Cycloaddition Reactions of 3,4-Diazacyclopentadienone Oxides with Olefins and Acetylenedicarboxylic Ester[1]

JEREMIAH P. FREEMAN* AND MICHAEL J. HOARE[2]

Department of Chemistry, University of Notre Dame, Notre Dame, Indiana 46556

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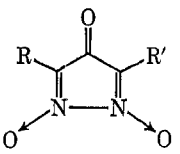
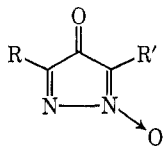
3,4-Diazacyclopentadienone *N,N'*-dioxides, **1**, and *N*-monoxides, **2**, undergo cycloaddition with olefins to produce isoxazolo[1,2-*b*]pyrazole derivatives **4** and **5**, respectively. These heterocycles undergo ring opening upon hydrolysis and hydrogenolysis to 4-ketopyrazoline derivatives. With acetylenedicarboxylic ester, **1** and **2** both yield 8-oxabicyclo[3.2.1]octane derivatives. Proof of the structure of these derivatives is based upon spectroscopic studies and a variety of oxidation and reduction products.

Recently, some representatives (**1**, **2**) of the 3,4-diazacyclopentadienone *N*-oxide family of heterocycles were reported.[3] The presence of the cross-conjugated keto-

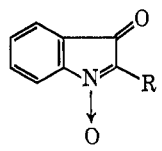


1a, R = C_6H_5; R' = CH_3
b, R = C_6H_5; R' = C_6H_5
c, R = CH_3; R' = CH_3
d, R = C_6H_5; R' = C_2H_5



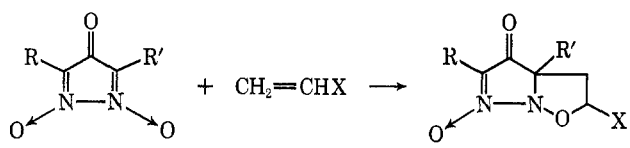
2a, R = C_6H_5; R' = CH_3
b, R = C_6H_5; R' = C_6H_5

nitrone system and their bright colors suggested that these compounds might bear some chemical similarity to the isatogens, **3**. The latter compounds have been reported to undergo a number of unusual cycloaddition reactions.[4]



3

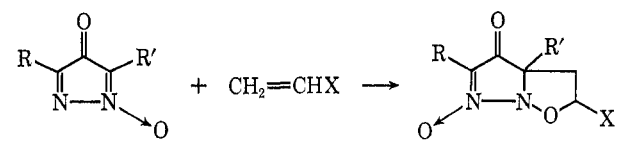
Olefin Additions.—Condensation of **1** with acrylonitrile, methyl acrylate, and butyl vinyl ether yielded 1:1 cycloadducts (Table I). All of these compounds resulted from the same regiospecific cycloaddition in which the nitrone oxygen is attached to the carbon atom of the olefin which bears the functional group. This orientation is that expected on the basis of previous re-



sults with simple nitrones[5] and supports the suggestion that steric factors are mainly responsible for this regiospecificity.[6] Proof for this orientation will be outlined below.

With unsymmetrical derivatives of **1**, such as **1a**, there is a second source of structural uncertainty in the cycloadducts and that is to which nitrone function addition occurs. In all cases examined, addition took place exclusively at the aliphatic nitrone group. This point was immediately apparent from a comparison of the nmr spectra of the adducts with those of the starting materials. The alkyl group hydrogens underwent an upfield shift of about δ 0.5, wholly compatible with the change of hybridization at the nitrone carbon from sp^2 to sp^3.

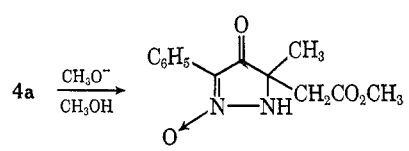
In the report[3] of compounds of structure **2**, it was noted that there was an unsettled ambiguity about the unsymmetrical derivatives. There was presumptive evidence that an alkyl rather than an aryl group was preferentially associated with the nitrone function, but spectral data alone could not unequivocally establish this point. The results of cycloaddition reactions of **2** (Table I) show conclusively that the original suggestion was correct as again the nmr spectra showed that the alkyl groups suffered an upfield shift upon cycloaddition.



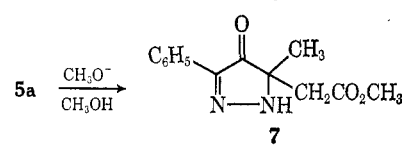
2, R = Ar
R' = Alkyl

5, R = Ar
R' = Alkyl

The heterocyclic adducts **4a** and **5a**, X = CN, underwent a base-catalyzed ring opening and solvolysis that served both to substantiate their structures and to produce new heterocyclic derivatives. This ring opening



6



7

is similar to that observed with isatogen cycloadducts.[7]

One previous example of the heterocyclic nucleus of **6** has been reported and it was established in that investigation that the keto–nitrone tautomer correctly represented the structure.[8] The spectral properties of **6** were very similar to those previously reported.[8]

* To whom correspondence should be addressed.

