Acyl azide photolysis. Proximity and ring-size factors and mechanism[1,2]

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Photolysis of hexanoyl azide in cyclohexane gave 6-methyl-2-piperidone (13%), 5-ethyl-2-pyrrolidone (8%), and *N*-cyclohexylhexanamide (3%). In contrast, photosensitized decomposition of the azide with acetophenone gave hexanamide (78%), cyclohexene (11%), and dicyclohexyl (11%), but no lactams. It is concluded that the direct photolysis gives singlet acyl nitrene as the reactive species, which yields the δ-lactam preferentially. The importance of proximity in determining the γ- to δ-lactam ratio is emphasized.

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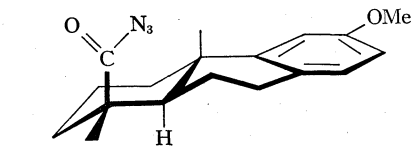
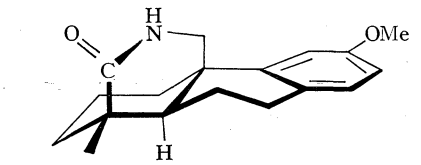
Early work on the photolysis of acyl azides showed that γ-lactams could be formed by internal attack on unactivated methylenes (2). However, in cases where both γ- and δ-lactam formation was possible (podocarpic and hexahydropodocarpic examples, ref. 3), δ-lactam formation predominated (e.g. I → II). The proximity of the axial methyl and azidocarbonyl groups could have been the major factor in this preference.

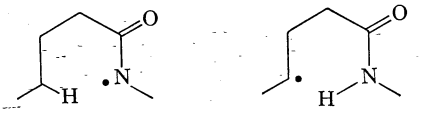
A second possibility was that the ring-size preference was related to the electronic state of the acyl nitrene. The photolysis of *N*-haloamides (4–6) and *N*-haloimides (7) most probably produces nitrogen radicals which abstract hydrogen preferentially from a γ-carbon (e.g. III → IV). This parallels the behavior of protonated nitrogen radicals in the Hofmann–Loffler reaction (8). Hence the geometry of the amide radicals (C—CO—N internal angle probably greater than 110°) does not appreciably modify the ring size of the favored cyclic transition state. By analogy, we conclude that the triplet state of the acyl nitrene would give predominantly the γ-lactam by internal hydrogen abstraction (six-membered cyclic transition state A), whereas the singlet state would probably favor the formation of δ-lactam via CH insertion (transition state B).



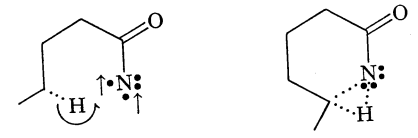
I



II



III IV



A B

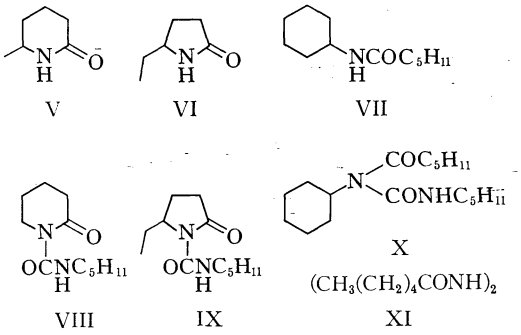
To evaluate the relative importance of these factors, we examined the simplest case in which two nearly equivalent methylenes were available for internal attack of the nitrene and no unusual proximity effect was present. This was the photolysis of hexanoyl azide.

[1]Issued as N.R.C. No. 9727.

[2]Presented in part at the Chemical Institute of Canada symposium on reactive intermediates in organic chemistry, Quebec, Quebec, September 1964. See also Abramovitch and Davis (1).

[3]National Research Council of Canada Postdoctorate Fellow, 1962–1964.

