N-(2-Acetamidoethylthio)phthalimide (**10**, 0.78 g, 3.0 mmol) in 5 ml of CH_2Cl_2 was allowed to react with *p*-**thiocresol** (0.36 g, 2.9 mmol). After a brief exothermic reaction, phthalimide precipitated and was removed by filtration. The filtrate was evaporated to dryness, and the residue was crystallized from benzene to give 0.43 g (61%) of **33** slightly contaminated (ir) with phthalimide; the ir spectrum was similar to that of authentic **33**, and tlc using 1:1 heptane–acetone separated a major product identical with authentic **33**.

Attempted Equilibration of Two Sulfenamides.—A 1:1 mixture of **12** and **16** was heated at 90° for 16 hr. Glpc analysis (10-ft column of 10% SE-30 on Gas Chrom Q at 160°) showed the presence of only **12** and **16**.

Registry No.—**4**, 25116-48-7; **5**, 25116-49-8; **6**, 25116-50-1; **7**, 25116-51-2; **8**, 25116-52-3; **9**, 25116-53-4; **10**, 25158-14-9; **11**, 25116-54-5; **12**, 25116-55-6; **13**, 25116-56-7; **14**, 3060-70-6; **16**, 25116-77-2; **17**, 25116-78-3; **19**, 5038-11-9; **20**, 25116-80-7; **21**, 25110-35-4; **22**, 25110-36-5; **23**, 25110-37-6; **24**, 25110-38-7; **24** HCl, 25110-39-8; **25**, 25110-40-1; **30**, 25110-41-2.

Photoaddition of Diphenylacetylene to Tetrahydro-2-quinolones[1]

A. I. MEYERS AND PIARA SINGH[2]

Department of Chemistry, Louisiana State University, New Orleans, Louisiana 70122

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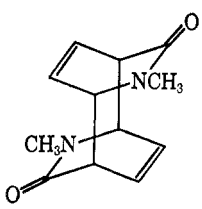
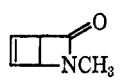
Diphenylacetylene has been observed to undergo photocycloaddition to a series of cycloalkano-2-pyridones **4** at 3500 Å to give the pentacyclic lactams **8**, the cyclobutene derivatives **16**, and the insoluble dimer **7**. Formation of **8** probably proceeds *via* the Diels–Alder adduct (4 + 2 addition) followed by photoreorganization. The pentacyclic lactams were highly labile to aqueous acid and base reverting back to starting materials, whereas the N-methyl derivatives were smoothly rearranged in methanolic acid to benzamides, **11**. Irradiation of **8** at 2537 Å resulted in rearrangement to the cyclobutene systems, **16**, a hitherto unknown photolytic reaction. This behavior was found to be general for a series of cycloalkano-2-pyridones containing various alkyl substitution and ring size.

Investigation of the photochemical behavior of simple 2-pyridones has been limited to the formation of dimers, **1**,[3–5] and valence isomers, **2**.[6] Recently,[7] the cycloaddition of olefins to the related carbostyril system has resulted in the cyclobutane derivative, **3**. Thermally induced cycloadditions to pyridones have also been observed in a few instances.[8–10] However, no photocycloadditions to pyridones have been described.[2] In view of the ready availability[11] of a series of cycloalkanopyridones, **4**, obtained by oxidative cyclization of cyano ketones, **5**, it was convenient to examine the photocycloaddition reaction with a suitable unsaturated substrate, *e.g.*, diphenylacetylene.



1



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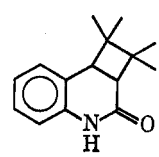

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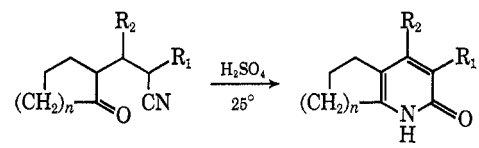
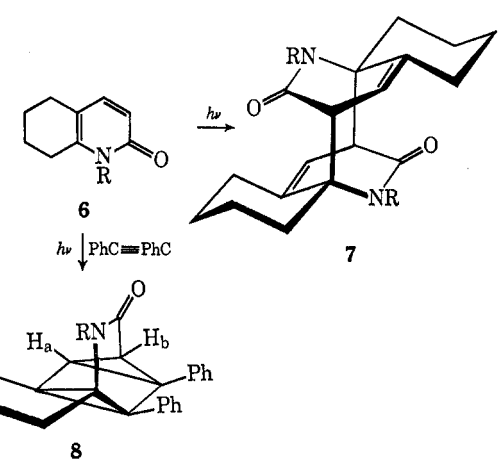


5 **4**

R_1 = H, Me
R_2 = H, Me
n = 1-3

Results and Discussion

Dimer Formation.—When a methanol–hexane solution of the 2-quinolone, **6** (R = H), and diphenylacetylene was irradiated (Pyrex) for 15 hr a crystalline material deposited along the walls of the vessel. The quantity of solid product was observed to increase with increasing exposure to the light source. The elemental analysis and mass spectrum under all practical ionizing conditions were identical with those of the starting material; yet the infrared spectrum displayed a single nonconjugated lactam band at 1660 cm^{-1} (Nujol) unlike the two strong bands (1653, 1625 cm^{-1}) present in **6** (R = H). Further, the melting point at various heat-



6 **7**

8

(1) (a) This study supported by the National Institutes of Health (NIG-MS-RG-06248-09) and the Greater New Orleans Cancer Association. (b) Address all inquiries to A. I. Meyers, Department of Chemistry, Wayne State University, Detroit, Mich. 48202.

(2) Taken from the Ph.D. Dissertation of P. Singh, June 1969. Preliminary accounts have already appeared (a) A. I. Meyers and P. Singh, *Chem. Commun.*, 576 (1968); (b) A. I. Meyers and P. Singh, *Tetrahedron Lett.*, 4073 (1968).

(3) W. A. Ayer, R. Hayatsu, P. de Mayo, S. T. Reid, and J. Stothers, *ibid.*, 648 (1961).

(4) L. A. Paquette and G. Slomp, *J. Amer. Chem. Soc.*, **85**, 765 (1963).

(5) E. C. Taylor and R. O. Kan, *ibid.*, **85**, 776 (1963).

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

(7) G. R. Evanega and D. L. Fabiny, *Tetrahedron Lett.*, 2241 (1968).

(8) B. S. Thayagarajan and K. Rajagopalan, *Tetrahedron*, **19**, 1483 (1963).

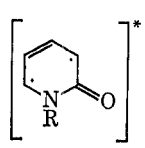
(9) L. Bauer, C. L. Bell, and G. E. Wright, *J. Heterocycl. Chem.*, **3**, 393 (1966).

(10) R. M. Acheson and P. A. Taskar, *J. Chem. Soc. C*, 1542 (1967).

(11) A. I. Meyers and G. Garcia Munoz, *J. Org. Chem.*, **29**, 1435 (1964).

ing rates was identical with that of **6** attesting to its thermal instability. The total insolubility of the photoproduct in all common solvents precluded the use of nmr for structural information. It was therefore concluded that the solid product was a labile dimer of **6** and assigned the structure **7** (R = H) based upon the analogous photodimerization leading to **1**. An attempt at examining its nmr spectrum in trifluoroacetic acid, which did give a homogeneous solution, proved to be useless since the spectrum was that of the monomer, **6**. The irradiation of **6** (R = H) was repeated in the absence of diphenylacetylene and resulted in the same product thus eliminating any concern over the role played by the diphenylacetylene in the dimerization. Since the available data on the dimer left much to be desired with regard to a firm structure elucidation, efforts were made to alter its solubility properties so that further spectral data could be obtained.[4] Nevertheless, all attempts to convert **7** (R = H) into **7** (R = Me) resulted in reversal to the monomer. Surprisingly, **6** (R = Me), obtained smoothly using sodium hydride and methyl iodide on **6** (R = H), failed to produce any trace of dimer **7** (R = Me) upon irradiation. Additional experiments designed to characterize **7** fully (R = H; ($LiAlH_4$ reduction, acidic or alkaline hydrolysis, catalytic reduction) likewise met with facile reversal to the monomer. A report[12] on the X-ray study of the dimer of N-methyl-2-pyridone (**1**) reveals that the C–C bond distance between the two pyridone rings is considerably greater (1.60 Å) than a normal C–C bond distance. In the present case, with the added bulk of the cyclohexane ring, it is conceivable that the amount of strain is greatly enhanced thus supporting its highly labile nature. The fact that the N-methyl derivative **6** (R = Me) failed to dimerize seems to be in further accord with the hypothesis that the added bulk of the N-methyl group prevents the joining of the two pyridone rings. Similarly, the 3-methyl derivative, **6b**, failed to yield any dimer, whereas the 4-methylpyridone, **6c**, did produce the dimer upon irradiation. This is also an expected result since the 3-methyl groups in the dimer would reside at the positions which link the two pyridone systems causing increased crowding, while the 4-methyls are attached to an sp^2 carbon and add little to the steric bulk between the joined rings.[13]

The photoinduced formation of the 3,6 "diradical" (**9**) in 2-pyridones has been suggested[4] as the excited species responsible for the dimerization leading to **1** and it is quite likely that a similar species (**10**) would be formed in the cycloalkanopyridone series, although the question regarding the multiplicity of **9** and **10** should be left open.



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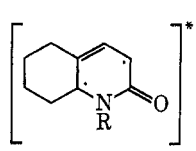
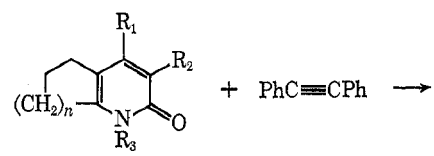


10

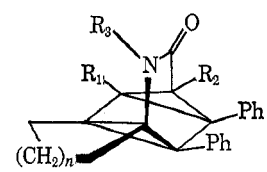
(12) M. Laing, *Proc. Chem. Soc.*, 343 (1964).

