

IV) column with pentane-ether- CH_2Cl_2 as eluent. Ketone **37** was purified further by column chromatography using a neutral alumina (activity I/II) column with pentane as eluent to give 109 mg (20%) of **37**: $\geq 99\%$ pure (by GLC; DEGS, 140°C); ^{13}C NMR, ^1H NMR, IR, and mass spectra of the product were identical with those of the ketone obtained by cyclization of **35** with NaH in THF. Evaporation of CH_2Cl_2 yielded crude 1-hydroxy-2-oxadamantane (**38a**), which was combined with the alcohol obtained from the ether extracts and sublimed in vacuo to give 67 mg (10%) of **38a**: $\geq 97\%$ pure (by GLC; DEGS, 150°C); ^{13}C NMR (CDCl_3), see text; ^1H NMR (CDCl_3), see text; IR (KBr) 3280 (s), 2900 (s), 1180 (m), 980 (m), 960 (m) cm^{-1} ; mass spectrum, m/e (relative intensity) 154 (M^+ , 57), 95 (56), 94 (100), 86 (59), 79 (74), 69 (64), 67 (61).

Acknowledgment. This work was supported by a grant from the Research Council of the Republic of Croatia (SIZ II). We thank Professor V. J. Shiner, Jr., for critical reading of the manuscript.

Registry No. **14a**, 35128-58-6; **14b**, 73683-14-4; **20**, 50529-96-9; **23**, 73683-17-7; **24a**, 57234-55-6; **24b**, 74987-37-4; **26**, 74987-38-5; **30**, 74987-39-6; **34a**, 67403-70-7; **34b**, 74987-40-9; *exo*-**35**, 74998-58-6; **37**, 74987-41-0; **38a**, 2879-40-5; **38b**, 2859-74-7; 4-homobrendane, 49700-65-4; 4-homobrendan-4'-one, 50529-80-1; 2-homobrendane, 42836-61-3; 2-methyl-2-adamantanol, 702-98-7; 7-chlorobicyclo[3.3.1]non-3-yl methyl ketone, 29844-79-9; 3-noradamantyl methyl ketone, 29844-80-2; 3-noradamantyl acetate, 74987-42-1; tricyclo[3.3.1.0^{2,7}]nonane, 766-67-6.

Cycloaddition Reaction of Dimethyl Acetylenedicarboxylate with 2,4,5-Triphenyl-3H-pyrrol-3-one 1-Oxide

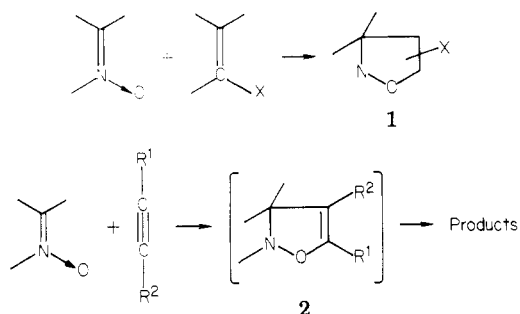
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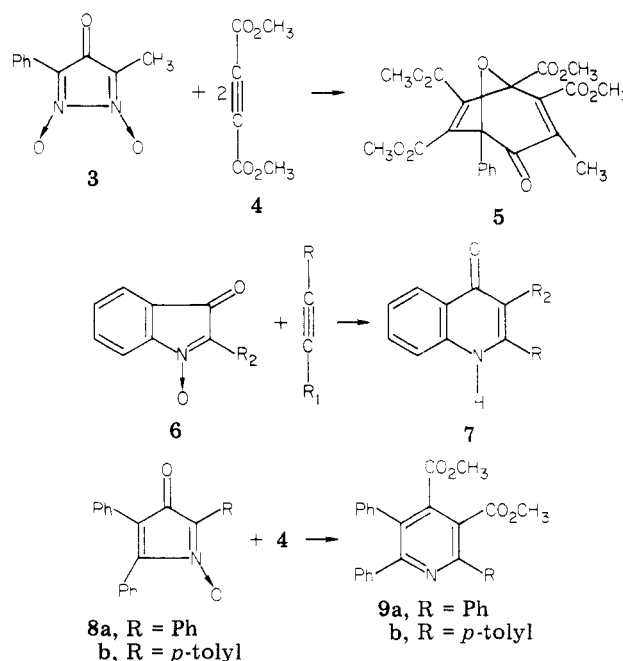
Received July 1, 1980

The reaction of 2,4,5-triphenyl-3H-pyrrol-3-one 1-oxide with dimethyl acetylenedicarboxylate gave pyridine **9a**, 4(3H)-pyridone **10a**, isoxazolidine **11**, and traces of pyridone **13**. Pyridone **10a** is not an intermediate in the formation of **9a**, yet on photolysis or pyrolysis above its melting point, **10a** yielded pyridine **9a**. Possible reaction mechanisms that rationalize the formation of these products are discussed.