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(2) National Defense Education Act Fellow, 1966–1969. Abstracted in part from the Ph.D. Thesis of M. J. Hoare.

(3) J. P. Freeman, J. J. Gannon, and D. L. Surbey, *J. Org. Chem.*, **34**, 187 (1969).

(4) W. E. Noland and R. F. Modler, *J. Amer. Chem. Soc.*, **86**, 2086 (1964).

(5) R. Huisgen, H. Hauck, R. Grashey, and H. Seidl, *Chem. Ber.*, **101**, 2568 (1968).

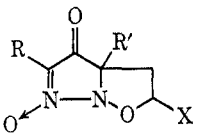
(6) N. A. LeBel, *Trans. N. Y. Acad. Sci.*, **27**, 858 (1965).

(7) W. E. Noland and D. A. Jones, *Chem. Ind. (London)*, 363 (1962).

(8) J. P. Freeman, *J. Org. Chem.*, **27**, 2881 (1962).

TABLE I

CYCLOADDUCTS



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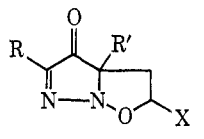

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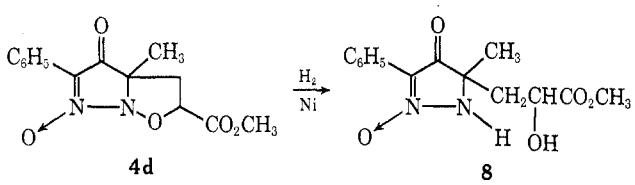
Compd no.	R	R′	X	Yield, %	Mp, °C	Ir (Nujol), cm⁻¹	Nmr (CDCl₃), δ	Calcd, % C	Calcd, % H	Calcd, % N	Found, % C	Found, % H	Found, % N
4a	C_6H_5	CH_3	CN	60	158–160	1735 (C=O), 1570 (-C=N→O), 1120 (N→O)	1.67 (s, 3, CH_3), 2.99 (m, 2, $-CH_2CH-$), 5.30 (q, 1, $>CHCH_2-$), 7.60 (m, 3), 8.30 (m, 2)	60.70	4.31	16.33	60.90	4.59	16.17
4b	CH_3	CH_3	CN	34	110–111	1725 (C=O), 1590, 1570 (-C=N→O), 970 (N→O)	1.67 (s, 3, CH_3), 2.05 (s, 3, CH_3), 2.75 (m, 2), 4.80 (m, 1)	49.20	4.65	21.50	48.92	4.66	21.69
4c	C_6H_5	C_2H_5	CN	72	117–118	1715 (C=O), 1565, 1100	1.06 (t, 3, J = 7.5 Hz), 2.05 (q, 2, J = 7.5 Hz), 2.80 (m, 2), 4.06 (m, 1), 7.50 (m, 3), 8.35 (m, 2)	61.99	4.83	15.49	62.20	4.90	15.52
4d	C_6H_5	CH_3	CO_2CH_3	62	145–147	1750 (ester C=O), 1720, 1565, 1120	1.40 (s, 3), 2.65 (m, 2), 3.80 (s, 3), 4.59 (m, 1), 7.50 (m, 3), 8.40 (m, 2)	57.93	4.86	9.65	57.65	5.06	9.79
4e	C_6H_5	C_6H_5	CO_2CH_3	68	150–151	1750, 1710, 1550, 1130	3.62 (s, 3), 3.33 (m, 2), 5.05 (m, 1), 7.45 (m, 10), 8.35 (m, 2)	64.77	4.58	7.95	64.84	4.59	8.23
4f	C_6H_5	C_6H_5	n-OC_4H_9	75	106–107	1725, 1550, 1380, 1050	1.00 (m, 7), 2.90 (q, 2), 3.65 (m, 2), 5.55 (t, 1), 7.50 (m, 10), 8.40 (m, 2)	68.84	6.05	7.65	68.70	6.22	7.69
5a	C_6H_5	CH_3	CN	46	150–152	1750, 1450	1.66 (s, CH_3), 2.62 (m, 2), 4.62 (m, 1), 7.50 (m, 3), 8.20 (m, 2)	64.72	4.60	17.42	64.87	4.85	17.35

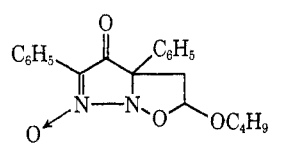
[a] See Experimental Section.

Hydrogenolysis of the cycloadducts also affords derivatives of the 4-ketopyrazoline 2-oxide system. Catalytic hydrogenation of **4d** yielded the α-hydroxy ester **8**, while similar treatment of **4f** yielded aldehyde **9** isolated as its 2,4-DNP derivative.