(13) Preliminary X-ray data show that the compound crystallizes in the centrosymmetric space group $P2_1/c$ with two dimer formula weights in the unit cell. Hence, unless it consists of four monomer units (contrary to the chemical evidence) it must be either a dimer which itself possesses a center of symmetry or else be disordered. However, since it scatters well out to $2\theta = 140°$ (using filtered Cu Kα radiation) it does not seem likely that it is disordered. The structure determination by direct methods is progressing satisfactorily and will be reported at a later date.

Photocycloaddition with Diphenylacetylene.—The filtrate obtained after removal of the dimer **7** (R = H), produced a residue which consisted of four products (tlc) in varying amounts. The major product (21%) was obtained *via* preparative layer chromatography and shown to be a 1:1 adduct of diphenylacetylene and the pyridone (elemental and mass analyses). All the spectroscopic data (ir, nmr, uv) were consistent with the pentacyclic lactam, **8** (R = H) (Experimental Section). Similar photocycloaddition occurred when the N-methylpyridone, **6a**, was irradiated in the presence of diphenylacetylene. The pentacyclic lactam, **8a**, was obtained in low yield (8%) and, as already stated, no dimer was found among the products. Examination of several related pyridones (**6b–6g**) under similar reaction conditions produced the pentacyclic lactams (**8b–8g**) in 13–49% yield and several minor products to be discussed later.



6, $n = 2$; $R_1 = R_2 = R_3 = H$



8, $n = 2$; $R_1 = R_2 = R_3 = H$

a, $n = 2$; $R_1 = R_2 = H$; $R_3 = Me$
b, $n = 2$; $R_1 = R_3 = H$; $R_2 = Me$
c, $n = 2$; $R_1 = Me$, $R_2 = R_3 = H$
d, $n = 2$; $R_1 = H$; $R_2 = R_3 = Me$
e, $n = 2$; $R_1 = R_3 = Me$; $R_2 = H$
f, $n = 1$; $R_1 = R_2 = R_3 = H$
g, $n = 1$; $R_1 = Me$; $R_2 = R_3 = H$

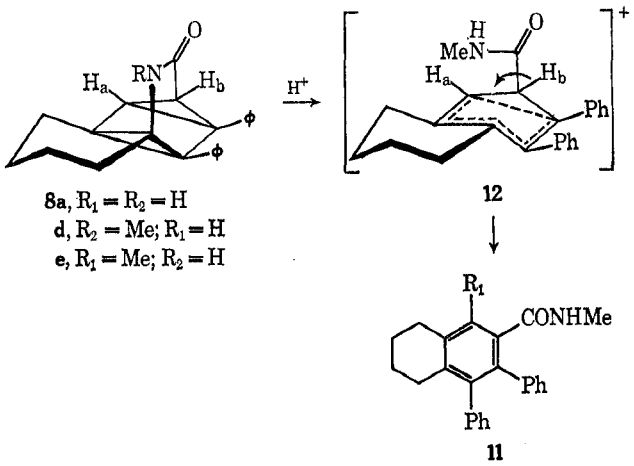
The only unique feature present in the nmr spectra of the pentacyclic lactams is the long range coupling between R_3 and R_2 when both are present as protons. Thus, the expected doublet of R_2 = H is split further into a doublet of doublets at 100 MHz (J = 1, 3 Hz) when R_3 = H. This long range coupling through the amide carbonyl group was found to be absent when the NH proton was exchanged by deuterium, irradiated for spin decoupling, or replaced by a methyl group.[14]

In order to accumulate some chemical evidence to support the structures of the photoadducts, a solution of **8** in methanolic potassium hydroxide was heated for several hours and produced considerable amounts of diphenylacetylene and the starting pyridone **6**. Reversal to starting materials was also found to occur in hot, acidic methanol. The fact that the presence of acid or base was responsible for the reversal of the pentacyclic lactams was clearly established when it was found that **8** was completely stable in boiling toluene even after prolonged heating. The driving force for the reversal is believed to be a function of the aromatic

(14) All the nmr spectra for the pentacyclic lactams and the deuterium exchanged analogs may be found in the doctoral dissertation of P. S., University Microfilms, Ann Arbor, Mich.

stability[11,15] of **6** and on this basis it was decided to examine the N-methyl derivative, **8a**.[16] The latter could also be readily obtained by alkylation of **8** by use of sodium hydride–methyl iodide. Alkaline treatment of **8a** resulted only in complete recovery of the pentacyclic lactam in sharp contrast to the lability of the normethyl system (**8**) under the same conditions.

On the other hand, treatment with methanolic hydrochloric acid produced a new product (tlc) along with small amount of diphenylacetylene undoubtedly due to reversal of **8a** to its components. After purification (tlc) the acid-generated product exhibited an NH band at 3440 cm^{-1} and the amide carbonyl at 1648 cm^{-1}. Elemental analysis and the mass spectrum revealed it to be an isomer of **8a**. A precise mass determination of 341.17756 (calcd 341.17796) indicated that the molecule possessed fourteen sites of unsaturation and/or rings. The uv spectrum exhibited the *o*-terphenyl chromophore (230 mμ) and the nmr spectrum (60 and 100 MHz) was in complete agreement with the assigned structure **11** (R = H). The facile rearrangement of **11** from **8a** may be formulated by protonation, either at nitrogen or oxygen, which produces a positively charged nitrogen atom followed by C–N bond rupture. The resulting delocalized cation **12** then loses a proton forming the aromatic system. Similar results were obtained when the dimethyl derivative, **8e**, was treated with methanolic acid solution, affording the 1-methyl derivative, **11** (R_1 = Me). The dimethyl lactam, **8d**, provided an interesting example in that the C-methyl group was in a position to block aromatization of the cation, **12**. When **8b** was refluxed in acidic medium, the product was again **11** (R_1 = Me) which can only have arisen *via* a methyl migration in **12**. Comparison



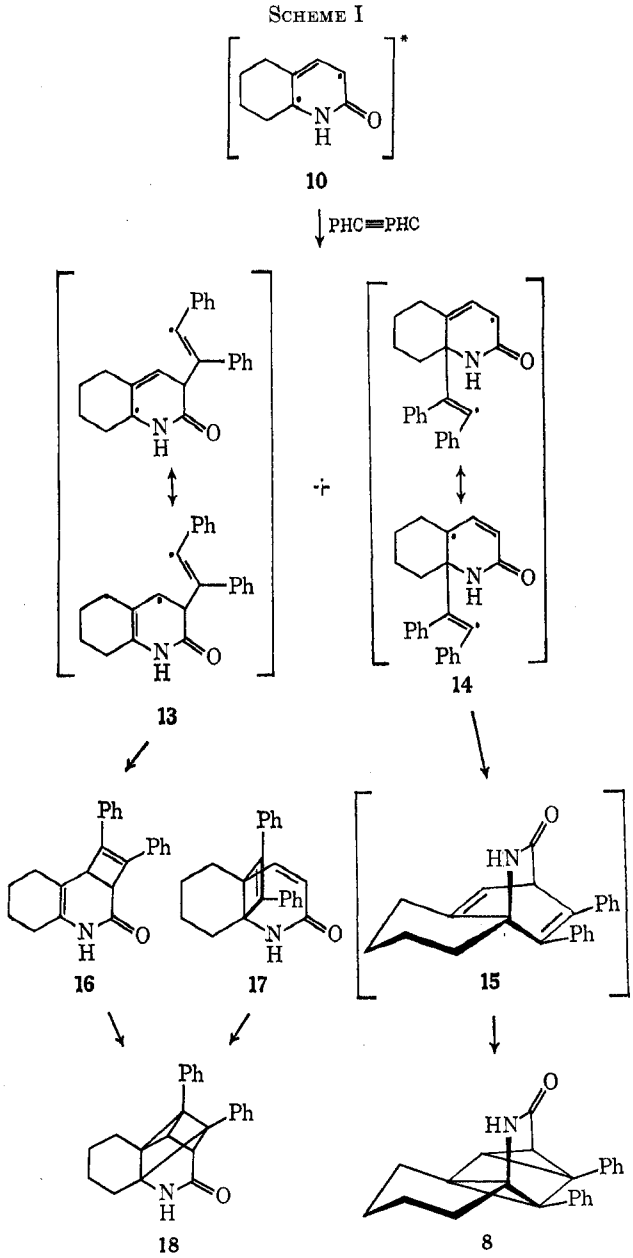
8a, $R_1 = R_2 = H$
d, R_2 = Me; $R_1 = H$
e, R_1 = Me; $R_2 = H$

12

11

of the benzamide derivatives obtained from **8e** and **8d** confirmed their identity. It is to be noted here that also present in the reaction were the starting pyridones, **6 a, d, e**, owing to some reversal under acidic conditions. The formation of the benzamides, **11**, support the site of addition of diphenylacetylene to the pyridones **6** as being at positions 3 and 9. If, as previously stated, the excited intermediate, **10**, may be envisioned as being responsible for dimerization of the pyridones, then it is significant that the presence of diphenylacetylene results in an apparent interception of the dimerization process. However, if the pyridone dimer is formed, not by a combination of two excited species, but instead by the excited pyridone adding to ground-state pyridone in a stepwise fashion, intervention by the acetylene is not unexpected. The latter appears to be the case since increasing the concentration of diphenylacetylene did result in an increase in pentacyclic lactam yield. The process leading to **8** may be formulated (Scheme I) as an

SCHEME I



attack by the diradical on ground-state diphenylacetylene[17] producing either **13** and/or **14** which proceed to the homoconjugated diene **15** and/or **16**. The former,

(15) J. A. Elvidge and L. M. Jackman, *J. Chem. Soc.*, 860 (1961). The ring current model, upon which these authors have based their conclusions, has been generally used to justify the use of chemical shifts as a qualitative criterion of aromatic character. However, quantitative conclusions in this regard have been challenged by various authors; see P. Beak, J. Bonhan, and J. T. Lee, Jr., *J. Amer. Chem. Soc.*, **90**, 1569 (1968), and references cited therein.