Irradiation of a dilute solution (ca. 0.04 *M*) of the azide in cyclohexane with a high-pressure mercury lamp at 0–5° gave approximately a 33% yield (by weight) of amides; the rest being isocyanate. No dicyclohexyl could be detected in the product. Since no suitable gas–liquid chromatographic column was found for the separation of the γ- and δ-lactams that were formed, thin-layer chromatography on fluorescent silica gel was used to separate the mixture. The major products[4] were 6-methyl-2-piperidone (V, 13%), 5-ethyl-2-pyrrolidone (VI, 8%), *N*-cyclohexylhexanamide (VII, 3%), and compounds produced by reaction of these amides with isocyanate. From the dilute solutions the only product of this type characterized was VIII. It was identical with the product obtained when pentyl isocyanate was heated with the δ-lactam V. Its nuclear magnetic resonance (n.m.r.) spectrum was consistent with the assigned structure (see the Experimental). Contrary to our early report (3), little if any hexanamide was produced in the direct photolysis (see below).



V VI VII

VIII IX X

XI

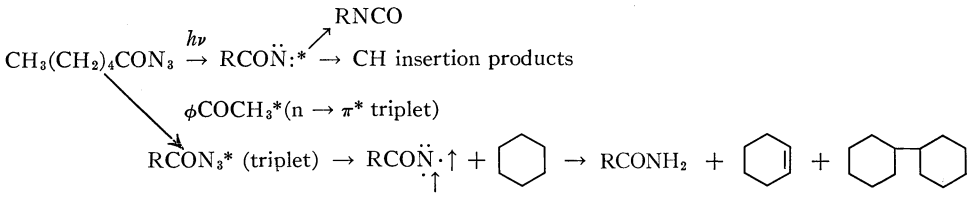
Photolysis of more concentrated solutions of the azide (ca. 0.5 *M*) resulted in more coupling products. This was at least partly a consequence of more prolonged heating during concentration of the final cyclohexane solution. After partial separation by distillation under 8 mm pressure, the products were separated by thin-layer chromatography. In addition to V, VI, and VII, the products IX and X from the reaction of isocyanate with the corresponding amides were characterized. Heating VI with isocyanate in cyclohexane gave authentic IX for comparison. The very high boiling fractions (>170° at 8 mm) yielded a small amount of crystals, identified by analysis and spectra as XI. This must have arisen by coupling of two nitrenes, followed by hydrogen abstraction from other components.

Our early attempts to realize a photosensitized decomposition of an acyl azide using triplet benzophenone failed (3). However, recently Lwowski and Mattingly (9) have shown that triplet acetophenone will transfer its energy to ethyl azidoformate. We have examined the photosensitized decomposition of hexanoyl azide with acetophenone. The results are in striking contrast to those of the direct photolysis. When a cyclohexane solution of hexanoyl azide and acetophenone was irradiated with light of wavelength over 3 000 Å, nitrogen was rapidly evolved. Hexanamide crystallized from the solution in a 78% yield. No isocyanate was detectable in the products, but dicyclohexyl and cyclohexene were.

After separation of acetophenone and dicyclohexyl by distillation, a fraction distilling over a short path between 100 and 170° at 8 mm was collected. This was separated by chromatography on alumina and further fractional distillation into three main fractions. The n.m.r. spectra and gas–liquid chromatography showed these to consist mainly of *N*-cyclohexylhexanamide, acetophenone substituted on the nucleus by cyclohexyl groups or a bicyclohexyl group, and molecules apparently containing amide, cyclohexyl, and aromatic rings (not acetophenone). These and the sizeable higher boiling residue were not further investigated. Gas–liquid chromatography failed to disclose the presence of δ-lactam V or γ-lactam VI. Thus the hoped-for comparison of the ratio of the yields of these products in the direct irradiation and photosensitized reactions was not realized.

It is now clear that, since considerable hexanamide was formed in our early experiments (3), enough acetone must

[4]The yields reported in ref. 1 have been revised as a result of care in avoiding the loss of the somewhat more volatile VI.