4d

8



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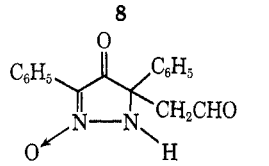
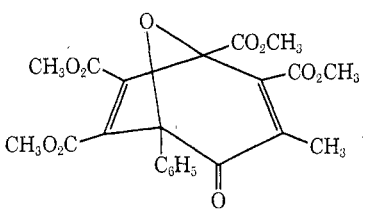


9

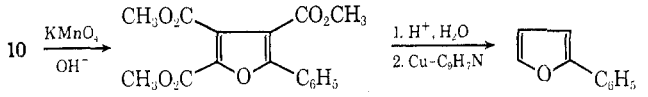
Acetylenes.—The dioxide **1a** condensed with acetylenedicarboxylic ester in boiling benzene to yield a nitrogen-free product derived from 2 equiv of the ester and 1 equiv of the dioxide. Nitrous oxide was evolved during the reaction. Structure **10** is proposed for the adduct: R = C_6H_5; R′ = CH_3.



10

Spectral Evidence.—The infrared spectrum of **10** contains carbonyl bands at 1760, 1740, 1720, and 1710 cm^{-1}, and a medium intensity band at 1660 cm^{-1}. Its nmr spectrum shows the ester methyl groups at δ 3.66 (3 H), 3.82 (6 H), and 3.88 (3 H), and a lone methyl singlet at δ 2.02. The phenyl group appears as a multiplet at δ 7.55. The mass spectrum of **10** showed a small molecular ion peak at m/e 444 and the 100% ion peak at 105 ($C_6H_5CO^+$). Its fragmentation pattern is consistent with the structure proposed. The ultraviolet spectrum of **10** showed absorption at λ_{max} 218, 245, and 370 nm, consistent with the α,β-unsaturated ketone and maleate ester chromophores.

Compound **10** was thermally stable at its melting point and it did not form carbonyl derivatives (under the usual conditions). Oxidation of **10** with alkaline permanganate yielded trimethyl 2-phenylfurantricarboxylate. The structure of this ester was established by its elemental analysis, its spectral properties, and its

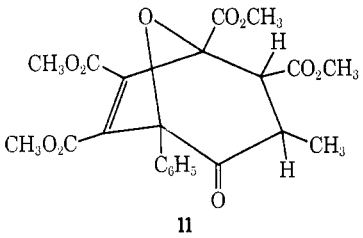


degradation to 2-phenylfuran by hydrolysis and decarboxylation.

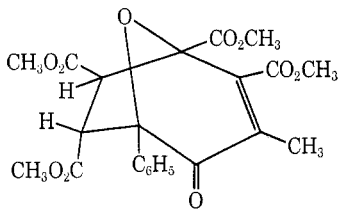
A series of reductions was also carried out to substantiate structure **10**. Catalytic hydrogenation yielded a mixture of two monohydrogenation products, **11** and **12**. The nmr spectrum of **11** had, in addition to signals due to the ester methyl groups, a doublet at δ 1.20 (3 H, J = 7 Hz) and multiplets at 7.50 (5 H), 3.45 (1 H), and 4.20 (1 H), fully consistent with structure **11** and confirming the structural feature in **10** of a methyl group attached to a double bond substituted with carbonyl functions.[9] The nmr spectrum of **12** showed that the C-

(9) Structures **11** and **12** represent the stable isomers (based upon study of models) obtained after base-catalyzed epimerization of the original hydrogenation products, which appeared to consist of mixtures of stereoisomers.

methyl group was still in the same magnetic environment as in **10** and was otherwise consistent with the structure proposed. All attempts to fully saturate **11** or **12** were unsuccessful. It may be of some interest that the ultraviolet spectra of compounds **10**, **11**, and **12** were virtually identical, but the significance of this fact is not known.

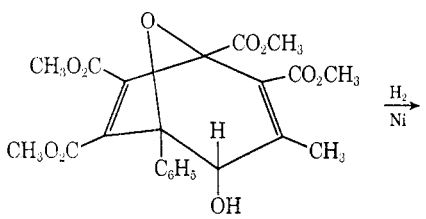


11

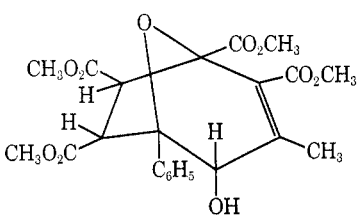


12

Sodium borohydride reduction of **10** yielded an alcohol **13** which could be reoxidized with chromic acid to **10**. The orientation of the hydroxyl group is not known although it is probably endo based upon the lactonization described below. Catalytic hydrogenation of **13** produced **14**. The structure of **14** is based

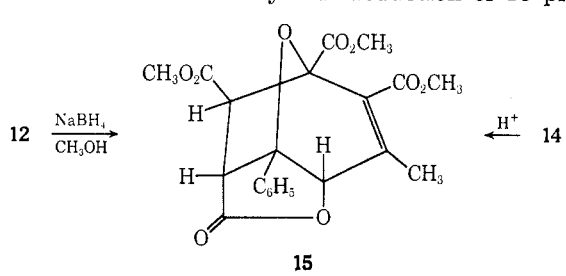


13



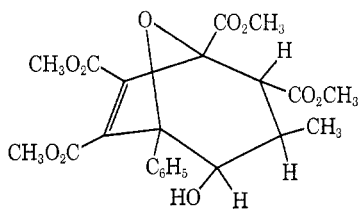
14

upon its nmr spectrum which showed that the *C*-methyl group was still a singlet and in the same magnetic environment as in **10** and **13**. In addition, oxidation of **14** yielded ketone **12**. Sodium borohydride reduction of **12** in methanol produced a lactone **15** which was identical with that produced by acid treatment of **14**. The lactone **15** is the only one that could be constructed using models and this requires that **14** have the structure shown. Thus borohydride reduction of **10** probably occurs from the exo side to give the endo alcohol **13**. The catalytic hydrogenation of **13** may yield the thermodynamically stable trans diester **14**, directly, but in any case the lactonization conditions are such as to produce the requisite epimer.



