered may be interpreted as showing that a small amount of VIIIa is present in equilibrium at room temperature. Since in the fast exchange approximation the position of the signal from the ring methyls is the weighted average of the positions of the ring protons of the two configurations,¹¹ if, at reduced temperature, VIIIa decreases in concentration, the ring proton signal should shift toward the position of the ring proton signal of VIIIb. This interpretation requires that the lower field absorptions in the *trans* compounds be due to the ring protons *cis* to the substituent on nitrogen.

The theory of intramolecular exchange of interacting nuclear spins requires that the coupling constants de-

(10) R. D. Clark and G. K. Helmkamp, *J. Org. Chem.*, **29**, 1316 (1964).

(11) J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High Resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959, Chapter 10.

terminated from the spectrum of a two-spin system at a given temperature correspond to the coupling constants for a single configuration, and that the observed chemical shifts be a function of the exchange rate at each temperature.¹² The coupling constants for the *trans*-2,3-dibenzoylaziridines compiled in Table I may be compared with the 3-c.p.s. coupling constant reported for *trans*-1,2-dideuterio-3-phenylaziridine.¹³ The apparent chemical shift differences between the protons *cis* and *trans* to the substituent on nitrogen are very much smaller than those (0.6 to 0.8 p.p.m.) reported for other aziridines.^{7,9} This discrepancy may be due to failure in the present investigation to attain a sufficiently low temperature that the slow exchange limit approximation may be applied. In the cases reported previously,^{7,9} the temperatures at which coalescence of the two peaks occur are greater than 50°. The fine structure of the signals from the ring protons of compounds 1B, 2B and 3B disappears between -10 and -20°, indicating that the barriers to inversion in the dibenzoylaziridines are much lower than in the aziridines previously studied. A bulk effect such as that reported for *t*-butylaziridine⁷ may be operating in these cases.

The difference in chemical shifts of the ring protons in the A and B series provides an independent confirmation of the assignment of stereochemistry. In the 1,2-dibenzoylcyclopropanes it has been reported¹⁴ that the protons α to the benzoyl groups absorb at 0.17 p.p.m. higher field in the *cis* compounds than in the *trans* compounds. From the data in Table I it may be seen that, at room temperature, the ring protons of the A series absorb at 0.67-0.73 p.p.m. higher field than do the ring protons of the B series. By analogy the A series should be assigned *cis* stereochemistry, confirming the assignment based on other considerations.

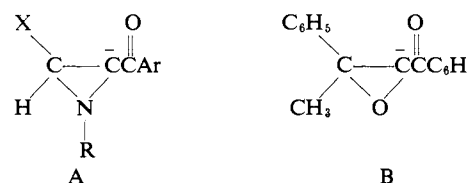
The ultraviolet absorption spectra of the *cis* and *trans* isomers of the 1-substituted 2-phenyl-3-benzoylaziridines, the chalcone oxides, and the 1,2-dibenzoylcyclopropanes in which *cis* and *trans* structures were assigned either on the basis of chemical evidence or p.m.r. spectra showed that the *cis* isomers absorb at a somewhat lower wave length and with less intensity than the *trans* compounds (Table II). Similar observations regarding the ultraviolet spectra of *cis*- and *trans*-phenyl- or -methylaroylaziridines¹⁵ and *cis*- and *trans*-chalcone oxides¹⁶ have been reported, and an explanation for the differences has been offered. Interestingly all the *cis* isomers of the above compounds melt higher than the *trans* isomers. It will be observed that the 1-substituted 2,3-dibenzoylaziridines of the A series all absorb at a lower wave length and with less intensity and have a higher melting point than the corresponding compounds of the B series.

One would expect the *cis*-1-benzyl-2,3-dibenzoylaziridine to have a larger dipole moment than the *trans* isomer. As was previously noted, the 1-benzyl-2,3-dibenzoylaziridine of series A has a considerably

larger dipole moment than the corresponding compound of the B series.

It has been noted that the infrared spectra of the *cis*-1-cyclohexyl- and -1-benzyl-2-phenyl-3-arylaziridines show a strong absorption band at about 9.2 μ , and that this band is weak or absent for the corresponding *trans* isomer.^{4c,17} The 2,3-dibenzoylaziridines of the A series exhibit a strong absorption band at about 9.1 μ and those of the B series do not.

