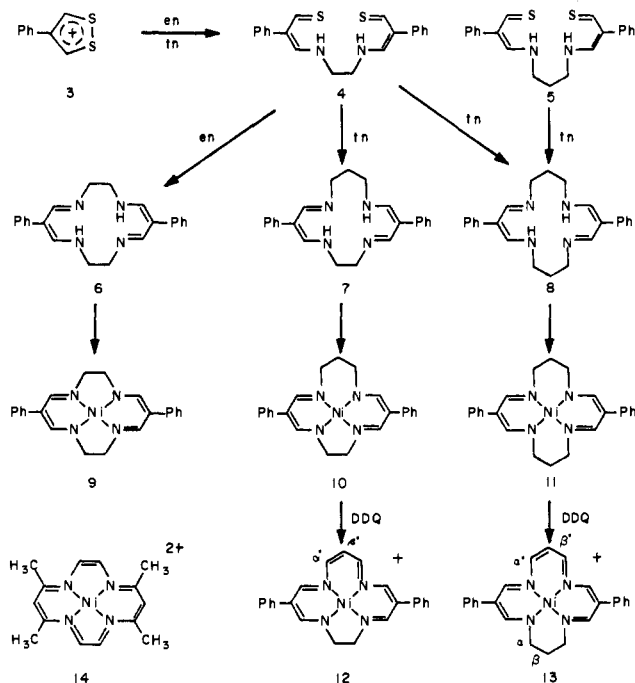


(tn; benzene, 25°) afforded the aminothiones¹⁰ **4** and **5** (60–80%), which proved susceptible to ring closure by further condensation. Reaction of **4** with en (2 equiv), tn (2 equiv), and tn (6 equiv) in benzene (70°, 1 hr) yielded after separation from by-products the macrocycles **6** (40%, mp 286–289°), **7**¹¹ (~30%, mp 220–222°), and **8** (30%, mp 147–148°), respectively, as white solids from chloroform–ethanol. Macrocycle **8** is better obtained from **5** and tn (2.5 equiv, benzene, 70°); yields of 90% have been achieved by this route.¹² Molecular weights of **6–8** were confirmed by high-resolution mass spectra (e.g., calcd for ¹²C₂₄¹H₂₈¹⁴N₄ (**8**), 372.2314; found, 372.2304).



Reaction of **6**, **7**, and **8** (plus 1 equiv of tn) with nickel(II) acetate in hot DMF gave the complexes **9** (84%, red, mp 320–322°), **10** (~80%, green, mp 276–277°), and **11** (50%, green, mp 269–270°), respectively. The three complexes are diamagnetic and their pmr spectra are consistent with the indicated structures. Complexes **10** and **11** were subjected to dehydrogenation reactions. Treatment of **11** with 4 equiv of 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ) in trichloroethylene (85°, 8 hr) followed by metathesis (NaPF₆–ethanol) and recrystallization (ethanol–acetone) yielded the partially dehydrogenated 14- π cation **13** as its PF₆⁻ salt (58%, green, mp 279–280°): pmr (CD₃CN) δ 8.00 (d, 2, α' -H), 7.85, 7.58 (both s, 2, ring H), 7.42 (10, Ph), 6.14 (t, 1, β' -H), 4.01 (t, 4, α -CH₂), 2.11 (CD₃NO₂, m, 2, β -CH₂). An analogous reaction of **10** afforded the PF₆⁻ salt of **12** (~30%, orange-brown, mp 257–258°): pmr (CD₃CN) δ 8.32, 7.83 (both s, 2, ring H), 8.22 (d, 2, α' -H), 7.41 (10, Ph), 6.32 (t, 1, β' -H), 4.01 (s, 4, CH₂). Increased ligand conjugation is evidenced by absorption bands at 489 (**12**, 17,400) and 516 nm

(10) All new compounds gave satisfactory elemental analyses and were further identified by pmr and, where necessary, by mass spectrometry.

(11) The crude product is contaminated with ~10% of **6** and **8** (identified by mass spectrum and pmr), which were removed by fractional recrystallization (benzene).

(12) Alternatively, the Ni(II) complex of **5** with excess neat tn (35°, 1 hr) afforded metal-free **8** (69%) in an apparent template reaction.