15

Borohydride reduction of ketone **11** produced an alcohol **16** isomeric with **14** but one which could not be lactonized. Oxidation of **16** regenerated **11**. Model studies indicated that no lactone could be formed between the ester at C-2 and the hydroxyl group at C-4.[10] The "α" relationship of the ketone carbonyl group and the *C*-methyl group is shown in the increased complexity of the nmr signal of the hydrogen coupled to the methyl group in **11** upon reduction to **16**. On the other hand,



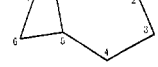
16

the signal for the CH group of the alcohol in **14** was a simple doublet (coupling to OH) which collapsed to a singlet when the spectrum was measured in the presence of trifluoroacetic acid.

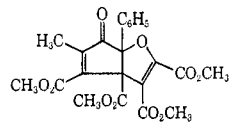
All the data assembled support the structure of the condensation product as **10**.[11] An attempt to convert **12** to a tropone by acid-catalyzed ring opening and dehydration in polyphosphoric acid was unsuccessful, possibly due to complicating side reactions with the several ester functions.

A possible route from dioxide **1a** to compound **10** may be envisioned as shown in Scheme I. The formation of adducts which are analogous to **17** has been postulated in other nitrone–acetylene cycloadditions. The rearrangement of **17** to **18** might be anticipated on the basis of the reported instability of the 4-isoxazoline nucleus.[12] Compounds similar to **19** have been postulated as the compounds responsible for the color produced upon heating epoxycyclopentadienones.[13] In one instance, such a compound was trapped by acety-

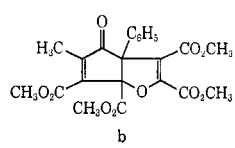
(10) Numbering according to Ring Index of the 8-oxabicyclo[3.2.1]octane skeleton.



(11) Other structures considered that were compatible with the spectral data were the following.



a



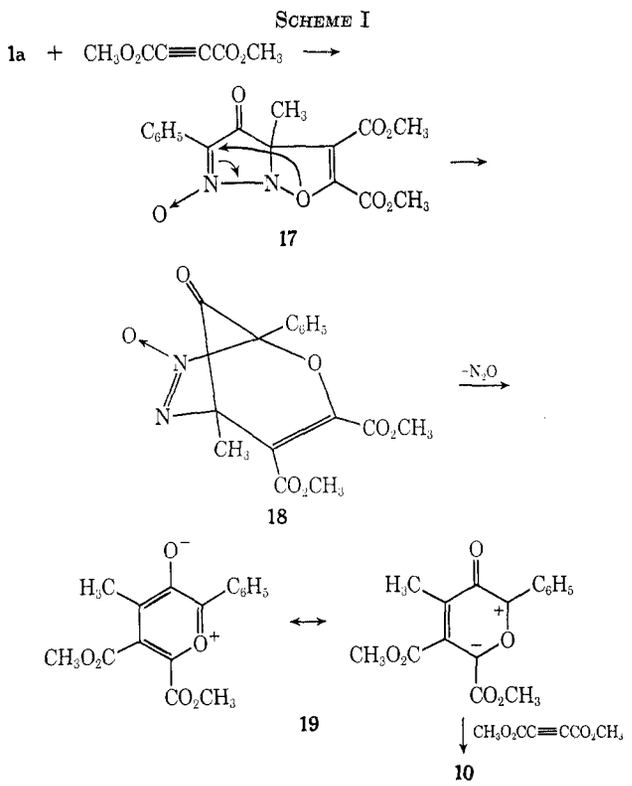
b

Both suffer from the fact that **10** is stable to acid-catalyzed hydrolysis, a reaction expected to cleave the vinyl ether function. Additionally b would yield trimethyl 3-phenylfurantricarboxylate instead of the 2-phenyl isomer.

(12) J. E. Baldwin, R. G. Pudussery, A. K. Qureshi, and B. Sklarz, *J. Amer. Chem. Soc.*, **90**, 5325 (1968).

(13) (a) E. F. Ullman and J. E. Milks, *ibid.*, **86**, 3814 (1964); (b) J. M. Dunston and P. Yates, *Tetrahedron Lett.*, 505 (1964).

SCHEME I



lenedicarboxylic ester to give a derivative analogous to **10**.[13a,14] As this mechanism would suggest, compound **10** was also obtained from the reaction of the mono-*N*-oxide **2a** with acetylenedicarboxylic ester.

