Generation, Reactions, and Multiplicity of Benzoylnitrene

Yoshiyuki Hayashi and Daniel Swern*

Contribution from the Fels Research Institute and Department of Chemistry, Temple University, Philadelphia, Pennsylvania 19122.

Received January 8, 1973

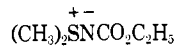
Abstract: Benzoylnitrene (**6**) has been generated by photolysis of benzoyl azide (**4**) and *N*-benzoyliminodimethylsulfurane (**5**) in various trapping substances. Singlet **6** is shown to be the primary species in these photolyses; **4** is by far the most satisfactory source of singlet **6**. In efficient olefinic traps for nitrenes, stereoselective addition to the double bond (aziridination) occurs (*ca.* 98%) with the isolation of *N*-benzoylaziridines in fair to good yields (25–65%). Yields of photo-Curtius rearrangement product, phenyl isocyanate (**9**), are about 30% in most instances. Photolysis of **4** in dimethyl sulfide (DMS), an efficient trap for singlet nitrene only, gives fair yields of **5** (38%) (owing to its photoinstability) and about 25–30% of **9** but only 3% of benzamide (**10**), the product formed from triplet **6** by hydrogen abstraction. In contrast with benzophenone, a known sensitizer for **4** also present in the DMS, yields of **5** are approximately halved but those of **10** increase about tenfold to 35% and those of **9** decrease by a factor of 4–7. In cyclohexane (**19**), a relatively inefficient singlet nitrene trap, a modest yield (19%) of CH insertion product is obtained from **4** and only a low yield is obtained from **10** (4%); the major product (37%) is the photo-Curtius rearrangement product, **9**. In contrast, photolysis of **5** in **19** yields no CH insertion product; products are **10** (32%) and **9** (23%). Pivaloyl azide (**7**) also adds stereospecifically to *cis*-4-methyl-2-pentene (**11a**) to afford a 31% yield of the *cis*-*N*-pivaloylaziridine (**26**), but in the trans olefin (**11b**) a complex mixture of products is obtained in poor yield. This is in marked contrast to the photolysis of **4**, which is equally successful and stereospecific in either **11a** or **11b**. Photolysis of *n*-butyl azide (**8**) in cyclohexene or DMS does not yield the anticipated nitrene products.

In the previous paper,[1] we described the photolysis of *N*-carbethoxyiminodimethylsulfurane (**1**) in *cis*- or *trans*-4-methyl-2-pentene, cyclohexene, cyclohexane, and diethyl sulfide, and we compared the results obtained in similar experiments with ethyl azidoformate (**2**) as the nitrene source.

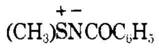
From the composition of the aziridine mixture obtained by the addition of carbethoxynitrene (**3**), prepared from **1**, to the cis olefin and the yields of the hydrogen abstraction product ethyl carbamate (63–65%) in reactions of **3** with either the cis or trans olefin, we concluded that **3** was being trapped predominantly as the triplet (>60%). Results of irradiation of solutions of **1** in cyclohexene and cyclohexane also suggested that considerable triplet **3** was present (30–60% yields of ethyl carbamate) but small yields of CH insertion products indicated that singlet **3** was also involved and may indeed have been the precursor of triplet **3**. The results of the cyclohexene and cyclohexane experiments were somewhat clouded, however, by the use of methylene chloride as an "inert" cosolvent to obtain a homogeneous solution. Only recently it has been shown that methylene chloride has a stabilizing effect on the singlet state of certain nitrenes, although **3** is reported to be exempt from such stabilization, at least in respect to CH insertion.[2]

In contrast with those results, photochemical transylidation of **1** in diethyl sulfide prompted us to conclude that **3** was being formed in the singlet state but, in the presence of an efficient singlet nitrene trap, such as diethyl sulfide,[3] intersystem crossing to triplet does not occur and in the presence of relatively poor singlet traps such as cyclohexane and cyclohexene intersystem crossing prevails and considerable triplet reaction products form.

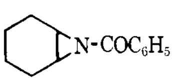
Concurrently with the work just described, we were also studying the photolysis of benzoyl azide (**4**) and *N*-benzoyliminodimethylsulfurane (**5**) in several cis and trans olefins, cyclohexene, cyclohexane, and dimethyl sulfide to obtain information on the generation, multiplicity, and reactions of benzoylnitrene (**6**) and also to compare the results obtained with those using **1** and **2** as nitrene sources. [In one study, pivaloyl azide (**7**) was the nitrene source and in another attempts were made to generate and trap a nitrene from *n*-butyl azide (**8**).] The results, not surprisingly, are sufficiently novel to warrant this report.


$(CH_3)_2\overset{+}{S}\overset{-}{N}CO_2C_2H_5$

1


$(CH_3)\overset{+}{S}\overset{-}{N}COC_6H_5$

5



13

18

Results and Discussion

Photolysis of either **4** or **5** in excess 4-methyl-2-pentene (**11a,b**) at 5 to 15° for 46–65 hr using 2538-Å radiation (Rayonet reactor) or for 7 hr using a Hanovia 450-W medium-pressure uv source gives modest yields of *N*-benzoylaziridines (19–28%) and an essentially constant yield of the photo-Curtius rearrangement product phenyl isocyanate (**9**) (29–33%) (Table I). The constancy of yields of **9**, independent from those of nitrene products, means that the nitrene is not the isocyanate precursor.

Most important, however, aziridination is stereoselective; only about 2% or less of the isomeric *N*-benzoylaziridine is formed. Furthermore, in the azide photolyses only traces of the hydrogen abstraction product benzamide (**10**) are formed but in the iminosulfurane (**5**) photolyses, in which methylene chloride is

---

[1] Iminosulfuranes. X. Part IX: Y. Hayashi and D. Swern, *Tetrahedron Lett.*, 1921 (1972).