(16) The reduction in aromatic character was seen by examining the nmr spectrum of **6a** which showed the 3-H and 4-H doublets centered at 6.33 and 7.04 ppm, respectively. This is compared with the normethyl pyridone (**6**) which exhibited the 3-H and 4-H resonances at 6.35 and 7.17 ppm.

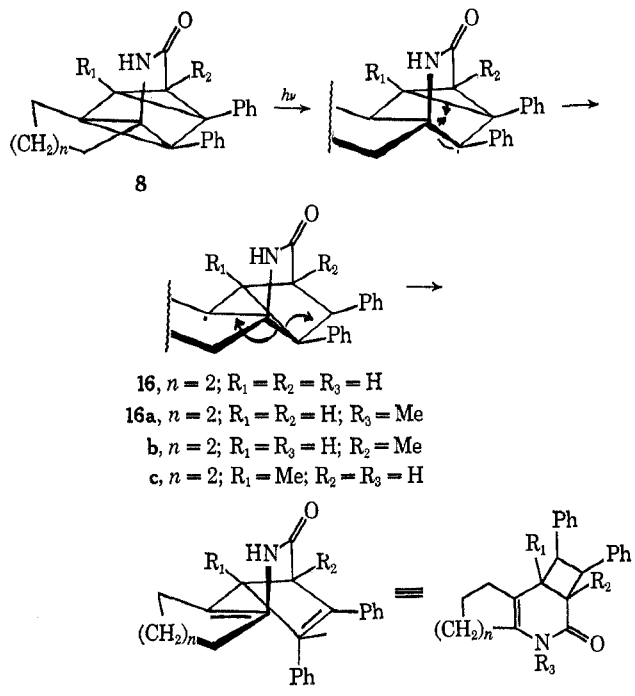
(17) The hypothesis that an activated pyridone attacks ground-state diphenylacetylene rather than vice versa was supported by the fact that the irradiation of a solution of diphenylacetylene at 3500 Å after 16 hr did not give rise to any new products.

under the influence of light, readily rearranges to the pentacyclic lactam **8**. The reorganization of **15** to **8** is now a well-known phenomenon having been observed in a variety of heterocyclic[18] and homocyclic[19] systems.

Scheme I also suggests that the initial adducts **13** and **14** should also provide the cyclobutene derivatives, **16** and **17**. Removal of the three additional bands from the preparative layer plate provided a small quantity of another product along with minute quantities of two additional components. The larger of these products exhibited elemental and mass spectral analyses consistent with **16**, **17**, or **18**. However, the infrared spectrum revealed absorption at 3390 and 1655 cm^{-1}, typical of the enamide moiety and the uv spectrum exhibited maxima at 226, 266, and 288 mμ. These spectral data are consistent with cyclobutene[20] and enamide[3,21] moieties present in **16**. The nmr spectrum was also in agreement with the *cis*-fused cyclobutenopyridone and details are presented in the Experimental Section. The two very minor products isolated from the preparative plate could not be fully characterized although both possessed molecular ions at 341 indicating that they were 1:1 adducts of the pyridone and diphenylacetylene. It is to be noted that, although we were not able to obtain meaningful quantities of the two additional products for complete characterization, both **16** and **17** might be expected *via* valence tautomerization to produce **18** in accord with a previous observation in the naphthalene series.[22] At this stage of the study, the comment concerning **17** and **18** must be regarded as speculative.

Photoisomerization of Pentacyclic Lactams 8.—The pentacyclic lactams **8** represent a highly strained system and it is well known that many analogous systems exhibit considerable photolability.[23] With this view in mind, we investigated the behavior of the pentacyclic lactams, **8**, by irradiation at 2537 Å, an energy source higher than that from which they were formed (3500 Å). When a benzene solution of **8** was irradiated, the starting material rapidly disappeared (tlc) and two new products formed in highly disproportionate amounts. The major product was isolated (tlc) and found to be identical with the cyclobutenopyridone, **16**, formed from diphenylacetylene and **6** (R = H). The conversion of **8** to **16** was 60%. Similar behavior was noted when the pentacyclic lactams **8a–8c** were irradiated in benzene solution. During the irradiation, it was observed that small amounts of diphenylacetylene were also produced. This suggested the possibility that reversal of **8** to its components may be occurring followed by recombination to give **16** directly. This pathway was precluded by the fact that no cyclobutenopyridone was found when the pyridone **6** and diphenylacetylene was irradiated (2537 Å) in methanol–ether (a solvent which also allowed conversion of **8** to **16**). When diphenylacetylene and **6** were irradiated (2537 Å) in benzene for 6 hr, a trace of the cyclobutenopyridone was observed (tlc) but no pentacyclic lactam **8** could be detected. It is thus evident that the formation of **16** from **8** is proceeding by a unimolecular process. The fact that the isomerization is fast in benzene (60% conversion in 4 hr) compared to methanol–ether (<10% in 12 hr) may be attributed to the efficient transfer of energy from benzene to the pentacyclic lactam **8**. Regarding the small amounts (1–2%) of cyclobutenopyridone formed from the pyridone **6** and diphenylacetylene during irradiation at 3500 Å, this was found to be a competing process originating from the postulated intermediates **13** and **14**. Confirmation of this was gathered when the pentacyclic lactam **8** showed no trace of the cyclobutenopyridone **16** upon prolonged exposure to light at 3500Å under the usual conditions. On the other hand, the cyclobutenopyridone was essentially stable to prolonged irradiation both at 2537 and 3500 Å producing only trace decomposition products. Thus, although the 2 + 2 cycloaddition of diphenylacetylene to the pyridones proceeds in poor yields in contrast to similar cycloadditions,[22,24] the photoisomerization of **8** occurs rather efficiently. See Scheme II.

SCHEME II



The photoisomerization of **8** to **16** at 2537 Å does not appear to have any close analogy in literature. The photoisomerization[25,26] of phenylcyclopropanes (**19**) to propenes has only a remote resemblance to this isomerization since the former involves a hydrogen trans-

(18) H. Prinzbach, R. Fuchs, and R. Kitzing, *Angew. Chem., Int. Ed. Engl.*, **7**, 67 (1968); G. R. Zeigler and G. S. Hammond, *J. Amer. Chem. Soc.*, **90**, 513 (1968).

(19) S. J. Cristol and R. L. Snell, *ibid.*, **76**, 5000 (1954); *ibid.*, **80**, 1950 (1958); W. G. Dauben and R. L. Cargill, *Tetrahedron*, **15**, 197 (1961); C. F. Wilcox, S. Winskin, and W. G. McMillan, *J. Amer. Chem. Soc.*, **82**, 5450 (1960); H. G. Richey and N. C. Buckley, *ibid.*, **85**, 3057 (1963); P. R. Story and S. R. Fahrenholtz, *ibid.*, **86**, 527 (1964); P. G. Gassman, D. H. Aue, and D. S. Patton, *ibid.*, **86**, 4211 (1964); H. Tanida, Y. Hata, Y. Matsui, and I. Tanada, *J. Org. Chem.*, **30**, 2259 (1965); K. E. Wilzbach and L. Kaplan, *J. Amer. Chem. Soc.*, **87**, 4004 (1965); *ibid.*, **90**, 5868 (1968).

(20) M. A. Battiste and M. E. Burns, *Tetrahedron Lett.*, 523 (1966); R. M. Dodson and A. G. Zielske, *Chem. Commun.*, 353 (1965); M. S. Newman and G. Kangers, *J. Org. Chem.*, **30**, 3295 (1965).

(21) W. A. Ayer and G. G. Iverach, *Tetrahedron Lett.*, 19 (1960); A. D. Campbell and I. D. R. Stevens, *J. Chem. Soc.*, 959 (1956).

(22) P. J. Collins and W. H. F. Sasse, *Tetrahedron Lett.*, 1689 (1968).

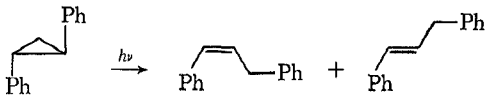
(23) "Organic Photochemistry," Vol. I, O. L. Chapman, Ed., Marcel Dekker, New York, N. Y., 1967.

(24) S. P. Pappas, B. C. Pappas, and N. A. Portnoy, *J. Org. Chem.*, **34**, 520 (1969). G. R. Evanega and D. L. Fabiny, *Tetrahedron Lett.*, 2241 (1968).

(25) G. W. Griffin, J. Covell, R. C. Petterson, R. M. Dodson, and G. Close, *J. Amer. Chem. Soc.*, **87**, 1410 (1965).