The cycloaddition reaction of nitrones with dipolarphiles is recognized as the most versatile method for the synthesis of isoxazolidines **1**.¹ On the other hand, the corresponding reaction with acetylene derivatives usually gives products that result from the rearrangement of the expected Δ^4 -isoxazoline **2**. For example, Freeman and Hoare² found



that the reaction of 3,4-diazacyclopentadienone 3,4-dioxide **3** with dimethyl acetylenedicarboxylate (DMAD), **4**, involved 2 mol of the latter to give the bicyclo[3.2.1] system **5**. Noland and co-workers³ reported the ring expansion of 2-phenylisatogen **6** into 4-quinolinone derivatives **7**. Recently, Jones and Sadighi⁴ described the reaction of 2,4,5-triphenyl-3H-pyrrol-3-one 1-oxide (**8a**) with DMAD to give pyridine **9a** as a "single product in high yield". Although each of the above *N*-oxides has a nitrone functional group, it is clear that they follow different pathways with acetylene derivatives.



As part of our interest in cycloaddition reactions,² we examined the reaction of **8a** with DMAD in some detail. Indeed, heating of a chloroform solution⁴ of **8a** with **4** resulted in the gradual disappearance of the violet color of **8a**. Workup and separation of the components of the reaction residue gave **9a**, identical with that reported by Jones and Sadighi⁴ and with that prepared by Eicher and co-workers⁵ (vide infra), and **10a**, **11a**/**12a**, and **13a**.

The formation of pyridone **13** is analogous to that of the quinolinones reported from isatogens and acetylenes;³

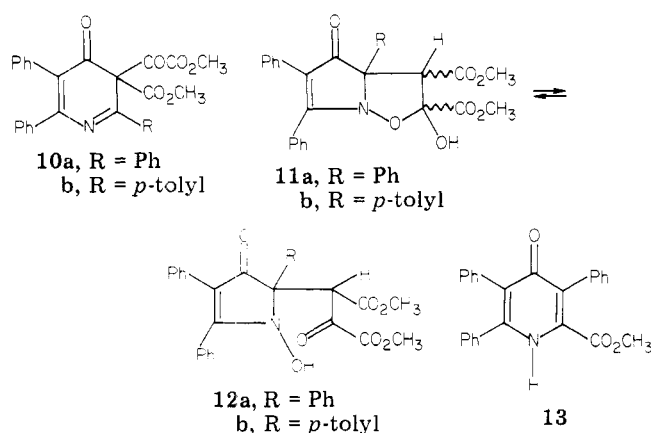
(1) (a) Black, D. St. C.; Crozier, R. F.; Davis, V. S. *Synthesis* **1975**, 205-221. (b) Takeuchi, Y.; Furusaki, F. *Adv. Heterocycl. Chem.* **1977**, **21**, 210-251.

(2) Freeman, J. P.; Hoare, M. J. *J. Org. Chem.* **1971**, **36**, 19-23.

(3) Noland, W. E.; Modler, R. J. *J. Am. Chem. Soc.* **1964**, **86**, 2086-2087.

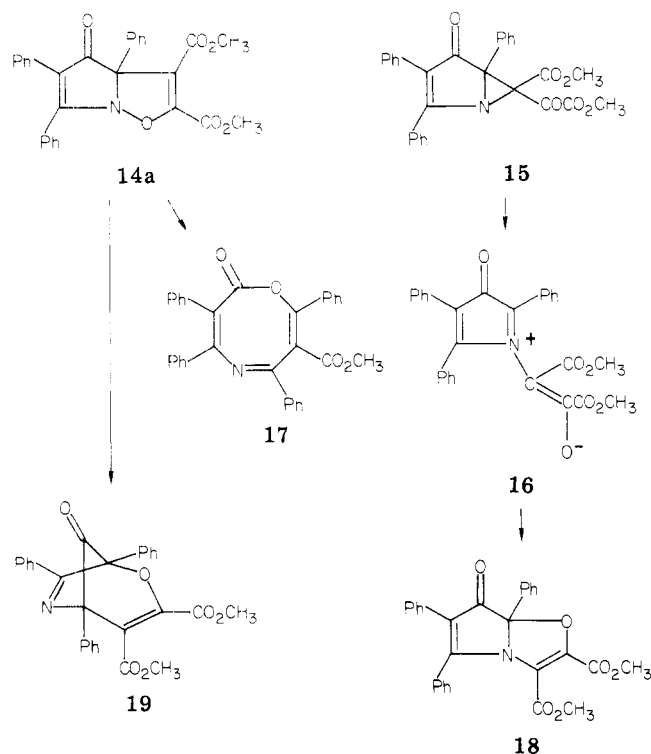
(4) Jones, R. A. Y.; Sadighi, N. J. *Chem. Soc., Perkin Trans. 1* **1976**, 2259-2264.