[2] G. R. Felt, S. Linke, and W. Lwowski, *Tetrahedron Lett.*, 2037 (1972).

[3] W. Ando, N. Ogino, and T. Migita, *Bull. Chem. Soc. Jap.*, **44**, 2278 (1971), report that singlet but not triplet nitrenes are trapped by dialkyl sulfides.

Table I. Photolysis of Benzoyl Azide (**4**), *N*-Benzoyliminodimethylsulfurane (**5**), and Pivaloyl Azide (**7**) in *cis*- and *trans*-4-Methyl-2-pentene (**11a,b**)

Yield of products, %	Photolyses **4 + 11a**	 **4 + 11b**	 **5**[a] **+ 11a**	 **7 + 11a**
cis-N-Acylaziridine	26[b] (**24**)	Trace (**24**)	28 (**24**)	31[d] (**26**)
trans-N-Acylaziridine	<2 (**25**)	19[c] (**25**)	<2 (**25**)	2 (**27**)
PhNCO (**9**)	33	29	32	*e*
$PhCONH_2$ (**10**)	Trace	Trace	7	

[a] Equal volumes of methylene chloride and olefin were used owing to the low solubility of **5** in neat olefin; see Experimental Section. Only about 60% of **5** decomposed. [b] Mp, 78–80°. [c] Bp, 85–87° (0.05 Torr). [d] Bp, 87–89° (17 Torr). [e] No attempt was made to isolate the photo-Curtius rearrangement product, butyl isocyanate. Linke, Tisue, and Lwowski[4] have shown that 40–43% yields are obtained in a wide range of substrates.

a cosolvent, yields of **10** are about 7%. When benzophenone was present during photolysis of **4** in **11a** the yield of *cis-N*-benzoyl-2-isopropyl-3-methylaziridine (**24**) was virtually unaffected (24%) but the yield of **10** increased to about 10% and that of the photo-Curtius product (**9**) decreased to 17%. The increased yield of **10** suggests that triplet **6** abstracts hydrogen more rapidly than it adds to the double bond, thus accounting for **10** and the maintenance of stereospecificity of olefin addition.

For comparison, the photodecomposition of **7** in the same olefins was also examined (Table I). This azide (**7**) has received detailed photolytic study in cyclohexane, *trans*-2-butene, and *trans*-4-methyl-2-pentene (**11b**) solutions by Lwowski and coworkers,[2,4,5] but not in *cis*-4-methyl-2-pentene (**11a**). We find that photolysis of **7** in neat **11a** yields the *cis-N*-pivaloyl-2-isopropyl-3-methylaziridine (**26**, 31%) with high stereoselectivity and less than 2% of the trans isomer (**27**). (No attempt was made by us to isolate *tert*-butyl isocyanate.) In contrast, photolysis of **7** in neat **11b** gives a complex mixture containing *both* isomeric *N*-pivaloylaziridines (**26** and **27**) in about 14% yield (cis: trans ratio = 1:4). This result is in good agreement with that of Felt, Linke, and Lwowski,[2] who obtained 7–20% yields of *N*-pivaloylaziridine from **7** and **11b**. Their yields *de*creased with *in*creasing olefin concentration (in olefin–methylene chloride mixtures) but they did not report any results with neat **11b**.

To determine the scope and stereochemistry of the direct aziridination reaction, we also photolyzed **4** in *cis*-2-hexene, *cis*-2-octene, and cyclohexene (**12**); yields of *N*-benzoylaziridines were 34, 46, and 64% (**13**), respectively. In the aliphatic cases, only *cis*-aziridines were isolated. Since the preparation of the relatively stable benzoyl azide (**4**) is easy and the photolysis–addition reaction occurs under mild conditions, direct aziridination may be an attractive route to certain aziridines from those unsaturated compounds that are unstable to strong acid or base and pseudohalogens, even though yields by the photolytic addition pathway are only fair to good. No attempt was made to define the scope and limitations of direct aziridination of unsaturated compounds by photolytic decomposition of **4**.

A more detailed study of products and material balance was conducted with cyclohexene (**12**). From **4** and excess **12** yields of products are as follows: *N*-benzoyl-7-azabicyclo[4.1.0]heptane (**13**), 64%; phenyl isocyanate (**9**), 17%; benzamide (**10**), 4%; 3-cyclohexenyl *N*-phenylcarbamate (**14**), 1%; 3-(*N*-benzoylamino)cyclohexene (**15**), trace; 3-hydroxycyclohexene (**16**), trace; 3,3′-biscyclohexenyl (**17**), trace; and undecomposed **4**, 6%. The yield of **13** is not only satisfactory from the preparative standpoint but that of the photo-Curtius rearrangement product **9** is only 17%. As shown in Table I, yields of **9** are about 30% with other olefins; we have no explanation for the apparent lower yield of **9** in this case. In addition, CH insertion products are usually almost totally absent.

To eliminate the possibility that aziridines are formed by initial triazoline formation followed by photochemical decomposition accompanied by loss of nitrogen, **4** was kept in **11a** or **12** in the dark at room temperature for up to 1 month. No spectral (ir, nmr) changes were observed. Under reflux in the dark, however, solutions of **4** in **11a** gave over 85% yields of **9** in 7 days but no aziridine could be detected. Thus, photolysis is essential to aziridine formation and triazoline formation may be excluded, except for the unlikely possibility that excited singlet azide adds to the double bond to give triazoline, which decomposes to aziridine.