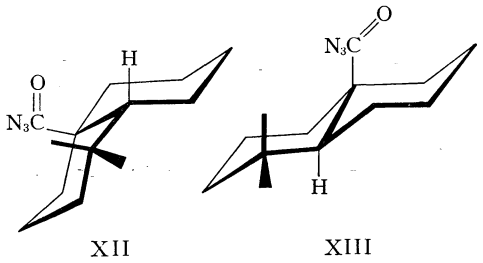


SCHEME 1.

have been carried through from the azide preparation to give some photosensitized decomposition of the azide. The photosensitized decomposition thus gives products characteristic of radical reactions[5] and hence of the triplet state of the excited azide or nitrene. Evidence is accumulating that excited nitrenes are the reactive intermediates (9–11); hence the reactions will be formulated as shown in Scheme 1. The fact that isocyanate was only formed during direct irradiation is consistent with the above conclusions. The migration of the pentyl group with its full complement of electrons onto singlet nitrene nitrogen should be favored over the corresponding radical migration onto triplet nitrene.

We conclude that the preferential δ-lactam formation in the hexanoyl azide case is a consequence of the preferred geometry for singlet nitrene insertion into the CH bond (see B).

The importance of the proximity factor is evident from the alicyclic terpenoid and steroidal examples. Brown (12) reported that azide XII gave more δ- than γ-lactam. Robinson found δ-lactam to be the major product in the photolysis of "lithocholic azide" (13), and Huneck obtained almost exclusively δ-lactam from 3α-acetoxyurs-12-en-24-oic acid (14). In all these cases primary hydrogens were replaced in preference to secondary, despite the intrinsic secondary to primary insertion ratio of 10:1 for nitrenes (15, 16). In the podocarpic cases cited above, there are two methylene hydrogens available to the nitrene as compared with only one methyl hydrogen. Using the 1:1.6 ratio for γ- to δ-lactam formation derived from the hexanoyl azide work, we would then expect that the ratio of γ- to δ-products would be roughly 12:1. As a consequence of the proximity of the azide and 10-methyl groups, however, the actual ratio is 1:4. Thus the proximity effect is a very large one, overriding all other effects.



XII XIII

Meyer and Levinson (17) have drawn attention to the fact that the accessible γ-hydrogens of I and related cases and of XII are in a 1,3-diaxial relation to an axial methyl group; hence attack on these is somewhat impeded. Thus the *trans*-decalin derivative XIII, in which the 6-hydrogen is not encumbered, gave a higher ratio of γ- to δ-lactam (1.5:1).

One noteworthy feature of the above acyl azide reactions is that, so far, only products apparently derived from electron-deficient nitrogen, rather than from electron-deficient oxygen, have been observed.

EXPERIMENTAL

Irradiation was carried out using a Vycor flask with internal ice-water cooling in a Rayonet apparatus[6] (lamps with reflector surrounding the sample, with photon density rated at 1.65×10^{16} photons cm^{-1} s^{-1} peaked at 2 537 Å), or using a Hanovia 100 W high-pressure mercury lamp in a Vycor well

[5]For unknown reasons, the triplet state selectively abstracts hydrogen from the solvent rather than internally. The successful cases of internal attack by nitrogen radicals (4–7) were observed with benzene or halogenated solvents. It hence appears desirable to compare the direct photolysis and photosensitized decomposition of acyl azides in proton-free solvents.

[6]Southern New England Ultraviolet Co., Middletown, Connecticut.

cooled by ice water, surrounded by the sample occupying a thin annular space in a Pyrex flask. The whole assembly was immersed in an ice bath. The amount of azide photolyzed was estimated by converting aliquots into isocyanate and then comparing the infrared intensities of the —NCO bands with those of solutions of known concentration. This proved rather inaccurate; hence recourse was had to measurement of the volume of nitrogen evolved. The products were distilled over a short path in a chain of bulbs under 8–10 mm pressure. Thin-layer chromatography was performed on Merck silica gel GF_{254} containing a fluorescent indicator. Infrared spectra were taken on a Perkin–Elmer model 537 grating spectrometer. Nuclear magnetic resonance spectra were determined in deuteriochloroform solutions on a Varian A-60A spectrometer with tetramethylsilane as internal reference.

