of water. The solution was stirred in an ice bath for 30 min. Then 0.625 mmol of NaI in 2.5 mL of water was added. The mixture was stirred in an ice bath for 2 h and warmed to 40 °C for 90 min. Sodium bisulfite was added to reduce any iodine. The product was filtered and recrystallized from methanol/water to yield 90 mg (56%) of **7**: mp 325–328 °C (lit.[13] 330–331 °C).

Registry No. 1, 364-98-7; **2**, 37157-79-2; **3a**, 71870-66-1; **3b**, 71870-67-2; **3c**, 71870-68-3; **5a**, 71870-69-4; **5b**, 71870-70-7; **5c**, 71870-71-8; **6**, 71870-72-9; **7**, 37148-02-0.

(13) J. G. Topliss and M. D. Yudis, *J. Med. Chem.*, **15**, 400 (1972).

Some Reactions of Enamine Adducts of 3,4-Diazacyclopentadienone 3,4-Dioxides

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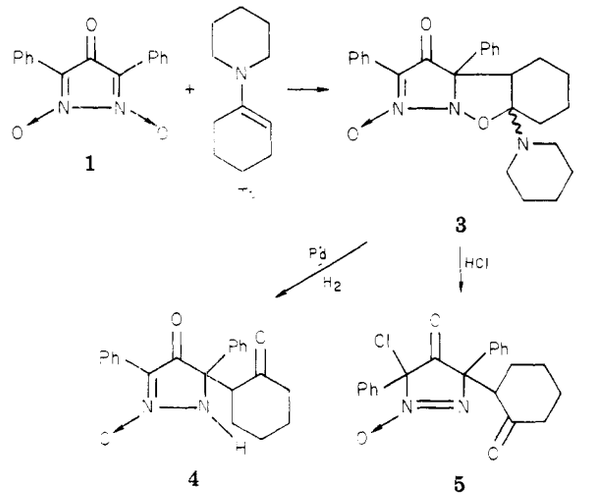
The formation of cycloadducts from diazacyclopentadienone dioxides and alkenes, and some of the reactions of these cycloadducts, have been reported.[1] Since the regiospecificity of enamine cycloadditions to the nitrone function[2] provides a masked carbonyl function, we have examined briefly the formation, hydrolysis, and hydrogenolysis of these cycloadducts in this novel system.

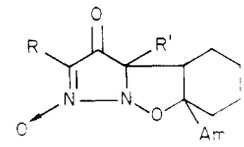
The diazacyclopentadienone dioxides react rapidly and almost quantitatively with enamines under mild conditions to yield the desired cycloadducts[3] (Table I). Cycloadduct **3**, formed from 2,5-diphenyl-3,4-diazacyclopentadienone



3,4-dioxide (**1**) and *N*-cyclohexenylpiperidine (**2**), was reduced rapidly at room temperature by hydrogen on palladium to yield the pyrazolone *N*-oxide **4** in good yield. This same compound was also obtained upon treatment of **3** with sodium dithionite, but this reaction was less clean.

The structure of **4** rests upon its spectral properties (see Experimental section), the similarity of its mass spectral

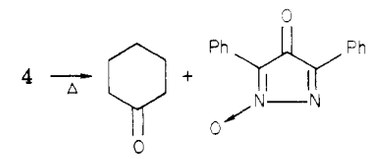
Table I. Enamine Cycloadducts



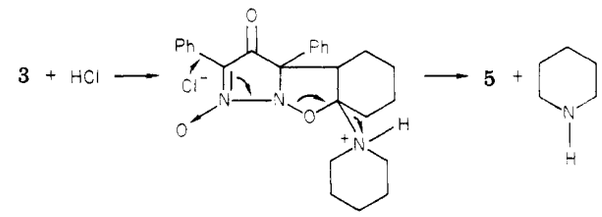
compd			mp, °C[a,b]	yield, %
R	R'	Am		
C_6H_5	C_6H_5	morpholine	113–115	96
C_6H_5	CH_3	morpholine	63–65	70
C_6H_5	C_6H_5	pyrrolidine	136–138	93
C_6H_5	CH_3CH_2	pyrrolidine	128–130	97
C_6H_5	CH_3	pyrrolidine	118–120	92
C_6H_5	C_6H_5	piperidine	143–145	93