(5) Eicher, Th.; Abdesaken, F.; Franke, G.; Weber, J. L. *Tetrahedron Lett.* **1975**, 3915-3918.



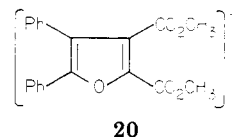
structure 13 was confirmed by spectroscopic and mass spectral data. Adduct 11a exists in equilibrium with 12a, probably as a mixture of diastereomers. Mixture 11a/12a did not melt sharply, and the crystalline form and the composition of the mixture as evidenced by its infrared and NMR spectra varied with solvent.⁶ Mixture 11a/12a reverted partially to pyrrolone oxide 8a on melting (160–165 °C). As 12a is a vinyllogous hydroxamic acid, the mixture dissolves in aqueous base and gives a positive ferric chloride test.

The structure of 10a was not easy to establish. Mechanistic considerations suggested that 10a might be one of the valence isomers 14–19. The formation of products or intermediates analogous to 15, 16, 18, and 19 has been reported.^{2,7}



The infrared spectrum of 10a showed strong carbonyl bands at 1745 and 1708 cm⁻¹ and a medium band at 1645 cm⁻¹. The ¹H NMR spectrum displayed, in addition to the two ester methyl singlets and the aromatic protons, a re-

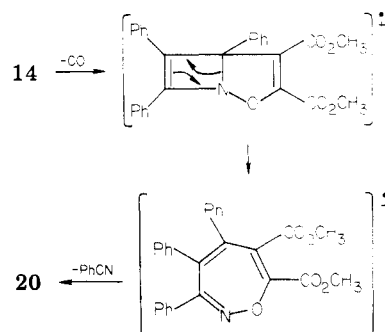
markably deshielded multiplet at δ 8.6–8.7 (2 H). Those two protons may be assigned to the ortho protons of a phenyl ring conjugated to a C=N function in analogy to similar deshielding effects reported in the literature.⁸ The mass spectrum of 10a showed strong peaks at m/e 467 (M⁺), 449 (M⁺ - 28), 336 (M⁺ - 28 - 103). The latter mass ion, the base peak, is assigned structure 20, derived from 10a by loss of carbon monoxide and benzonitrile.



The ¹³C NMR spectrum of 10a contains one small but persistent peak (except for the ester methyl peaks) at higher field than δ 100 and five signals between δ 150–200. This spectrum can best be accommodated by structure 10a which has four carbonyl carbons and an imine carbon in addition to one quaternary carbon.

On the basis of these data structures 14a–19 appear to be ruled out. Compounds 14a, 15, and 18 would not be expected to show the low-field multiplet for two ortho protons nor do they or 19, the product that might have been anticipated on the basis of the conversion of 3 to 5,² fit the ¹³C NMR spectrum. Compounds 15, 16, and 18 could not produce ion 20.

Although the known chemical instability^{2,3,7,9} of cyclo-adducts analogous to 14 and the ¹H and ¹³C NMR spectra do not support this structure, we examined the possibility that structure 14a could yield ion 20 via the fragmentation pattern shown in which the benzonitrile is derived from a phenyl group of the pyrrolone ring rather than that at the ring junction.



To determine the origin of this phenyl group we prepared 10b from 8b by the same method. The NMR spectrum of 10b showed a doublet centered at δ 8.55 (2 H, J = 8 Hz) which must arise from the *p*-tolyl group. The deshielded protons in 10a then must be the ortho protons of the phenyl ring originally attached to the nitrone function of 8a. Moreover, the mass spectrum of 10b showed a strong peak at m/e 336 (ion 20) which would not be expected of structure 14b. This experiment also rules out structure 19 since the *p*-tolyl group would be at a bridgehead in that structure.

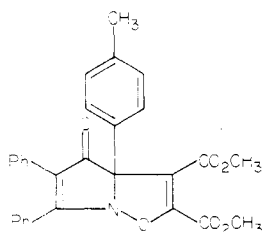
Structure 17 deserves special comment. It is easy to rationalize the mass spectral and ¹H NMR data on the basis of this structure as well as the conversion to pyridine 9a and CO₂ upon heating or irradiation. However, it lacks a carbon atom to which the signal at δ 69 can be attributed,

(6) A similar product was obtained from the reaction of 2-phenylisatogen with DMAD: D. A. Jones, Ph.D. Thesis, University of Minnesota, 1961; R. F. Modler, Ph.D. Thesis, University of Minnesota, 1965.