(26) H. Kristinsson and G. W. Griffin, *Tetrahedron Lett.*, 3259 (1966).

fer as well as isomerization. More suitable analogies of the type **20** to **21** and **22** to **23** do not appear to be



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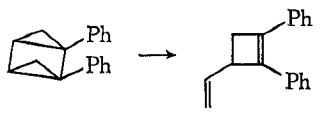
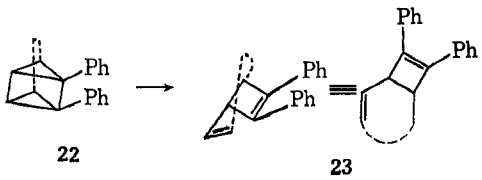


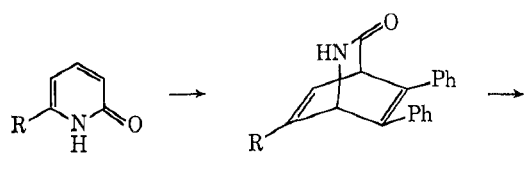
20 **21**



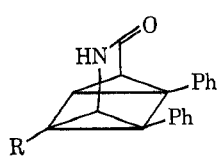
22 **23**

known. The isomerization of **8** to **16** may be envisioned to proceed by a concerted three-bond fission and recombination or may occur in a stepwise manner involving the intermediate shown in Scheme II. This photoisomerization has been found to be a general process and a number of pentacyclic lactams have been converted in a similar manner to the corresponding cyclobutenopyridones (Experimental Section).

Several attempts to induce photocycloaddition of diphenylacetylene to monocyclic pyridones **24** (R = H) and **24** (R = Me) resulted in trace amounts of 1:1 adducts which revealed through their mass, spectra to be possibly **25** and/or **26**. However, the quantities



24 **25**



26

were too minute for meaningful characterization and further studies in this respect as well as those relating to the multiplicity of the reactive species are planned. Meanwhile, the synthetic utility of this photocycloaddition process for preparing unusual heterocyclic caged systems need not await its in-depth understanding.

Experimental Section

All irradiations involving addition of diphenylacetylene to cycloalkano[*e*]-2-pyridones were carried out under nitrogen in Pyrex containers. Two types of light sources were used: (a) an assembly of sixteen external low pressure 8 Wmercury resonance lamps (Sylvania F8Ts/BLB) in an air cooled Rayonet Srinivasan-Griffin photochemical reactor manufactured by the Southern New England Ultraviolet Company, Middletown, Connecticut (the wavelength of this light source is a tits maximum[27] intensity at 3500 Å); (b) an internal water-cooled Hanovia high pressure quartz mercury vapor lamp, Type S, No. 654A36, 200 W with an arc length of 4.5 in., manufactured by Englehard Hanovia, Inc., Newark, N. J.

Isomerization of the pentacyclic lactams (**8**) leading to the cyclobutene derivatives (**16**) were carried out under nitrogen in quartz vessels with an assembly of sixteen external low pressure 8W mercury resonance lamps (Sylvania G8 T5) in the air-cooled Rayonet reactor. About 90% of the light intensity of this source is at 2537 Å. In all cases the solutions were degassed either by the freeze–thaw technique or by passing in pure nitrogen for at least 30 min.

Thin layer and preparative layer chromatography were done on silica gel G (PF_{254}), Brinkmann Company, Long Island, N. Y. All melting points were determined on a Fisher-Johns melting point apparatus, and are uncorrected. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn., and by Medizinisch-Chemisches Institut und Pregl Laboratorium, Graz, Austria. Mass spectra were taken on a Hitachi Perkin-Elmer RMU-6E or the Varian instruments. Infrared and ultraviolet spectra were taken on Perkin-Elmer 257 and 450 instruments respectively.

Cycloalkano[*e*]-2-pyridones (4).—The cycloalkanopyridones were all prepared by the method of Meyers and Garcia[11] except for 6 g which was obtained using the method of Sakurai and Midorikawa.[28]

1-Methyl-5,6,7,8-tetrahydro-2-quinolone (6a).—A solution of 5,6,7,8-tetrahydro-2-quinolone (3.73 g, 25 mmol) and sodium hydride (1.04 g, 25 mmol, 58% oil dispersion) in 450 ml dry xylene was heated to reflux under nitrogen for 20 hr. The solution was allowed to cool under a stream of nitrogen and 14.2 g (100 mmol, 4 equiv) of methyl iodide was added dropwise with stirring. The reaction mixture was refluxed for another 6 hr and the hot xylene solution filtered to remove precipitated sodium iodide. The solvent was then removed under reduced pressure to give a yellow oil which was crystallized from ethyl acetate–hexane to give 2.44 g (59%) of 1-methyl-5,6,7,8-tetrahydro-2-quinolone (**6a**): mp 215–217°; ir 1660, 1582, 1550 cm^{-1}; nmr ($CDCl_3$) 1.5–2.1 (m, 4, methylene H), 2.3–2.8 (m, 4, allylic H), 3.43 (w, 3, N-CH_3), 6.33 (d, J = 9 Hz, 1, 3 H), 7.02 δ (J = 9 Hz, 1, 4 H).

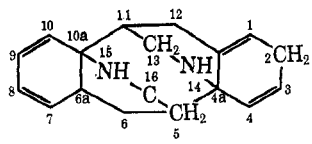
Anal. Calcd for $C_{10}H_{13}NO$: C, 73.59; H, 8.03; N, 8.58. Found: C, 73.56; H, 7.97; N, 8.64.

1,3,4,7,8,9,10,11-Octahydro-2H,5H-4a,11:10a,5-bis(iminomethano)dibenzo[*a*,*e*]cyclooctene-13,16-dione (7).[29]—A solution of 5,6,7,8-tetrahydro-2-quinolone (**6**) (500 mg, 3.4 mmol) in 20

(28) A. Sakurai and H. Midorikawa, *Bull. Chem. Soc. Jap.*, **41**, 165 (1968).

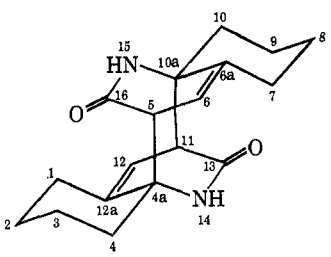
(29) The nomenclature utilized for the compounds described herein has been kindly suggested by Dr. Kurt L. Loening of Chemical Abstract Service, Columbus, Ohio, for which we are grateful.

The fundamental ring system in the proposed structure for the dimer of 5,6,7,8-tetrahydro-2-quinolone (**32**) is oriented, numbered, and, named as follows.



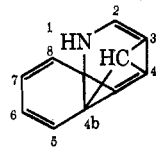
2H,5H-4a,11:10a,5-bis(iminomethano)dibenzo[*a*,*e*]cyclooctene

Thus, the nomenclature for the dimer is as follows.



1,3,4,7,8,9,10,11-octahydro-2H,5H-4a,11:10a,5-bis(iminomethano)dibenzo-[*a*,*e*]cyclooctene-13,16-dione

The fundamental ring system in pentacyclic lactams **8a–g** is oriented, numbered, and named as follows.



1H-3,4,4b-methenobenzo[1,3]-cyclopropa[1,2-*b*]pyridine

(27) J. H. Stocker and D. H. Kern, *J. Org. Chem.*, **31**, 3755 (1966).

ml of methanol was irradiated under N_2 for 80 hr at 3500 Å to give 300 mg (60%) of the solid dimer. Higher yields of dimer could be obtained by irradiating in more concentrated solution for longer periods of time. The dimer was washed with methanol and dried at room temperature: mp 205–206°; mixture melting point with authentic 5,6,7,8-tetrahydro-2-quinolone **6** was undepressed; ir (Nujol) 1653, 1625 cm^{-1}; nmr (TFA) identical to nmr (TFA) of 5,6,7,8-tetrahydro-2-quinolone (**6**, R = H).

Anal. Calcd for $C_{18}H_{22}N_2O_2$: C, 72.49; H, 7.38; N, 9.39. Found: C, 72.21; H, 7.38; N, 9.15.

Calcd *m/e* for $C_{18}H_{22}N_2O_2$: 298. Found: 149.

Attempted Methylation of the Dimer 7.—The dimer (200 mg, 0.34 mmol) was stirred with an equivalent of sodium hydride in 100 ml anhydrous tetrahydrofuran under nitrogen in an oil bath maintained at 50°. After 0.5 hr a small portion of the solution was withdrawn and diluted with 95% ethanol for ultraviolet examination. The spectrum revealed (318 mμ, ε 6500) that reversal to the pyridone **6** had taken place.

Irradiation of 1-Methyl-5,6,7,8-tetrahydro-2-quinolone (6a) at 3500 Å.—A solution of 1-methyl-5,6,7,8-tetrahydro-2-quinolone (1.0 g, 6.1 mmol) in 10 ml methanol was irradiated under nitrogen at 3500 Å and the solution monitored periodically. No dimer separated during the irradiation which lasted one week. The methanol was removed *in vacuo* and examination of the residue revealed unchanged starting material.