(**13**, ϵ 17,200), whereas the 12- π precursors **9–11** show only weak d–d bands above 450 nm.

The nickel(II) cation **12** is the initial example of a complex whose cyclic ligand framework is comprised exclusively of the 14- π corrin inner ring structure.¹³ This structure is evidently mildly perturbed by the phenyl substituents since the lowest energy intense band in Ni(II) corrinoid complexes with exterior saturated ring framework occurs at 420–450 nm.¹⁴ Voltammetry of **12** reveals a one-electron reduction whose potential ($E_{1/2}$, –0.79 V vs. sce, acetonitrile) is slightly more cathodic than that recently predicted¹⁵ (ca. –0.55 V) for Ni(II) corrins. Reduction of **13**, a possible precursor to the porphyrin inner ring structure by further oxidative dehydrogenation, occurs at –0.76 V. These values are less negative than those for reduction of Ni(II) porphyrins¹⁶ but substantially more negative than the potentials (+0.70, +0.10 V) for stepwise reduction of the 14- π Ni(II) cation **14**.⁷ These results, which provide further demonstration of the influence of ligand structures on redox properties of macrocycles,¹⁷ together with elaboration of the synthetic methods herein will be the subject of future reports.

Acknowledgment. This research was supported by grants from the National Institutes of Health (GM-15471) and the National Science Foundation (GP-18978X).

(13) Recently several dibenzo corrin-type (“dibenzocorrin”) complexes have been reported: D. St. C. Black and A. J. Hartshorn, *J. Chem. Soc., Chem. Commun.*, 706 (1972).

(14) E. Bertele, H. Boos, J. D. Dunitz, F. Elsinger, A. Eschenmoser, I. Felner, H. P. Gribi, H. Gschwend, E. F. Meyer, M. Pesaro, and R. Scheffold, *Angew. Chem., Int. Ed. Engl.*, **3**, 490 (1964); I. D. Dicker, R. Grigg, A. W. Johnson, H. Pinnock, K. Richardson, and P. van den Broeck, *J. Chem. Soc. C*, 536 (1971); A. W. Johnson and W. R. Overend, *Chem. Commun.*, 710 (1971).

(15) N. S. Hush and I. S. Woolsey, *J. Amer. Chem. Soc.*, **94**, 4107 (1972).

(16) A. Wolberg and J. Manassen, *ibid.*, **92**, 2982 (1970).

(17) See, e.g., J. C. Dabrowiak, F. V. Lovecchio, V. L. Goedken, and D. H. Busch, *ibid.*, **94**, 5502 (1972).

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Cyclobutadiene¹

Sir:

Cyclobutadiene has been the object of significant research effort since the initial attempt at its synthesis by Kekulé 100 years ago.² Synthetic methods for generation of cyclobutadiene as a reactive intermediate have been developed.^{3–6} Physical evidence for the

(1) Photochemical Transformations. XLVIII. Presented at the European Photochemistry Association Symposium, Reading, England, July 1972.

(2) A. Kekulé, *Justus Leibigs Ann. Chem.*, **162**, 77 (1872).

(3) M. Avram, I. G. Dinulescu, E. Marcia, G. Mateescu, E. Sliam, and C. D. Nenitzescu, *Chem. Ber.*, **97**, 382 (1964).

(4) G. D. Burt and R. Pettit, *Chem. Commun.*, 517 (1965); L. Watts, J. D. Fitzpatrick, and R. Pettit, *J. Amer. Chem. Soc.*, **87**, 3253 (1965); **88**, 623 (1966).

(5) E. Hedaya, R. D. Miller, D. W. McNeil, P. F. D'Angelo, and P. Schissel, *ibid.*, **91**, 1875 (1969).

(6) For reviews, see the following references: (a) M. P. Cava and M. J. Mitchell, “Cyclobutadiene and Related Compounds,” Academic Press, New York, N. Y., 1967; (b) R. Criegee, *Angew. Chem., Int. Ed. Engl.*, **1**, 519 (1962); (c) G. Subrahonyam, *J. Sci. Ind. Res.*, **26**, 158 (1967); (d) W. Baker and J. F. W. McOmie, *Non-Benzenoid Aromat. Compounds*, 43 (1959).

