denser with drying tube. The reaction mixture was stirred magnetically. All additions were done at ice-bath temperatures and all reactions were carried out under a nitrogen atmosphere.

To the ester **2** (6.2 g, 11.6 mol) suspended in 300 ml of dry THF was added 1 *M* BH_3–THF (20 ml, 20 mmol) in 20 ml of dry THF as rapidly as possible. The reaction mixture was refluxed for 1.5 hr and cooled in an ice bath and 50 ml of acetic acid saturated with HBr(g) was added dropwise. The reaction was stirred at room temperature for 1 hr and filtered to give 5.0 g of the reduced ester **3** HBr, mp 196–197° dec. Reduction in volume of the filtrate and dilution with ether gave an additional 1.6 g of **3** HBr: mp 193–194° dec; 96% total crude yield; ir (Nujol) 3250, 1800 cm^{-1}; NMR (Me_2SO-d_6) 2.43 (s, 3, CHAr), 3.22, 4.00, 4.74 (a series of three singlets which change such that the singlet at 4.74 decreases, the singlet at 4.00 increases, and the singlet at 3.22 becomes a multiplet, as the ester reacts with Me_2SO-d_6, 6, CH_2N), 7.46 and 7.84 (d, 2, J = 9 Hz, Ar), 8.00 (s, 1, $NHSO_2$), 9.4 ppm (s, 2, NH_2^+).

An analytical sample was prepared by recrystallization from a mixture of dimethylformamide–THF–ether to give the pure ester **3** HBr, mp 196.5–197° dec. Anal. Calcd for $C_{17}H_{15}Cl_5N_2O_4S$·HBr (601.60): C, 33.94; H, 2.68; Br, 13.28; Cl, 29.47; S, 5.33. Found: C, 33.84; H, 2.58; Br, 13.43; Cl, 29.57; S, 5.43.

Triethylamine (1.25 ml, 9 mmol) in 75 ml of dry chloroform was added to a stirred suspension of **3** HBr (5.4 g, 9 mmol) in 75 ml of dry chloroform. The reaction mixture was stirred until solution occurred and then concentrated to dryness in vacuo. The residue was warmed gently with 200 ml of benzene and the triethylamine hydrobromide was removed by filtration. The benzene filtrate was concentrated in vacuo to 50 ml to give 4.0 g of the free base **3** (85%, mp 123–125°): ir (Nujol) 3300, 3140, 1785 cm^{-1}.

The free base was unstable and formed the diketopiperazine **7** on attempted purification. A sample of **7** was recrystallized from ethanol–dimethylformamide to give a solid: mp 251–252°; ir (Nujol) 3260, 1635 cm^{-1}. Anal. Calcd for $C_{22}H_{28}N_4O_6S_2$ (**7**) (508.63): C, 51.95; H, 5.55; N, 11.02; S, 12.61. Found: C, 51.96; H, 5.45; N, 11.05; S, 12.77.

***N*-Acetyl-*N*-(2-tosylaminoethyl)glycine Pentachlorophenyl Ester (4).** The base **3** (3.9 g, 7.5 mmol) was stirred in redistilled acetic anhydride (25 ml) until solution occurred. The reaction mixture was then stirred for an additional 2 hr at room temperature. A solid precipitated. The solid was filtered and washed with a small portion of acetic anhydride and then with ether to give 3.0 g of **4** (73%, mp 147–148°): ir (Nujol) 3140, 1786, 1645 cm^{-1}.

***N*-Ethyl-*N*-(2-tosylaminoethyl)glycine Hydrochloride (6a).** The amido ester **4** (1.1 g, 3 mmol) in 40 ml of dry THF was added dropwise to 1 *M* BH_3–THF (3.4 ml, 3.4 mmol) in 15 ml of cold, dry THF. The reaction mixture was stirred at room temperature for 2 hr and then cooled in an ice bath. Hydrochloric acid (0.5 ml, 6 *N*) was added dropwise and the reaction mixture stirred for 1 hr. The solid was filtered and washed with THF to give 0.2 g of the amino acid salt **6a**, mp 154–160° dec. Reduction in volume of the filtrate and dilution with ether gave 0.15–0.20 g more of **6**: ir (Nujol) 3300 (broad), 3060, 1730 cm^{-1}.