Experimental Section

Cycloaddition Reactions with Alkenes. 1. The Cycloadducts (Table I).—2-Phenyl-4-methyl-6-cyano-3-ketoisoxazolo[1,2-*b*]pyrazole *N*-Oxide (4a).—A 2.0-g (9.8 mmol) sample of 2-phenyl-5-methyl-3,4-diazacyclopentadienone *N,N'*-dioxide[3] (**1a**) and 20 ml (0.30 mol) of acrylonitrile were refluxed for 4 hr. There was a color change from bright orange to pale yellow as the reaction proceeded. The acrylonitrile was removed under vacuum and the residual oil slowly crystallized. A single recrystallization from methylene chloride–hexane gave colorless needles, mp 158–160°, 60% yield.

2-Phenyl-4-methyl-6-cyano-3-ketoisoxazolo[1,2-*b*]pyrazole (5a).—A 0.5-g (2.66 mmol) sample of **2-methyl-5-phenyl-3,4-diazacyclopentadienone 3-oxide (2a)**[3] and 10 ml (0.15 mole) of acrylonitrile were dissolved in 10 ml of benzene and the solution was refluxed for 4 hr. The solution turned from dark red to pale yellow during the reaction period. The benzene and excess acrylonitrile were removed under vacuum and the solid residue was crystallized from methanol. Recrystallization from methylene chloride–hexane gave pale yellow crystals, 0.30 g (46%), mp 150–152°.

2. The Cycloadduct Derivatives. 5-Carbomethoxymethyl-5-methyl-3-phenyl-2-pyrazolin-4-one 2-Oxide (6).—A solution containing 0.5 g (2 mmol) of **4a** in 50 ml of methanol and 2 ml of 10% NaOH solution was refluxed for 3 hr, and then cooled and acidified to congo red with HCl. After a long period of cooling, 0.3 g (60%) of white needles were isolated: mp 113–115°; ir (Nujol) 3300 (NH), 1720 (ester C=O), 1550 and 1250 cm^{-1}; nmr ($CDCl_3$) δ 1.34 (s, 3, CH_3), 2.94 (d, 2), 3.55 (s, 3, OCH_3), 7.50 (m, 3), and 8.20 (m, 2). *Anal.* Calcd for $C_{13}H_{14}N_2O_4$: C, 59.5; H, 5.38; N, 10.68. Found: C, 59.60; H, 5.56; N, 10.60.

5-Carbomethoxymethyl-5-methyl-3-phenyl-2-pyrazolin-4-one (7).—To a solution of 0.5 g (2.0 mmole) of **5a** in 50 ml of methanol was added 2 ml of 10% NaOH. The solution was refluxed for 4 hr and worked up as described for **6**. Pale yellow crystals were isolated: 0.3 g (60%); mp 99–100°; ir (Nujol) 3320 (NH), 1720 and 1705 (CO); nmr ($CDCl_3$) δ 1.42 (s, 3, CH_3), 2.66 (d, 2), 3.73 (s, 3, OCH_3), 7.40 (m, 3), and 8.15 (m, 2). *Anal.* Calcd for $C_{13}H_{14}N_2O_5$: C, 63.40; H, 5.73; N, 11.38. Found: C, 61.68; H, 5.73; N, 11.55.

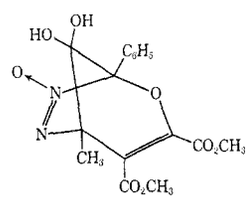
5-(2-Hydroxy-2-carbomethoxy)ethyl-5-methyl-3-phenyl-2-pyrazolin-4-one 2-Oxide (8).—A 0.8-g (2.7 mmol) sample of **4d** was hydrogenated in 50 ml of ethyl acetate with Raney Ni (0.5 g) over a 4-hr period. The solution was filtered and the solvent removed under reduced pressure. The residual oil was swirled in 25 ml of CCl_4. Pale green crystals were isolated by this method. Recrystallization from $CHCl_3$–*n*-C_6H_{12} gave 0.6 g (76%) of pale yellow crystals: mp 95–96°; ir (Nujol) 3400 (NH), 3120 (OH), 1735 and 1683 (C=O), and 1545 cm^{-1} (O=CC=N→O) vs; nmr ($CDCl_3$) δ 1.48 (s, 3, CH_3), 2.35 (m, 2), 3.34 (m, 1), 3.76 (s, 3, OCH_3), 4.23 (m, 1), 7.35 (m, 3), and 8.30 (m, 2 H). *Anal.* Calcd for $C_{14}H_{16}N_2O_5$: C, 57.5; H, 5.52; N, 9.58. Found: C, 57.15; H, 5.79; N, 9.80.

5-Formylmethyl-3,5-diphenyl-2-pyrazolin-4-one 2-Oxide.—A 0.8-g (2.2 mmol) sample of **4f** was hydrogenated in 50 ml of ethyl acetate with Raney Ni (0.5 g) for 4 hr. The residual oil after removal of solvent and catalyst was dissolved in ethanol and added to 15 ml of 0.17 *M* 2,4-dinitrophenylhydrazine reagent in ethanol. The resulting yellow 2,4-dinitrophenylhydrazone was recrystallized from $CHCl_3$-*n*-hexane: mp 196–198°; yield 0.45 g (42%); nmr ($CDCl_3$) δ 3.50 (m, 2), 7.70 (m, 12), 8.32 (m, 2), and 8.89 (d, 1). *Anal.* Calcd for $C_{23}H_{18}N_6O_6$: C, 58.3; H, 3.80; N, 17.70. Found: C, 58.0; H, 4.04; N, 1781.

