On the Mechanism of the 1,2-Cycloaddition
of Azobenzenes to Ketenimines

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The 1,2-cycloaddition of unsymmetrical azobenzenes has been found to be stereoselective and the rate is essentially solvent independent. These observations lead to the postulation of a near concerted process which encounters a steric effect after alignment.

Ketenimines (nitrogen analogs of ketenes) have been reported to undergo cycloaddition reactions with symmetrically substituted azobenzenes to produce 3-imino-substituted-1,2-diazetidines (2) (Eq. 1). The requirement

Eq. 1

II
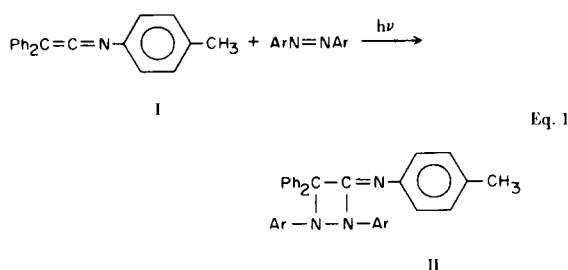
for light in the reaction was stated, but other details of the mechanism were not explored. This cycloaddition is similar to the production of 3-diazetidinones from ketenes and azobenzenes for which Cook and Jones have shown that the function of light is to convert *trans* to *cis* azobenzenes which then condense readily with ketenes (3). Kerber and Ryan have suggested that the ketene-*cis*-azobenzene cycloaddition is concerted (4). We have studied the mechanism of the ketenimine-azobenzene cycloaddition to determine how analogous it is to the ketene-azobenzene reaction since other ketenimine cycloadditions have been shown to be polar (5) or photochemical (6) but not concerted. Furthermore, knowledge of the mechanism of this reaction will enhance its utilization as a synthetic route to diazetidines with exocyclic unsaturation.

To determine if the function of light in this cycloaddition (Eq. 1) is to convert *trans* to *cis*-azobenzenes, an ethereal solution of *cis* enriched azobenzene (3) and I were allowed to stand in the absence of light at room temperature. Pure *cis*-azobenzene could not be obtained, but the *cis* enriched mixture obtained reacted with I at room temperature in the dark to give a 40% yield of II (Ar = Ph).

Commercial (*trans*) azobenzene gave no product under the same conditions. Since pure *cis*-azobenzene was not obtained, the reaction of I with dibenzo[c,f]diazepine (III) (7) in the dark at room temperature was investigated. This azo compound which must have a configuration similar to *cis*-azobenzene (8), gave adduct IV in a 68% yield (Eq. 2). Interestingly, benzocinnoline which has the *cis*-geometry

III

IV

Eq. 2
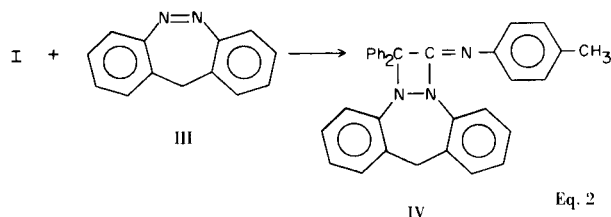
but is a planar structure whose azo linkage is part of the aromatic system does not react with I. Thus, the ketenimine-azobenzene cycloaddition is analogous to the ketene-azobenzene reaction in that the function of light is to product the nonplanar *cis*-azobenzenes from the *trans* forms. The actual cycloaddition reaction between the ketenimines and the *cis*-azobenzenes is not photochemical.