The filtrate was concentrated in vacuo. The residue was dissolved in a small volume of THF and diluted with ether to remove the pentachlorophenol. The material that was insoluble in ether was treated with a small portion of THF to give 0.15 g of the amino ester **5**: mp 134–136° dec; ir (Nujol) 3210, 1795 cm^{-1}. Reduction of the filtrate and treatment of the residue with THF–ether gave about 0.1 g of crude **5**.

The amino ester **5** (0.45 g, 0.77 mmol) was saponified with sodium hydroxide (1.54 ml, 1.54 mmol) to give both the amino acid salt **6a**, 0.2 g, ir (Nujol) 1730 cm^{-1}, contains sodium chloride (theory for NaCl 80 mg), and the free amino acid **6**, mp 185–187°, ir (Nujol) 3010, 1650 cm^{-1}, which is a 98% recovery of the material based on recovery of the amino acid salt **6a**.

An analytical sample of **6a** was prepared by recrystallization from 2-propanol: mp 155–161°; ir (Nujol) 3300 (broad), 3050, 1730 cm^{-1}; NMR (Me_2SO-d_6) 1.23 (t, 3, J = 8 Hz, CH_3CH_2), 2.42 (s, 3, CH_3Ar), 3.25 (m, 6, CH_2N), 3.8 (broad t) and 4.1 (s, 2, NCH_2CO), 7.42 and 7.78 (d, 2, J = 9 Hz, Ar), 8.22 ppm (s, 1, SNH). Anal. Calcd for $C_{13}H_{21}N_2O_4ClS$ (336.83): C, 46.36; H, 6.28; Cl, 10.53; N, 8.32; S, 9.52. Found: C, 46.19; H, 6.34; Cl, 10.39; N, 8.28; S, 9.53.

Acknowledgment. The authors wish to thank Dr. Ralph C. Northrup of Microbiological Associates, Inc., for his encouragement and helpful discussions.

Registry No.—**1**, 556-50-3; **2**, 57066-12-3; **3**, 57066-13-4; **3** HBr, 57066-14-5; **4**, 57066-15-6; **5**, 57066-16-7; **6**, 57066-17-8; **6a**, 57066-18-9; **7**, 57066-19-0; acetic anhydride, 108-24-7; tosyl chloride, 98-59-9; *N*-tosylglycylglycine, 4703-34-8; pentachlorophenol, 87-86-5.

References and Notes

(1) (a) C. Buehler and D. Pearson, "Survey of Organic Syntheses", Wiley-Interscience, New York, N.Y., 1970, pp 413–507; (b) I. Harrison and S. Harrison, "Compendium of Organic Synthetic Methods", Wiley-Interscience, New York, N.Y., 1971, pp 230–266; (c) J. March, "Advanced Organic Chemistry; reactions, Mechanisms and Structure", McGraw-Hill, New York, N.Y., 1969; (d) J. D. Roberts and M. C. Caserio, "Basic Principles of Organic Chemistry", W. A. Benjamin, New York, N.Y., 1964, pp 652–663.
(2) Reference 1a, p 421.
(3) (a) N. M. Yoon, C. S. Pak, H. C. Brown, S. Krishnamurthy, and T. P. Stocky, *J. Org. Chem.*, **38**, 2786–2792 (1973); (b) H. C. Brown and P. Heim, *J. Org. Chem.*, **38**, 912–916 (1973); (c) H. C. Brown, P. Heim, and N. M. Yoon, *J. Am. Chem. Soc.*, **92**, 1637–1646 (1960); (d) H. C. Brown and P. Heim, *Ibid.*, **86**, 3566–3567 (1964); (e) H. C. Brown and B. C. Subba Rao, *Ibid.*, **82**, 681–686 (1960).
(4) C. F. Lane, *Aldrichimica Acta*, **6**, 21–34 (1973).
(5) J. P. Greenstein and M. Wintlz, "Chemistry of the Amino Acids", Vol. 2, Wiley, New York, N.Y., 1961, p 886.
(6) M. J. Kornet, P. A. Thio, and S. I. Tan, *J. Org. Chem.*, **33**, 3637–3639 (1968).
(7) O. Yonemitsu, T. Hamad, and Y. Kanaoka, *Tetrahedron Lett.*, 3575–3578 (1968).
(8) Reference 5, pp 1016–1023.
(9) Reference 5, p 1027.