2-Phenyl-5-methyl-3,4-diazacyclopentadienone *N,N'*-Dioxide and Dimethyl Acetylenedicarboxylate. Preparation of 4-Keto-3-methyl-5-phenyl-1,2,6,7-tetracarbomethoxy-8-oxabicyclo[3.2.1]octa-2,6-diene (10).—A solution of 5 g (25 mmol) of dioxide **1a** in 10 ml of benzene and 10 ml of dimethyl acetylenedicarboxylate [Aldrich, bp 65% (0.1 mm)] was heated under reflux for 4 hr while its color changed from bright red to pale yellow. The mixture was cooled and the benzene and excess ester were removed under vacuum. The residual oil crystallized from methanol as fine needles. Recrystallization from $CHCl_3$–*n*-C_6H_{12} gave 6 g (55%) of yellow needles of **10**: mp 110–112°; ir (Nujol) 1760, 1740, 1720, and 1710 (C=O), and 1660 cm^{-1}; uv max (95% EtOH) 370 nm (ϵ 300), 218 (9800), and 245 (5000); nmr ($CDCl_3$) δ 3.66 (s, 3), 3.82 (bs, 6), 3.88 (s, 3), 2.02 (s, 3), and 7.55 (m, 5); mass spectrum (70 eV) *m/e* (rel intensity) 444 (10), 105 (100).[15] *Anal.* Calcd for $C_{22}H_{20}O_{10}$: C, 59.90; H, 4.97. Found: C, 59.94; H, 4.92.

Sodium Borohydride Reduction of 10. 4-Hydroxy-3-methyl-5-phenyl-1,2,6,7-tetracarbomethoxy-8-oxabicyclo[3.2.1]octa-2,6-diene (13).—A solution of 4.44 g (10 mmol) of **10** and 0.2 g (5.5 mmol) of $NaBH_4$ in 200 ml of methanol was stirred for 4 hr at 10–15°. The solution was acidified to congo red with HCl, concentrated, and then poured into 50 ml of distilled water. The white precipitate was collected, washed a few times with water, and crystallized from methanol. Recrystallization from methanol gave 3.5 g (80%) of white crystals of **13**: mp 146–148°; ir (Nujol) 3405 (OH), 1760, 1735, and 1705 (C=O), and 1645 cm^{-1}; nmr ($CDCl_3$) δ 2.20 (s, 3), 3.87 (s, 6), 3.78 (s, 3), 3.66 (s, 3), 4.75 (d, 1, J = 8.5 Hz), 4.05 (d, 1, J = 8.5 Hz), and 7.60 (m, 5); uv max (95% EtOH) 217 nm (ϵ 12,000). The mass spectrum (70 eV) showed a molecular ion peak at *m/e* 446. *Anal.* Calcd for $C_{22}H_{22}O_{10}$: C, 59.19; H, 4.97. Found: C, 59.04; H, 5.12. Compound **13** was oxidized back to **10** by the Jones Method.[16]

(14) Some evidence for the intermediacy of compound **18** was obtained when the cycloaddition was carried out at room temperature. The hydrate of a 1:1 adduct was obtained whose spectral properties could be interpreted in terms of structure **20**. See Experimental Section for details.



(15) The mass spectral analysis was prepared by the High Resolution Mass Spectrometry Center, Battelle Memorial Institute, Columbus, Ohio.

(16) A. Bowers, T. G. Halsall, E. R. H. Jones, and A. J. Lemin, *J. Chem. Soc.*, 2548 (1953).

Catalytic Hydrogenation of 10. 4-Keto-3-methyl-5-phenyl-1,2,6,7-tetracarbomethoxy-8-oxabicyclo[3.2.1]octene-6 (11) and 4-Keto-3-methyl-5-phenyl-1,2,6,7-tetracarbomethoxy-8-oxabicyclo[3.2.1]octene-2 (12).—A solution of 5 g (11 mmol) of **10** in 200 ml of methanol containing 0.2 g of Pd–C was stirred under 1 atm of hydrogen for 5 days. The catalyst was removed, the colorless solution concentrated to 100 ml, and the precipitate was recrystallized from methanol giving 1.85 (36%) of white crystals of **11**: mp 150–153°; ir (Nujol) 1760, 1740, and 1735 (C=O), and 1650 cm^{-1}; nmr ($CDCl_3$) δ 3.83 (s, 3), 3.76 (s, 6), 3.67 (s, 3), 1.20 (d, 3, J = 7.5 Hz, $CH_3CH<$), 3.45 (q, 1, J = 7.5 Hz, $CH-CH_3$), 4.20 (m, 1), and 7.50 (m, 5); uv max (95% EtOH) 320 nm (ϵ 500), 240 (4000), 217 (9200). The mass spectrum showed a M^+ at m/e 446. *Anal.* Calcd for $C_{22}H_{22}O_{10}$: C, 59.19; H, 4.97. Found: C, 58.95; H, 5.06.