(7) Baldwin, J. E.; Pudussery, R. G.; Qureshi, A. K.; Sklarz, B. *J. Am. Chem. Soc.* 1968, 90, 5325–5326. Seidl, H.; Huisgen, R.; Knorr, R. *Chem. Ber.* 1969, 102, 904–914.

(8) Berti, C.; Colonna, M.; Greci, L.; Marchetti, L. *Tetrahedron* 1975, 31, 1745–1753, fnt p 1746. (b) Berti, C.; Greci, L.; Marchetti, L. *J. Chem. Soc., Perkin Trans. 2* 1979, 233–236. (c) Acheson, R. M.; Wallis, J. D.; Woollard, J. *J. Chem. Soc., Perkin Trans. 1* 1979, 584–590.

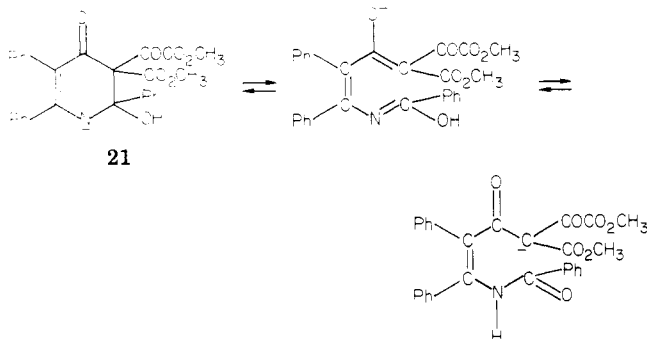
(9) Niklas, K. J. Ph.D. Thesis, University of Munich, 1975, p 16–20.



14b

although lack of suitable models makes this judgment somewhat arbitrary. What is most unsatisfactory about this structure, which the British authors⁴ had originally suggested as an unisolated precursor to the pyridine **9a**, is the behavior of this product in alkaline solution (vide infra). It would be expected that **17** would dissolve in alcoholic base by hydrolysis of the enol lactone, but it is hard to envision recyclization upon acidification.

Elimination of possible structures **14a**–**19** leaves structure **10a**, which is consistent with the infrared, ¹H and ¹³C NMR, and mass spectral data. Some chemical properties of **10a** also seem more consistent with the pyridone structure than do those of any of the other isomers. It dissolves in dilute alcoholic base from which it can be recovered upon acidification. This treatment provides the best method of separating **10a** from pyridine **9a**. Presumably this reaction involves addition of hydroxide ion to the imine function to provide delocalized ion **21** and possibly its open-chain tautomers. (Prolonged exposure to base or higher temperatures caused decomposition of **10a** but no products were identified.)



21

Compound **10a** is stable at its melting point (171–172 °C) but starts to decompose above 185 °C to finally yield pyridine **9a** and carbon dioxide. Photolysis of **10a** in methanol with sunlight also yielded **9a**. However, **10a** was recovered unchanged on prolonged treatment under the original cycloaddition reaction conditions (refluxing chloroform) and therefore cannot be an intermediate in the formation of **9a** from the reaction of **8a** and DMAD.

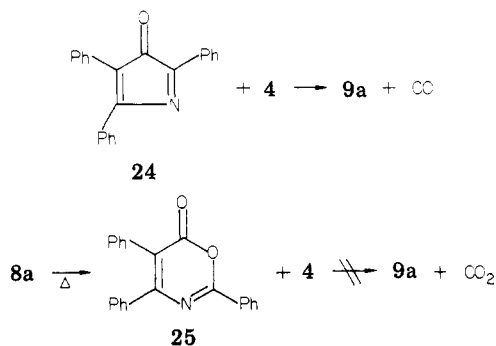
We propose that products **9**–**13** result from the common cycloaddition intermediate **14** (Scheme I). This reaction path is consistent with the fact that the reaction of **8a** + **4** is accompanied by the gradual evolution of carbon dioxide (monitored by its infrared band at 2338 cm⁻¹) and the formation of **9a** and **10a** in almost equal amounts. The path from **14** to **9a** and **10a** is highly speculative but the closure of **22** to **23** is analogous to that proposed for the formation of 2,3-diphenylbenzofuran from (*o*-(benzoyloxy)phenyl)phenylketene,¹⁰ and the closure of **22** to **10a** has precedent in proposals for closely related systems.¹¹

(10) Freeman, J. P.; Grabiak, R. C. *J. Org. Chem.* **1976**, *41*, 2531–2535.