Hexanoyl Azide

(*a*) To an ice-cold solution of 500 mg of hexanoic hydrazide, m.p. 73.5° (18), in 10 ml of water containing 2 ml of acetic acid was added, with stirring, a saturated aqueous solution of 0.5 g of sodium nitrite. After 1 min, 10 ml of ice water was added and the oil extracted with 40 ml of pure ice-cold cyclohexane. The solution was washed successively with sodium carbonate solution and water, and then dried over sodium sulfate.

(*b*) To a stirred solution of 6 g of sodium azide in 15 ml of water at 0° was added 2.5 g of hexanoyl chloride. The mixture was stirred for 2.5 h at 0°, after which no acid chloride remained. Cold cyclohexane was added, followed by sodium carbonate. The layers were separated and the aqueous layer was washed once with cyclohexane. The organic layer was dried and diluted further with cold hexane. Both products gave comparable results on photolysis. The azide solutions in cyclohexane had ν_{max} 2 130 and 1 720 cm^{-1}.

Photolysis of Hexanoyl Azide

(a) Dilute Solution

The azide solution from 2.5 g of acid chloride was diluted to 350 ml with cold cyclohexane, and then irradiated with the Hanovia lamp for 4 h 50 min. Nitrogen evolution had then ceased, 379 ml (25°) being collected. This corresponded to 2.18 g (83%) of hexanoyl azide. The solution now had ν_{max} 2 270 (RNCO) and 1 680 cm^{-1} (amides). Most of the cyclohexane was removed on a rotating evaporator at 40°. The rest of the cyclohexane and the isocyanate were removed by careful distillation in the chain of bulbs; then the volatile amides were collected at a bath temperature up to 170° at 8 mm. A small orange residue remained. The more volatile amides weighed 705 mg (33% by weight). An ice-cold pentane solution of this deposited 121 mg of δ-lactam V.

In preliminary runs it was found that gas–liquid chromatography with silicone grease, polypropylene glycol, tetraethylene glycol dimethyl ether, silicone gum rubber, and Apiezon L grease separated some components but failed to resolve the γ- and δ-lactams. Hence recourse was had to separation by thin-layer chromatography.

A total of 473 mg of the product, after removal of the crystals, was spotted on four 20 × 20 cm plates (0.5 mm thickness when wet) and developed with 50% benzene–ether. Five zones were separated, of which only A_1 and C were strongly fluorescent. The amides were recovered by extraction three times with methanol in ether.

Zone	R_f	Weight (mg)	Corrected weight* (mg)
A	0.27	184	227
A_1	0.29	8	10
B	0.53	112	137
C	0.68	88	109
D	0.88	32	40

*(To correspond to total oil.)

The loss was probably mainly γ- and δ-lactams, the most strongly adsorbed components.

Part of the product from zone A (138 mg) was separated on two 20 × 20 plates, using double development with ether, into 39 mg of pure γ-lactam VI and 90 mg of mixed γ- and δ-lactam. The latter was shown by plate separation and by comparison of the methyl peak heights in the n.m.r. spectrum with those of known mixtures to contain 58 mg of δ-lactam and 32 mg of γ-lactam. Hence the total yield of γ-lactam was 117 mg, and of δ-lactam 217 mg.[7] The compound from zone A_1 was not identified. The one from zone B was mainly *N*-hexanoylcyclohexylamine (VII). Zone C gave mainly ureide VIII, and zone D gave a mixture containing a ureide (characteristic quartet at δ 3.3), but no product was identified.