Further concentration of the mother liquor gave a second crop of crystals. Recrystallization from methanol gave 2.0 g (50%) of pale yellow crystals of **12**: mp 100–102°; ir (Nujol 1750 and 1725 cm^{-1}; nmr ($CDCl_3$) δ 2.26 (s, 3), 3.87 (s, 3), 3.82 (s, 3), 3.67 (s, 6), 3.90 (d, 1, J = 12 Hz), 4.40 (d, 1, J = 12 Hz), and 7.38 (s, 5); uv max (95% EtOH) 370 nm (ϵ 280) 248 (7300), 211 (7300). The mass spectrum showed M^+ at m/e 446. *Anal.* Calcd for $C_{22}H_{22}O_{10}$: C, 59.19; H, 4.97. Found: C, 58.99; H, 5.10.

Catalytic Hydrogenation of 13. 4-Hydroxy-3-methyl-5-phenyl-1,2,6,7-tetracarbomethoxy-8-oxabicyclo[3.2.1]octene-2 (14).—A solution of 1 g (2.2 mmol) of **13** in 100 ml of methanol, containing 0.2 g of Pd–C was stirred under H_2 gas at 1 atm for 2 hr. The catalyst and solvent were removed and the residue was crystallized from methanol. Recrystallization from ethanol gave 0.8 g (80%) of white crystals of **14**: mp 170–173°; ir (Nujol) 3480 (OH), 1775, 1750, and 1695 cm^{-1} (C=O); nmr ($CDCl_3$) δ 2.17 (s, 3), 3.61 (s, 3), 3.70 (s, 3), 3.73 (s, 3), 3.84 (s, 3), 4.20 (m, 4), and 7.50 (m, 5). *Anal.* Calcd for $C_{22}H_{24}O_{10}$: C, 58.53; H, 5.39. Found: C, 58.87; H, 5.47. Compound **14** was oxidized to compound **12** with the Jones reagent.[16]

Sodium Borohydride Reduction of 11. 4-Hydroxy-3-methyl-5-phenyl-1,2,6,7-tetracarbomethoxy-8-oxabicyclo[3.2.1]octene-6 (16).—To a cold solution of 2 g (4.5 mmol) of **11** in 200 ml of methanol was added 0.1 g (2.5 mmol) of $NaBH_4$. The solution was stirred constantly in an ice bath for 4 hr and worked up as described for compound **13**. Recrystallization from methanol gave 1.6 g (80%) of white crystals of **16**: mp 140–142°; ir (Nujol) 3440, 1750, 1730, and 1710 (C=O), and 1650 cm^{-1} (C=C); nmr ($CDCl_3$) δ 1.06 (d, 3, J = 8.0 Hz), 2.90 (q, 1, J = 8.0 Hz), 3.55 (d, 1, J = 7.0 Hz), 3.67 (s, 3), 3.72 (s, 3), 3.82 (s, 6), 4.00 (d, 1, J = 12 Hz), 4.45 (q, 1), and 7.50 (m, 5). *Anal.* Calcd for $C_{22}H_{24}O_{10}$: C, 58.53; H, 5.39. Found: C, 59.09; H, 5.57. Jones oxidation[16] of **16** regenerated ketone **11**.

Sodium Borohydride Reduction of 12. Formation of Lactone 15.—To a cold solution of 1 g (2.2 mmol) of compound **12** in 50 ml of methanol was added 0.1 g (2.5 mmol) of $NaBH_4$. The mixture was stirred constantly and allowed to warm to room temperature during a 4-hr period. The reaction was worked up as described for compound **13**. Recrystallization of the white powder from methanol gave 0.2 g (24%) of white crystals of **15**: mp 131–133°; ir (Nujol) 1790 (lactone C=O), 1760 (ester C=O), and 1700 cm^{-1} (unsaturated ester C=O); nmr ($CDCl_3$) δ 2.26 (s, 3), 3.70 (s, 3), 3.73 (s, 3), 3.84 (s, 3), 3.28 (d, 1, J = 12 Hz), 4.28 (d, 1, J = 12 Hz), 5.06 (d, 1), and 7.45 (s, 5). *Anal.* Calcd for $C_{21}H_{20}O_9$: C, 60.58; H, 4.84. Found: C, 60.67; H, 5.03.

Potassium Permanganate Oxidation of 10. Trimethyl 2-Phenylfuran-3,4,5-tricarboxylate.—A mixture of 5 g (11 mmol) of compound **10** and 10 g (64 mmol) of $KMnO_4$ in 300 ml of acetone was stirred at 25° for 2 hr, and then heated on the steam bath for 1 hr. The solution was filtered and concentrated, and the solid residue was crystallized from ethanol and recrystallized from CH_2Cl_2–C_6H_{12} to give 2 g (58%) of white needles: mp 67–69°; ir (Nujol) 1745, 1725, and 1615 cm^{-1}; nmr ($CDCl_3$) 3.83 (s, 3), 3.92 (s, 3), 3.99 (s, 3), and 7.70 (m, 5); uv max (95% EtOH) 290 nm (ϵ 15,000), 217 (9200). The mass spectrum showed a M^+ peak at m/e 318. *Anal.* Calcd for $C_{16}H_{14}O_7$: C, 60.38; H, 4.43. Found: C, 60.55; H, 4.52.