[a] After recrystallization from CH_2Cl_2-petroleum ether. [b] Satisfactory analytical data (±0.3 for C, H, N) were obtained and reported for all compounds except for the first entry which tenaciously retained solvent.

cracking pattern to that of other 4-ketopyrazoline 2-oxides,[1,4] and its decomposition at its melting point to produce cyclohexanone and 2,5-diphenyl-3,4-diazacyclopentadienone 3-oxide.[5,6]



Treatment of **3** with hydrochloric acid in methanol at room temperature produced the halogenated pyrazolone *N*-oxide **5**. This compound may arise as follows:[7]



In the absence of a nucleophilic anion, **3** was stable to acid treatment. Thus similar treatment with aqueous perchloric acid produced no cleavage; harsher conditions were not examined, however.

The structure of **5** rests upon its elemental analysis and its spectral properties (M^+ in mass spectrum, $\gamma_{N=NO}$ 1570 cm^{-1} in its infrared spectrum). The proposed mechanism is consistent with the known reactivity of the nitrone carbon toward nucleophiles (cf. the rearrangement of the acetylene adducts of **1**[1]) and with other nucleophilic additions, even to aromatic rings, which accompany heterolytic cleavage of N–O bonds.[8]

The importance of the nucleophilic addition to the cleavage of the oxazolidine ring was also shown by the stability of the cycloadducts **6** and **7** (obtained in two diastereomeric forms) to acid hydrolysis; neither reacted

(1) J. P. Freeman and M. J. Hoare, *J. Org. Chem.*, **36**, 19 (1971).
(2) (a) D. St. C. Black, R. F. Crozier, and V. C. Davis, *Synthesis*, 205 (1975); (b) Y. Takeuchi and F. Furusaki, "Advances in Heterocyclic Chemistry", Vol. 21, A. R. Katritzky and A. J. Boulton, Eds., Academic Press, New York, 1977, p 201.
(3) As with other dipolarophiles, cycloaddition of unsymmetrical derivatives of **1** always occurred at the alkyl-substituted nitrone function,[1] as revealed by the upfield shift of the alkyl group hydrogens in their NMR spectra.
(4) J. P. Freeman, *J. Org. Chem.*, **27**, 2881 (1962).
(5) J. P. Freeman, J. J. Gannon, and D. L. Surbey, *J. Org. Chem.*, **34**, 187 (1969).
(6) In other work we have observed that adducts of **6** and stable enolates, e.g., that from ethyl benzoylacetate, form but readily reverse to starting materials upon heating.
(7) The reaction need not be concerted but could involve prior addition of HCl to the nitrone function followed by elimination to form the N=N bond.
(8) Inter Alia: R. Fielden, O. Meth-Cohn, and H. Suschitsky, *J. Chem. Soc., Perkin Trans. 1*, 705 (1973); A. Picot and X. Lisinchi, *Tetrahedron Lett.*, 903 (1973); P. G. Gassman, G. A. Campbell, and G. Mehta, *Tetrahedron*, **28**, 2749 (1972).

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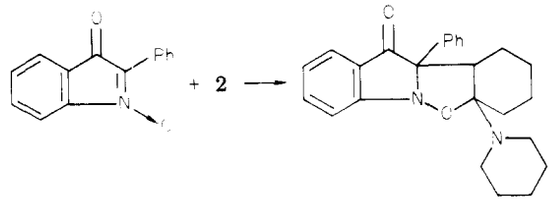
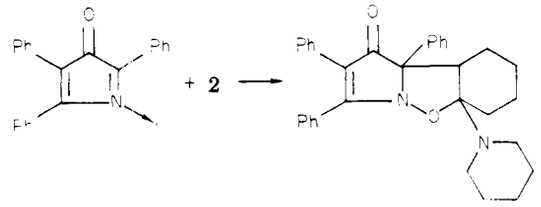
with aqueous hydrochloric acid under the same conditions under which **3** reacts.