Photoreduction of Substituted Benzo[*b*]furans by Aliphatic Amines

Cyril Párkányi*

Department of Chemistry, The University of Texas at El Paso, El Paso, Texas 79968

Alain Lablache-Combier,* I. Marko, and Harry Ofenberg[1]

Laboratoire de Chimie Organique Physique, Université des Sciences et Techniques de Lille, B. P. 36, F-59650 Villeneuve d'Ascq, France

Received June 27, 1975

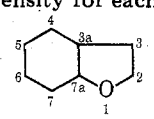
In one of our previous papers we have reported that uv irradiation (254 nm) of benzo[*b*]thiophene in aliphatic amines leads to the corresponding adducts and we have postulated the intermediate formation of an exciplex.[2] In contrast to benzo[*b*]thiophene, no detectable reaction was observed when benzo[*b*]furan was irradiated with uv light in an aliphatic amine.[2] Assuming that the photoexcited heterocycle reacts with the amine via intermediate formation of an exciplex[3,4] in which the heteroaromatic derivative possesses the character of a radical anion, we were able to explain the difference in the photochemical behavior of these two heterocycles as due to the fact that the maximum spin density in the benzo[*b*]furan radical anion is found in the 4 position whereas in the benzo[*b*]thiophene radical anion it is the 2 position where the spin density is the highest.[2] This means that, if a photoreaction between benzo[*b*]furan and an aliphatic amine, HNR_2, were possible, it would lead to the formation of product **1** which would be unstable under the conditions used in our study.[2]

To verify this assumption, we have synthesized some benzo[*b*]furan derivatives in which the spin density of their radical anion is the highest in the 4 position, and we have also prepared some other derivatives whose radical anions have the highest spin density in the 2 position. According to our hypothesis, the former group of compounds should not give any isolable products when irradiated in an aliphatic amine, whereas uv irradiation of the compounds belonging to the latter group is expected to lead to the formation of stable photoproducts.

Table I
Calculated HMO Spin Densities of Radical Anions Derived from Substituted Benzo[b]furans[a]

Position[b]	2,3-Dimethyl	2-Phenyl	3-Phenyl	2,4,7-Trimethyl-3-phenyl	2,3-Diphenyl
1	0.0040	0.0302	0.0236	0.0083	0.0351
2	0.1074	0.1019	0.2257	0.1408	0.1334
3	0.0097	0.0941	0.0295	0.0074	0.0653
3a	0.0735	0.0103	0.0013	0.0297	0.0000
4	0.3018	0.1333	0.1370	0.0122	0.0740
5	0.0605	0.0249	0.0715	0.0554	0.0299
6	0.1009	0.0641	0.0229	0.0123	0.0260
7	0.2972	0.1138	0.1531	0.0172	0.0763
7a	0.0382	0.0002	0.0286	0.0346	0.0002