2-Phenylfuran-3,4,5-tricarboxylic Acid.—Trimethyl 2-phenylfuran-3,4,5-tricarboxylate (1 g, 3 mmol) was refluxed for 1 hr with 20 ml of 35% aqueous KOH. The solution was filtered and acidified to congo red with HCl. On cooling, the potassium salt precipitated. Recrystallization from water gave 0.7 g of white needles, mp 300° dec. The potassium salt (0.7 g) was dissolved in 50 ml of 20% aqueous HCl. On cooling, white needles were deposited. Recrystallization from water gave 0.5 g (74%) of long needles: mp 212–215°; ir (KBr) 3540 and 3440 (OH), 1730 and 1685 (C=O), and 1210 cm^{-1}; nmr (acetone-d_6) δ 7.70 (m, 5), and 8.20 (s, 3). *Anal.* Calcd for $C_{13}H_8O_7$: C, 56.53; H, 2.92. Found: C, 55.84; H, 3.11.

Decarboxylation of 2-Phenylfuran-3,4,5-tricarboxylic Acid to 2-Phenylfuran.—A 1.0-g sample of **2-phenylfuran-3,4,5-tricarboxylic acid** was placed in a small flask with 5 ml of freshly distilled quinoline and 0.2 g of Cu powder. The mixture was heated in an oil bath at 240° for 4 hr while N_2 gas was passed over it. The mixture was cooled and filtered, and the filtrate was distilled under reduced pressure. Quinoline and 2-phenylfuran were isolated as one fraction [115° (20 mm)]. The quinoline was removed from this fraction by treatment with ethereal HCl. 2-Phenylfuran was isolated as a high boiling liquid: bp 110° (20 mm) [lit.[17] 107–108° (18 mm)]; ir (CCl_4) 1600 (C=C), 1475 and 1155 cm^{-1}; nmr (CCl_4) δ 6.35 (q, 1, J_{AB} = 1.5 Hz, J_{BC} = 3.5 Hz), 6.53 (d, 1, J_{BC} = 3.5 Hz), and 7.40 (m, 6). This spectrum corresponds to that reported.[18]

Reaction of 2-Methyl-5-phenyl-3,4-diazacyclopentadienone 3-Oxide (2a) with Dimethyl Acetylenedicarboxylate.—To a solution of 0.3 g (1.6 mmol) of **3a** in 5 ml of anhydrous benzene was added 5 ml of dimethyl acetylenedicarboxylate. The solution was refluxed at 90° for 4 hr. The benzene and the acetylenic ester were removed under reduced pressure and the residual oil was dissolved in CH_2Cl_2 and chromatographed on a silica gel column. The first fraction obtained was a pale yellow oil which crystallized from methanol to give 0.2 g (30%) of pale yellow crystals, **10**, mp 106–108°.

Reaction of 2-Methyl-5-phenyl-3,4-diazacyclopentadienone *N,N'*-Dioxide (1a) with Dimethyl Acetylenedicarboxylate at 25°.—A 2.0-g (9.6 mmol) sample of **1a** was suspended in 25 ml of dimethyl acetylenedicarboxylate. The suspension was stirred at room temperature for 72 hr. An additional 2 g of **1a** was added and stirring was continued for 72 hr. The mixture was filtered to give 1 g of white powder, **20**, mp 162–165°. This process was repeated and subsequent 2.0-g samples of **1a** added to the above dimethyl acetylenedicarboxylate solution gave 2.3 g and 2.6 g of compound **20** (total yield 5.9 g, 42%): ir (Nujol) 3400 and 3220 (OH), 1750 and 1705 (C=O), and 1520 cm^{-1} (N=NO); nmr (acetone-d_6) δ 1.50 (s, 3), 3.78 (s, 3), 3.82 (s, 3), 6.06 (s, 1), 6.67 (s, 1), and 7.50 (m, 5). *Anal.* Calcd for $C_{16}H_{16}N_2O_8$: C, 52.75; H, 4.43; N, 7.69. Found: C, 52.39; H, 4.48; N, 7.76.

Registry No.—**4a**, 26732-93-4; **4b**, 26732-94-5; **4c**, 26732-95-6; **4d**, 26732-96-7; **4e**, 26732-97-8; **4f**, 26732-98-9; **5a**, 26732-99-0; **6**, 26733-00-6; **7**, 26733-01-7; **8**, 26785-68-2; **9** (2,4-DNP), 12441-10-0; **10**, 26733-02-8; **11**, 26733-03-9; **12**, 26733-04-0; **13**, 26866-79-5; **14**, 26733-05-1; **15**, 26733-06-2; **16**, 26733-07-3; **20**, 26733-08-4; trimethyl 2-phenylfuran-3,4,5-tricarboxylate, 26733-09-5; 2-phenylfuran-3,4,5-tricarboxylic acid, 26733-10-8; 2-phenylfuran, 17113-33-6.

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