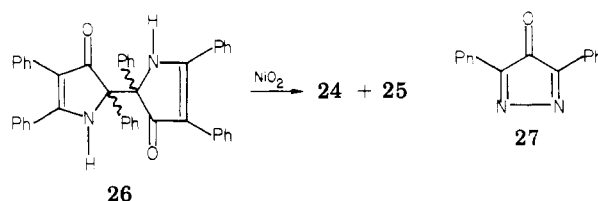
(11) Grigg, R.; Hayes, R.; Jackson, J. L.; King, T. J. *J. Chem. Soc., Chem. Commun.* **1973**, 349. Chaloupka, S.; Heimgartner, H. *Chimia* **1978**, *32*, 468–470. Potts, K. T.; Elliott, A. J.; Sorm, M. *J. Org. Chem.* **1972**, *37*, 3838–3845. The latter authors obtained carbocyclic analogues of **9a** and **10c** by thermal isomerization of an 8-oxabicyclo[3.2.1]octadienone system, a carbologue of the bicyclo[3.3.0] system of **14**.

Cis elimination¹² of carbon dioxide to give **9a** is a thermally allowed electrocyclic reaction of **23**. The thermal and photochemical conversion of **10a** to **9a** is believed to occur by way of intermediate **22** with which **10a** can equilibrate by an allowed electrocyclic process. Under the influence of heat or light the conversion of **22** to **10a** is reversible but the conversion of **22** to **9a** (by way of **23**) is irreversible, allowing the complete conversion of **10a** to **9a**.

The possibility that **9a** arose from Diels–Alder reactions of pyrrolone **24** (formed in some prior deoxygenation process) and/or oxazinone **25**¹³ (a rearrangement product of **8a**) and DMAD was considered and dismissed since the reaction of **24** and DMAD gave **9a**⁵ at a much slower rate than that of **8a** and DMAD, and oxazinone **25** failed to react with DMAD. Also no carbon monoxide, required of the former reaction, was detected.



Eicher and co-workers⁵ briefly described the generation of **24** (presumably in low concentration in solution) and its trapping with DMAD to give pyridine **9a**. The dark-violet pyrrolone **24** (IR 1710 cm⁻¹) can be conveniently generated in a CH₂Cl₂ solution at room temperature along with oxazinone **25** through the oxidation of dimer **26**¹⁴ with nickel peroxide. Pyrrolone **24** is unstable and all attempts



to isolate it in the solid state failed. However, it is quite stable in CH₂Cl₂ solution at room temperature over a period of at least 2 months. Although the major product of the oxidation is oxazinone **25**, the relative inertness of this compound combined with the ease with which this method provides **24** renders it the synthetic method of choice. The instability of **24** is similar to that of the pyrazolone **27**.¹⁵

Experimental Section

Melting points were determined on a Mel-Temp apparatus and are uncorrected. Infrared spectra were measured with a Per-

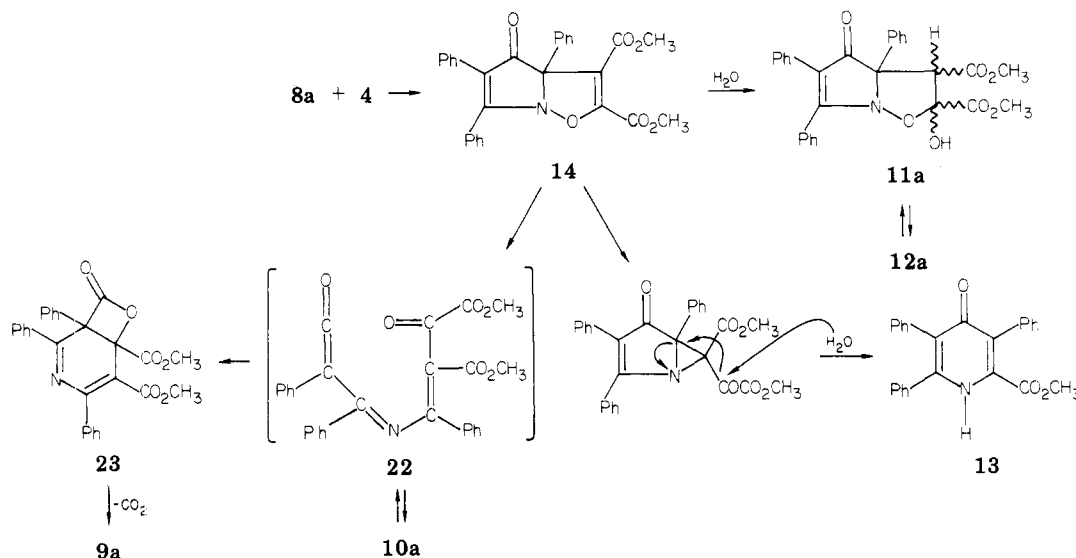
(12) Mageswaran, S.; Sultanabawa, M. U. S. *J. Chem. Soc., Perkin Trans. 1*, **1976**, 884–890.