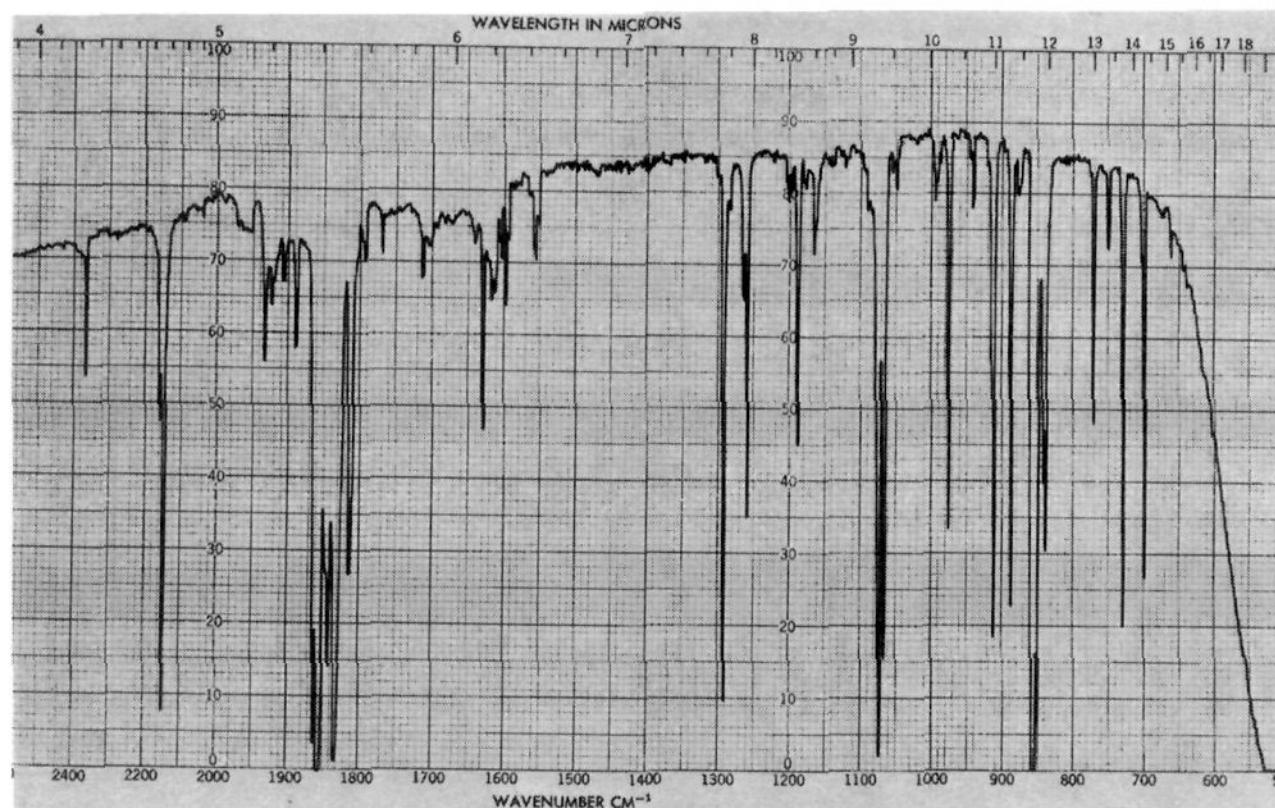


Figure 1. Photo- α -pyrone (**2**) matrix isolated in argon, prepared by 11.5 hr of irradiation ($>2910 \text{ \AA}$) of α -pyrone at 8°K .