(b) Concentrated Solution

The azide was prepared as above from 3.5 g of hexanoyl chloride and 6 g of sodium azide in 15 ml of water. The final volume of cyclohexane solution was 45 ml. The photolysis was complete in 3.5 h. Most of the cyclohexane was distilled through a short column at 1 atmosphere pressure, using an oil bath for heating. The product was distilled as in method (*a*), yielding 617 mg distilling below 170° at 10 mm pressure. A residue of 182 mg crystallized in part, giving 13 mg of XI.

The distilled amides were spotted on 20 × 20 cm plates (ca. 120 mg per plate) and developed with 1:1 benzene–ether. The plate was sectioned to give five zones, of which only a very narrow band (zone 2) and a broad one (zone 4) were very fluorescent.

The compounds in each zone were extracted with three portions of methanol in ether (intermediate

Zone	R_f	Weight (mg)
1	0–0.25	99
2	0.27	16
3	0.5	108
4	0.65	250
5	0.85	33

[7]In a number of runs in which a rotating evaporator was used to remove cyclohexane and most of the isocyanate, the apparent ratio of γ- to δ-lactam was 1:4. The selective loss of γ-lactam is probably responsible for this.

filtration). Zone 1 was separated on a preparative plate with 1% methanol in ether to give 19 mg of γ- and 72 mg of δ-lactam. Zone 2 (crystalline) was not identified.

Zone 3 was an oil. A pentane solution gave 75 mg of a crystalline mixture of VII and ureide X when cooled to −78°. The rest was separated on a preparative plate, giving three fractions: 58 mg of VII, 37 mg of ureide X, and 15 mg not identified.

Zone 4 was an oil which could be separated partially on preparative plates, using double development with 30% ether in benzene. The zone was arbitrarily cut one-third of its width from the front edge. The faster moving fraction was a mixture. Its n.m.r. spectrum coincided with that expected for a mixture of ureides VIII and IX. The slower moving two-thirds of the band was also a mixture, but, on distillation at ca. 145° and 8 mm, isocyanate (ν_{max} 2 270 cm^{-1}) and crystalline δ-lactam distilled first, followed by an oil, whose n.m.r. spectrum indicated it to be pure ureide IX. Clearly ureide VIII is less thermally stable than IX, reverting to isocyanate and the lactam.

Zone 5 gave a poorly defined n.m.r. spectrum, and no attempt was made to characterize it.

N-Cyclohexylhexanamide (VII)

The yield from the photolysis of the dilute solution was 3%. The white solid could be recrystallized from aqueous methanol. After sublimation *in vacuo*, it had m.p. 71.5–72°.

Anal. Calcd. for $C_{12}H_{23}NO$: C, 73.04; H, 11.75; N, 7.10. Found: C, 73.14; H, 11.75; N, 7.21.

It had $\nu_{max}^{CHCl_3}$ 3 440, 1 655, and 1 509 cm^{-1}, and its n.m.r. spectrum had peaks at δ 5.7 (NH), 3.8 (—CON—CH), 2.04 and 2.16 (—CH_2CO—), and 0.9 (center of a triplet, CH_3CH_2—). It was identical with a sample prepared from hexanoyl chloride and cyclohexylamine in dry benzene.

5-Ethyl-2-pyrrolidone (VI)

The yield from the photolysis of the dilute solution, was 8% The colorless oil distilled over a short path at 130° and 8 mm. It had $\nu_{max}^{CS_2}$ 1 695 cm^{-1} and $\nu_{max}^{CHCl_3}$ 1 690 cm^{-1}, and its n.m.r. spectrum had bands at δ 7.28 (NH), 3.6 (—CON—CH), 2.3 (—CH_2CO—), and 0.96 (center of a three-proton triplet). Its infrared spectrum in carbon disulfide and n.m.r. spectrum were identical with those of authentic 5-ethyl-2-pyrrolidone kindly supplied by Dr. R. B. Moffatt (19).