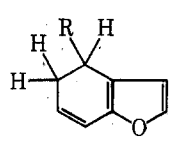
[a] The spin density ρ_r at atom r was approximated by the square of the coefficient of the corresponding atomic orbital in the respective molecular orbital, $\rho_r = c^2_{m+1,r}$, where $c_{m+1,r}$ is the expansion coefficient of the rth atomic orbital in the $(m+1)$st molecular orbital, i.e., the lowest unoccupied π molecular orbital of the parent heterocyclic system. The HMO calculations were made in the usual way using an IBM 360/50 computer. The heteroatom model of the methyl group was used in the calculations and the methyl group was assumed to contribute a pair of electrons to the π system. The following parameters were adopted:[2,5] $\alpha_O = \alpha + 2\beta$; $\alpha_{Me} = \alpha + 2\beta$; $\alpha_{C(Me)} = \alpha - 0.2\beta$; $\beta_{CO} = \sqrt{2}\beta$; $\beta_{CMe} = 0.7\beta$. The highest spin density for each radical anion is underlined. [b] Numbering:



The calculated HMO spin densities of the radical anions of the compounds under study are summarized in Table I.

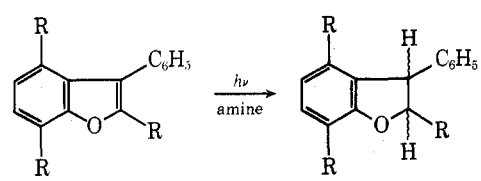
As expected, 2,3-dimethylbenzo[b]furan, which has the highest value of spin density in its radical anion in the 4 position, does not give any identifiable photoproducts when irradiated in n-propylamine or triethylamine, regardless of the presence or absence of methanol (methanol is known to facilitate the photoreaction of benzene with triethylamine[6]). 2-Phenylbenzo[b]furan, which belongs to the same group as 2,3-dimethylbenzo[b]furan, photodimerizes in n-propylamine similarly as in other solvents.[7,8]

On the other hand, 3-phenylbenzo[b]furan (**2a**) and 2,4,7-trimethyl-3-phenylbenzo[b]furan (**2b**), i.e., compounds in which the spin density in their respective radical anions in the highest in the 2 position, are photoreduced to the corresponding 2,3-dihydro derivatives **3a** and **3b**, respectively, when irradiated in an aliphatic amine. Similarly



1

R = H or NR_2



2 **3**

a, R = H

b, R = Me

as in other solvents, 2,3-diphenylbenzo[b]furan, which belongs to this group as well, undergoes photocyclization when irradiated under these conditions.[9]

The chemical yield of photoreduction of **2a** by aliphatic amines increases when going from a primary amine to a tertiary amine. The yields of 2,3-dihydro-3-phenylbenzo[b]furan (**3a**) in n-propylamine, diethylamine, and triethylamine (with 10% of methanol added) are 10, 20, and 30%, respectively, and thus increase with decreasing ionization potential of the amine (the first ionization potentials of the above amines are 8.78, 8.01, and 7.50 eV, respectively[10]). This finding is consistent with the hypothesis about the intermediate formation of an exciplex during the photoreaction of benzo[b]furan derivatives with an aliphatic amine, at least in the case of those derivatives which undergo photoreduction.

Experimental Section

Materials. 2-Phenylbenzo[b]furan and 3-phenylbenzo[b]furan (**2a**) were synthesized as described in the literature.[11] Previously described procedures were used to prepare 2,4,7-trimethyl-3-phenylbenzo[b]furan[12-14] (**2b**) and 2,3-dimethylbenzo[b]furan.[15]

Instruments and Methods. NMR spectra were obtained with a Jeol C-60HL spectrometer. Mass spectra were determined on an AEI Model MS 12 spectrometer (Laboratoire de Chimie Appliquée de l'Université de Bordeaux I, Bordeaux, France) operating at 70 eV ionizing potential. Preparative gas chromatography was performed on an Autoprep A 700 gas chromatograph using a column of 10% Apiezon L on Chromosorb W (8 ft × 0.375 in.). Gas chromatographic analyses were made on an F & M Model 810 gas chromatograph using a 30% SE column (6 ft × 0.25 in.).