In contrast, photolysis of **5** in **12** under similar conditions (33% methylene chloride was required to obtain a homogeneous solution) gave the following products and yields: **13**, 28%; **10**, 9%; **9**, 5%; **14**, **16**, and **17**, trace %; and undecomposed **5**, 46%. Decomposition of **5** is considerably slower and less clean than that of **4** and tarry products form on the vessel walls. Thus, **5** is a far less satisfactory source of **6** than is **4**. Furthermore, methylene chloride is not exerting any special stabilizing effect on singlet **6**, otherwise considerably less **10** should have been obtained with concomitant increases in CH insertion products. In this photolysis, no CH insertion product (**15**) was detected.

The stereoselectivity of aziridine formation in the photolyses of **4** and **5** in olefin solutions leads to the conclusions that (a) benzoylnitrene (**6**) is being generated in the singlet state from both **4** and **5** and (b) it is rapidly trapped by the olefin before intersystem crossing to triplet occurs. In contrast, the poor yield of aziridines, low stereoselectivity, and the formation of a complex mixture of tarry, unidentified products from photolyses of **7** and **11b** are not clear. This anomalous result may be a consequence of the lower thermodynamic stability of *trans-N*-pivaloylaziridine than its cis isomer,[2] causing isomerization, photodecomposition, and possibly polymerization (tar) as well. From the earlier reported work[2] on the photodecomposition of **7** in **11b**, we had expected a low yield of aziridine; however, we also found that the recovered olefin contained about 2% of **11a**, its cis isomer (starting material was >99.9% trans). This suggests that photoisomerization of trans to cis may be occurring and the addition of singlet pivaloylnitrene may indeed be stereospecific to both olefins but the trans product does not survive.

Evidence has accumulated that singlet nitrenes are the main reactive species in the direct photolyses of

---

(4) S. Linke, G. T. Tisue, and W. Lwowski, *J. Amer. Chem. Soc.*, **89**, 6308 (1967).

(5) G. T. Tisue, S. Linke, and W. Lwowski, *J. Amer. Chem. Soc.*, **89**, 6303 (1967).

acyl azides.[6] Horner and coworkers,[7] for example, have proven the existence of singlet **6** as the primary photocleavage product of **4** by trapping experiments with water, acetic acid, aniline, and dimethyl sulfoxide, among others. In our experience[1] and that of Ando and coworkers,[8] dimethyl or other dialkyl sulfides are perhaps the best traps for singlet nitrenes yielding iminosulfuranes. Accordingly, **4** was photolyzed in excess dimethyl sulfide at room temperature with and without benzophenone, an efficient photosensitizer for **4**,[7] using a medium pressure Hanovia lamp (450 W).

As Table II shows, the yield of iminosulfurane (**5**, 35–38%) relative to that of the dehydrogenation product benzamide (**10**, 3%) leads to the conclusion that singlet **6** is the major, and perhaps even the exclusive, *initial* photodecomposition product of **4**. Failure to obtain higher yields of **5** reflects the instability of **5** under the photochemical reaction conditions.[1] The yield of the photo-Curtius rearrangement product phenyl isocyanate (**9**) is about 25–32%, in the same range as that shown in Table I (olefin trapping).

Table II. Photolysis[a] of Benzoyl Azide (**4**) in Excess Dimethyl Sulfide (DMS)

	Photolyses	
Yield of products, %	**4** + DMS (Vycor filter)	**4** + DMS + benzophenone (0.5–1 g) (Pyrex)
$PhCON^{-}S^{+}Me_2$ (**5**)	35–38	20
PhNCO (**9**)	25–32	7
$PhCONH_2$ (**10**)	3	35

[a] Medium pressure Hanovia lamp (450 W) for 24 hr or Rayonet reactor for 50 hr; both at 5–15°. In the latter case only 60% of **4** had decomposed, whereas in the former complete decomposition occurred.

In contrast, photolysis of **4** in excess dimethyl sulfide in the presence of benzophenone, reported to be an effective sensitizer for **4**,[7] produces substantially lower yields of **5** and the yield of **10** increases to 35%. The conclusion seems inescapable that singlet nitrene **6** is the primary product in the absence of sensitizer. A particularly interesting result whose significance is not apparent is the marked reduction in yield of the photo-Curtius rearrangement product **9** from about 30 to 7% in the presence of sensitizer. Sensitized photodecomposition of **4** in **19** is also reported to give no isocyanate.[7]

Photolysis of *n*-butyl azide (**8**) in cyclohexene or excess dimethyl sulfide did not yield the expected products 7-*n*-butyl-7-azabicyclo[4.1.0]heptane (**18**) or *N*-*n*-butyliminosulfurane, respectively. The lower limit of detection of **18** was about 0.1%.

Table III. Photolysis of Benzoyl Azide (**4**) and *N*-Benzoyliminodimethylsulfurane (**5**) in Cyclohexane (**19**)

	Photolyses[a]		
Yield of products, %	**4** + **19**[b]	**4** + **19** + Ph_2CO (lit.[7])	**5** + **19**[b, c]
$C_6H_{11}NHCOPh$ (**20**)	19		0
$PhCONH_2$ (**10**)	4	63	32
PhNCO (**9**)	37	0	23
PhCONHCONHPh (**21**)			3

[a] Photolysis times 43–68 hr at 5–15°. [b] Only about 60% of the azide had decomposed, presumably because of the copious precipitation of **20** on the vessel walls which may have blocked out the radiation. [c] Equal volumes of methylene chloride and **19** were used owing to the low solubility of **5** in neat **19**; see Experimental Section. Only about 50% of **5** decomposed.