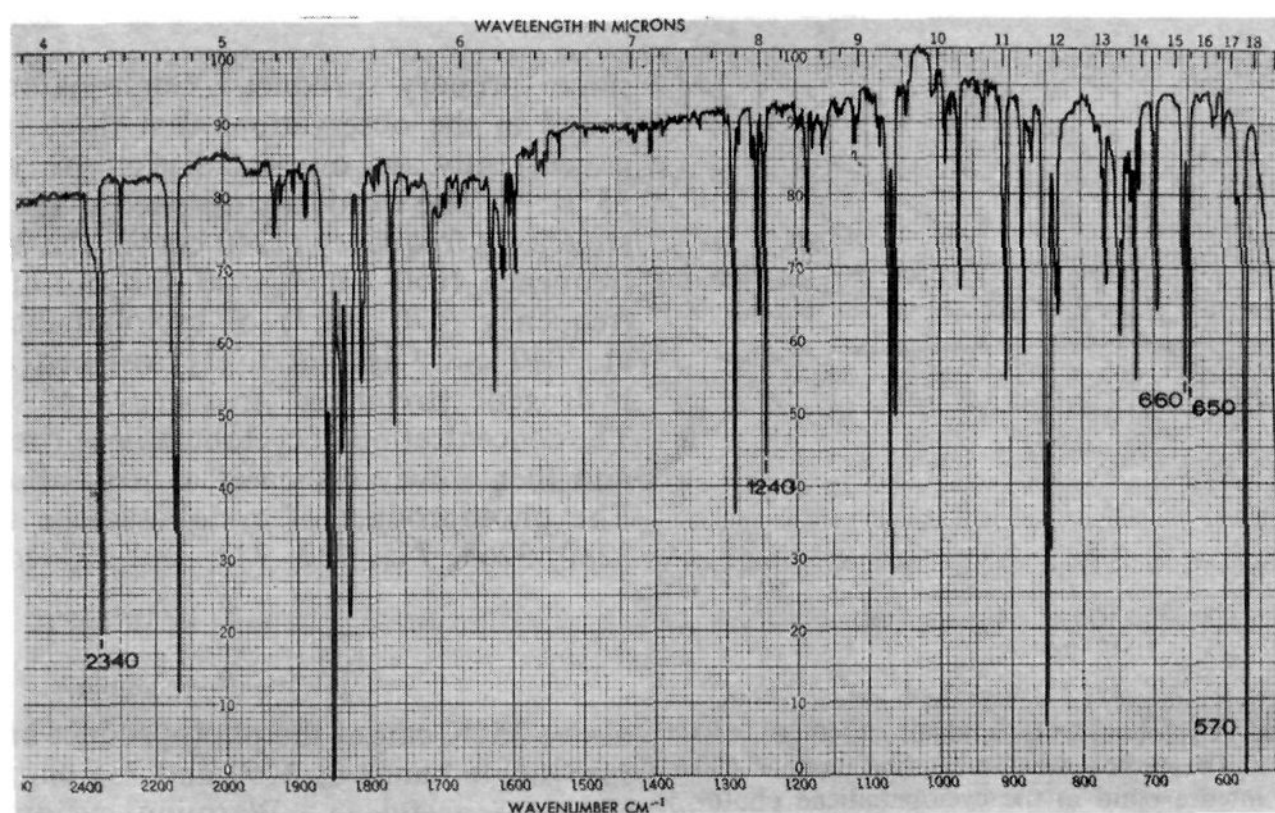


Figure 2. Sample shown in Figure 1 after irradiation for 62 min through quartz at 8°K . Bands at 2340 and 660 cm^{-1} are due to carbon dioxide. Bands at 1240 , 650 , and 570 cm^{-1} are due to cyclobutadiene.

structure of cyclobutadiene, however, is completely lacking⁷ despite the intense theoretical interest in this molecule.⁸⁻¹¹ We now wish to report the photochemical synthesis of cyclobutadiene under conditions conducive to spectroscopic study of this reactive molecule and the infrared spectrum of cyclobutadiene.

Corey has reported the photochemical conversion of α -pyrone (**1**) to an isomeric β -lactone (**2**) at -20° and

(7) A report of the electronic spectra of alkyl substituted cyclobutadienes has appeared: G. Maier, G. Fritschi, and B. Hoppe, *Angew. Chem., Int. Ed. Engl.*, **9**, 529 (1970).

(8) For reviews see H. E. Simmons and A. G. Anastassiou in ref 6a, p 368, and D. P. Craig, *Non-Benzenoid Aromat. Compounds*, **1** (1959).

(9) R. J. Buenker and S. D. Peyerimhoff, *J. Chem. Phys.*, **48**, 354 (1968).

(10) N. L. Allinger, C. Gilardeau, and L. W. Chow, *Tetrahedron*, **24**, 2401 (1968).