Hexahydro-4,4a-diphenyl-1H-3,4,4b-methenobenzo[1,3]cyclopropa[1,2-*b*]pyridin-2(3H)-one (8). A. From Irradiation at 3500 Å.—A solution of 1.0 g (6.7 mmol) 5,6,7,8-tetrahydro-2-quinolone **6** and 2.5 g (14.0 mmol) diphenylacetylene in 8 ml anhydrous methanol and 5 ml *n*-hexane in a 25 × 200 mm Pyrex tube was stoppered with a rubber serum cap, securely held with copper wire. The air in the tube was then replaced by pure nitrogen using the freeze-thaw technique. The vessel was suspended from a clamp by a copper wire into an air cooled photochemical reactor (Rayonet) equipped with sixteen low pressure 8W lamps emitting light at 3500 Å. After overnight irradiation crystals of the dimer of the pyridone (**7**) began to deposit along the sides of the tube. The irradiation was continued for one week (188 hr). The separated solid was removed by filtration, the residue was washed first with anhydrous methanol and then with anhydrous ether, and the washings were combined with the filtrate. The amount of the separated solid dimer was 610 mg (61%). The combined filtrate and washings were concentrated under reduced pressure and the residue was dissolved in minimum amount of methylene chloride. The mixture was separated by preparative layer chromatography on five 20 × 40 cm plates coated to 1.5 mm thickness using ether eluent. The bands corresponding to the product with R_f (ether) = 0.27 were cut from each plate, combined and put in a 500-ml erlenmeyer flask containing 300 ml anhydrous ether. The flask was then stoppered with a cork and the silica stirred vigorosuly by means of a magnetic stirrer for 0.5 hr. It was then filtered through a sintered glass funnel and the silica thoroughly washed with anhydrous ether. The washings were combined and ether removed under reduced pressure to give 270 mg (12.5%, based on pyridone **6**) of the pentacyclic lactam, **8**. The product was homogeneous on a thin layer chromatogram. Crystallization from benzene–petroleum ether gave colorless needles: mp 203–205°; ir ($CHCl_3$) 1690 (–CONH–), 3410 cm^{-1} (–NH–); nmr ($CDCl_3$) 1.5–2.4 (m, 8, methylene H); 2.55 (d, J = 3 Hz, 1, Ha); 3.60 (doublet of doublets, J = 1, 3 Hz, 1, H_b); 6.9–7.5 (m, 10, aromatic H); 7.61 δ (broad singlet, 1, NH). Upon treatment with deuterium oxide, the signal at 7.61 ppm due to NH disappeared and the doublet of doublets at 3.60 ppm collapsed to a true doublet (J = 3 Hz). A 100-MHz spectrum ($CDCl_3$) showed the doublet of doublets sharply resolved. Irradiation of the NH signal at 7.61 ppm again resulted in collapse of doublet of doublets at 3.60 ppm to a true doublet (J = 3 Hz).

Anal. Calcd for $C_{23}H_{21}NO$: C, 84.36; H, 6.48; N, 4.28. Found: C, 84.62; H, 6.58; N, 4.37.

Calcd *m/e* for $C_{23}H_{21}NO$: 327. Found: 327.

Fragments peaks at *m/e* 149 (pyridone) and *m/e* 178 (diphenylacetylene) were also observed.

In a subsequent experiment low boiling petroleum ether was used as the irradiation solvent in place of *n*-hexane without significant change. Another run using 3.5 g (19.6 mmol) diphenylacetylene and 500 ml methanol (no *n*-hexane or petroleum ether) gave 450 mg (20.5%) of **8**. Thus, the yield of the cycloadduct, **8**, increases if a larger excess of diphenylacetylene is used and irradiations are performed for longer periods.

B. Using a Hanovia 200-W High Pressure Lamp.—A solution of 1.0 g (6.7 mmol) of pyridone (**6**) and 5.0 g (28.1 mmol) diphenylacetylene in 100 ml of hexane–methanol (6:4) in a Pyrex vessel was irradiated under nitrogen using an internal water cooled, high pressure 200-W Hanovia lamp for 36 hr. Work-up of the mixture produced 500 mg of the dimer and 350 mg (16%) of lactam, **8**. The product was identical in every respect with that obtained at 3500 Å.

Reversal of Hexahydro-4,4a-diphenyl-1H-3,4,4b-methenobenzo[1,3]cyclopropa[1,2-*b*]pyridin-2(3H)-one (8) to Its Components. A. In Base.—A solution of 50 mg (0.15 mmol) of **8** in 2 ml methanol and 2 ml 20% aqueous potassium hydroxide was heated to

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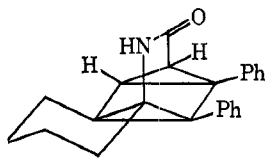
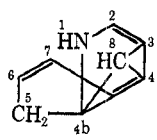
Thus, the nomenclature for the pentacyclic lactams is as follows, with the methyl substituents appropriately included as needed.



hexahydro-4,4a-diphenyl-1H-3,4,4b-methenobenzo[1,3]cyclopropa[1,2-*b*]pyridin-2(3H)-one

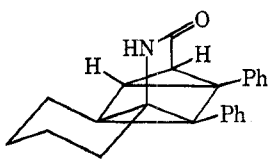
8

The fundamental ring system in the pentacyclic lactams **6f** and **6g** is oriented, numbered, and named as follows.



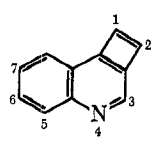
5H-3,4,4b-metheno-1H-cyclopenta-[1,3]cyclopropa[1,2-*b*]pyridine

Thus, the nomenclature of the above-mentioned pentacyclic lactams is given below.



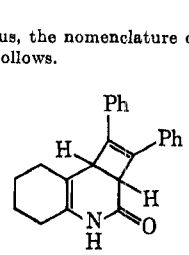
tetrahydro-4,4a-diphenyl-5H-3,4,4b-metheno-1H-cyclopenta[1,3]-cyclopropa[1,2-*b*]pyridin-2(3H)-one

The fundamental ring system in the cyclobutene derivatives **16a–e** is oriented, numbered, and named as follows.



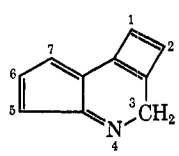
cyclobuta[*c*]quinoline

Thus, the nomenclature of the above-mentioned cyclobutene derivatives is as follows.



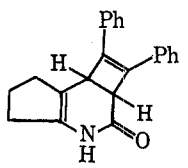
4,5,6,7,8,8b-hexahydro-1,2-diphenyl-cyclobuta[*c*]quinolin-3(2aH)-one

The fundamental ring system in the cyclobutene derivatives **16f,g** is oriented, numbered, and named as follows.



3H-cyclobuta[*d*]cyclopenta[*b*]pyridine

Thus, the nomenclature of the cyclobutene derivatives is as follows.



2a,4,5,6,7,7b-hexahydro-1,2-diphenyl-3H-cyclobuta[*d*]cyclopenta[*d*]cyclopenta[*b*]pyridin-3-one

reflux under nitrogen for 8 hr. Examination of the reaction contents by tlc indicated that a considerable amount of diphenylacetylene had formed.

B. In Acid.—A solution of 50 mg (0.15 mmol) of compound **8** in 2 ml methanol and 2 ml 6 *N* hydrochloric acid was refluxed under nitrogen for 4 hr and an aliquot removed for tlc examination. Visualization of the plates indicated an abundant quantity of diphenylacetylene.

Thermal Stability of Hexahydro-4,4a-diphenyl-1H-3,4,4b-methenobenzo[1,3]cyclopropa[1,2-*b*]pyridin-2(3H)-one (8).—A solution of 50 mg (0.15 mmol) of **8** in 15 ml dry benzene was heated to reflux under nitrogen; aliquots were removed at the end of 6, 24, 48, 72, and 96 hr. Thin layer examination exhibited one spot due to **8** and there was no evidence of any new products. Heating was discontinued and benzene removed, first on rotavapor and then on a vacuum pump. To the residue, 15 ml toluene was added and solution refluxed for 20 hr under nitrogen. A tlc check revealed that no new products had formed and only one homogeneous spot due to **8** was present.

Hexahydro-1-methyl-4,4a-diphenyl-1H-3,4,4b-methenobenzo-[1,3]cyclopropa[1,2-*b*]pyridin-2(3H)-one (8a). A. From 1-methyl-5,6,7,8-tetrahydro-2-quinolone and Diphenylacetylene.—A solution of 1.0 g (6.1 mmol) of 1-methyl-5,6,7,8-tetrahydro-2-quinolone **6a** and 2.5 g (14.0 mmol) of diphenylacetylene in 8 ml ethanol and 6 ml of *n*-hexane was irradiated in a Pyrex tube under nitrogen at 3500Å for one week (188 hr). During this period no solid dimer appeared. The solution was evaporated to dryness under reduced pressure and the residue dissolved in methylene chloride. The mixture was separated *via* preparative layer chromatography to give 170 mg (8.2%) of lactam **8a**, R_f (ether) = 0.43. The product was crystallized from benzene–petroleum ether to give colorless needles: mp 166–169°; ir ($CHCl_3$) 1675 cm^{-1} (–$CONCH_3$–), the band at 3400 cm^{-1} (NH) was absent; nmr ($CDCl_3$) 1.1–2.5 (m, 8, methylene H), 2.61 (d, J = 3 Hz, 1, H_a), 3.03 (s, 3, N–CH_3), 3.61 (d, J = 3 Hz, 1, H_b), 6.85–7.1 δ (m, 10, aromatic H).

Anal. Calcd for $C_{24}H_{23}NO$: C, 84.42; H, 6.79; N, 4.10. Found: C, 84.78; H, 7.02; N, 3.78.

Calcd *m/e* for $C_{24}H_{23}NO$: 341. Found: 341.

Fragment peaks at *m/e* 163 (pyridone) and *m/e* 178 (diphenylacetylene) were also observed.

B. From Hexahydro-4,4a-diphenyl-1H-3,4,4b-methenobenzo-[1,3]cyclopropa[1,2-*b*]pyridin-2(3H)-one (8) (Reaction with CH_3I).—**8** (109 mg, 0.33 mmol) in 15 ml of dry benzene was treated with 18 mg of sodium hydride, previously washed with anhydrous benzene, and the solution was allowed to reflux for 10 hr. The reaction mixture, after cooling under a stream of N_2, was treated with 188 mg (2.54 mmol, 8.0 equiv) of methyl iodide and the solution refluxed for another 4 hr. The solution was filtered through a sintered-glass funnel with the aid of *filter gel* and the residue was washed with benzene. The filtrate and the washings were combined and concentrated under reduced pressure. The residue was dissolved in methylene chloride and purified *via* preparative layer chromatogaphy on one 20 × 20 cm plate coated to 1.5 mm thickness to give 102 mg (90%) of **8a**. Crystallization from benzene–petroleum ether furnished colorless needles identical in all respects with the product obtained by irradiation of 1-methyl-5,6,7,8-tetrahydro-2-quinolone and diphenylacetylene at 3500 Å. A small amount of diphenylacetylene was also formed during the alkylation reaction, confirmed by comparison with an authentic sample (tlc).