(13) We observed that pyrrolone oxide **8a** slowly rearranged to oxazinone **27** when refluxed in toluene or more rapidly in triglyme. Since the rate of this rearrangement was not accelerated by carbonyl compounds, it is probable that the reported⁴ formation of the oxazinone **27** from **8a** and certain carbonyl compounds was due, in fact, simply to a thermal rearrangement.

(14) Freeman, J. P.; Haddadin, M. J. *Tetrahedron Lett.* **1979**, 4813–4816.

(15) Fagan, P. J.; Neidert, E. E.; Nye, M. J.; O'Hare, M. J.; Tang, W.-P. *Can. J. Chem.* **1979**, *57*, 904–912.

Scheme I



kin-Elmer 457 grating spectrophotometer. ¹H NMR spectra were measured on a Varian A-60 instrument in CDCl₃ with Me₄Si as internal standard. Mass spectral measurements were done on AEI 902 and/or DuPont DP-102 spectrometers at 70 eV. ¹³C NMR spectra were determined on a Varian XL-100 spectrometer.

Reaction of 2,4,5-Triphenyl-3H-pyrrol-3-one 1-Oxide (8a) with Dimethyl Acetylenedicarboxylate. Pyrrolone 1-oxide 8a (1.62 g) was dissolved in 15 mL of CHCl₃ and dimethyl acetylenedicarboxylate (4, 1.42 g) was added. The solution was refluxed for 2.5 h after which the violet color of 8a had disappeared. The yellow solution was evaporated to dryness and the oily yellow residue was treated with methanol (15 mL). After the mixture stood at room temperature for 0.5 h, the resulting solid was collected by suction filtration, washed with methanol, and dried (0.77 g). The yellowish solid was warmed gently for a few minutes with 10 mL of 5% methanolic KOH. Dilution with water produced a white precipitate that was collected by suction filtration, washed with water, and dried to yield 0.3 g (15%) of dimethyl 2,5,6-triphenylpyridine-3,4-dicarboxylate (9a): mp 231 °C⁴ (CHCl₃-CH₃OH); IR 1740, 1730 cm⁻¹; ¹H NMR (CDCl₃) δ 3.61 (s, 3 H), 3.72 (s, 3 H), 7.1-7.9 (m, 15 H).¹⁷

The basic methanolic filtrate was acidified with 5% HCl, and the yellowish curdy precipitate was collected, washed, and dried to give 0.35 g (14%) of pale yellow 3-(methoxalyl)-3-(carbo-methoxy)-2,5,6-triphenyl-4(3H)-pyridone (10a): mp 171-172 °C (CH₃OH); IR 1745, 1708 1645 cm⁻¹; ¹H NMR (CDCl₃) δ 3.8 (s, 3 H), 4.0 (s, 3 H), 6.8-7.32 (m, 10 H), 7.55-7.8 (m, 3 H), 8.6-8.8 (m, 2 H); ¹³C NMR (CDCl₃) 52.064 (OCH₃), 53.125 (OCH₃), 69.394 (quaternary C), 110.227, 112.63, 126.16, 127.45, 127.56, 127.86, 128.30, 128.61, 128.69, 132.97, 133.51, 133.85, 155.39, 159.66, 161.92, 167.94, 195.76; UV (C₆H₅OH) λ_{max} 292 nm (sh) (ε_{max} 3000), 270-280 nm (11 400); mass spectrum, *m/e* (70 eV) 467 (M⁺, 47), 439 (M⁺ - CO, 32), 353 (70), 336 (M⁺ - CO - PhCN, 100), 249 (41), 105 (C₆H₅CO⁺, 30).

Anal. Calcd for C₂₈H₂₁NO₆: C, 71.94; H, 4.53; N, 3.00. Found: C, 71.70; H, 4.49; N, 3.08.

The original methanol solution was allowed to evaporate to 10-mL volume. A yellow fluorescent solid separated and was collected, washed with methanol, and dried to give 0.3 g of mixture 11a/12a, mp 162-166 °C (CH₃OH). An additional crop of 0.15 g (total yield, 19%) was obtained during chromatography of the residue from the mother liquor (*vide infra*).