6



7

Experimental Section

Synthesis of Enamine Adducts (Table I). All of the adducts were prepared in the following manner. To a slurry of 2 g (7.0 mmol) of 2,5-diphenyl-3,4-diazacyclopentadienone 3,4-dioxide[5] in 30 mL of CH_2Cl_2 was added 2 mL of *N*-cyclohexenylpiperidine. This mixture was warmed on a steam bath for 15 min, and then allowed to stand at room temperature for 5 min. The solvent was evaporated, and the dark yellow oily residue was triturated with methanol to produce a yellow solid. Recrystallization from CH_2Cl_2–petroleum ether gives bright yellow crystals: mp 143–145 °C dec; yield 2.9 g (90%); IR (Nujol) 1725 (C=O), 1550 cm^{-1} (C=N(→O)–); ^1H NMR ($CDCl_3$) δ 1.2–1.5 (br d, 16 H), 2.6 (m, 3 H), 7.2–7.6 (m, 6 H), 7.7–7.9 (m, 2 H), 8.6–8.8 (m, 2 H); *m/e* (70 eV) 431 (M^+, 1), 300 (34), 115 (100), 105 (77).

Adduct 6 was prepared by the same general procedure as that used above from 0.3 g of 2-phenylisatogen:[9] yield 0.45 g (87%); mp 163–165 °C; IR (Nujol) 1718, 1600 cm^{-1}; NMR ($CDCl_3$) δ 7.7, 7.3 (m, 9), 3.2, 2.7, 2.3 (m, 19).

Anal. Calcd for $C_{25}H_{25}N_2O_2$: C, 77.29; H, 7.27; N, 7.21. Found: C, 77.18; H, 7.07; N, 7.47.

Upon prolonged standing in light, this adduct took on an orange color suggesting reversion to free isatogen.

Adduct 7 was prepared in two diastereomeric forms by the same procedure as that used above from 0.1 g of 2,4,5-triphenyl-3*H*-pyrrol-3-one 1-oxide[10] and separated by thick layer chromatography on silica; yield 0.125 g (83%).

7a: mp 172–174 °C; IR (Nujol) 1669, 1660 cm^{-1}; NMR ($CDCl_3$) δ 0.8–2.8 (br m, 18), 3.3 (m, 1), 7.3 (m, 13), 7.8 (m, 2); *m/e* (70 eV) M^+ 490 (15), 462 (2), 407 (3), 378 (3), 350 (3), 325 (7), 178 (30), 165 (100).

Anal. Calcd for $C_{33}H_{34}N_2O_2$: C, 80.78; H, 6.98; N, 5.71. Found: C, 79.09; H, 6.86; N, 5.60.

7b: mp 194–196 °C; IR (Nujol) 1710, 1600 cm^{-1}; NMR ($CDCl_3$) δ 1.2–2.6 (m, 18), 3.45 (m, 1), 7.25 (m, 11), 7.8 (4); mass spectrum identical with that of **7a**.

Anal. Calcd for $C_{33}H_{34}N_2O_2$: C, 80.78; H, 6.98; N, 5.71. Found: C, 80.69; H, 6.88; N, 5.70.

Reaction of Adduct 3 and Hydrochloric Acid. To 1 g of adduct **3** in 50 mL of CH_3OH was added 6 mL of concentrated HCl, and this mixture was allowed to stand at room temperature overnight. Water was added and **5**, a white solid (mp 188–190 °C), was collected: yield 0.8 g (91%); IR (Nujol) 1770 cm^{-1} (C=O, 5-membered ring), 1700 (C=O, 6-membered ring), 1570 (–N=N(→O)–); NMR ($CDCl_3$) δ 1.4–2.5 (m, 8), 3.48 (m, 1), 7.18–7.5 (m, 9), 7.93 (m, 1); *m/e* (CI) $M^+ + 1$, 383 (20), 385 (5), 348 (24), 326 (22), 324 (61), 303 (100), 250 (48), 119 (68), 105 (39).

Anal. Calcd for $C_{21}H_{19}ClN_2O_3$: C, 65.87; H, 5.00; Cl, 9.27; N, 7.31. Found: C, 65.68; H, 4.90, Cl, 9.47, N. 7.27.

(9) F. Kröhnke and M. Meyer-Delius, *Chem. Ber.*, **84**, 932 (1951).
(10) E. P. Kohler and C. R. Addinall, *J. Am. Chem. Soc.*, **52**, 1590 (1930).