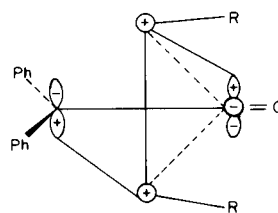Further insight into the mechanism of the cycloaddition was provided by treating I with a series of 2, 3, and 4 monosubstituted azobenzenes.
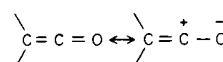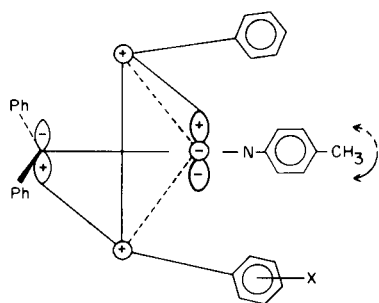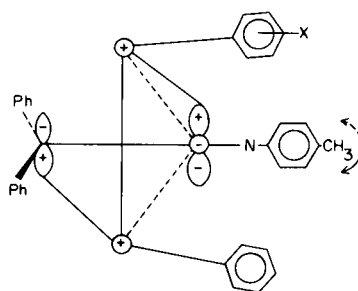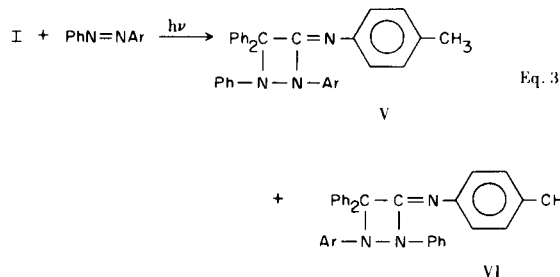

Figure 1

Figure 2

Figure 3

Figure 4

The reactions resulted in the production of both 1 and 2-arylsubstituted-3-iminodiazetidines (Eq. 3). In no case could the separation of the two isomers be effected (crys-
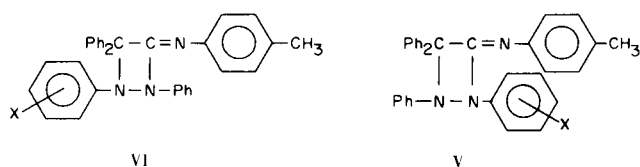

Eq. 3

tallization and chromatography techniques were utilized); but in all cases thermal degradation of the product mixture permitted determination of the ratio of V to VI. Although thermal degradation of V or VI might be expected to occur in two ways, only the imine and carbodiimide were actually obtained (Scheme).

SCHEME
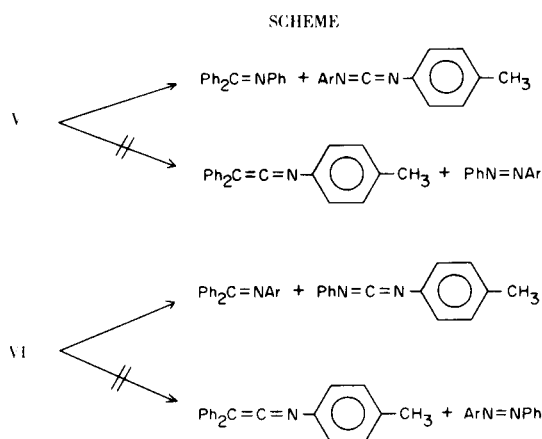
The decompositions were quantitative. Analysis of solutions of the decomposition mixtures showed no diazetidines (ir), no residue or tarry products, and vpc peaks for the imines and carbodiimides only. Thus, the ratio of the

two imines obtained reflects the ratio of V and VI in the product of cycloaddition. The results of the effect of substituents on the cycloaddition of I and cis-azobenzenes are given in the Table.

TABLE

Isomer Distribution for the Cycloaddition of I
and Unsymmetrical Azobenzenes (a)

X	% (b)	% (b)
	VI	V
p-CH3	65	35
m-CH3	72	28
o-CH3	100	0
p-Cl	71	29
m-Cl	78	22
o-Cl	100	0
p-CN	65	35
o-CN	100	0
p-Br	77	23
p-N(CH3)	100	0
p-N(CH2CH3)2	100	0
p-OCH3	93	7
m-NO2	85	15

(a) Determined by thermal degradation to the imines. (b) All values are the average of four runs. The maximum deviation for any substituent was ± 2%.

The data in the Table shows that isomer VI is obtained in excess for every substituent although the amount of VI in excess seems to vary with the substituent's position.