(11) M. J. S. Dewar and G. J. Gleicher, *J. Amer. Chem. Soc.*, **87**, 3255 (1965); M. J. S. Dewar, M. C. Kohn, and N. Trinajstic, *ibid.*, **93**, 3437 (1971).

suggested that the β -lactone would be a possible precursor of cyclobutadiene.¹² A cobalt complex of cyclobutadiene has, in fact, been prepared by irradiation of the β -lactone in the presence of the appropriate cobalt carbonyl,¹³ and evidence has been presented that flash thermolysis of **2** gives cyclobutadiene.⁵ Irradiation ($>2910 \text{ \AA}$) of α -pyrone matrix isolated in argon (1:500-1:1000) at 8°K equilibrates the α -pyrone and the aldehyde-ketene and slowly converts the α -pyrone to the β -lactone (Figure 1).¹⁴ The ultimate conversion (10-12 hr irradiation) is very high and only small amounts of α -pyrone and ketene can be detected

(12) E. J. Corey and J. Streith, *ibid.*, **86**, 950 (1964).

(13) M. Rosenblum, B. North, D. Wells, and W. P. Giering, *ibid.*, **94**, 1239 (1972).

(14) O. L. Chapman, C. L. McIntosh, and J. Pacansky, *ibid.*, **95**, 244 (1973). The β -lactone was identified by infrared comparison (argon matrix, 8°K) with a sample prepared as described previously.¹²

