Registry No.—**1**, 30625-58-2; **2**, 3815-30-3; **3**, 32979-83-2; **4**, 1896-62-4; **5**, 30626-03-0; **6**, 3815-31-4; **7**, 30626-00-7; **8**, 30625-98-0.

Acknowledgment.—Acknowledgment is made to the donors of The Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

[4,5-*c*(*d*)]Pyrazolotropone. A New Aromatic Ring System

CLAUDE V. GRECO* AND MICHAEL PESCE[1]

Department of Chemistry, St. John's University, Jamaica, New York 11432

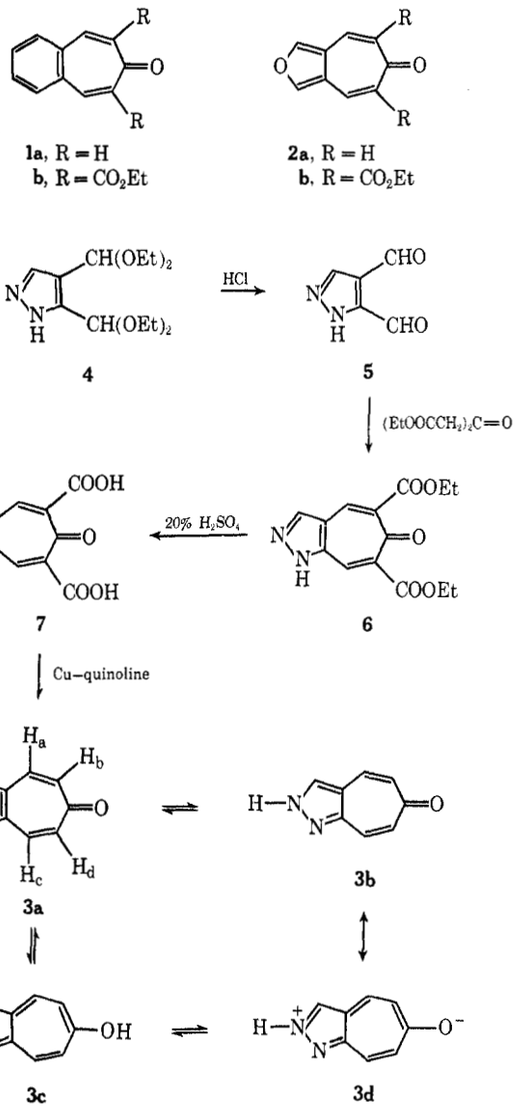
Received August 13, 1971

Heterocyclic analogs of 4,5-benzotropone (**1a**) were unknown until the recent preparations of 2-thiaazulen-6-ones,[2,3] 2-phenyl-1,3,5,7-tetramethyl-2-azaazulen-6-one,[3] and [4,5-*c*]furotropone (**2a**).[4] A hitherto unknown member of this series is [4,5-*c*(*d*)]pyrazolotropone (or 1,2-diaza-1*H*-azulen-6-one) (**3**), which could exist in any of several tautomeric structures **3a–d** (Scheme I). It was of interest to determine if the difference in basicity of the carbonyl group and the annular nitrogens would be relinquished for the stabilization which would result from further delocalization of the ten π electrons in the tautomer, 6-hydroxy-1,2-diazaazulene (**3c**).

A good yield of 2,7-dicarbethoxy[4,5-*c*(*d*)]pyrazolotropone (**6**)[5] was obtained as outlined in Scheme I. Its infrared spectrum (KBr) showed a broad band at 3226 cm^{-1} for the associated NH group in the pyrazole ring. The tropone ring carbonyl absorption was assigned to both bands at 1600 and 1520 cm^{-1} based on comparable bands reported[4] for the furotropone **2b** (1614 cm^{-1} in CH_2Cl_2) and the benzotropone **1b** (1625 and 1550 cm^{-1} in CH_2Cl_2). However, the intense band at 1600 cm^{-1} characteristic of the C=N absorption in pyrazoles[6] makes it difficult to definitely assign this band specifically as the carbonyl stretching frequency in **6**.

The ultraviolet absorption (methanol) at 222 nm (log ϵ 4.24) was attributed to the pyrazole ring, since alkyl-substituted pyrazoles absorb at 210–225 nm and arylpyrazoles at 250–280 nm.[6] The bands associated with the tropone ring (in isooctane at 225, 297, and 310 nm for tropone itself)[7] were shifted by the fused pyrazole chromophoric ring to 262 nm (log ϵ 4.43) and 316 (3.98), the latter band assigned to the conjugated keto function. Comparable absorptions were reported[4] for **2b**: λ_{max}^{EtOH} 219 nm (log ϵ 4.14) and 260 (4.49). The nmr spectra of **1**, **2**,[4] and **6** (*cf.* Experimental Section) were also very similar with respect to chemical shift values and absorption patterns for the tropone rings.