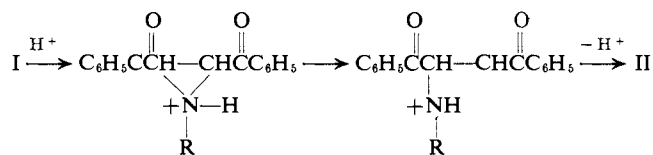
The base-catalyzed epimerization of the *trans*-1-substituted 2,3-dibenzoylaziridines and the *trans*-1-substituted 2-phenyl-3-arylaziridines into the *cis* isomers may be explained by the formation of an enolate anion such as A. An analogous anion intermediate B has been demonstrated by deuterium studies



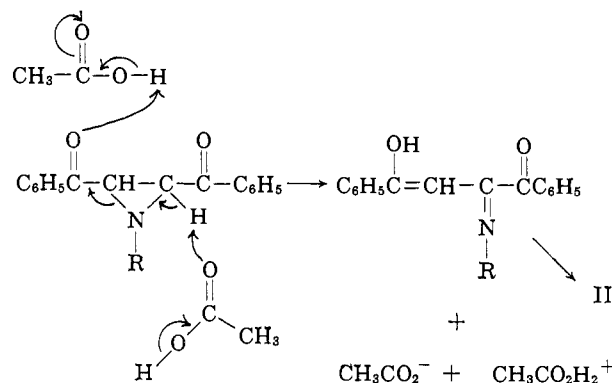
to be involved in the base-catalyzed epimerization of *trans*-dypnone oxide (phenyl and benzoyl *trans*) into *cis*-dypnone oxide.^{18a} Other epimerizations of related epoxy ketones by base have also been observed.^{18b}

In contrast to the base-catalyzed rearrangement of *trans* aziridine and epoxide systems to the *cis* isomers, ethanolic sodium hydroxide rearranges *cis*-1,2-dibenzoylcyclopropane to the *trans* isomer.¹⁴

A possible mechanism for the isomerization of the various 2,3-dibenzoylaziridines (I) into enamines (II) involves protonation of the aziridinyll nitrogen, ring scission to a phenacyl cation, and elimination of a proton.



An attractive alternate mechanism which avoids the postulation of a phenacyl cation (for which there is but scant evidence in the literature) is



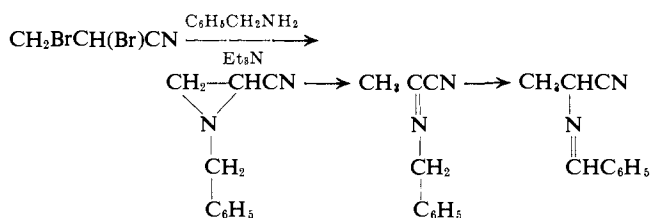
A similar rearrangement may be involved when 2,3-dibromopropionitrile, benzylamine, and triethylamine

(17) M. A. Stolberg, J. J. O'Neill, and T. Wagner-Jauregg, *ibid.*, **75**, 504 (1953).

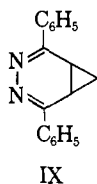
(18) (a) H. O. House and R. S. Ro, *ibid.*, **80**, 2428 (1958); (b) H. H. Wasserman, N. E. Aubrey, and H. E. Zimmerman, *ibid.*, **75**, 96 (1953); H. H. Wasserman and N. E. Aubrey, *ibid.*, **77**, 590 (1955).

(12) S. Alexander, *J. Chem. Phys.*, **37**, 967 (1962).
 (13) A. Hassner and C. C. Heathcock, *Tetrahedron Letters*, 1125 (1964); *ibid.*, 1502 (1964).
 (14) G. W. Griffin, E. J. O'Connell, and H. A. Hammond, *J. Am. Chem. Soc.*, **85**, 1001 (1963).
 (15) N. H. Cromwell, R. E. Bambury, and J. L. Adelfang, *ibid.*, **82**, 4241 (1960).
 (16) N. H. Cromwell, F. H. Schumacher, and J. L. Adelfang, *ibid.*, **83**, 974 (1961).

are heated in benzene. An isomeric mixture of 1-benzyl-2-cyanoaziridine, N-benzyliminopropionitrile, and α -N-benzylidenaminopropionitrile was obtained, the latter two compounds being formed presumably by isomerization of the aziridine.¹⁹ The isomerization was possibly catalyzed by triethylamine hydrobromide that was generated in the first step.