Table III shows the results of the photolyses (Rayonet reactor) of **4** and **5** in cyclohexane (**19**) for 43–68 hr at 5–15°. Cyclohexane is a much less effective singlet nitrene trap than either dimethyl sulfide or olefins; also, considerable tar and solid material deposited on the vessel surface and only 50–60% of **4** and **5** decomposed under these conditions. From **4** a modest yield of CH insertion product, *N*-cyclohexylbenzamide (**20**, 19%), was obtained; the major product was the photo-Curtius rearrangement product (**9**, 37%). Only a small amount of dehydrogenation product (**10**, 4%) was also formed, presumably from triplet **6**. In the presence of photosensitizer,[7] the yield of dehydrogenation product is reported to be 63%; this result permits the conclusion that triplet nitrenes are *not* of substantial importance in nonphotosensitized photolyses of **4** (see Table II also).

With **5**, however, no CH insertion product (**20**) was found, a somewhat surprising result in view of our earlier work on transylidation[1] and the results reported in Table I, in which **5** appears to be producing singlet **6** predominantly. We have no ready explanation for this result except to propose that singlet **6** from **5** contains more energy than that from **4** and undergoes intersystem crossing to triplet considerably faster than it can insert into a CH bond of cyclohexane. With more efficient singlet nitrene traps (olefins, sulfides) described earlier, trapping of the singlet species **6** must be substantially faster than intersystem crossing. The conclusion that intersystem crossing from singlet to triplet **6** is occurring in photolyses of **5** in cyclohexane is supported by the high yield of dehydrogenation product (**10**, 32%) obtained. The cyclohexane photolysis systems in which **5** was employed also contained equal volumes of methylene chloride, a singlet nitrene stabilizer,[2] yet no CH insertion products were observed.

1-Benzoyl-3-phenylurea (**21**) is formed in about 3% yield in the photolyses of **5** in 1:1 methylene chloride–**19** but not in the absence of methylene chloride. The formation of **21** is rationalized in Scheme I. Methylene chloride provides a source of chlorine atoms which can attack **10** to form *N*-chlorobenzamide (**22**). Compound **22** contains an active hydrogen and reacts with **9** to yield 1-benzoyl-1-chloro-3-phenylurea (**23**), which is converted to **21** by chlorine–hydrogen exchange, a known reaction of *N*-halo compounds. In a separate study, we prepared authentic **21** in 55% yield from **10** plus *tert*-butyl hypochlorite, followed by reaction of the intermediate **22** with **9** to yield **21**, identical with the product from photolysis of **5** in cyclohexane–methylene chloride. Compounds **9** and **10** do not react either in the dark (2 months) or upon irradiation in benzene solution, but produce **21** in 14% yield if methylene chloride is the solvent during irradiation, thus lending credence to our conclusion concerning the origin of **21**.

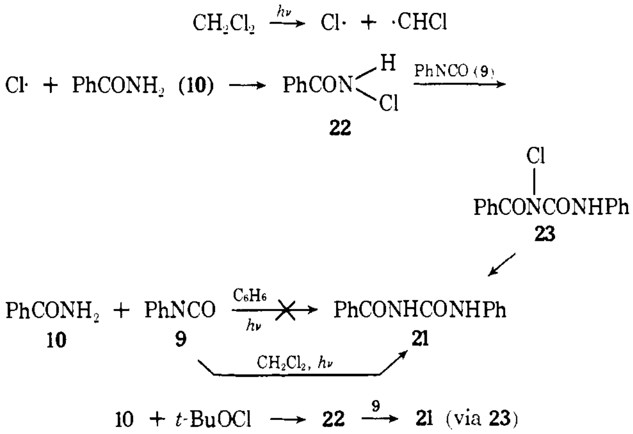
---

(6) O. E. Edwards in "Nitrenes," Chapter 7, W. Lwowski, Ed., Interscience, New York, N. Y., 1970, p 239, and references cited.

(7) L. Horner, G. Bauer, and J. Dörges, *Chem. Ber.*, **98**, 2631 (1965).

(8) W. Ando, N. Ogino, and T. Migita, *Bull. Chem. Soc. Jap.*, **44**, 2278 (1971).

Scheme I



The photo-Curtius rearrangement product **9** is obtained in 23% yield in the photolysis of **5** in **19**.

In summary, on photolysis, **4** and **5** yield singlet benzoylnitrene (**6**) predominantly. If efficient nitrene traps are present in excess (olefins, sulfides), products expected from a singlet nitrene species are obtained often in good yield based on **4** and **5** decomposed. Stereoselective aziridination of olefins occurs in most instances. With a less efficient nitrene trap (cyclohexane) and/or in the presence of photosensitizers considerably more triplet **6** is formed from both **4** and **5**; however, we presume that the initially formed **6** is in the singlet state from both **4** and **5**.

Experimental Section

Ir spectra were obtained as KBr disks or liquid films using a Perkin-Elmer model 225 grating or model 137B infracord spectrophotometer. Nmr spectra were obtained with a Varian XL-100 or A-60A spectrometer using suitable solvents and internal standards. Uv spectra were obtained with a Perkin-Elmer model 202 spectrophotometer. Tlc and glc analyses and assessments of purity were conducted using appropriate solvent and developing systems (tlc) and gas chromatographs with suitable column packings and operating conditions. Internal standards and pure reference compounds (see below) were used throughout in tlc and glc probes. Melting points were determined with a Thomas-Hoover capillary melting point apparatus. Melting points and boiling points are uncorrected. Elemental analyses were performed by Micro-Analysis, Inc., Wilmington, Del.