Irradiations were conducted in a quartz vessel using light from a Hanau NN 1544 15-W low-pressure mercury arc lamp. All samples were irradiated for 24 hr and a nitrogen atmosphere was maintained during irradiation. The concentration of the solutions was 1 g of the heterocyclic substrate in 100 ml of n-propylamine, diethylamine, or triethylamine (or a mixture of 90 ml of triethylamine and 10 ml of methanol in the case of the irradiation of **2a** in triethylamine). After evaporation of the solvent, the crude reaction product was filtered through a silica gel column with petroleum ether as eluent and then isolated by preparative gas chromatography. The yields were determined by analytical VPC.

All melting points are uncorrected. Elemental microanalyses were carried out by the Centre de Microanalyse du CNRS, Thiais, France.

Irradiation of 2-Phenylbenzo[b]furan. The dimer of 2-phenylbenzo[b]furan formed during irradiation deposited on the walls of the photochemical vessel (0.51 g, 51%). After recrystallization from benzene, it had mp 283–284°; NMR (dimethyl sulfoxide) δ 4.95 (2 H, s), 6.75 (8 H, m), 7.20 ppm (10 H, m).

Anal. Calcd for $C_{28}H_{20}O_2$: C, 86.57; H, 5.19; O, 8.24. Found: C, 86.19; H, 5.26; O, 8.52.

Irradiation of 3-Phenylbenzo[b]furan. Irradiation of this compound gave 2,3-dihydro-3-phenylbenzo[b]furan (**3a**): mp 35–37° (ethanol); NMR (CCl_4) δ 4.5 (3 H, m), 6.8 (4 H, m), 7.15 ppm (5 H, m); mass spectrum m/e (rel intensity) 196 (M^+, 100), 181 (14), 167 (25), 165 (28), 91 (16). Yields, reduced photoproduct (RP), unreacted starting material (SM): in triethylamine, 30% RP, 70% SM; in diethylamine, 20% RP, 80% SM; in n-propylamine, 10% RP, 90% SM.

Anal. Calcd for $C_{14}H_{12}O$: C, 85.68; H, 6.16; O, 8.15. Found: C, 85.61; H, 6.18; O, 8.12.

Irradiation of 2,4,7-Trimethyl-3-phenylbenzo[b]furan (2b). In this case, an inseparable mixture of *cis*- and *trans*-2,3-dihydro-2,4,7-trimethyl-3-phenylbenzo[b]furan (**3b**) was obtained, in an overall yield of 20% (the unreacted starting material represented 80%) when the reaction was carried out in triethylamine. The two isomers were present in 1:2 ratio, the trans isomer seeming to be the preponderant isomer. NMR of the mixture (CCl_4): δ 1.06 (3 H, d), 1.47 (3 H, d), 1.87 (3 H, s), 2.19 (3 H, s), 4.00 (1 H, d), 4.25 (1 H, d), unresolved between 4.4 and 5.1 (1 H, m), unresolved between 6.3 and 7.25 ppm (7 H, m). Mass spectrum m/e (rel intensity): 238 (M^+, 100), 223 (69), 209 (23), 195 (19). M^+ calcd for $C_{17}H_{18}O$: 238. Found: 238.

Irradiation of 2,3-Dimethylbenzo[b]furan. Under the conditions described above, irradiation of this compound gave no photoreduction. No product could be identified by gas chromatography.

Irradiation of 2,3-Diphenylbenzo[b]furan. The photocyclization of this compound has been described in one of our previous publications.[9]

Acknowledgments. Financial support of this research by the Délégation Générale à la Recherche Scientifique et Technique (Grant 74-7-0977) and by the Robert A. Welch Foundation (Grant AH-461) is gratefully acknowledged. We thank Dr. G. Bourgeois for the measurement of the mass spectra.