The isolation of 2,5-diphenyl-3,4-diaza-2,4-norcaradiene (IX) has been reported recently.²⁰ The stability of this system does not seem impaired by substitution of a nitrogen moiety in the 7-position such as is the case with III. Interestingly, heating of 7-benzyl-2,5-diphenyl-3,4,7-triaza-2,4-norcaradiene gave benzonitrile as a product. This reaction is currently being studied in our laboratories.



Experimental

trans-1-Benzyl-2,3-dibenzoylaziridine (1B). A suspension of 64.1 g. (0.16 mole) of *meso*-1,2-dibenzoyl-1,2-dibromoethane²¹ in 600 ml. of dry benzene was heated until almost all the dibromide dissolved. The solution was cooled to 40° and 51.0 g. (0.48 mole) of benzylamine was slowly added with stirring, care being taken to keep the temperature below 40°. The reaction mixture was stirred at room temperature for an additional hour and then allowed to stand for 2 hr. The benzylamine hydrobromide was filtered and the filtrate evaporated to dryness. The crude product was recrystallized three times from 95% ethanol to give 38.8 g. of 1B, m.p. 134–136°.

Anal. Calcd. for C₂₃H₁₉NO₂: C, 80.90; H, 5.60; N, 4.10. Found: C, 81.36; H, 5.62; N, 4.10.

trans-1-Cyclohexyl-2,3-dibenzoylaziridine (2B) was prepared analogously as 1B using 79.2 g. (0.20 mole) of *meso*-1,2-dibenzoyl-1,2-dibromoethane, 600 ml. of benzene, and 59.6 g. (0.60 mole) of cyclohexylamine with the exception that stirring was continued for 24 hr. Two recrystallizations from methanol gave 43.2 g. of 2B, m.p. 138.5–140°.

Anal. Calcd. for C₂₂H₂₃NO₂: C, 79.25; H, 6.95; N, 4.20. Found: C, 79.43; H, 6.94; N, 4.50.

trans-1-Methyl-2,3-dibenzoylaziridine (3B) was prepared by adding 22.8 g. of *meso*-1,2-dibenzoyl-1,2-dibromoethane to a flask immersed in an ice bath and containing 500 ml. of ether and 5.30 g. of methylamine. The reaction mixture was stirred for 3 hr. and the

methylamine hydrobromide filtered. The flask containing the ether filtrate was immersed in a water bath held at 25–40° and the ether evaporated rapidly until a copious light yellow precipitate was obtained. The solid was filtered and recrystallized from 70% methanol. The ether should not be completely evaporated or else the residue is very difficult to purify. The procedure is similar to the one outlined by Lutz³ but with the important modifications specified above. The yield of recrystallized 3B was 7.7 g., m.p. 87°; lit.³ m.p. 88–88.5°.

cis-1-Benzyl-2,3-dibenzoylaziridine (1A). Five grams of 1B was added to 100 ml. of 0.26 M sodium ethoxide solution and the reaction mixture heated until the solution became clear (about 1 min. longer periods of heating cause considerable decomposition). A small quantity of the solvent was evaporated, water was added until the solution became turbid, the solution was cooled in an ice bath, and the crude 1A, 4.25 g., was filtered. Two recrystallizations from 95% ethanol gave 3.75 g. of 1A, m.p. 152–154°. The crude and recrystallized 1A had identical infrared spectra.

Anal. Calcd. for C₂₃H₁₉NO₂: C, 80.90; H, 5.60; N, 4.10. Found: C, 80.44; H, 5.79; N, 4.12.

cis-1-Cyclohexyl-2,3-dibenzoylaziridine (2A) was prepared in the same manner as 1A using 10.00 g. of 2B and 200 ml. of 0.43 M sodium ethoxide solution. The crude yield was 6.98 g., m.p. 138–142°. Four recrystallizations from methanol gave 3.2 g. of 2A, m.p. 148–150°.