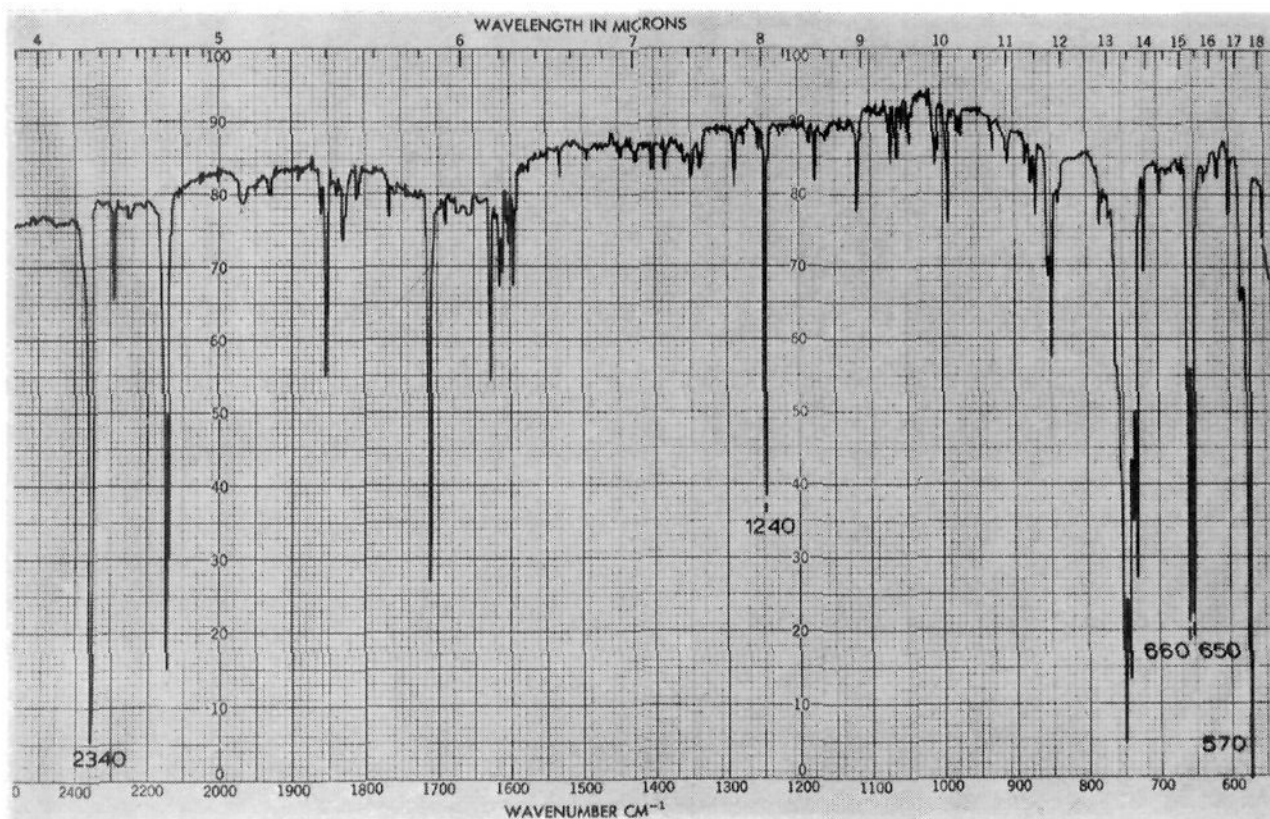


Figure 3. Sample shown in Figure 1 after 267 min of irradiation through quartz at 8°K. The new bands in the 745-cm⁻¹ region of the spectrum are due to the photoproduct of cyclobutadiene.

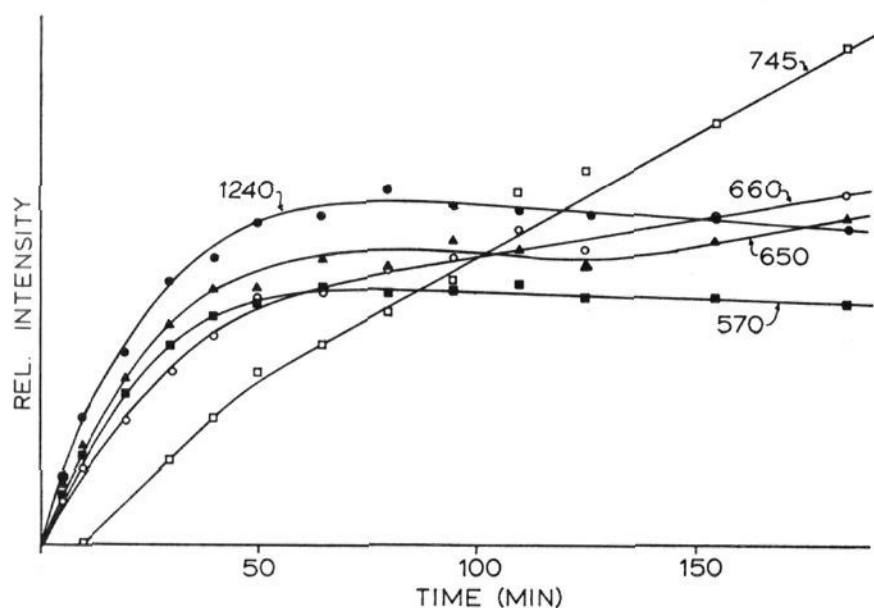
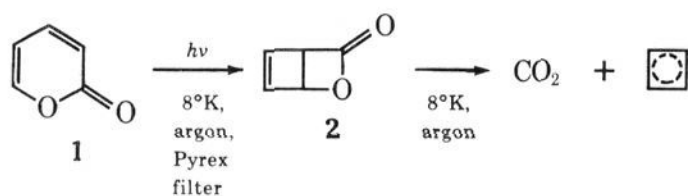


Figure 4. Plot of relative intensity of significant bands as a function of irradiation time. Cyclobutadiene bands are 1240 (●), 650 (▲), and 570 cm⁻¹ (■). The carbon dioxide bending mode is 660 cm⁻¹ (○). The most intense band in the cyclobutadiene photoproduct is 745 cm⁻¹ (□).

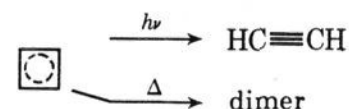
in the β -lactone. Removal of the Pyrex filter and continued irradiation (through quartz) at 8°K causes destruction of the matrix isolated β -lactone and gives rise to new bands at 1240, 650, and 570 cm⁻¹ in addition to the carbon dioxide bands at 2340 and 660 cm⁻¹ (Figures 2 and 3).¹⁵ In experiments with an unusually



thick matrix an additional band at 3040 cm⁻¹ can be observed. An intensity *vs.* time plot (Figure 4) shows that the 1240-, 650-, and 570-cm⁻¹ bands are due to the