Registry No.—**2a**, 29909-72-6; **2a** radical ion (RI), (1−), 57049-55-5; **2b**, 57049-56-6; **2b** RI, (1−), 57049-57-7; **3a**, 57049-58-8; *cis*-**3b**, 57049-59-9; *trans*-**3b**, 57049-60-2; 2-phenylbenzo[*b*]furan, 1839-72-1; 2-phenylbenzo[*b*]furan RI, (1−), 57049-61-3; 2-phenylbenzo[*b*]furan dimer, 57049-62-4; 2,3-dimethylbenzo[*b*]furan, 3782-00-1; 2,3-dimethylbenzo[*b*]furan RI, (1−), 57049-63-5; 2,3-diphenylbenzo[*b*]furan, 13054-95-0; 2,3-diphenylbenzo[*b*]furan RI, (1−), 57049-64-6; *n*-propylamine, 107-10-8; diethylamine, 109-89-7; triethylamine, 598-56-1.

References and Notes

(1) On leave of absence from the University of Iaşi, Iaşi, Rumania.
(2) P. Grandclaudon, A. Lablache-Combier, and C. Párkányi, *Tetrahedron*, **29**, 651 (1973).
(3) A. Lablache-Combier, *Bull. Soc. Chim. Fr.*, 4791 (1972).
(4) S. G. Cohen, A. Parola, and G. H. Parsons, Jr., *Chem. Rev.*, **73**, 141 (1973).
(5) A. Couture, A. Delevallee, A. Lablache-Combier, and C. Párkányi, *Tetrahedron*, **31**, 785 (1975).
(6) D. Bryce-Smith, M. T. Clarke, A. Gilbert, G. Klunklin, and G. Manning, *Chem. Commun.*, 916 (1971).
(7) C. H. Krauch, W. Metzner, and G. O. Schenck, *Chem. Ber.*, **99**, 1723 (1966).
(8) S. Farid, S. E. Hartman, and C. D. DeBoer, *J. Am. Chem. Soc.*, **97**, 1723 (1975).
(9) A. Couture, A. Lablache-Combier, and H. Ofenberg, *Tetrahedron Lett.*, 2497 (1974); *Tetrahedron*, **31**, 2023 (1975).
(10) K. Watanabe, *J. Chem. Phys.*, **26**, 542 (1957).
(11) W. Davies and S. Middleton, *J. Chem. Soc.*, 822 (1958).
(12) B. I. Arventiev, *Ann. Sci. Univ. Iaşi*, **24**, 72 (1938); *Chem. Abstr.*, **33**, 1693 (1939).
(13) B. I. Arventiev and H. Ofenberg, *Ann. Sci. Univ. Iaşi*, **15**, 28 (1969).
(14) B. I. Arventiev, H. Wexler, and M. Strul, *Acad. Repub. Pop. Rom., Fil. Iaşi, Stud. Cercet. Stiint., Chim.*, **12**, 87 (1961); *Chem. Abstr.*, **57**, 9772 (1962).
(15) E. Bisagni and R. Royer, *Bull. Soc. Chim. Fr.*, 925 (1962).

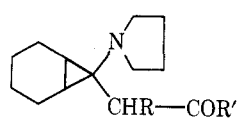
Cyclobutanones from Cyclopropanone Precursors. Addition of Nitroalkanes to Cyclopropanone Aminals