Anal. Calcd. for C₂₂H₂₃NO₂: C, 79.25; H, 6.95; N, 4.20. Found: C, 78.72; H, 6.84; N, 4.31.

cis-1-Methyl-2,3-dibenzoylaziridine (3A) was prepared by heating a mixture of 1.00 g. of 3B and 20 ml. of 0.5 M sodium ethoxide for 1 min. and allowing the mixture to stand overnight at room temperature. The mixture was placed in an ice bath and 70 ml. of water added dropwise. The precipitate was filtered and weighed 0.88 g., m.p. 115–119°. Recrystallization from 1:1 benzene-petroleum ether (b.p. 60–90°) gave 0.60 g. of the *cis* isomer, m.p. 125–126°.

Anal. Calcd. for C₁₇H₁₅NO₂: C, 76.96; H, 5.69; N, 5.28. Found: C, 76.95; H, 5.91; N, 5.40.

Isomerization of 1B into 1-Benzylamino-1,2-dibenzoyl-ethene. Five grams of 1B was added to 50 ml. of glacial acetic acid and the mixture was stirred overnight. The solution was cooled and water added until precipitation occurred. Filtration gave 4.7 g. of crude product, m.p. 99–103°. Recrystallization from petroleum ether (b.p. 60–110°) gave yellow crystals, m.p. 104–106°.

Anal. Calcd. for C₂₃H₁₉NO₂: C, 80.90; H, 5.60; N, 4.10. Found: C, 80.98; H, 5.79; N, 4.20.

Isomerization of 1A into 1-Benzylamino-1,2-dibenzoyl-ethene. To 1.78 g. of 1A was added 37 ml. of glacial acetic acid. The reaction mixture was held at about 35° and stirred for 24 hr. Water was added to the cooled reaction mixture until turbidity was observed. The mixture was kept in an ice bath for 1 hr. and the precipitate filtered. The crude product weighed 1.28 g. and recrystallization from petroleum ether gave the enamine melting at 101–103°.

1-Benzylamino-1,2-dibenzoyl-ethene was also prepared by the addition of 0.6 g. of benzylamine to 10 ml. of

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(20) G. Maier, *Angew. Chem.*, **75**, 920 (1963).

(21) E. Campaigne and W. O. Foyle, *J. Org. Chem.*, **17**, 1405 (1952).

dry benzene containing 1.16 g. of dibenzoylacetylene.²² Heat was generated during the addition of the benzylamine. After 0.5 hr. at room temperature the solvent was evaporated and petroleum ether was added to the residue. The flask was scratched to induce crystallization. Filtration gave 1.7 g. of product, m.p. 90–93°. Recrystallization from petroleum ether (b.p. 60–110°) yielded 1.2 g. of yellow crystals, m.p. 98–102°. The infrared spectrum of this material was identical with those obtained from the isomerization of 1A and 1B.

Isomerization of 2B into 1-Cyclohexylamino-1,2-dibenzoyl ethene. To 20 ml. of glacial acetic acid was added 1.02 g. of 2B. The reaction mixture was stirred for 1 hr. at about 35° then cooled in an ice bath and water added dropwise until precipitation was complete. The mixture was filtered and the crude enamine, 0.94 g., m.p. 120–123°, recrystallized from 95% ethanol to give 0.63 g. of yellow crystals, m.p. 130–132°.

Anal. Calcd. for C₂₂H₂₃NO₂: C, 79.25; H, 6.95; N, 4.20. Found: C, 78.83; H, 7.25; N, 4.09.

Isomerization of 2A into 1-cyclohexylamino-1,2-dibenzoyl ethene occurred by the addition of 1.64 g. of 2A to 32 ml. of glacial acetic acid. The reaction mixture was stirred for 8 hr. at 38° and then 50 ml. of water was added dropwise to give 1.24 g. of enamine, m.p. 120–124°. Two recrystallizations from 95% ethanol gave 0.90 g. of enamine, m.p. 130–132°.

1-Cyclohexylamino-1,2-dibenzoyl ethene was also synthesized by addition of 0.50 g. of cyclohexylamine to 1.17 g. of dibenzoylacetylene dissolved in 10 ml. of benzene. Three-fourths of the benzene was evaporated and the side of the flask scratched to induce crystallization. The crude enamine was stirred with petroleum ether and then filtered. The crude product weighed 1.35 g. and melted at 127–129°. Recrystallization from petroleum ether gave 0.90 g. of enamine, m.p. 128–130°. The infrared spectrum was identical with those obtained by isomerization of 2A and 2B in glacial acetic acid.