For instance VI is obtained quantitatively for o-methyl, in 78% for m-methyl, and in 65% for p-methylazobenzene. Similar results are observed for the o, m, and p-chloro system. Furthermore one observes that for all ortho substituents studied (methyl, chloro, and cyano) only isomer VI is obtained, and for all meta systems studied (methyl, chloro, and nitro) VI is approximately 75% of the product mixture. The difference in electron-withdrawing properties of these substituents seems not to affect the product distribution ratio. From the para substituted systems studied, one observes that the small methyl, chloro, and bromo substituents and the linear cyano substituent give similar amounts of VI; the angular methoxy substituent gives considerably more of VI; and the bulky dialkylamino substituents give only VI. Thus, product distribution is apparently determined more by the position and size of the substituent than by the electronic character of the substituent. Furthermore we have found that dibenzo[c,f]-diazepine (III) and I only react five times faster in acetonitrile than in ether. This minimal rate acceleration in a more polar solvent and a product distribution based on substituent size not electronic character essentially rule out a polar mechanism for the ketenimine-cis-azobenzene cycloaddition.

Kerber and Ryan have postulated that the cycloaddition of diphenylketene and cis- azo compounds is concerted (4). They envision an alignment of reactants as shown in Figure 1 in which during cycloaddition the ketene molecule bonds in an antarafacial manner and the azo component in a suprafacial manner. The configuration is stabilized by the vinylium ion character of the ketene (Figure 2). This postulation agrees with Woodward and Hoffman's explanation of the cycloaddition of ketenes and olefins (9).

If unsymmetrical azobenzenes and ketenimines behave in a similar manner, then two transition configurations can be drawn (Figures 3 and 4). These are the only alignments possible since steric interaction will prevent the azobenzene from approaching in a manner where its rings interact with the phenyl groups on the ketenimine.

Models show that with the advent of bond formation in either figure 3 or 4 the ketenimine p-tolyl group will rotate from the plane of the page to a plane perpendicular to the page. Jochims and Anet have shown that the energy barrier for inversion at the nitrogen of the ketenimine moiety is about 10 kcal/mole (10). One would thus expect sufficient inversions to occur at the conditions used (refluxing ether) to merit drawing structures indicating racemization at this position. The p-tolyl group will sterically interact with the azobenzene ring situated at the top of each of Figures 3 and 4. Figure 3 would indicate a configuration where the alignment would produce the least interaction and therefore lead to product with lower

energy involvement. This Figure also predicts the isomer always observed in excess. Reversal of signs on the ketenimine orbitals will lead to exactly the same conclusions. No steric problems are associated with the two phenyl rings of the ketenimine because the carbon they are attached to undergoes a hybridization change during bond formation which moves the phenyl groups out of the way of the bonding azobenzene moiety. Therefore we propose that the reaction of ketenimines and unsymmetrical azobenzenes is nearly concerted and that a steric effect in a transition configuration determines the principle product.

EXPERIMENTAL

Melting points were determined on Fisher-Johns and Mel-Temp apparatuses and are uncorrected. The ir were determined on Perkin-Elmer Model 137 and 137G Infracords using potassium bromide, solution, and mull techniques. The uv and visible spectra were determined on a Perkin-Elmer Model 202 spectrophotometer. A Beckman DU Model 2400 spectrophotometer was used to follow the disappearance of ketenimine absorption during rate studies. The Aerograph Autoprep Model A-700 was utilized to obtain all gas chromatographs. Analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tennessee.

o-Chloroazobenzene.

Twenty-two g. (0.24 mole) of aniline was dissolved in 150 ml. of glacial acetic acid in a 500 ml. erlenmeyer flask. Thirty-five g. (0.24 mole) of o-chloronitrosobenzene was then added to the acetic acid solution. The mixture was swirled until all of the nitroso compound dissolved. The solution was warmed on a steam bath until the reaction occurred, as evidenced by the heat evolved from the reaction. The flask was stoppered and the solution allowed to stand at room temperature for 24 hours. After this period of time, the acetic acid was removed under reduced pressure (aspirator). The residue was then vacuum distilled. Redistillation of the o-chloroazobenzene afforded an analytically pure sample of the materical, b.p., 120-125° at 0.4 mm-Hg.