6-Methyl-2-piperidone (V)

The yield from the photolysis of the dilute solution, with addition of the amount contained in ureide VIII, was 13%. After recrystallization from *n*-hexane, it melted at 86–88° and had $\nu_{max}^{CHCl_3}$ 1 656 cm^{-1} and n.m.r. peaks at δ 6.8 (NH), 3.5 (—CON—CH), 2.3 (—CH_2CO—), and 1.17 and 1.27 (doublet, CH_3). It was identical with an authentic sample prepared according to Conley (20).

Ureide VIII

This was an oil with $\nu_{max}^{CHCl_3}$ 1 711 cm^{-1} and n.m.r. peaks at δ 9.47 (NH), 4.79 ($(CO)_2$N—CH), 3.25 (center of a two-proton "quartet", CONHCH_2), 2.51 (CH_2CO), 1.21 and 1.32 (CH_3—CH—N), and 0.9 (center of a three-proton triplet, CH_3CH_2—).

A solution of 225 mg of pentyl isocyanate and 50 mg of δ-lactam V in 5 ml of cyclohexane was heated on the steam bath for 4 h, the cyclohexane being allowed to evaporate slowly. Distillation of the product gave unchanged urethane, δ-lactam, and ureide VIII (55 mg) in order of volatility. The latter distilled over a short path at 150° and 10 mm. The oil had an n.m.r. spectrum superposable on that of the compound from the photolysis product. The ureide reverted in part to δ-lactam and isocyanate when distilled at 150° under 10 mm pressure; for this reason, a specimen pure enough for analysis was not obtained.

Ureide IX

This was an oil distilling readily over a short path at 160° and 10 mm. It had ν_{max} 3 310, 1 711, and 1 545 cm^{-1} and n.m.r. peaks at δ 8.5 (NH), 4.3 (one-proton multiplet, $(CO)_2$N—CH), 3.6 (quartet, actually two overlapping triplets collapsing to a triplet when NH exchanged for deuterium, —CONH—CH_2—), 2.6 (center of a one-proton quartet) and 2.49 (one-proton singlet) (CH_2CO—), and 0.95 (center of a triplet, CH_3CH_2—).

Anal. Calcd. for $C_{12}H_{22}N_2O_2$: C, 63.68; H, 9.80; N, 14.14. Found: C, 64.10; H, 9.71; N, 13.87.

A solution of γ-lactam VI (30 mg) and 225 mg of pentyl isocyanate in 5 ml of cyclohexane was slowly distilled during 4 h. The volume was then ca. 2 ml. The products were distilled, giving 45 mg of ureide IX, whose n.m.r. spectrum was identical with that of the product from the photolysis mixture.

Ureide X

A mixture of 80 mg of pentyl isocyanate and 135 mg of *N*-cyclohexylhexanamide (VII) in 3 ml of cyclohexane was slowly distilled during 4 h. The final volume was ca. 1 ml. The products were distilled over a short path under 10 mm pressure. Most of the mixture came over at 150–160°, and crystallized spontaneously when cooled. It contained ureide (n.m.r. signals centered at δ 3.2), but was estimated to be approximately 50% unchanged VII.

The product from zone 3*b* solidified to a waxy solid after distillation over a short path at 120° and 0.2 mm. It had n.m.r. peaks at δ 6.1 (broad NH), 3.8 (broad, $(CO)_2$N—CH), 3.24 (multiplet, —CONH—CH_2), 2.07 and 2.18 (—CH_2—CO), and 0.91 (center of a triplet, CH_3CH_2—).

Anal. Calcd. for $C_{18}H_{34}N_2O_2$: C, 69.63; H, 11.04. Found: C, 68.57; H, 10.93.

1,2-Bishexanoyl Hydrazine

When recrystallized from acetone–hexane, this gave needles, m.p. 162–163° (lit. m.p. 159° (21)).

Anal. Calcd. for $C_{12}H_{24}N_2O_2$: C, 63.12; H, 10.60; N, 12.27. Found: C, 62.94; H, 10.43; N, 12.35.