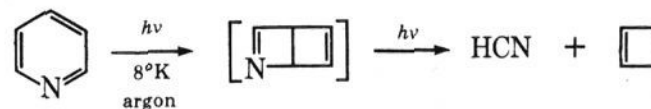
(15) Experiments starting with the β -lactone prepared as described by Corey¹² give the same results. The β -lactone unfortunately undergoes rearrangement to the bicyclobutane lactone during the matrix deposition. It is for this reason that we have preferred to start with 2-pyrone and prepare the β -lactone *in situ*.

same primary product. Confirmatory evidence is found in the observations that these bands disappear concurrently on over-irradiation or warming above 35°K.¹⁶ The bands are assigned to the carbon-carbon stretching frequency (1240 cm⁻¹), the in-plane bending frequency (650 cm⁻¹), and the out-of-plane bending frequency (570 cm⁻¹) of cyclobutadiene. The band at 3040 cm⁻¹ is tentatively assigned to the carbon-hydrogen stretching frequency of cyclobutadiene. The concentration of cyclobutadiene rises to a maximum and then slowly decreases as irradiation is continued. The photoproduct of cyclobutadiene shows bands at 3280, 3265, 745, 737, 733, and 727 cm⁻¹. Warming



above 35°K causes the photoproduct bands to coalesce into single bands at 3260 and 735 cm⁻¹ identical with those of acetylene. Warming cyclobutadiene above 35°K gives the dimer which is observed in the infrared and by high-resolution mass spectrometry.

Irradiation of pyridine matrix isolated in argon at 8°K gives rise to hydrogen cyanide and cyclobutadiene (1245, 655, and 575 cm⁻¹) but not as primary products. Presumably the reaction proceeds *via* the pyridine valence tautomer reported by Wilzbach and Rausch.¹⁷



(16) The band at 650 cm⁻¹ parallels the bands at 1240 and 570 cm⁻¹ for about 100 min irradiation and then increases owing to the intrusion of a new band at the same position. This can be shown clearly by warming experiments. When samples which have been irradiated for a short period of time are warmed above 35°K, the 650-cm⁻¹ band completely disappears. When samples irradiated for longer periods of time are warmed, the band does not completely disappear. If the cyclobutadiene is completely destroyed by irradiation, the residual band at 650 cm⁻¹ coalesces with the 660-cm⁻¹ band of carbon dioxide on warming. The secondary band at 650 cm⁻¹ is probably the bending mode of carbon dioxide in the environment of the secondary products.

(17) K. E. Wilzbach and D. J. Rausch, *J. Amer. Chem. Soc.*, **92**, 2178 (1970).

Group theory predicts four infrared-active fundamentals for D_{4h} (square, planar) cyclobutadiene and seven for D_{2h} (rectangular, planar) cyclobutadiene. It is interesting to note that group theory predicts four infrared-active fundamentals for any D_{nh} $c\text{-C}_n\text{H}_n$ species.¹⁸ Table I shows the four fundamentals for

Table I. Infrared-Active Fundamental Modes for D_{nh} $c\text{-C}_n\text{H}_n$ Molecules and Ions^a

Mode,	C_nH_n					
	$C_3H_3^+$	C_4H_4	$C_5H_5^-$	C_6H_6	$C_7H_7^+$	$C_8H_8^{2-}$
Out-of-plane bend	736	570	701	673	633	684
In-plane bend	908	650	1008	1037	992	880
C-C stretch	1276	1240	1442	1482	1477	1431
C-H stretch	3105	(3040)	3021	3064	3020	2994

^a Data are from ref 18 except for $C_3H_3^+$ which is from R. Breslow, *Pure Appl. Chem.*, **28**, 111 (1971), and C_4H_4 from the present report.

the known D_{nh} $c\text{-C}_n\text{H}_n$ species. The simplicity of the cyclobutadiene infrared spectrum consisting of four fundamentals reinforced by the absence of additional bands even in unusually thick matrices leads us to the tentative conclusion that cyclobutadiene has D_{4h} symmetry.

Attempts to obtain the electronic spectra, electron spin resonance spectra, and laser Raman spectra of cyclobutadiene are in progress.

Acknowledgment. This research was supported by Grant GP-28152X from the National Science Foundation, Grant 5252-AC4 from the Petroleum Research Fund, administered by the American Chemical Society, and Grant AM-14624 from the National Institute of Arthritis and Metabolic Diseases, U. S. Public Health Service.