Anal. Calcd. for $C_{12}H_9ClN_2$: C, 66.53; H, 4.11; N, 12.94. Cl, 16.38. Found: C, 66.69; H, 4.20; N, 13.08; Cl, 16.17.

Adducts of Diphenylketene-N-(p-tolyl)imine (I) with Unsymmetrical Azobenzenes.

1. With cis-Azobenzene (1,2,4,4-Tetraphenyl-3-p-tolylimino-1,2-diazetidine).

To 0.3 g. (0.001 mole) of diphenylketene-N-(p-tolyl) imine in 5 ml. of ether was added an excess of cis enriched azobenzene (3) in 5 ml. of ether. The 25 ml. erlenmeyer flask was stoppered and placed in the absence of light. After two days the product began to crystallize. Concentration of the ether solution afforded 0.2 g. (40% yield indicating a minimum of 40% cis-azobenzene in the azobenzene mixture) of the adduct. Recrystallization of the adduct from acetone (74% recovery) gave a pure sample of the material, m.p., 181-182°. A mixture melting point with an authentic sample gave no depression.

2. With Dibenzo[c,f]diazepine (4,4-Diphenyl-1,2-o,o'-diphenyl-methane-3-p-tolylimino-1,2-diazetidine).

To 0.2 g. (0.001 mole) of diphenylketene-N-(p-tolyl)imine in 5 ml. of anhydrous ether was added an excess of dibenzo[c,f]diazepine in 5 ml. of ether. The 25 ml. erlenmeyer flask was stoppered and placed in the absence of light. After 12 hours, the solution had an appreciable absorption at 5.9 μ in its infrared spectrum.

This was indicative of the expected adduct (2). After an additional 12 hours, the solution was cooled to approximately -20°. This resulted in crystallization of 0.3 g. (68% yield) of the adduct. It was recrystallized from ether (80% recovery), affording an analytically pure sample of the material, m.p., 193-194°.

Anal. Calcd. for $C_{34}H_{27}N_3$: C, 85.49; H, 5.71; N, 8.80. Found: C, 85.42; H, 5.87; N, 8.67.

3. With p-Methylazobenzene (1-p-Tolyl-3-p-tolylimino-2,4,4-triphenyl-1,2-diazetidine and 2-p-Tolyl-3-p-tolylimino-1,4,4-triphenyl-1,2-diazetidine).

In a 500 ml. round botoom flask were placed 250 ml. of anhydrous ether, 4.9 g. (0.025 mole) of p-methylazobenzene and 7.0 g. (0.025 mole) of diphenylketene-N-(p-tolyl)imine (1). The flask was attached to a long bubble condenser fitted with a drying tube. The solution was irradiated with a General Electric ultraviolet sunlamp from a distance of one inch. The solution was allowed to reflux vigorously from the heat of the lamp until the insoluble adduct blocked the entrance of additional light or the solution began to bump. Then the adduct was filtered and washed free of the reaction mixture with 20 ml. of ether. The filtrate was poured back into the 500 ml. flask. Ether washings of the filtration vessel were also poured into the flask. The process of irradiation and filtration was repeated until no additional adduct formed (approximately three or four days). Ten and nine-tenths g. (92% yield) of the impure adduct was collected. The adduct was purified by recrystallization from approximately 75 ml. of an acetone-water solvent pair, then from pure acetone (78% recovery). This afforded an analytically pure sample of the material, m.p., 178°.

Anal. Calcd. for $C_{34}H_{29}N_3$: C, 85.18; H, 6.05; N, 8.77. Found: C, 85.39; H, 5.88; N, 8.73.

4. With p-Chloroazobenzene (1-p-Chlorophenyl-3-p-tolylimino-2,4,4-triphenyl-1,2-diazetidine and 2-p-Chlorophenyl-3-p-tolylimino-1,4,4-triphenyl-1,2-diazetidine).

In a procedure similar to that described, 5.4 g. (0.025 mole) of p-chloroazobenzene was treated with 7.0 g. (0.025 mole) of diphenylketene-N-(p-tolyl)imine. Ten and nine-tenths g. (88% yield) of the impure adduct was recrystallized from an acetone-water solvent pair, then from pure acetone (57% recovery), affording an analytically pure sample of the material, m.p. 179°.