Its n.m.r. spectrum had peaks at δ 9.5 (NH), 2.29 (multiplet, CH_2CO—), and 0.9 (triplet, CH_3CH_2—), with areas in the ratio of 1:2:3. It was identical (mixture melting point and n.m.r. spectrum) with an authentic sample prepared by adding a cyclohexane solution of 98% hydrazine to a cyclohexane solution of hexanoyl chloride.

Photosensitized Decomposition of Hexanoyl Azide

Hexanoyl azide (prepared from 1.46 g of hexanoyl chloride) and 1.14 g of acetophenone in 90 ml of cyclohexane were irradiated at 5° in a Rayonet apparatus,[6] using 16 lamps with radiation peaked at 3 500 Å. Steady gas evolution ensued. After 6 h, the azide had disappeared (infrared) and 200 ml of gas at 25° had been evolved. This corresponds to 1.15 g (0.0082 mole) of azide.

The solution was separated from 668 mg of crystals which had precipitated. No isocyanate could be detected in the filtrate by infrared absorption. The filtrate was concentrated to a volume of ca. 15 ml; then the residue was transferred to a chain of bulbs. Careful distillation, finally under 8 mm pressure gave two fractions: A, up to 100° bath temperature (1.0 g), and B, up to 170° (0.55 g). A residue of 500 mg of pentane-soluble oil and a small amount of pentane-insoluble gum remained.

Hexanamide

The 668 mg of crystals consisted of hexanamide contaminated with a small amount of colored gum. A further 47 mg of hexanamide crystallized from a pentane solution of B, and another 40 mg was obtained on chromatography of B (see below). After recrystallization from acetone–hexane, the product (78% yield) had m.p. 96–98°, undepressed on admixture with authentic hexanamide. It had n.m.r. peaks at δ 6.0 (NH_2), 2.22 and 2.11 (CH_2CO—), and 0.91 (CH_3CH_2—), with areas in the ratio of 2:2:3.

Cyclohexene

The cyclohexane distillate (75 ml) was examined on a 2 m column (Perkin–Elmer column H) of silver nitrate in ethylene glycol, in a Perkin–Elmer model 154 C gas chromatograph at 40°. Cyclohexene had a retention time of 9.4 min. By comparison with standard solutions, its concentration was estimated to be 0.098 mg/ml. Hence 73 mg was present in the distillate (yield 11% based on photolyzed azide).

Dicyclohexyl

Fraction A was dissolved in 50% aqueous methanol and reduced with sodium borohydride. The solution was extracted with pentane, and the extract was dried and added to a column of 8 g of alumina (activity I). The first 50 ml of pentane eluted 124 mg of pure dicyclohexyl, and the next 5 ml eluted 46 mg of a mixture of dicyclohexyl and 34% of another unknown component (gas–liquid chromatographic examination). The pure material had the same n.m.r. spectrum and retention time in gas chromatography as authentic dicyclohexyl (yield 11% based on photolyzed azide).

Fraction B

Gas chromatography failed to disclose the presence of lactams V or VI, but a component with the same retention time as *N*-cyclohexylhexanamide was present in fraction B. It was separated into 10 fractions by chromatography on 10 g of alumina (activity 1). The main fractions were 150 mg of oil (eluted rapidly with benzene), 117 mg of oil (eluted with ca. 5% methanol in ether), and 40 mg of strongly adsorbed hexanamide.

The main weakly adsorbed fraction was distilled over a short path at 8 mm, giving cuts 1 (up to 130°) and 2 (130–160°). The former was shown by its n.m.r. spectrum to be a mixture of hexanamides and acetophenone. The higher boiling cut gave an n.m.r. spectrum suggestive of acetophenone substituted by dicyclohexyl.

The main strongly adsorbed fraction gave an n.m.r. spectrum containing peaks ascribable to hexanoylamido and aryl methyl carbinol functions.

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