Starting Materials (a) Benzoyl azide (**4**),[9] mp 30°, *n*-butyl azide (**8**),[10] and pivaloyl azide (**7**),[5] bp 30° (18 Torr), were prepared by literature procedures. *Caution:* **7** has been distilled several times in our laboratory without explosion but it is thermally unstable even at room temperature, thus precluding elemental analysis; it was always prepared on a small scale (*ca.* 4 g or less) with adequate protection and it was handled in a hood at all times as it is toxic and its vapors cause unpleasant physiological effects.[5] Compound **7** was always freshly prepared and used up immediately. Olefins and cyclohexane were the purest available reagent grades; just before use they were thoroughly shaken with concentrated aqueous sodium hydroxide solution, washed with water, dried over anhydrous magnesium sulfate, and then fractionally distilled under nitrogen. Glc analysis indicated a purity of at least 99.9%. Dimethyl sulfide was used as received; its purity was in the same range. Solvents were dried and purified following accepted procedures.[11]

(b) *N*-Benzoyliminodimethylsulfurane (5). To a stirred mixture of benzamide (**10**) (24.2 g, 0.2 mol) in methylene chloride (200 ml), *tert*-butyl hypochlorite (21.6 g, 0.2 mol) was added dropwise while maintaining the temperature at about 25° by means of a cooling bath. The mixture became homogeneous after 1 hr but was stirred for an additional hour. The stirred solution was cooled to −5 to −10° and anhydrous powdered sodium carbonate (21.2 g, 0.2 mol) was added, followed immediately by the dropwise addition of dimethyl sulfide (12.6 g, 0.2 mol) at −5 to −10°. The reaction mixture was then allowed to warm to room temperature with stirring overnight and filtered. The precipitate was washed with methylene chloride and the combined filtrates were evaporated to dryness at room temperature in a rotary evaporator. The residue was stirred well with water (100 ml) and cooled to 0° to precipitate unreacted **10** (8–10 g), which was filtered off and washed with cold water. The combined aqueous filtrates were extracted with a total of 300 ml of methylene chloride and the methylene chloride was again evaporated to dryness. The residue was recrystallized from diethyl ether; the yield of **5** was 13 g (35%), mp 107–108° (lit.[12,13] 108–109.5°). Compound **5** was also prepared by photolysis of **4** in dimethyl sulfide (see below).

Photolyses of 4. (a) In *cis*-Methyl-2-pentene (11a) (Table I). A solution of **4** (4 g, 0.027 mol) in the olefin (50 ml) was irradiated under a nitrogen atmosphere in a Rayonet reactor (2537 Å) for 46 hr at 5–15°. During photolysis, the reaction wall became coated with precipitate. Excess olefin was evaporated in a rotary evaporator and the total residue was fractionally distilled under vacuum. Fraction 1, bp 50° (0.05 Torr), consisted of undecomposed **4** (2.3 g, 58% of the starting material) and **9**. Exposure of this fraction to the atmosphere for several days yielded a precipitate of diphenylurea (33% yield) whose ir and nmr spectra were identical with those of an authentic specimen. Fraction 2, bp 70–90° (0.01 Torr), solidified upon cooling to room temperature. Tlc and nmr examination of the distillate without further workup showed that it contained over 98% of *cis*-*N*-benzoyl-2-isopropyl-3-methylaziridine (**24**, 26% yield) and less than 2% of trans isomer **25**. Pure **24**, mp 78–80°, was obtained by recrystallization from benzene–hexane (1:9); it was identical in every way (ir, nmr, tlc, and mp) with an authentic specimen.

Anal. Calcd for $C_{13}H_{10}NO$: C, 76.85; H, 8.37; N, 6.90. Found: C, 76.83; H, 8.52; N, 6.77.

Approximately the same ratios and yields of products were obtained when **4** (3 g, 0.02 mol) was photolyzed in **11a** (100 ml) using a medium pressure 450-W Hanovia lamp; the azide was completely decomposed in about 7 hr. However, when **4** (2 g, 0.0135 mol) was irradiated for 7 hr in **11a** (120 ml) containing benzophenone (0.5 g), only 50% of **4** decomposed. Yields of products were: **24**, 24%; **9**, 17%; and **10**, 11%.

(b) In *trans*-4-Methyl-2-pentene (11b) (Table I). Photolysis and workup were conducted essentially as described under (a). The *trans*-aziridine (**25**), however, is a liquid, bp 85–87° (0.05 Torr). It was identical in every way with an authentic specimen.

Anal. Calcd for $C_{13}H_{10}NO$: C, 76.85; H, 8.37; N, 6.90. Found: C, 76.57; H, 8.46; N, 6.93.

(c) In *cis*-2-Hexene. Photolysis and workup were conducted essentially as described under (a). *cis*-*N*-Benzoyl-2-methyl-3-*n*-propylaziridine, bp 93–95° (0.01 Torr), was isolated in 34% yield; it was identical in every respect with an authentic sample.

Anal. Calcd for $C_{13}H_{10}NO$: C, 76.85; H, 8.37; N, 6.90. Found: C, 77.06; H, 8.85; N, 6.42.

(d) In *cis*-2-Octene. *cis*-*N*-Benzoyl-2-methyl-3-*n*-pentylaziridine, bp 115° (0.02 Torr), was isolated in 46% yield; it was identical in every respect with an authentic sample.

Anal. Calcd for $C_{15}H_{21}NO$: C, 77.92; H, 9.09; N, 6.07. Found: C, 77.92; H, 9.22; N, 6.20.

Nmr signals of the ring protons of *cis*-aziridines from **11a**, *cis*-2-hexene, and *cis*-2-octene appear as one multiplet between δ 2.25–2.70; signals of the corresponding *trans*-aziridines appear as two multiplets.