Anal. Calcd for C₂₈H₂₃NO₇: C, 69.27; H, 4.78; N, 2.89. Found: C, 69.40; H, 4.96; N, 2.87.

Chromatography of the residue from the methanolic filtrate on alumina (60 g) and elution with CH₂Cl₂ yielded 125 mg (2%) of methyl 3,5,6-triphenyl-4(1H)-pyridinone-2-carboxylate (13): mp 250-251 °C (CH₃OH); IR 1730, 1670, 1600 cm⁻¹; ¹H NMR (CDCl₃) δ 3.61 (s, 3 H), 7.7-7.1 (m, 15); mass spectrum, *m/e* (70 eV) 381 (M⁺, 60), 340 (100), 321 (80).

Anal. Calcd for C₂₅H₁₉NO₃: C, 78.72; H, 5.02; N, 3.67. Found: C, 78.28; H, 4.94; N, 3.77.

Reaction of 2-p-Tolyl-4,5-diphenyl-3H-pyrrol-3-one 1-Oxide (8b) with DMAD. The same procedure as described above was employed with 8b (1.3 g) and DMAD (3 mL) in CHCl₃ (15 mL). After this solution was refluxed for 3 h, the solvent was evaporated and treated with methanol. The solid was collected and dissolved in 5% methanolic KOH. Dilution of this solution with water produced a white precipitate. Recrystallization from CH₃OH-CHCl₃ gave 0.18 g (11%), of dimethyl 2-p-tolyl-5,6-diphenylpyridine-3,4-dicarboxylate (9b): mp 219-220 °C; IR (Nujol) 1740, 1728, 1550 cm⁻¹; ¹H NMR (CDCl₃) δ 2.40 (s, 3 H), 3.58 (s, 3 H), 3.72 (s, 3 H), 7.5-7.1 (m, 12 H), 7.66 (d, *J* = 8 Hz, 2 H); mass spectrum, *m/e* (70 eV) 437 (M⁺, 100), 436 (80).

Anal. Calcd for C₂₈H₂₃NO₄: C, 76.88; H, 5.49; N, 3.20. Found: C, 76.73; H, 5.23; N, 3.43.

The basic methanolic solution was acidified with dilute HCl and a fluorescent yellow solid was collected and recrystallized from CH₃OH-CHCl₃ to give 0.32 g (24%) of mixture 11b/12b, mp 150-160 °C.

Anal. Calcd for C₂₉H₂₅NO₇: C, 69.73; H, 5.04; N, 2.80. Found: C, 70.53; H, 5.10; N, 2.93.

The original methanolic solution was evaporated and chromatographed twice on a thick layer of silica with CHCl₃ to give 14 mg (1%) of 3-(methoxalyl)-3-(carbo-methoxy)-2-p-tolyl-5,6-diphenyl-4(3H)-pyridone (10b): mp 119-120; IR (Nujol) 1750, 1710, 1645, 1600 cm⁻¹; ¹H NMR (CDCl₃) δ 2.40 (s, 3 H), 3.58 (s, 3 H), 3.94 (s, 3 H), 7.5-7.2 (m, 12 H), 8.55 (d, *J* = 8 Hz, 2 H); mass spectrum, *m/e* (70 eV) 481 (M⁺, 37), 453 (M⁺ - CO, 35), 336 (M⁺ - CO - C₇H₇CN, 60), 105 (C₆H₅CO⁺, 100).

Thermal and Photochemical Conversion of 10a into 9a. Pyridone 10a (70 mg) was heated in a test tube in an oil bath at 200-215 °C for 1 h. There was slow evolution of a gas identified as CO₂. The molten residue was triturated with methanol to give 30 mg of a white solid, mp 230-231 °C, identical with 9a.

Exposure of a solution of 30 mg of 10a in 100 mL of CH₃OH in a Pyrex flask to sunlight for 10 h gave 20 mg of 9a.

[5,5'-Bi-2-pyrrolinyl]-2,2',3,3',5,5'-hexaphenyl-4,4'-dione (26). To a solution of benzaldehyde (6 g) in methanol (25 mL) was added NH₄OH (25 mL) and then a solution of diphenylcyclopropenone¹⁸ (5 g) in CH₃OH (50 mL). The mixture turned yellow

(16) Kohler, E. P.; Addinall, C. R. *J. Am. Chem. Soc.* **1930**, *52*, 1590-1604.

(17) The spectral data for 9a reported in ref 5 contain some errors. We found no carbonyl bands as high as 1775 cm⁻¹. While the NMR signals for the methyl groups are reported accurately in δ values, it appears that the aromatic hydrogens have been reported in τ values. Unfortunately, ref 4 reports no spectral data.