Anal. Calcd. for $C_{33}H_{26}ClN_3$: C, 79.28; H, 5.21; N, 8.41. Found: C, 79.42; H, 5.02; N, 8.38.

5. With p-Bromoazobenzene (1-p-Bromophenyl-3-p-tolylimino-2,4,4-triphenyl-1,2-diazetidine and 2-p-Bromophenyl-3-p-tolylimino-1,4,4-triphenyl-1,2-diazetidine).

In a procedure similar to that described 4.6 g. (0.018 mole) of p-bromoazobenzene was treated with 5.0 g (0.018 mole) of diphenylketene-N-(p-tolyl)imine. Eight and eight-tenths g. (92% yield) of the impure adduct was recrystallized from an acetone-water solvent pair, then from pure acetone (74% recovery), affording an analytically pure sample of the material, m.p., 185°.

Anal. Calcd. for $C_{33}H_{26}BrN_3$: C, 72.81; H, 4.78; N, 7.72. Found: C, 72.80; H, 4.79; N, 7.63.

6. With p-N,N-Dimethylaminoazobenzene (1-p-N,N-Dimethylaminophenyl-3-p-tolylimino-2,4,4-triphenyl-1,2-diazetidine).

In a procedure similar to that described, 7.4 g. (0.032 mole) of p-N,N-dimethylaminoazobenzene was treated with 9.2 g. (0.032 mole) of diphenylketene-N-(p-tolyl)imine. Twelve and three-tenths g. (74% yield) of the impure adduct was recrystallized from ether (60% recovery), affording an analytically pure sample of the material, m.p., 151°.

Anal. Calcd. for $C_{35}H_{32}N_4$: C, 82.68; H, 6.30; N, 11.02. Found: C, 82.54; H, 6.39; N, 11.14.

7. With p-N,N-Diethylaminoazobenzene (1-p-N,N-Diethylaminophenyl-3-p-tolylimino-2,4,4-triphenyl-1,2-diazetidine).

In a procedure similar to that described 4.5 g. (0.018 mole) of N,N-diethylaminoazobenzene was treated with 5.0 g. (0.018 mole) of diphenylketene-N-(p-tolyl)imine. Five and nine-tenths g. (62% yield) of the impure adduct was recrystallized from ether (64% recovery), affording an analytically pure sample of the material, m.p., 143°.

Anal. Calcd. for $C_{37}H_{36}N_4$: C, 82.84; H, 6.72; N, 10.45. Found: C, 82.96; H, 6.71; N, 10.28.

8. With p-Methoxylazobenzene (1-p-Methoxylphenyl-3-p-tolylimino-2,4,4-triphenyl-1,2-diazetidine and 2-p-Methoxylphenyl-3-p-tolylimino-1,4,4-triphenyl-1,2-diazetidine).

In a procedure similar to that described 2.0 g. (0.010 mole) of p-methoxylazobenzene was treated with 2.7 g. (0.010 mole) of diphenylketene-N-(p-tolyl)imine. Three and three-tenths g. (71% yield) of the impure adduct was recrystallized from an acetone-water solvent pair, then from pure acetone (73% recovery), affording an analytically pure sample of the material, m.p., 176°.

Anal. Calcd. for $C_{34}H_{29}N_3O$: C, 82.42; H, 5.86; N, 8.48. Found: C, 82.68; H, 5.96; N, 8.70.

9. With o-Methylazobenzene (1-o-Tolyl-3-p-tolylimino-2,4,4-triphenyl-1,2-diazetidine).

In a procedure similar to that described 3.0 g. (0.015 mole) of o-methylazobenzene was treated with 4.3 g. (0.015 mole) of diphenylketene-(p-tolyl)imine. Three and five-tenths g. (48% yield) solvent pair, then from pure acetone (57% recovery), affording an analytically pure sample of the material, m.p., 189°.

Anal. Calcd. for $C_{34}H_{29}N_3$: C, 85.18; H, 6.05; N, 8.77. Found: C, 84.99; H, 6.11; N, 8.60.

