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SYNTHESES OF 2-DIAZO-4-CYCLOPENTENE-1,3-DIONE AND 2-DIAZO-4,6-CYCLOHEPTADIENE-1,3-DIONE. A MARKED DIFFERENCE IN THE DEGREE OF RESONANCE CONTRIBUTION OF THE CANONICAL FORMS

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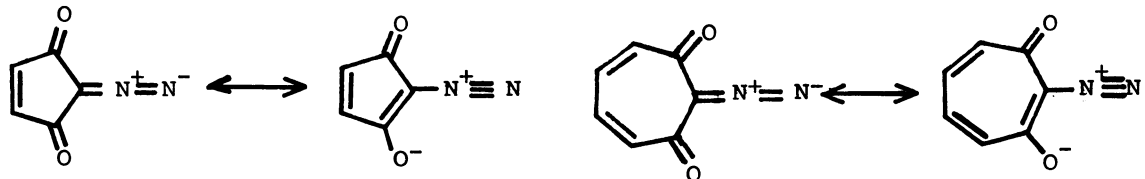
2-Diazo-4-cyclopentene-1,3-dione 1 and 2-diazo-4,6-cycloheptadiene-1,3-dione 2 are synthesized. The spectral data of these compounds indicate that there are considerable difference between them in the degree of resonance contribution of the canonical forms: the contribution of the enolate canonical form 1b to the resonance hybrid of 1 is less important than the corresponding form of usual 2-diazo-1,3-diones, while the enolate form 2b to 2 is very important.

Among a large number of organic diazo compounds, 2-diazo-1,3-diones are compounds having appreciable stability owing to the considerable contribution of the enolate canonical forms to their resonance hybrids.[1] When such forms as 1b and 2b are considered for 2-diazo-4-cyclopentene-1,3-dione 1 and 2-diazo-4,6-cycloheptadiene-1,3-dione 2 respectively, one may expect considerable difference in the importance of 1b and 2b to the resonance hybrid of each compound because 1b has a structure of antiaromatic cyclopentadienone while 2b does a structure of aromatic cycloheptatrienone (tropone). Although a few derivatives of these compounds are known,[2,3] no discussion has been made on this subject. We wish here to report the syntheses and some properties of the parent compounds, 1 and 2.



1a 1b 2a 2b

Synthesis of 2-diazo-4-cyclopentene-1,3-dione 1:

Usually 2-diazo-1,3-diones can be readily prepared from the corresponding 1,3-diones by diazo transfer reaction using *p*-toluenesulfonyl azide and base.[1] The reaction is, however, not applicable to 4-cyclopentene-1,3-dione 3 itself because of its extreme instability to bases.[4] Taking account of ready transformation of saturated 1,3-diones into 2-diazo-1,3-diones and moderate thermal stability of them, the synthesis of 1 was accomplished as described below.

Heating to reflux of 3 in excess furan for a week gradually separated out the 1:1 adduct 4 as solids in 75% yield [m.p. 156-157°C dec.; ν (KBr) 1570, 1325, 810,

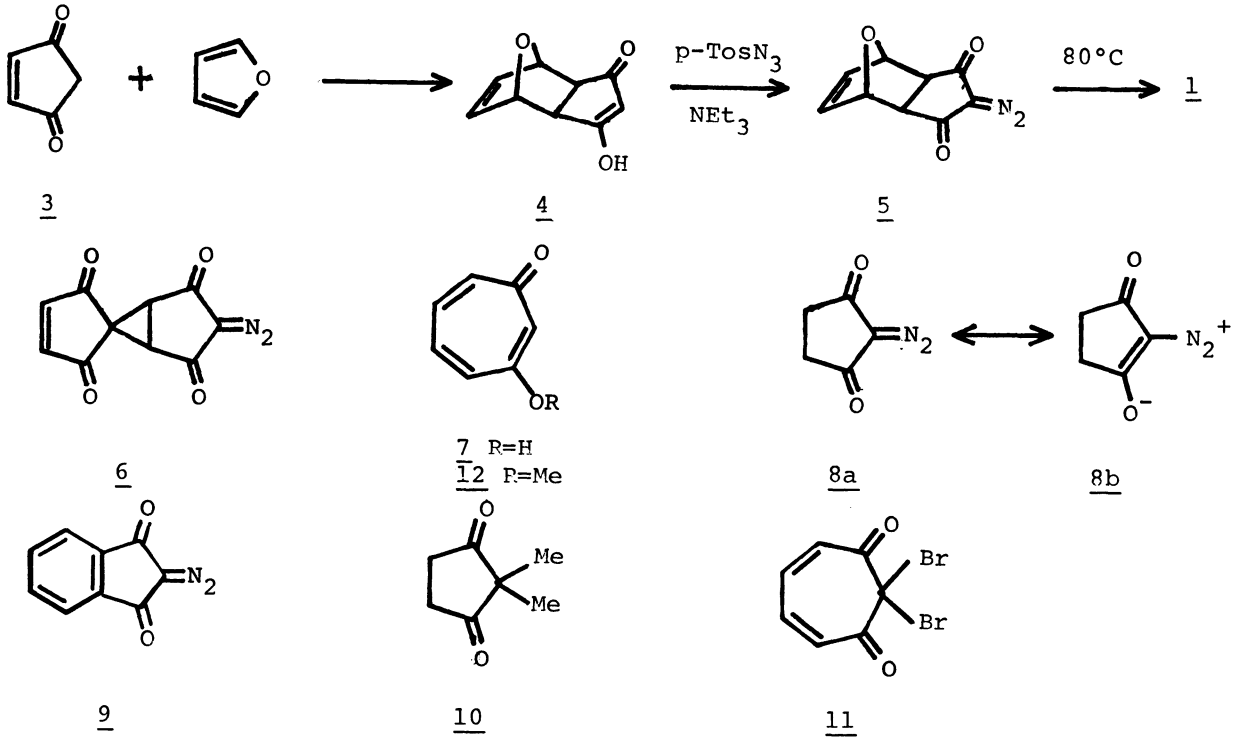
and 720 cm^{-1}; δ (DMSO-d_6) 2.61 (2H, s), 4.94 (2H, br. s), 5.21 (1H, s), and 6.51 (2H, br. s)].[5] The spectral data indicate the existence of 4 in the enol-form, and the absence of observable coupling between the juncture and the bridgehead protons suggests the *exo*-configuration.[6]