(e) In Cyclohexene (12). Photolysis of **4** (5 g, 0.034 mol) in the olefin (100 ml) was conducted as in (a) but for 50 hr; about 94% of the azide had decomposed in that period. Excess olefin was evaporated in a rotary evaporator and the residue was fractionally distilled under vacuum. The following fractions were obtained: I, bp 40–45° (0.1 Torr); II, bp 105–108° (0.1 Torr); and III, bp 125–130° (0.1 Torr). I was shown by nmr and ir to consist of a mixture of undecomposed **4** (6%) and **9** (5–17%). II rapidly solidified (62% yield) and, upon recrystallization from hexane–benzene, it had mp 76–78° (lit.[14] mp 78–80°). Its ir spec-

---

[9] E. W. Barrett and C. W. Porter, *J. Amer. Chem. Soc.*, 63, 3434 (1941).

[10] E. Lieber, T. S. Chao, and C. N. R. Rao, *J. Org. Chem.*, 22, 238 (1957).

[11] J. A. Riddick and W. B. Bunger, "Organic Solvents," Wiley-Interscience, New York, N. Y., 1970.

[12] D. Swern, I. Ikeda, and G. F. Whitfield, *Tetrahedron Lett.*, 2635 (1972).

[13] J. G. Moffat and U. Lerch, *J. Org. Chem.*, 36, 3391 (1971).

[14] P. E. Fanta and E. N. Walsh, *J. Org. Chem.*, 30, 3574 (1965).

trum and glc retention time were identical with those of authentic **13**. III (**14**) also solidified and, upon crystallization from hexane, it had mp 102–104° (lit.[15] 105°). It was identical with an authentic specimen of **14**. Crude **14** was contaminated with a very small quantity of **15**, mp 101–102° (lit.[16] 101.8–102.8°), which was separated by tlc. The other products (**10**, **16**, and **17**) were identified and characterized by the nmr spectrum of the original residue after evaporation of excess cyclohexene, using authentic samples as standards.

Photolyses of 5. (a) In 11a (Table I). A solution of **5** (1.4 g, 0.0077 mol) in **11a** (50 ml) and methylene chloride (50 ml) was irradiated under nitrogen in a Rayonet reactor for 65 hr at 5–15°. The solvent and excess olefin were evaporated and the residue was treated with water (20 ml) and then extracted with ether. Reextraction of the aqueous layer with methylene chloride and evaporation of the solvent yielded undecomposed **5** (0.6 g, 43%). The wet ether layer was allowed to stand for several days and the precipitate that formed was filtered off and washed with hexane; the insoluble residue consisted of diphenylurea (32%) and benzamide (7%). The filtrates were combined and evaporated to dryness, and the residue was fractionally distilled, bp 85–90° (0.5 Torr) and mp 72–76°. The distillate was shown to consist of almost pure **24** (28%) contaminated with only a small quantity of its trans isomer **25**.

(b) In Cyclohexane (12). A solution of **5** (2.5 g, 0.014 mol) in **12** (100 ml) and methylene chloride (50 ml) was irradiated as in (a). Workup was as described under the photolysis of **4** in **12**. Yields of products were: **13**, 28%; **10**, 9%; **9**, 5%; **14**, **15**, **16**, and **17**, traces; and undecomposed **5**, 46%.

Photolyses of 7. (a) In 11a. A solution of **7** (4 g, 0.03 mol) in **11a** (40 ml) was irradiated under nitrogen in a Rayonet reactor for 24 hr at 5–15°. Excess olefin and other low boiling products, such as *tert*-butyl isocyanate, were removed in a rotary evaporator (17 Torr) at room temperature and discarded. The residue (glc) consisted almost exclusively of *cis*-*N*-pivaloyl-2-isopropyl-3-methylaziridine (**26**) contaminated with its trans isomer (**27**, <2%) and undecomposed **7**. Fractional distillation of the residue yielded pure **26**, bp 87–89° (17 Torr), in 31% yield. It was identical with an authentic sample.

Anal. Calcd for $C_{11}H_{21}NO$: C, 72.08; H, 11.55; N, 7.64. Found: C, 71.94; H, 11.37; N, 7.61.

(b) In 11b. Identical reaction of **7** in **11b** yielded an extremely complex reaction mixture. Glc analyses of the nonvolatile residue showed many peaks, two of which had the same retention times as **26** and **27** (peak enhancement employed). The ratio of **26**:**27** was 1:4. Distillation of the residue yielded only a small quantity (0.65 g) of distillate, bp 85–90° (17 Torr), which contained about 60% of the aziridines and several other unidentified components.

Glc analysis of **26** and **27** was conducted using dilauryl phthalate (20%) on Chromosorb P [typical temperatures: injection port, 200°; column, 115° (column temperatures above 150° cause product decomposition)].

Photolysis of 4 in DMS. A solution of **4** (2 g, 0.0135 mol) in dimethyl sulfide (DMS) (80–120 ml) was irradiated at 5–15° under a nitrogen atmosphere using a medium pressure Hanovia lamp (450 W) for 24 hr or a Rayonet reactor for 50 hr, in the absence or presence of benzophenone (0.5–1 g). With the Hanovia lamp **4** was completely decomposed but only 60% had decomposed using the Rayonet reactor. Evaporation of excess DMS yielded a brown oily residue whose composition was determined by nmr, ir, and glc using authentic compounds for reference. Results are summarized in Table II.

Photolyses of 8. A solution of **8** (4 g, 0.04 mol) in cyclohexene (120 ml) was irradiated for 24 hr at 5–15° under a nitrogen atmosphere using a Rayonet reactor. Considerable tarry material formed. Excess olefin and volatiles were separated by distillation to a maximum temperature of 140° and the residue was then fractionally distilled. A fraction, bp 60–90° (18 Torr), weighing only 0.8 g was obtained. Glc analysis showed only a trace of **18** (*ca.* 0.1%). Addition of a drop of the distillate to a saturated alcoholic solution of picric acid gave no precipitate; authentic **18** yields a picrate, mp 140°.[17] Addition of a drop of the distillate to an alcoholic solution of 2,4-dinitrophenylhydrazine gave a small quantity of the crystalline 2,4-DNPH of butyraldehyde, mp 117°, identical with an authentic specimen. The precursor of butyraldehyde is assumed to be butylimine.