10. With m-Chloroazobenzene (1-m-Chlorophenyl-3-p-tolylimino-2,4,4-triphenyl-1,2-diazetidine and 2-m-Chlorophenyl-3-p-tolylimino-1,4,4-triphenyl-1,2-diazetidine).

In a procedure similar to that described 2.3 g. (0.011 mole) of m-chloroazobenzene was treated with 3.0 g. (0.011 mole) of diphenylketene-N-(p-tolyl)imine. One and six-tenths g. (30% yield) of the impure adduct was recrystallized from an acetone-water solvent pair, then from pure acetone (75% recovery), affording an analytically pure sample of the material, m.p. 183°.

Anal. Calcd. for $C_{33}H_{26}ClN_3$: C, 79.28; H, 5.21; N, 8.41. Found: C, 79.08; H, 5.19; N, 8.29.

11. With o-Chloroazobenzene (1-o-Chlorophenyl-3-p-tolylimino-2,4,4-triphenyl-1,2-diazetidine).

In a procedure similar to that described 1.2 g. (0.0055 mole) of o-chloroazobenzene was treated with 1.6 g. (0.0055 mole) of diphenylketene-N-(p-tolyl)imine. One g. (36% yield) of the impure adduct was recrystallized from acetone (46% recovery), affording an analytically pure sample of the material, m.p., 207°.

Anal. Calcd. for $C_{33}H_{26}ClN_3$: C, 79.28; H, 5.21; N, 8.41. Found: C, 78.99; H, 5.05; H, 8.23.

12. With m-Methylazobenzene (1-m-Tolyl-3-p-tolylimino-2,4,4-triphenyl-1,2-diazetidine and 2-m-Tolyl-3-p-tolylimino-1,4,4-triphenyl-1,2-diazetidine).

In a procedure similar to that described 5.0 g. (0.026 mole) of m-methylazobenzene was treated with 7.2 g. (0.026 mole) of diphenylketene-N-(p-tolyl)imine. Six g. (49% yield) of the impure adduct was recrystallized from acetone (87% recovery), affording

an analytically pure sample of the material, m.p., 174-175°.

Anal. Calcd. for $C_{34}H_{29}N_3$: C, 85.18; H, 6.05; N, 8.77. Found: C, 85.39; H, 5.88; N, 8.73.

13. With *o*-Cyanoazobenzene (1-*o*-Cyanophenyl-3-*p*-tolylimino-2,4,4-triphenyl-1,2-diazetidine).

In a 200 ml. round bottom flask were placed 150 ml. of anhydrous ether, 2.2 g. (0.011 mole) of *o*-cyanoazobenzene, and 3.0 g. (0.011 mole) of diphenyl-*N*-(*p*-tolyl)imine. The flask was attached to a long bubble condenser fitted with a drying tube. The solution was irradiated with a General Electric ultraviolet sun lamp from a distance of one inch. The solution was allowed to reflux vigorously from the heat of the lamp for several days, after which time the solution had a strong 5.9 μ absorption in its infrared spectrum. This indicated that the reaction had almost gone to completion. The ether was removed under reduced pressure (aspirator). Then the residue was extracted with boiling hexane to remove the unreacted materials. The impure insoluble adduct was washed with hexane and recrystallized from methanol. This resulted in the isolation of 1.1 g. (21% yield) of the pure adduct. An additional recrystallization of the adduct from methanol afforded an analytically pure sample of the material, m.p., 207-208°.

Anal. Calcd. for $C_{34}H_{26}N_4$: C, 83.26; H, 5.31: N, 11.43. Found: C, 83.28; H, 5.25; N, 11.28.

14. With *p*-Cyanoazobenzene (1-*p*-Cyanophenyl-3-*p*-tolylimino-2,4,4-triphenyl-1,2-diazetidine and 2-*p*-Cyanophenyl-3-*p*-tolylimino-1,4,4-triphenyl-1,2-diazetidine).

In a procedure similar to that described 3.0 g. (0.015 mole) of *p*-cyanoazobenzene was treated with 4.1 g. (0.015 mole) of diphenylketene-*N*-(*p*-tolyl)imine. The impure adduct was recrystallized from methanol (24% yield), affording an analytically pure sample of the material, m.p., 177-178°.