(18) Eicher, Th.; Weber, J. L.; Chatila, G. *Justus Liebigs Ann. Chem.* **1978**, 1203-1221.

immediately and was allowed to stand at room temperature overnight. The yellow solid that appeared was collected, washed with CH_3OH , and dried to give 7 g (80%) of **26**, mp 284–287 °C, identical in all respects with the compound previously reported.^{4,14,19}

Generation of 2,4,5-Triphenyl-3H-pyrrol-3-one (24). A suspension of dimer **26** (62 mg) in CH_2Cl_2 (20 mL) was treated with 0.8 g of freshly prepared nickel peroxide.²⁰ The violet color of product **24** appeared within minutes, but the mixture was allowed to stand at room temperature overnight. Evaporation of the solvent allowed the isolation of 18.5 mg (57%) of **2,4,5-triphenyl-6H-oxazin-6-one (25)**, mp 207 °C (lit.²¹ mp 207 °C),

identical in all ways with an authentic sample.²¹

When the purple CH_2Cl_2 solution, filtered to remove nickel oxides, and 5 drops of DMAD in 10 mL of toluene were mixed and the solution was refluxed for 4 h (after removal of CH_2Cl_2), the purple color was discharged. Thick-layer chromatography on silica with CHCl_3 allowed separation of oxazinone **25** and pyridine **9a** (10 mg), mp 231 °C.

Acknowledgment. We thank Professor D. J. Pasto for many stimulating discussions.

Registry No. 4, 762-42-5; **8a**, 62224-74-2; **8b**, 75233-32-8; **9a**, 58329-12-7; **9b**, 75233-33-9; **10a**, 75233-34-0; **10b**, 75233-35-1; **11a**, 75233-36-2; **11b**, 75233-37-3; **12a**, 75233-38-4; **12b**, 75233-39-5; **13**, 75233-40-8; **24**, 58329-06-9; **25**, 30237-78-6; **26**, 74149-24-9; benzaldehyde, 100-52-7; diphenylcyclopropenone, 886-38-4.

(19) Takahashi, M.; Inara, N.; Kirihaara, H.; Watanabe, S.-I. *Bull. Chem. Soc. Jpn.* **1978**, *51*, 3312–3315.

(20) Nakagawa, K.; Konaka, R.; Nakata, T. *J. Org. Chem.* **1962**, *27*, 1597–1601.

(21) Sprio, I. R. *Gazz. Chim. Ital.* **1955**, *85*, 569–577.

Determination of the Stereochemistry in the Addition of Thiols to Indene^{1a}

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A methodology for the determination of the stereoselectivity in the addition of thiols to indene is described. The chemical method employs an *S*-deuterio thiol, the thermal elimination reaction of the sulfoxides derived from the adducts, and the determination of the D content in the resulting indene. The preferred spectroscopic method employs 1,1,3-trideuterioindene and the LIS technique in the NMR analysis of the sulfones derived from the thiol-olefin adduct. The methodology employed is illustrated with a set of addition reactions carried out at room temperature under photochemically induced conditions and employing equimolar mixtures of 1,1,3-trideuterioindene and a series of substituted thiophenols. Under these conditions the relative amount of *cis* adduct increased proportionally with the σ constants of the substituents.

The stereochemistry of the addition of thiols to olefins has been reviewed^{1b,2} in the context of the stereochemistry of radical chemistry. In the case of cyclic olefins, most of the results have dealt with systems that contain either a substituent at the double bond, in which the *exo* or *endo* approach of the sulfur-containing reagent leads to isomeric products of different stability, or systems in which there is a choice of axially or equatorially substituted intermediates. This is the case when the addition reaction occurs with 4-*tert*-butylcyclohexene,³ *trans*- Δ^2 -octalin,⁴ norbornene,^{5–7} bornylene,⁸ norbornadiene,⁹ and related bicyclic olefins^{7,10–17} or with 1-chlorocyclohexene,^{18,19} 1-chloro-4-

tert-butylcyclohexene,²⁰ 2-chloro-4-*tert*-butylcyclohexene,²¹ 2-methylnorborn-2-ene,⁶ or 1-methylcyclopentene.²² In all of these olefins there exists a built-in bias with respect to either the preferential approach of the sulfur moiety to the olefinic site or a difference in the relative stability of the potential intermediate species or final products. Our concern here is the relative orientation of the thiol and hydrogen moieties in the thiol-olefin adduct irrespective of the kinetic or thermodynamic factors induced by the structure of the olefinic reagent. Thus, for our purposes the most appropriate system is an olefin that is symmetrical with regard to the *syn* or *anti* approach of the thiol. The isomeric 2-butenes fit this criterium, and these olefins

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