Similar photolysis of **8** in DMS gave none of the anticipated iminosulfurane.

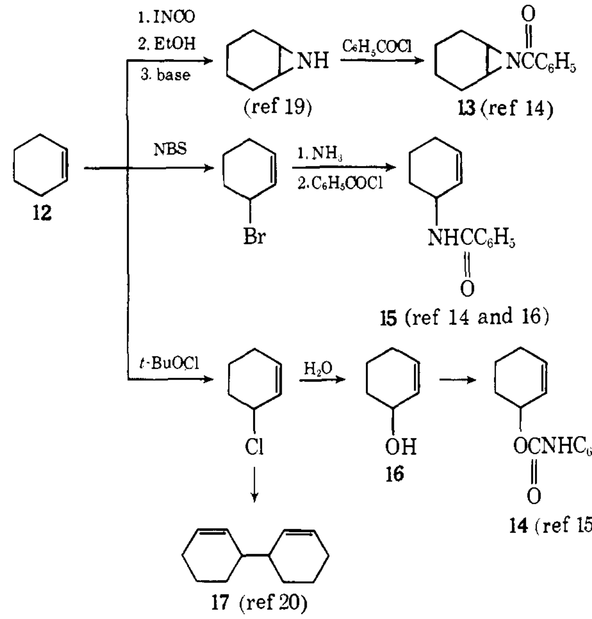
Photolyses in Cyclohexane (19). A solution of **4** (2 g, 0.014 mol) in **19** was irradiated under a nitrogen atmosphere in a Rayonet reactor for 43 hr at 5–15°. As the reaction proceeded, **20**, as well as tarry material, precipitated on the vessel wall. Evaporation of excess **19** was followed by washing of the reaction vessel with cold ether (20 ml). The insoluble material was crystallized from ethanol; it (0.24 g, 19%) was shown by ir, tlc, and mp to be identical with authentic *N*-cyclohexylbenzamide (**20**).[18] The ether was evaporated from the original extraction and the residue was fractionally distilled under reduced pressure (*ca.* 0.1 Torr) in the normal way to yield undecomposed **4** (49%), **9** (37%), and **10** (4%) (Table III).

Similar treatment of **5** (3 g, 0.017 mol) in a mixture of **19** (60 ml) and methylene chloride (60 ml) for 68 hr resulted in only 60% photodecomposition of **5**. No CH insertion product (**20**) could be detected by tlc or glc. Yields of **9**, **10**, and **21**, mp 204–205°, were 23, 32, and 3%, respectively (Table III). Compound **21** was identified by elemental analysis, by comparison of its ir spectrum with that of an authentic sample, and by mixture melting point (undepressed).

Anal. Calcd for $C_{14}H_{12}N_2O_2$ (**21**): C, 70.00; H, 5.00; N, 11.67. Found: C, 69.95; H, 4.64; N, 11.38.

Preparation of Reference Compounds. Compounds **13–17** were prepared by standard or slightly modified literature procedures, summarized in Scheme II.

Scheme II



Compound **18** was prepared by the method of Paris and Fanta.[17] Compound **20** was prepared from cyclohexylamine and benzoyl chloride in a standard Schotten–Baumann reaction.[18] Compound **21**, mp 204–205°, was prepared in 55% yield by reaction of **10** with an equimolar quantity of *t*-BuOCl in CH_2Cl_2 at room temperature, followed by addition of an equimolar quantity of **9**, filtration of the precipitated **21**, and recrystallization from ethanol. Compound **21** was also prepared in 14% yield by irradiation of an equimolar mixture of **9** and **10** in CH_2Cl_2 for 48 hr but **9** and **10** do not react in the dark (2 months) or on irradiation in benzene solution. Compound **24** was prepared from *cis*-*N*-carbethoxy-2-isopropyl-3-methylaziridine[21] (8.5 g, 0.05 mol) by refluxing it for several hours with aqueous ethanolic potassium hydroxide solution (20 g of 50% aqueous potassium hydroxide in 60 ml of ethanol) and then pouring

---

[15] R. Criegee, *Justus Liebigs Ann. Chem.*, **481**, 263 (1930).

[16] L. Goodman, S. Winstein, and R. Boschan, *J. Amer. Chem. Soc.*, **80**, 4312 (1958).

[17] O. E. Paris and P. E. Fanta, *J. Amer. Chem. Soc.*, **74**, 3007 (1952).

[18] R. L. Shriner, R. C. Fuson, and D. Y. Curtin, "The Systematic Identification of Organic Compounds," Wiley, New York, N. Y., 1967, pp 114 and 326.

[19] G. Swift and D. Swern, *J. Org. Chem.*, **32**, 511 (1967).

[20] W. Lwowski and T. W. Mattingly, *J. Amer. Chem. Soc.*, **87**, 1947 (1965).

[21] J. S. McConaghy and W. Lwowski, *J. Amer. Chem. Soc.*, **89**, 2357, 4450 (1967).

the darkly colored solution into water (150 ml). The aqueous system was extracted with ether (2 × 100 ml) and the ether solution was washed with saturated aqueous sodium chloride solution and then dried over anhydrous magnesium sulfate. Triethylamine (10 g) was added to the ether filtrate, followed by benzoyl chloride (10 g, 0.07 mol). The reaction mixture was stirred for 3 hr at room temperature, washed with water, and distilled. After removal of ether at atmospheric pressure, the residue was distilled under vacuum yielding ethyl benzoate, bp 45° (0.05 Torr), followed by **24**, bp 80° (0.03 Torr). The distillate quickly solidified, mp 79–80° (4.5 g, 44% yield). Compound **25**, bp 85–87° (0.05 Torr), was similarly prepared in 65% yield from *trans-N*-carbethoxy-2-isopropyl-3-methylaziridine. Compounds **26** (30% yield) and **27** [bp 83–85° (17 Torr)] were prepared similarly, substituting pivaloyl chloride for benzoyl chloride in the acylation step.