(18) H. P. Fritz, *Advan. Organometal. Chem.*, **1**, 239 (1964).

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Mercury Photosensitized Oxidation of Primary and Secondary Aliphatic Amines

Sir:

Our interest in the interaction between electronically excited reagents and nitrogen-containing systems has prompted us to investigate the mercury photosensitized chemistry of some aliphatic amines in the gas phase. We report here the results of some of our studies which show that (a) Hg ³P-photosensitized decomposition of primary and secondary aliphatic primary and secondary carbinamines results in oxidation to give the corresponding imines in high yield; (b) the reactions involve the intermediacy of hydrogen atoms and amine-derived radicals; and (c) in the case of isopropylamine, if not in general, hydrogen atoms formed in the primary process react selectively with amine to give H₂ and the corresponding α -aminoalkyl radical.

Equations 1 and 2 and Table I show the results of mercury photosensitized decomposition of some representative primary and secondary aliphatic amines.

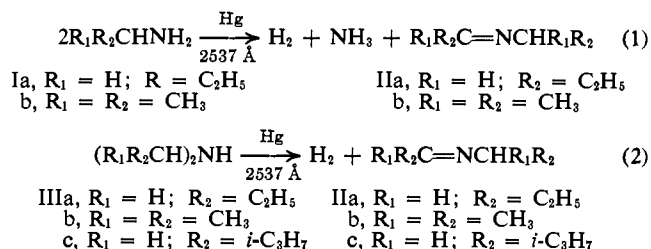


Table I. Imine Yields from Mercury Photosensitized Decomposition of Aliphatic Amines

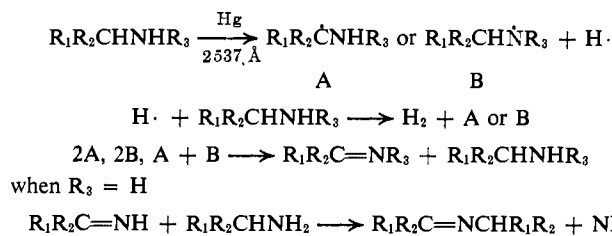
Amine	% conversion	Imine (% yield) ^a
<i>n</i> -Propylamine (Ia)	45	IIa (66)
Isopropylamine (Ib)	29	IIb (84)
Di- <i>n</i> -propylamine (IIIa)	54	IIa (58)
Diisopropylamine (IIIb)	77	IIb (49)
Diisobutylamine (IIIc)	36	IIc (73)

^a Based on starting material consumed.

Primary amines are oxidatively deaminated, and secondary amines are oxidized when subjected to these reaction conditions.¹

When these reactions were carried out in the presence of *cis*-2-butene, the product mixtures at low conversion were found to contain *n*-butane, 1-butene, and the 3,4-dimethylhexanes in addition to the amine oxidation products. In these cases the initial rate of formation of hydrogen was substantially reduced even after correction for competition between amine and olefin for excited mercury atoms.² These results suggest that the above amine oxidations involve a two-step process in which hydrogen atoms and amine-derived radicals are intermediates. Radical disproportionation would then give products in the correct oxidation level. With secondary amines these are the final products; with primary amines initially formed unsubstituted imines undergo condensation with amine followed by loss of ammonia to give the observed products. These mechanistic features are summarized in Scheme I.

Scheme I. Mechanism of Hg ³P-Photosensitized Amine Oxidation



At present it is not possible to unequivocally distinguish between the α -aminoalkyl- or neutral amino radical structures (Scheme I, A and B, respectively) for the products of the reactions between Hg ³P atoms and aliphatic amines. On the other hand, we have deter-

(1) Photolyses were performed at ambient temperatures in a 5-l. globe containing a drop of mercury and charged with reactants at pressures such that direct absorption by reactant was negligible. Mercury resonance radiation (2537 Å) was provided by a 50-W helical low-pressure resonance lamp contained in a Corning 7910 Vycor sleeve which protruded into the globe. Photolysates were worked up on a conventional vacuum line, and products were identified by comparison with authentic materials.

(2) A. A. Baum and L. A. Karnischky, *J. Amer. Chem. Soc.*, submitted for publication.