Isomerization of 3B into 1-Methylamino-1,2-dibenzoyl ethene. A mixture of 320 mg. of 3B and 3.2 ml. of glacial acetic acid was kept at room temperature for 19 hr. Ice-water was added until a slight turbidity was observed, and then were added a few drops of dilute sodium hydroxide. The precipitate was filtered and the enamine, 250 mg., m.p. 98–101°, recrystallized from 50% methanol. The enamine melted at 102–104°; lit.³ m.p. 101–102.5°.

Isomerization of 3A into 1-methylamino-1,2-dibenzoyl ethene was accomplished by dissolving 470 mg. of 3A in 9 ml. of glacial acetic acid and stirring the solution for 28 hr. at 37°. The solution was cooled in an ice bath and 15 ml. of water added dropwise. The

(22) R. E. Lutz and W. R. Smithey, Jr., *J. Org. Chem.*, **16**, 51 (1951).

precipitated enamine was filtered and weighed 250 mg. Recrystallization gave 206 mg. of enamine, m.p. 100–102°.

Epimerization of trans-1-Cyclohexyl-2-phenyl-3-p-tolylaziridine. A mixture of 425 mg. of the aziridine^{4c} and 10 ml. of 0.35 M sodium methoxide was heated for 1 or 2 min. and then allowed to stand at room temperature for 35 hr. Water was added until no further precipitation occurred. A crude yield of 405 mg. of the *cis*-aziridine was obtained. Recrystallization from 95% ethanol gave material melting at 109–111°; lit.^{4c} m.p. 111–112°. The infrared spectra of the crude and recrystallized *cis*-aziridine were identical with the published spectrum.

Epimerization of trans-1-Cyclohexyl-2-phenyl-3-benzoylaziridine. A mixture of 2.02 g. of the *trans*-aziridine^{4c} and 40 ml. of 0.43 M sodium ethoxide was heated for 2 min. and then maintained at room temperature for 49 hr. Water (30 ml.) was added dropwise to give 1.41 g. of the crude *cis* isomer. Addition of more water precipitated a mixture of *cis* and *trans* isomers. One recrystallization from methanol gave 1.10 g. of material melting at 104–107°; lit.^{4c} m.p. 107–109°.

Epimerization of trans-1-Benzyl-2-phenyl-3-benzoylaziridine. A solution of 265 mg. of the *trans*-aziridine^{4c} in 3 ml. of 1.2 M sodium ethoxide was heated for 1 min. and then kept at room temperature overnight. The reaction mixture was filtered to give 218 mg. of crude *cis* isomer. One recrystallization from absolute ethanol gave material melting at 105–108°; lit.^{4c} m.p. 108°.

7-Benzyl-2,5-diphenyl-3,4,7-triaza-2,4-norcaradiene. A mixture of 0.86 g. of 1A, 0.3 g. of 95% hydrazine, and 20 ml. of 95% ethanol was stirred for approximately 2 hr. and the temperature gradually increased to 55°. As soon as the aziridine had dissolved the solution was filtered and cooled. A precipitate formed and was filtered and recrystallized from a 3:1 mixture of benzene-petroleum ether (b.p. 30–60°) to give 0.57 g. of material melting at 98–100°. This primary adduct which had absorption peaks at 3.0 and 3.1 μ and no absorption at 6.5 μ gradually lost weight on exposure to air or more quickly by means of a lamp to yield 0.50 g. of the norcaradiene derivative, m.p. 113–115°. The norcaradiene derivative contained no absorption peaks at 3.0 nor 3.1 μ but did show C=N absorption at 6.5 μ . A similar absorption spectrum was noted by Maier for 2,5-diphenyl-3,4-diaza-2,4-norcaradiene.²⁰ Recrystallization of the norcaradiene from 3:1 benzene-petroleum ether gave crystals melting at 115–117°.

Anal. Calcd. for C₂₃H₁₉N₃: C, 81.87; H, 5.68; N, 12.45. Found: C, 81.96; H, 5.82; N, 12.15.

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