Harry H. Wasserman,* Michael J. Hearn, Bernard Haveaux, and Marco Thyes

Department of Chemistry, Yale University, New Haven, Connecticut 06520

Received July 29, 1975

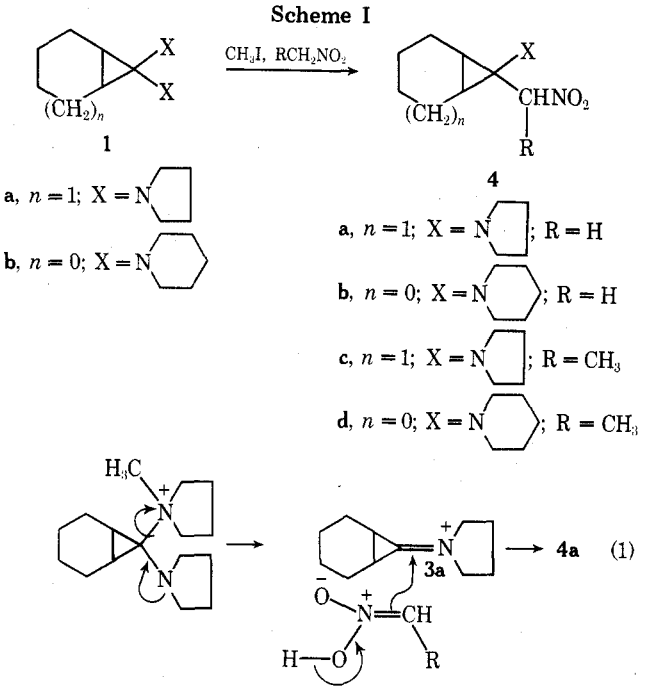
We have previously reported[1] that 1,1-dipyrrolidinocyclopropanes of type **1**[3] undergo ready reaction with ketones under mildly acidic conditions to form addition products such as **2**. We have now found that these aminals undergo



2

ready alkylation by nitroalkanes under conditions in which the cyclopropyl iminium salts are probable intermediates. The addition takes place on treatment of **1a** or **1b** with excess nitromethane or nitroethane under a nitrogen atmosphere in the presence of methyl iodide at room temperature and leads to derivatives corresponding to **4** (Scheme I). Presumably, the alkylation of **1** with methyl iodide yields a

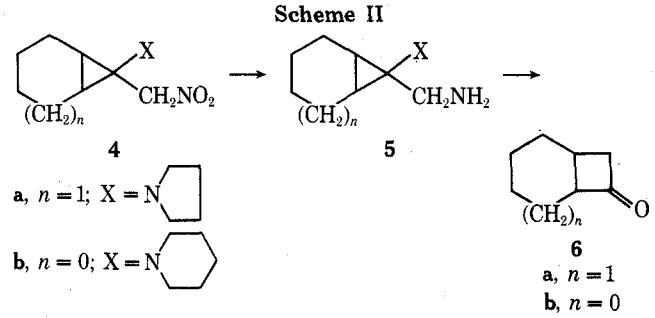
Scheme I



quaternary derivative which then dissociates to an iminium salt such as **3a**. Reaction of the iminium salt with the nitroalkane (through the aci form) leads to **4**.

Reduction of the nitroalkanes with lithium aluminum hydride yields the primary amines **5**, which may serve as substrates for the Tiffeneau–Demjanov ring enlargement (acetic acid and isoamyl nitrite in benzene followed by aqueous work-up)[2] forming fused ring cyclobutanones **6** (Scheme II).

Scheme II



In the work outlined below, this procedure has been adapted for the preparation of bicyclo[4.2.0]octan-7-one (**6a**)[4] and bicyclo[3.2.0]heptan-6-one (**6b**). The structures of these cyclobutanone derivatives were established by spectroscopic methods and by comparison with authentic materials.

Experimental Section

Microanalyses were performed by Dr. R. Rittner of the Olin Mathieson Chemical Co., New Haven, Conn. Infrared spectra were determined on a Perkin-Elmer Model 421 grating spectrophotometer as neat liquids unless otherwise noted. NMR spectra were recorded on Varian Model A-60, A-60A (60 MHz), or Jeolco Minimar 100 (100 MHz) spectrometers, as indicated. Chemical shifts are reported in δ units using tetramethylsilane as the internal standard. Mass spectra were recorded on an AEI Model MS-9 instrument, courtesy of Dr. W. McMurray. Boiling points are uncorrected. VPC analyses and sample preparations were performed with an Aerograph Model A90-P3 instrument. A 12 ft × 0.375 in. 9% SE-30 column packed on 60–80 mesh Anakrom A support was used, column temperature 95–100°C, helium flow rate 60 ml/min. Retention times were as noted below. Sample purity checks were made on a Waters Associates Model ALC-100 analytical liquid chroma-