Hexahydro-3-methyl-4,4a-diphenyl-1H-3,4,4b-methenobenzo-[1,3]cyclopropa[1,2-*b*]pyridin-2(3H)-one (8b).—Pure, dry nitrogen was bubbled through a solution of 1.5 g (9.2 mmol) of 3-methyl-5,6,7,8-tetrahydro-2-quinolone (**6b**) and 7.5 g (42 mmol) diphenylacetylene in 80 ml methanol and 80 ml anhydrous ether for 40 min. The solution was then irradiated (Hanovia) for 48 hr. There was no separation of a solid dimer. The reaction was worked up by preparative layer chromatography (ether eluent) to give 647 mg (20.6%) of desired product **8b**. Crystallization from benzene petroleum ether afforded colorless needles: R_f (ether) = 0.46; mp 228–230°; ir ($CHCl_3$) 1708 (–CONH–), 3408 cm^{-1} (–NH–); nmr ($CDCl_3$) 1.0–2.3 (m, methylene H), 1.33 (s, CH_3) (total area = 11 protons), 2.39 (s, 1, H_a), 6.85–7.5 (m, 10, aromatic H), 7.7 δ (broad singlet, 1, NH).

Anal. Calcd for $C_{24}H_{23}NO$: C, 84.42; H, 6.79; N, 4.10. Found: C, 84.70; H, 7.00; N, 4.04.

Calcd *m/e* for $C_{24}H_{23}NO$: 341. Found: 341.

Fragment peaks at *m/e* 163 (pyridone) and *m/e* 178 (diphenylacetylene) were also observed.

Hexahydro-9-methyl-4,4a-diphenyl-1H-3,4,4b-methenobenzo-[1,3]cyclopropa[1,2-*b*]pyridin-2(3H)-one (8c).—Irradiation of a solution of 1.5 g (9.2 mmol) of 4-methyl-5,6,7,8-tetrahydro-2-quinolone (**6c**) and 7.5 g (42.0 mmol) of diphenylacetylene in 160 ml methanol–ether (1:1) (Hanovia) yielded 425 mg (28.3%) of the dimer. After preparative layer chromatography, 694 mg (22.1%) of the lactam, **8c**, was isolated. The product was crystallized from benzene–petroleum ether to obtain colorless needles: R_f (ether) = 0.40; ir ($CHCl_3$) 1690 (CONH), 3416 cm^{-1} (NH); nmr ($CDCl_3$) 1.1–2.4 (m, methylene H), 1.34 (s, CH_3) (total area = 11 protons), 3.51 (diffuse singlet, 1, H_b); 6.9–7.5 (m, 10, aromatic H), 8.61 δ (broad singlet, 1, NH) (mp 189–190°).

Anal. Calcd for $C_{24}H_{23}NO$: C, 84.42; H, 6.79; N, 4.10. Found: C, 84.66; H, 6.94; N, 4.00.

Calcd *m/e* for $C_{24}H_{23}NO$: 341. Found: 341.

Fragment peaks at *m/e* 163 (pyridone) and *m/e* 178 (diphenylacetylene) were also observed.

Tetrahydro-4,4a-diphenyl-5H-3,4,4b-metheno-1H-cyclopenta-[1,3]cyclopropa[1,2-*b*]pyridin-2(3H)-one (8f).—A solution of 1.35 g (10.0 mmol) of cyclopentano [*e*]-2-pyridone (**6f**) and 7.5 g (42.0 mmol) of diphenylacetylene in 80 ml methanol and 80 ml anhydrous ether was irradiated for 48 hr (Hanovia) to give 865 mg (63.6%) of the dimer and, after preparative layer chromatographic separation, 402 mg (12.8%) of the pentacyclic lactam, **8f** [R_f (ether) = 0.30]. The product was crystallized from benzene–petroleum ether to give colorless needles: mp 158–159°; ir ($CHCl_3$) 1693 (NH–C=O), 3410 cm^{-1} (NH); nmr ($CDCl_3$) 1.5–2.5 (m, 6, methylene H), 2.99 (d, J = 3 Hz, 1, H_a), 3.89 (diffuse doublet, J = 3 Hz, 1, H_b), 6.65–7.5 (m, 10, aromatic H), 8.0 δ (broad singlet, 1, NH).

Anal. Calcd for $C_{22}H_{19}NO$: C, 84.32; H, 6.11; N, 4.47. Found: C, 84.41; H, 6.24; N, 4.33.

Calcd *m/e* for $C_{22}H_{19}NO$: 313. Found: 313.

Fragment peaks at *m/e* 135 (pyridone) and *m/e* 178 (diphenylacetylene) were also present.

Tetrahydro-8-methyl-4,4a-diphenyl-5H-3,4,4b-metheno-1H-cyclopenta[1,3]cyclopropa[1,2-*b*]pyridin-2(3H)-one (8g).—A solution of 1.371 g (9.2 mmol) of 4-methyl-cyclopentano[*e*]-2-pyridone (6 g) and 7.5 g (42.0 mmol) of diphenylacetylene in 160 ml methanol–ether (1:1) was irradiated under nitrogen (Hanovia) for 48 hr to obtain 347 mg (25.3%) of dimer and 1.480 g (49.0%) of the lactam, **8g** (R_f ether = 0.29). Crystallization from benzene–petroleum ether furnished colorless needles: mp 185–186°; ir ($CHCl_3$) 1690 (NHC=O), 3413 cm^{-1} (NH); nmr ($CDCl_3$) 1.5–2.5 (m, methylene H), 1.6 (s, CH_3) (total area = 9 protons), 3.75 (diffuse singlet, 1, H_b), 6.8–7.5 (m, 10, aromatic H), 7.75 δ (broad singlet, 1, NH). Upon treatment with deuterium oxide the signal at 7.75 ppm vanished and the diffuse singlet at 3.75 ppm due to H_b collapsed to a sharp singlet.

Anal. Calcd for $C_{23}H_{21}NO$: C, 84.37; H, 6.46; N, 4.28. Found: C, 84.44; H, 6.55; N, 4.25.

Calcd *m/e* 327. Found: 327.

Hexahydro-1,3-dimethyl-4,4a-diphenyl-1H-3,4,4b-methenobenzo[1,3]-cyclopropa[1,2-*b*]pyridin-2(3H)-one (8d).—A solution of 512.0 mg (1.5 mmol) of pentacyclic lactam (**8b**) and 190 mg (4.5 mmol) of 58% oil dispersion of sodium hydride in 50 ml benzene was refluxed under nitrogen for 8 hr. Methyl iodide was then added and the solution refluxed again for 6 hr. The isolation procedure followed was similar to that used for the preparation of **8a** from **8**. Purification by preparative layer chromatography gave 455.0 mg (86%) of the desired product, **8d**. Crystallization from benzene–petroleum ether afforded colorless needles: mp 228–230°; ir ($CHCl_3$) 1670 cm^{-1} ($CONCH_3$); nmr ($CDCl_3$) 1.0–2.65 (m, methylene H), 1.28 (s, C–CH_3), 2.44 (s, H_a), 3.07 (s, 3, N–CH_3), 6.7–7.5 δ (m, 10, aromatic H).

Anal. Calcd for $C_{25}H_{25}NO$: C, 84.47; H, 7.09; N, 4.50. Found: C, 84.55; H, 7.19; N, 4.38.

Calcd *m/e* 355. Found: 355.

Hexahydro-1,9-dimethyl-4,4a-diphenyl-1H-3,4,4b-methenobenzo[1,3]cyclopropa[1,2-*b*]pyridin-2(3H)-one (8e).—The procedure followed was similar to that described in the preceding experiment. The product was isolated using preparative layer chromatography producing 460 mg (87%) of desired lactam, **8e**. Crystallization from benzene–petroleum ether gave colorless needles: R_f (ether) = 0.51; mp 158–159°; ir ($CHCl_3$) 1669 cm^{-1} ($CONCH_3$); nmr ($CDCl_3$) 1.1–2.4 (m, methylene H), 1.37 (s, C–CH_3), 2.97 (s, 3, N–CH_3), 3.48 (s, 1, H_b), 6.8–7.5 δ (m, 10, aromatic H).

Anal. Calcd for $C_{25}H_{25}NO$: C, 84.47; H, 7.09; N, 4.50. Found: C, 84.63; H, 7.12; N, 4.49.

Calcd *m/e* 355. Found: 355.

5,6,7,8-Tetrahydro-N-methyl-3,4-diphenyl-2-naphthamide (11, R = H).—A solution of 100 mg (0.29 mmol) of the pentacyclic lactam **8a** in 4 ml methanol and 4 ml 6 *N* hydrochloric acid was refluxed under nitrogen for 16 hr. A thin layer check indicated complete disappearance of starting material and appearance of a new, faster moving product [R_f (ether) = 0.61]. Refluxing was discontinued and the solution taken to dryness under reduced pressure by repeatedly adding benzene and evaporating. Purification *via* preparative layer chromatography on a 20 × 20 cm plate coated to 1.5 mm thickness gave 58 mg (58%) of **11**. The analytical sample was obtained by crystallization from benzene–petroleum ether as colorless needles: mp 199–202°; ir ($CHCl_3$) 1648 (–CONH–), 3440 cm^{-1} (–NH–); nmr ($CDCl_3$) 1.5–1.9 (m, 4, methylene H), 2.3–2.8 (m, 4, benzylic H), 2.5 (d, J = 5 Hz, 3, N–CH_3), 5.12 (broad singlet, 1, NH), 7.10–7.6 δ (m, 11, aromatic H). Upon treatment with deuterium oxide the signal at 5.12 vanished and the doublet at 2.5 collapsed to a singlet. Furthermore, irradiation of the NH signal at 5.12 ppm lead to the collapse of the doublet at 2.5 ppm to a singlet: uv (cyclohexane) λ_{max} 230 mμ.