Anal. Calcd. for $C_{34}H_{26}N_4$: C, 83.26; H, 5.31; N, 11.43. Found: C, 83.06; H, 5.25; N, 11.26.

15. With *m*-Nitroazobenzene (1-*m*-Nitrophenyl-3-*p*-tolylimino-2,4,4-triphenyl-1,2-diazetidine and 2-*m*-Nitrophenyl-3-*p*-tolylimino-2,4,4-triphenyl-1,2-diazetidine).

In a procedure similar to that described 2.9 g. (0.014 mole) of *m*-nitroazobenzene was treated with 3.9 g. (0.014 mole) of diphenylketene-*N*-(*p*-tolyl)imine. The impure adduct was recrystallized from methanol (15% yield), affording an analytically pure sample of the material, m.p., 182-184°.

Anal. Calcd. for $C_{33}H_{26}N_4O_2$: C, 77.65; H, 5.10; N, 10.98. Found: C, 77.40; H, 5.19; N, 10.80.

Decomposition Studies.

Gas Chromatography Column Preparation.

A copper column 0.6 cm. in external diameter and 2 m. in length was packed with 15% SE 30 liquid phase on Chromat CE solid support. The packing material was prepared by the addition of 23 g. of dry Chromat CE to a slurry composed of 4 g. of SE 30 dissolved in 200 ml. of chloroform. The chloroform was removed from the resulting mixture on a Buchler flash evaporator. After the packing material was air dried, it was heated for two hours at 140°.

Decomposition Procedure.

Approximately one-tenth of a g. of a pure, dry diazetidine product was sealed in a Pyrex sodium fusion tube. The tube was placed in an oven preheated to 220° for the length of time required to melt the diazetidine plus one minute. The total heating

period never exceeded eight minutes for any diazetidine. The hot tube was cooled in a stream of cool air to room temperature and broken. An infrared spectrum of the decomposition mixture was taken to make sure that all of the diazetidine had decomposed, as indicated by the absence of a 5.9 μ band. The remainder of the decomposition mixture was dissolved in benzene and concentrated to the extent that 8 or 9 μ 1 of the solution gave the desired peak intensity with the gas chromatograph attenuation set at 1. For a typical run, the flow rate was 30 ml./min., the chart rate was 1 division/min., and the column, injector, detector, and collector temperatures were 234°, 262°, 267°, and 253°, respectively. The injection of benzophenone-anil gave a single peak used as a standard, since the decomposition of a diazetidine product consisting of two isomers will always result in the formation of benzophenone-anil in the decomposition mixture. The retention times of the carbodiimides in all of the diazetidine decomposition mixtures were always less than that of benzophenone-anil. When only one diazetidine isomer was obtained in a decomposition mixture, there were always three carbodiimide peaks arising from the disproportionation of resulting unsymmetrical carbodiimides (11). Therefore, a peak with a longer retention time than benzophenone-anil was attributed to a substituted imine component.

If two isomers were present in a diazetidine product, the isomer ratio was determined by cutting out the areas under the two imine peaks of the decomposition mixture gas chromatograph and determining the mass of each peak. No evidence was obtained by spectroscopy techniques or by Glc to indicate the presence of anything other than imines and carbodiimides in the decomposition mixtures.

Rate Studies.

In a 5 ml. volumetric flask were weighed 0.0010 g. (5.15 x 10^{-6} mole) of dibenzo [c,f]diazepine and 0.00145 g. (5.12 x 10^{-6} mole) of I. The flask was diluted to the mark in ether and the absorbance at 360 mm. (ketenimine) determined with time. The same procedure was used for acetonitrile. Second order plots were made for the reaction in each solvent. The rate constants of the reaction in ether and acetonitrile were determined from the slope of the lines obtained from the second order plots. In ether the rate constant for the reaction was found to be 4 x 10^{-3} l. mole^{-1} sec.$^{-1}$. The rate constant for the reaction in acetonitrile was 2 x 10^{-2} l. mole^{-1} sec.$^{-1}$.

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