Diazo transfer reaction of 4 with *p*-toluenesulfonyl azide using Et_3N as a base (CH_2Cl_2, room temp.) afforded the diazo diketone 5 in 81% yield [m.p. 132-134°C dec.; ν (KBr) 2160, 1670, and 1310 cm^{-1}; δ ($CDCl_3$) 2.86 (2H, s), 5.32 (2H, t, J 0.9 Hz), and 6.57 (2H, t, J 0.9 Hz)].

On heating at 80°C in benzene for 28 hr, 5 underwent a cycloreversion to afford the desired compound 1 as fairly stable yellow solids (m.p. 99-101°C dec.) in 77% yield, accompanied with a small amount (5%) of a spiro compound 6 which was later verified to be arisen from two molecule of 1.[7]

Synthesis of 2-diazo-4,6-cycloheptadiene-1,3-dione 2:

This compound was prepared directly from 3-hydroxytropone 7[8] by diazo transfer reaction (tosyl azide, Et_3N, CH_2Cl_2) as pale yellow solids (m.p. 108-110°C dec.) in 25% yield.



3 4 5 1

6 7 R=H 12 R=Me 8a 8b

9 10 11

The IR, UV, and ^{1}H-NMR spectral data of 1 and 2 are listed in the Table 1 compared with those of 2-diazocyclopentane-1,3-dione 8,[9] 2-diazoindane-1,3-dione 9,[10] 2,2-dimethylcyclopentane-1,3-dione 10,[11] and 2,2-dibromo-4,6-cycloheptadiene-1,3-dione 11.[12]

The carbonyl absorption of 1 (ν=1670 cm^{-1}) is almost the same position as that of 5 in spite of additional conjugation with the double bond and only 30 cm^{-1} lower than that of 3 (ν=1700 cm^{-1}). This contrasts with the considerably large difference (Δν=70 cm^{-1}) between 8 and 10. On the other hand, the carbonyl absorption of 2 (ν= 1562 cm^{-1}) is at remarkably low frequency, which is almost the same as that of 3-

Table 1. The IR, UV, and ^{1}H-NMR data of 1, 2, 8, 9, 10, and 11.

Compds.	IR (KBr), ν cm^{-1}		UV (MeOH), λ nm (logε)	^{1}H-NMR ($CDCl_3$), δ ppm
	diazo	carbonyl		
1	2130	1670	225 (4.36), 285 (sh, 2.99) 337 (2.82)	6.86 s
2	2180	1562	237 (4.27) 304 (sh, 3.35) 318 (3.69) 329.5 (3.69)	6.72 AA'BB'
8	2130	1660	212.5 (4.30) 244.5 (4.13)	2.76 s
9	2120	1675	———	———
10	——	1730	———	2.75 s
11	——	1661	310 (3.50)	6.62 AA'BB'

Table 2. The ^{13}C-Chemical shifts of 1, 2, 8, and 9.[a]