Calcd *m/e* for $C_{24}H_{23}NO$: 341. Found: (70 eV) 341.

Calcd *precise m/e* for $C_{24}H_{23}NO$: 341.17796. Found: 341.17756.

Anal. Calcd for $C_{24}H_{23}NO$: C, 84.42; H, 6.79. Found: C, 84.22; H, 6.40.

5,6,7,8-Tetrahydro-N,1-dimethyl-3,4-diphenyl-2-naphthamide (11, R = Me). A. From 8e.—The procedure followed was similar to that used for the preparation of **11** (R = H). A solution of 97 mg (0.27 mmol) of the pentacyclic lactam, **8e**, in 3 ml methanol and 3 ml 6 *N* hydrochloric acid was refluxed under nitrogen for 12 hr. Work-up of the reaction mixture *via* preparative layer chromatography afforded 45 mg (47%) of the desired product, **11** (R = Me). Crystallization from benzene–petroleum ether gave colorless needles: R_f (ether) = 0.82; mp 233–234°; ir ($CHCl_3$) 1653 (CONH), 3440 cm^{-1} (NH); nmr ($CDCl_3$) 1.2–1.9 (m, methylene H), 1.98 (s, C–CH_3), 2.2–2.8 (m, benzylic H), 2.51 (d, J = 5 Hz, N–CH_3), 5.25 (broad singlet, 1, NH), 7.0–7.7 δ (m, 10, aromatic H).

Anal. Calcd for $C_{25}H_{25}NO$: C, 84.47; H, 7.09. Found: C, 84.31; H, 7.26.

Calcd *m/e* 355. Found: 355.

In addition to **11**, 35 mg (36%) of an unidentified product (R_f ether = 0.67) and a small amount of diphenylacetylene was also detected by tlc.

B. From 8d.—The procedure followed was similar to the procedure employed for the preparation of **11** (R = H). A solution of 97 mg (0.27 mmol) of pentacyclic lactam, **8d**, in 6 ml methanol and 3 ml 6 *N* hydrochloric acid was refluxed in an oil bath under nitrogen and the reaction monitored by tlc. It was found that even after heating for 82 hr, some **8d** was still present. The reaction mixture was worked up as usual to give 27 mg (28%) of **11** (R = Me). Crystallization from benzene–petroleum ether gave colorless needles, mp 233–234°. A mixture mp with the product obtained from **8e** was undepressed, and the two infrared spectra were superimposable. An abundant amount of diphenylacetylene was also formed in the reaction indicating reversal of the product to pyridone.

4,5,6,7,8,8b-Hexahydro-1,2-diphenylcyclobuta[*c*]quinolin-3(2aH)-one (16). A. From Irradiation of 8 at 2537 Å.—A solution of 290 mg (0.89 mmol) hexahydro-4,4a-diphenyl-1H-3,4,4b-methenobenzo[1,3]cyclopropa[1,2-*b*]pyridin-2(3H)-one (**8**) in 60 ml benzene was irradiated in a quartz tube under nitrogen at 2537Å in an air cooled Rayonet reactor. Irradiation was stopped after 3.75 hr and the product worked up by preparative layer chromatography to give 135 mg (47%; 60% based on unrecovered pentacyclic lactam **8**) of the cyclobutene derivative, **16**. Crystallization from benzene–petroleum ether furnished colorless needles (R_f ether = 0.68): mp 167–169°; ir ($CHCl_3$) 1655 (C=C–NH·CO), 3990 cm^{-1} (NH); nmr ($CDCl_3$) 1.2–2.4 (m, 8, methylene H), 3.74 (diffuse doublet, J = 5 Hz, 1, H_a), 4.02 (d, J = 5 Hz, 1, H_b), 7.1–8.0 δ (m, 11, aromatic **H** and **NH**). Upon treatment with deuterium oxide the NH proton exchanged and signals at 7.1–8.0 ppm integrated to 10 protons only: uv max (EtOH) 226 (log ε 4.36), 266 (4.14), 288 mμ (sh) (4.08).

Anal. Calcd for $C_{23}H_{21}NO$: C, 84.36; H, 6.48; N, 4.28. Found: C, 84.50; H, 6.31; N, 4.25.

Calcd *m/e* 327. Found: 327.

Fragment peaks at *m, e* 149 (pyridone) and *m, e* 178 (diphenylacetylene) were also seen. The minor product in this reaction was obtained in trace amounts and was not characterized further.

B. From Pyridone 6 and Diphenylacetylene.—Irradiation of a mixture of 1.0 g (6.7 mmol) 5,6,7,8-tetrahydro-2-quinolone and 2.5 g (14.0 mmol) diphenylacetylene as described previously, afforded (tlc) 35 mg (1.5%) of cyclobutene derivative (**16**). The product was crystallized from benzene–petroleum ether and was identical with that obtained by irradiation of hexahydro-4,4a-diphenyl-1H-3,4,4b-methenobenzo[1,3]cyclopropa[1,2-*b*]pyridin-2(3H)-one (**8**) at 2537 Å.

4,5,6,7,8,8b-Hexahydro-4-methyl-1,2-diphenylcyclobuta[*c*]quinolin-3(2aH)-one (16a). A. From Irradiation at 2537 Å.—Irradiation of a solution of 300 mg (0.88 mmol) of hexahydro-1-methyl-4,4a-diphenyl-1H-3,4,4b-methenobenzo[1,3]cyclopropa[1,2-*b*]pyridin-2(3H)-one (**8a**) in 60 ml benzene in a quartz tube under nitrogen at 2537 Å for 10 hr followed by work-up *via* preparative layer chromatography afforded 110 mg (37%) of the cyclobutene derivative **16a** (R_f ether = 0.78). Crystallization from benzene–petroleum ether furnished colorless needles: mp 120–122°; ir ($CHCl_3$) 1635 cm^{-1} (–N–C=O); nmr ($CDCl_3$) 1.2–2.4 (m, 8, methylene H), 3.12 (s, 3, N–CH_3), 3.63 (diffuse doublet, half band width ≅ 5 Hz, J = 5 Hz, 1, H_a), 4.04 (d, J = 5 Hz, 1, H_b), 7.1–8.0 δ (m, 10, aromatic H); spin decoupling of the signals at 2.22 led to the collapse of diffuse doublet at 3.63 ppm to a true doublet, J = 5 Hz; uv max (EtOH) 226 (log ε 4.32), 268 (4.11), 292 sh (432).

Anal. Calcd for $C_{24}H_{23}NO$: C, 84.42; H, 6.79. Found: C, 84.69; H, 6.99.

Calcd *m/e* 341. Found: 341.

Fragment peaks at *m/e* 163 (pyridone) and *m/e* 178 (diphenylacetylene) were also observed.

B. From Pyridone 6a and Diphenylacetylene.—Irradiation of a mixture of 1.0 g (6.1 mmol) of pyridone **6a** and 2.5 g (14.0 mmol) of diphenylacetylene as described previously, gave the cyclobutene derivative, **16a**, in trace amounts as seen *via* tlc. The amount was too small to isolate. Comparison (tlc) of this product with that obtained from A confirmed their identity.

4,5,6,7,8,8b-Hexahydro-2a-methyl-1,2-diphenylcyclobuta[*c*]quinolin-3(2aH)-one (16b). A. From Irradiation at 2537 Å.—A solution of 110 mg (0.32 mmol) of **8b** in 25 ml dry benzene was irradiated at 2537Å for 6 hr and the product **16b** isolated *via* preparative layer chromatography in 64% yield (R_f ether = 0.80). Crystallization from benzene–petroleum ether gave colorless needles: mp 234–236° dec; ir ($CHCl_3$) 1655 (C=C–NH–C=O), 3388 cm^{-1} (NH); nmr ($CDCl_3$) 1.2–2.5 (m, methylene H), 1.67 (s, C–CH_3) (total area = 11 protons), 3.33 (diffuse singlet, 1, H_a), 7.15–8.0 δ (m, 11, aromatic H and NH); uv max (EtOH) 228 (log ε 4.59), 287 mμ (4.22).

Anal. Calcd for $C_{24}H_{23}NO$: C, 84.42; H, 6.79. Found: C, 84.55; H, 6.84.

Calcd *m/e* 341. Found: 341.

Fragment peaks at *m/e* 163 (pyridone) and *m/e* 178 (diphenylacetyl) were also observed.

B. From Pyridone 6b and Diphenylacetylene.—Irradiation of a mixture of 1.5 g (9.2 mmol) of pyridone **6b** and 7.5 g (42.0 mmol) of diphenylacetylene with a 200-W high pressure Hanovia lamp as described before furnished 200 mg (6.6%) of the cyclobutene derivative. The product was identical with that obtained by 2537-Å irradiation of the pentacyclic lactam, **8b**, as determined by mixture melting point, ir, and nmr.