Acknowledgment. The authors thank the National Institutes of Health for partial support of this investigation under Grants CA-12227 and 07803 of the National Cancer Institute, and the Samuel S. Fels Fund.

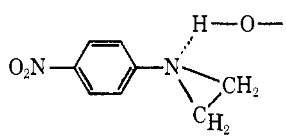
Hydrogen Bonding by Protic Solvents to Nitro Oxygens. Effects on Electronic Spectra of Nitroaniline Derivatives

Mortimer J. Kamlet,*[1a] Eleonore G. Kayser,[1a] John W. Eastes,[1b] and William H. Gilligan[1a]

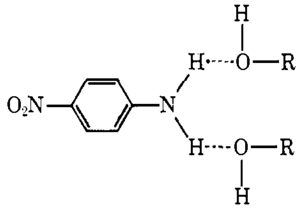
Contribution from the Advanced Chemistry Division,
U. S. Naval Ordnance Laboratory, White Oak, Silver Spring, Maryland 20910,
and the Engineer Topographic Laboratory, Fort Belvoir, Virginia 22060.
Received January 5, 1973

Abstract: Positions of uv maxima for *N,N*-diethyl-4-nitroaniline (**4**) in nonprotic solvents show good linear correlation with corresponding ν_{max} values for 4-nitroanisole (**5**). In proton-donor solvents, however, $\nu(\mathbf{4})_{max}$ values are shifted to the red relative to positions predicted from this linear relationship. These longer wavelength displacements $[-\Delta\Delta\nu(\mathbf{4}\text{–}\mathbf{5})^{A}{}_{\rightarrow NO_2}]$ are considered to be measures of the bathochromic influence of enhanced type-A hydrogen bonding *by* the protic solvents *to* the nitro oxygens of **4** compared with **5**. Magnitudes of the solvatochromic effects are related to solvent structures and acidities.

Earlier papers in this series dealt with spectral effects of two types of specific solvation phenomena involving hydroxylic solvents and nitroaromatic amine substrates: type-A hydrogen bonding,



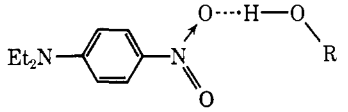
type-A hydrogen bonding *by* R-OH solvent *to* *N*-(4-nitrophenyl)aziridine (**1a**)



type-B hydrogen bonding *by* 4-nitroaniline (**2**) *to* R-OH solvent

wherein the solvent acts as proton donor and the amine nitrogen of the solute as acceptor (bonding *by* solvent *to* substrate); and type-B, wherein hydrogen bonding is *by* the amine protons of the solute *to* the solvent oxygen.[2–6] The effect of type-A solvation is to decrease ground state electron density on the amine nitrogen; hence it serves as a hypsochromic influence on the $[^{+}R_2N{=}C(1) \rightarrow C(4){=}NO_2^{-}]$ band in the uv spectrum.[7] Type-B hydrogen bonding has the converse effect; an increase in ground state charge density on the amine nitrogen results in a bathochromic displacement of the uv spectrum.[8,9]

In the present paper we will deal with the spectral consequences of still a third type of hydrogen-bonded complex formation which may occur in such systems. This again involves the solvent as proton donor, and thus represents another form of type-A bonding. Here, however, the oxygens of the nitro group are the proton acceptors. By decreasing ground state electron densities on the nitro oxygens (hence facilitating electronic transitions which feed charge into these sites), type-A hydrogen bonds to nitro would be expected to shift $[^{+}R_2N{=}C(1) \rightarrow C(4){=}NO_2^{-}]$ bands bathochromically.



type-A hydrogen bonding *by*R-OH solvent *to* nitro group oxygen of *N,N*-diethyl-4-nitroaniline (**4**)

Hammond and Modic[10] have postulated that such solvent-to-nitro bonding accounts for longer wavelength displacements in the spectrum of nitrobenzene on going from water to progressively stronger sulfuric

---

[1] (a) Naval Ordnance Laboratory; (b) Engineer Topographic Laboratory.

[2] R. R. Minesinger, E. G. Kayser, and M. J. Kamlet, *J. Org. Chem.*, **36**, 1342 (1971).

[3] M. J. Kamlet, R. R. Minesinger, E. G. Kayser, M. H. Aldridge, and J. W. Eastes, *ibid.*, **36**, 3852 (1971).

[4] M. J. Kamlet, R. R. Minesinger, and W. H. Gilligan, *J. Amer. Chem. Soc.*, **94**, 4744 (1972).

[5] J. W. Eastes, M. H. Aldridge, and M. J. Kamlet, *J. Chem. Soc. B*, 922 (1969).

[6] M. J. Kamlet, *Isr. J. Chem.*, **1**, 428 (1963).

[7] J. C. Deardon and W. F. Forbes, *Can. J. Chem.*, **38**, 896 (1960).

[8] J. H. P. Utley, *J. Chem. Soc.*, 3252 (1963).

[9] B. D. Pearson, *Proc. Chem. Soc., London*, 78 (1962).

[10] G. S. Hammond and F. J. Modic, *J. Amer. Chem. Soc.*, **75**, 1385 (1953).