Compds.	Chemical shifts, δ ppm[b]			
	C-2	C-1,3	C-4,5 (6,7)	Aromatic
1	64.0	185.7	142.2	———
2	101.2	179.0	134.9 137.6	———
8	74.1	193.7	34.9	———
9	70.5	182.7	———	123.4 136.2 138.2

[a] The measurements were performed in acetone-d_6 by adding $Cr(acac)_3$ to reduce considerably long spin-lattice relaxation time of C-2.[13]

[b] from Me_4Si.

methoxytropone 12 and 99 cm^{-1} lower that that of 11 (ν=1661 cm^{-1}). Although, in view of usually high frequency shift effect of α-bromo substituent on carbonyl infrared absorption, compound 11 may not be a suitable one for the comparison, the large differnce seems to be still valid. In case of 4-cyclopentene-1,3-dione 3, the carbonyl absorption is shifted to high frequency only by 5 cm^{-1} in 2,2-dibromo-4-cyclopentene-1,3-dione.[14] The diazo absorption of 2 is observed at 50 cm^{-1} higher frequency than that of 1; however exact reasoning can not be made in the lack of sufficient data on the infrared absortion of diazo compounds.

These results suggest that the degree of contribution of the enolate canonical form 1b to resonance hybrid of 1 is less than 8b to 8, and that 2b to 2 is, on the contrary, very important.

The chemical shift of the olefin protons of 1 is 0.3 ppm higher than those of 3, suggesting the presence of still some resonance contribution of 1b which should increase electron density on the double bond. In sharp contrast, the olefin protons of 2 is observed at 0.1 ppm lower field than those of 11 in spite of the IR spectral suggestion of large resonance contribution of 2b. The chemical shift of 2 is comparable to that of C-4$\sim$C-7 protons of 12 (δ=6.70), being indicative of their resemblance in the electronic property.

Further support on the above spectral suggestion was obtained from ^{13}C-chemical

shifts of Carbon-2 of 1, 2, and the related compounds (Table 2). The chemical shift of C-2 of 1 is 10.1 ppm higher than that of 8 and that of 9 lies between them. Strikingly, C-2 of 2 is observed at considerably low field of δ=101.2 ppm which is lower than that of 1 by so large as 37.2 ppm and approaches the chemical shifts of usual olefin carbons. The difference in the chemical shifts may reflect double bond character of C-1 (C-3)—C-2 single bond of these compounds: the order of the double bond character is 2 > 8 > 1 in accordance with the results from IR spectra.

The chemistry of 1 and 2 will be reported in due course.

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References and Notes

1) For a review see: M. Regitz, Synthesis, 351 (1972).
2) a) G. Seitz and W. Klein, Tetrahedron, 29, 253 (1973); b) F. B. Culp, K. Kurita, and J. A. Moore, J. Org. Chem., 38, 2945 (1973).
3) W. Ried and R. Conte, Chem. Ber., 104, 1573 (1971).
4) C. H. Depuy and E. F. Zwaeski, J. Amer. Chem. Soc., 81, 4920 (1959).
5) Satisfactory elemental analyses were obtained for all the new compounds described in this paper.
6) The coupling constants between bridgehead and *endo*-protons of 7-oxabicyclo[2.2.1]-hepta-2-enes have been observed to be nearly zero Hz, while those between bridgehead and *exo*-protons to be ca 4 Hz: see, a)F. A. L. Anet, Tetrahedron Lett., 1219 (1962); b) P. E. Eaton and K. Lin, J. Amer. Chem. Soc.,87, 2052 (1965); c) R. W. LaRochelle and B. M. Trost, Chem. Commun., 1353 (1970); d) Y. Kayama. M. Oda, and Y. Kitahara, Chemistry Lett., 345 (1974).
7) 6: m.p. 185-188°C dec.; ν (KBr) 2160, 1710, 1680, and 1340 cm^{-1}; δ ($CDCl_3$) 3.06 (2H, s) and 7.40 (2H, s). The mechanism of the formation of 6 from 1 will be reported in due course.
8) W. G. Dauben, K. Koch, O. L. Chapman, and S. L. Smith, J. Amer. Chem. Soc., 85, 2616 (1963).
9) This compound was prepared from cyclopentane-1,3-dione by diazo transfer reaction [m.p. 64-66°C; ν (KBr) 2130, 1660, and 1312 cm^{-1}; δ ($CDCl_3$) 2.76 s].
10) M. Regitz and O. G. Heck, Chem. Ber., 97, 1482 (1964).
11) W. C. Agosta and A. B. Smith III, J. Org. Chem., 35, 3856 (1970).
12) This compound was prepared from 7 by treatment with two equivalents of bromine in acetic acid in the presence of sodium acetate in 88% yield [yellow crystals; m.p. 93-94°C].
13) G. C. Levy and R. A. Komoroski, J. Amer. Chem. Soc., 96, 678 (1974).

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