4,5,6,7,8,8b-Hexahydro-8b-methyl-1,2-diphenylcyclobuta[*c*]quinolin-3(2aH)-one (16c). A.—A solution of 100 mg (0.29 mmol) of **8c** in 20 ml of benzene was irradiated for 5.5 hr at 2537 Å; the product (**16c**) was isolated *via* preparative layer chromatography (R_f ether = 0.84) in 62% yield (62 mg). Crystallization from benzene–petroleum ether gave colorless needles: mp 205–207° dec; ir ($CHCl_3$) 1660 (C=C·NH·C=O), 3388 cm^{-1} (NH); nmr ($CDCl_3$) 1.2–2.3 (m, methylene H), 1.5 (s, CH_3) total area = 11 protons), 3.58 (s, 1, H_b), 7.05–7.9 δ (m, 11, aromatic H and NH); uv max (EtOH) 230 (sh) (log ε 4.39), 260 mμ (4.19).

Anal. Calcd for $C_{24}H_{23}NO$: C, 84.42; H, 6.79. Found: C, 84.67; H, 7.07.

Calcd *m/e* 341. Found: 341.

Fragment peaks at *m/e* 163 (pyridone) and *m/e* 178 (diphenylacetylene) were also observed.

B. From Pyridone 6c and Diphenylacetylene.—Irradiation of a mixture of 1.5 g (9.2 mmol) of pyridone **6c** and 7.5 g (42.0 mmol) of diphenylacetylene as described previously, gave 210 mg (6.7%) of the cyclobutene derivative, **16c**. The product was

identical with that obtained by 2537-Å photolysis of the pentacyclic lactam, **8c**.

2a,4,5,6,7,7b-Hexahydro-1,2-diphenyl-3H-cyclobuta[*d*]cyclopenta[*b*]pyridin-3-one (16f).—Irradiation of a mixture of 1.359 g (10.0 mmol) of the pyridone **6f** and 7.5 g (42.0 mmol) of diphenylacetylene as described above gave, in addition to **8f**, 275 mg (8.7%) of cyclobutene derivative, **16f** (R_f ether = 0.65). The product was crystallized from benzene–petroleum ether producing colorless needles: mp 184–186° dec; ir ($CHCl_3$) 1663 (C=C·NH·C=O), 3398 cm^{-1} (NH); nmr ($CDCl_3$) 1.6–2.6 (m, 6, methylene H), 3.88 (diffuse doublet J = 6 Hz, 1, H_a), 4.02 (d, J = 5 Hz, 1, H_b), 7.0–8.0 δ (m, 11, aromatic H and NH); uv max (EtOH) 224 (log ε 4.45), 277 mμ (4.08).

Anal. Calcd for $C_{22}H_{19}NO$: C, 84.31; H, 6.11. Found: C, 84.45; H, 6.36.

Calcd *m/e* 313. Found: 313.

Fragment peaks at *m/e* 135 (pyridone) and *m/e* 178 (diphenylacetylene were also observed. No attempt was made to obtain this product from the photoisomerization of **8f**.

2a,4,5,6,7,7b-Hexahydro-7b-methyl-1,2-diphenyl-3H-cyclobuta[*d*]cyclopenta[*b*]pyridin-3-one (16g).—Irradiation of a mixture of 1.371 g (9.2 mmol) of 4-methylcyclopentano-[*e*]-2-pyridone (**6g**) and 7.5 g (42.0 mmol) of diphenylacetylene as described before gave, in addition to other products, 400 mg (13.3%) of the cyclobutene derivative (**16g**) (R_f ether = 0.75). Crystallization from benzene–petroleum ether furnished colorless needles: mp 202–203°; ir ($CHCl_3$) 1661 (C=C·NH·C=O), 3398 cm^{-1} (NH); nmr ($CDCl_3$) 1.3–2.7 (m, methylene H), 1.5 (s, CH_3), 3.58 (s, 1, H_b), 7.0–7.85 (m, 10, aromatic H), 8.05 δ (broad singlet, 1, NH); uv max (EtOH) 225 (log ε 4.37), 263 mμ (4.17).

Anal. Calcd for $C_{23}H_{21}NO$: C, 84.37; H, 6.46. Found: C, 84.51; H, 6.60.

Calcd *m/e* 327. Found: 327.

Fragment peaks at *m/e* 149 (pyridone) and *m/e* 178 (diphenylacetylene) were also observed.

Stability of 8 at 3500 Å.—A solution of 10 mg (0.03 mmol) of pentacyclic lactam, **8**, in 20 ml of methanol was irradiated under nitrogen at 3500 Å and the reaction monitored by tlc at various intervals. After 100 hr no spot corresponding to the cyclobutenopyridone, **16**, was detected.

Photoisomerization of 8 to 16 in Methanol–Ether at 2537 Å.—A solution of 10 mg (0.03 mmol) of the pentacyclic lactam (**8**) in 2 ml of methanol and 2 ml of anhydrous ether was irradiated at 2537 Å and the reaction followed by tlc. After 12 hr, it was found that isomerization to the cyclobutenopyridone, **16**, had taken place.

Irradiation of the Pyridone (6) and Diphenylacetylene in Methanol–Ether at 2537 Å.—A solution of 300 mg (2.0 mmol) of 5,6,7,8-tetrahydro-2-quinolone (**6**) and 750 mg (4.2 mmol) of diphenylacetylene in 8 ml of MeOH and 8 ml of Et_2O was irradiated at 2537 Å for 12 hr. A tlc examination revealed that a minute trace of the pentacyclic lactam, (**8**), was present but no spot due to cyclobutenopyridone (**16**), could be detected.

Irradiation of the Pyridone (6) and Diphenylacetylene in Benzene at 2537 Å.—Irradiation of a solution of 100 mg (0.67 mmol) of **6** and 119.3 mg (0.67 mmol) of diphenylacetylene in 10 ml of benzene at 2537 Å for 4 hr followed by an examination by tlc revealed that a trace of cyclobutenopyridone, **16**, was present but no spot corresponding to the pentacyclic lactam, **8**, was visible.

Photostability of 16 at 2537 Å.—A solution of 13 mg (0.04 mmol) of cyclobutenopyridone (**16**) in 3 ml of benzene was irradiated at 2537 Å and the reaction checked by tlc after 6 and 17 hr. It was found that some decomposition had taken place as shown by streaking on the plate but the predominant spot was due to unchanged **16**.

Photostability of 16 at 3500 Å.—A solution of 27 mg (0.08 mmol) of cyclobutenopyridone (**16**) in 15 ml of methanol was irradiated for 16 hr and the reaction followed by tlc. It was found that some decomposition had taken place but no spots corresponding to new products were seen on the tlc plate.

Registry No.—Diphenylacetylene, 501-65-5; **6a**, 25183-42-0; **7**, 25183-43-1; **8**, 20670-50-2; **8a**, 20199-81-9; **8b**, 25183-46-4; **8c**, 25183-47-5; **8d**, 25183-48-6; **8e**, 25183-49-7; **8f**, 25183-50-0; **8g**, 25183-51-1; **11**, R = H, 19734-36-2; **11**, R = Me, 25183-53-3; **16**, 20177-91-7; **16a**, 20177-92-8; **16b**, 25183-56-6; **16c**, 25183-57-7; **16f**, 25183-58-8; **16g**, 25184-11-6.

Alkylation Reactions of 2-Fluoro-2,2-dinitroethanol[1]

VYTAUTAS GRAKAUSKAS

Environmental Systems Division, Aerojet-General Corporation, Azusa, California 91702

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2-Fluoro-2,2-dinitroethanol in aqueous alkali reacted with dimethyl sulfate, allyl bromide, acetic anhydride, ethyl chloroformate, and oxalyl chloride yielding 2-fluoro-2,2-dinitroethyl methyl ether, allyl 2-fluoro-2,2-dinitroethyl ether, 2-fluoro-2,2-dinitroethyl acetate, ethyl 2-fluoro-2,2-dinitroethyl carbonate, and 2-fluoro-2,2-dinitroethyl oxalyl chloride, respectively. Ethylene oxide, propylene oxide, epihalohydrins, and butadiene dioxide yielded 2-fluoro-2,2-dinitroethyl 2-hydroxyethyl ether, 2-fluoro-2,2-dinitroethyl 2-hydroxylpropyl ether, 2-fluoro-2,2-dinitroethyl glycidyl ether, and 4-(2-fluoro-2,2-dinitroethoxy)-3-hydroxybutene 1,2-oxide, respectively. Pyridine-catalyzed reactions of 2-fluoro-2,2-dinitroethanol with thionyl chloride and sulfuryl chloride gave bis(2-fluoro-2,2-dinitroethyl) sulfite and 2-fluoro-2,2-dinitroethyl chloride, respectively. Tris(2-fluoro-2,2-dinitroethyl) borate was obtained in the ester-exchange reaction. Reactions of 2-fluoro-2,2-dinitroethyl 2-hydroxyethyl ether, 2-fluoro-2,2-dinitroethyl 2-hydroxypropyl ether, and 2-fluoro-2,2-dinitroethyl oxalyl chloride were investigated.

Although the synthesis of 2-fluoro-2,2-dinitroethanol was only recently reported,[2,3] the reactions of this unusual polynitro alcohol have been already explored by several groups of investigators.[2-6] 2-Fluoro-2,2-dinitroethanol undergoes deformylation in aqueous alkaline solutions in a manner similar to other 2,2-dinitro alcohols,[7] but unlike the other polynitro alcohols 2-fluoro-2,2-dinitroethanol in basic medium may also exist in equilibrium with its alkoxide ions. The dissociation to alkoxide ions, attributed to the reported

$$FC(NO_2)_2CH_2OH \overset{OH^-}{\rightleftharpoons} FC(NO_2)_2CH_2O^- \rightleftharpoons FC(NO_2)_2^- + CH_2O$$

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