Reduction of Adduct 3. A solution of 1.25 g of **3** in 30 mL of tetrahydrofuran was stirred at room temperature under 1 atm of H_2 in the presence of 0.1 g of Pd/C. After 2 h, the mixture was filtered and concentrated. The residue was chromatographed on silica gel, and the product was eluted with $CHCl_3$. Recrystallization from $CHCl_3$–Skelly B gave **4**: yellow needles: mp 187–189 °C; yield 0.7 g (70%); IR (Nujol) 3220, 1700, 1540 cm^{-1}; *m/e* (70 eV) M^+, 348 (11), 250 (10), 236 (80), 119 (95), 105 (100).

Anal. Calcd for $C_{21}H_{20}N_2O_3$: C, 72.41; H, 5.74; N, 8.04. Found: C, 72.30, H, 5.56; N, 7.89.

Registry No. **1**, 17952-96-4; **2**, 2981-10-4; **3** (R = R^1 = C_6H_5; Am = piperidine), 71964-78-8; **3** (R = R^1 = C_6H_5; Am = morpholine), 71964-79-9; **3** (R = C_6H_5; R^1 = CH_3; Am = morpholine), 71964-80-2; **3** (R = R^1 = C_6H_5; Am = pyrrolidine), 71964-81-3; **3** (R = C_6H_5; R^1 = CH_3CH_2; Am = pyrrolidine), 71964-82-4; **3** (R = C_6H_5; R^1 = CH_3; Am = pyrrolidine), 71964-83-5; **4**, 71964-84-6; **5**, 71964-85-7; **6**, 71964-86-8; **7**, 71964-87-9; 2-methyl-5-phenyl-3,4-diazacyclopentadienone 3,4-dioxide, 16901-38-5; 2-ethyl-5-phenyl-3,4-diazacyclopentadienone 3,4-dioxide, 16858-30-3; *N*-cyclohexenylmorpholine, 670-80-4; *N*-cyclohexenylpyrrolidine, 1125-99-1; 2-phenylisatogen, 1969-74-0; 2,4,5-triphenyl-3*H*-pyrrol-3-one 1-oxide, 62224-74-2.

Sodium–Ethanol: A Superior Reagent for the Reductive Dehalogenation of Polychlorinated Alicyclic Molecules

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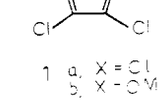
Diels–Alder reactions of hexachlorocyclopentadiene (**1a**) and 1,2,3,4-tetrachloro-5,5-dimethoxycyclopentadiene (**1b**) with a wide range of dienophiles generally give excellent yields of adducts with a high degree of stereospecificity. For these reasons **1a** and **1b** are often used as synthons for cyclopentadiene and cyclopentadienone, respectively.[1-5] Unfortunately, the attractiveness of these synthons is offset by the necessity to reductively dechlorinate the resulting adducts. The Gassman–Pape method[4] (Na, *tert*-butyl alcohol, THF), a modification of the Bruck–Thompson–Winstein procedure[2] (Li, *tert*-butyl alcohol, THF), is currently the most popular way of carrying out reductive dechlorinations of adducts of both **1a** and **1b**. However,



1 a, X = Cl
b, X = OMe

this method, carried out on a large scale, suffers from several disadvantages: it is time consuming, the workup procedure is inconvenient and hazardous, and the yields are often less than 50%.[6] The Birch reduction (Na, liquid NH_3, EtOH) has shown promise in reductively dechlorinating adducts of **1b**.[5] However, we have applied this method to a series of adducts of hexachlorocyclopentadiene

(1) H. E. Ungnade and E. T. McBee, *Chem. Rev.*, **58**, 249 (1958).
(2) P. Bruck, D. Thompson, and S. Winstein, *Chem. Ind. (London)*, 405 (1960); P. Bruck, *Tetrahedron Lett.*, 449 (1962).
(3) J. Haywood-Farmer, H. Malkus, and M. A. Battiste, *J. Am. Chem. Soc.*, **94**, 2209 (1972).
(4) (a) P. G. Gassman and P. G. Pape, *J. Org. Chem.*, **29**, 160 (1964); (b) P. G. Gassman and J. L. Marshall, *Org. Synth.*, **48**, 68 (1968).
(5) M. E. Jung and J. P. Hudspeth, *J. Am. Chem. Soc.*, **99**, 5508 (1977).
(6) For example, the reductive dechlorination of **6a** via this method required 38 h of reaction time to give **6b** in only ca. 31–43% yield.[3b]

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