SCHEME I



Hydrolysis of **6** with 20% sulfuric acid gave 2,7-dicarboxy[4,5-*c*(*d*)]pyrazolotropone (**7**) in 87% yield. The parent structure was then obtained in 35% yield by decarboxylation of **7** at 205° with a copper–quinoline mixture. This represents a different, convenient, and improved method for decarboxylation of the precursor dicarboxylic acids to yield tropones. Usually acid hydrolysis in sealed tubes affords very low yields.[4]

The extent of aromaticity in **3** was estimated by a comparison of some spectral characteristics with the data available on the related unsubstituted systems, **1a** and **2a**. The bands at 1635 and 1582 cm^{-1} in the infrared spectra of tropones were previously considered carbonyl group vibrations. A study[8] on a number of tropones revealed that the lower frequency band was solvent dependent and therefore it was concluded that

(1) Taken from the Ph.D. dissertation of M. Pesce, St. John's University, June 1971.

(2) M. Winn and F. G. Bordwell, *J. Org. Chem.*, **32**, 1610 (1967).

(3) (a) A. V. El'tsov, A. A. Guinesina, and L. N. Kivokurtseva, *Zh. Org. Khim.*, **3**, 1343 (1967); *Chem. Abstr.*, **66**, 94581 (1967); (b) A. V. El'tsov, L. N. Kivokurtseva, and A. A. Guinesina, *Zh. Org. Khim.*, **4**, 907 (1968); *Chem. Abstr.*, **69**, 18958 (1968); (c) A. V. El'tsov, A. S. Guinesina, and L. N. Kivokurtseva, *Tetrahedron Lett.*, 735 (1968).

(4) M. S. Cook and E. J. Forbes, *Tetrahedron*, **24**, 4501 (1968).

(5) The nomenclature employed is analogous to that accepted for benzotropone and [4,5-*c*]furotropone,[4] the letters *c* and *d* referring to the numbering of the pyrazole ring in **3a** and **3b**, the numbers 4,5 referring to the side of the tropone ring fused to the pyrazole ring.

(6) A. N. Kost and I. I. Grandberg, "Advances in Heterocyclic Chemistry, Vol. 6, A. R. Katritzky and A. J. Boulton, Ed., Academic Press, New York, N. Y., 1966, pp 355–358, and references cited therein.

(7) W. von E. Doering and F. L. Detert, *J. Amer. Chem. Soc.*, **73**, 876 (1951).

(8) H. Goetz, E. Heilbronner, A. R. Katritzky, and R. A. Jones, *Helv. Chim. Acta*, **40**, 957 (1957).

this band was the carbonyl stretching mode. The lower frequency absorptions of furotropone **2a** and benzotropone **1a** were also found to be solvent dependent.[4] By correlating the frequency of this absorption with calculated bond orders it was inferred[4] that **2a** was less aromatic than tropone or **1a**. Since the carbonyl in **3** does not have a similar geometric disposition[9] to that in **1a** and **2a**, we were unable to compare the infrared absorptions at 1620–1590 cm^{-1} in the same manner.

The ultraviolet absorption bands of **3** (methanol) at 215 nm (log ϵ 4.01) for the pyrazole ring, 252 (4.40) for the tropone ring, and 320 (3.81) for the conjugated keto group compare well with those for benzotropone **1a** [λ_{max}^{EtOH} 231 nm (log ϵ 4.50), 272 (4.69), 332 (3.64), and 348 (3.45)] and for furotropone **2a** [λ_{max}^{EtOH} 211 nm (log ϵ 4.08), 216 (4.05), 250 (4.57), 255 (4.55), 292 (3.67), and 301 (3.67)]. We had an opportunity here to compare the extent of delocalization of the ring electrons by comparing the long-wavelength absorptions. The shift in maxima of about 47 nm toward the blue from the band for benzotropone was attributed[4] to a decrease in delocalization in furotropone. By analogy, the blue shift of only 28 nm by pyrazolotropone indicates the order of aromaticity to be benzotropone > pyrazolotropone > furotropone. The dipolar structure **3d** must make a significant contribution to the resonance hybrid of **3**.

In Table I, pyrazolotropone is compared with the other pertinent tropones with regard to their nmr properties. It is apparent that the three bicyclic structures can sustain an induced ring current. A comparison with tropone, which shows only a broadened singlet, reveals the bicyclic tropones to be less aromatic. Benzotropone and furotropone show their symmetry in the very similar absorption pattern for the peripheral protons. The unsymmetrical distribution of heteroatoms in **3** produces four absorptions consisting of two singlets and two doublets.

TABLE I
CHEMICAL SHIFTS FOR TROPONES[a]

Compd	Assignment, δ ppm: Fused ring protons	Tropone ring doublets
Tropone[b]		6.95 (broad singlet)
1a[c]	7.47 (4 H, s)	7.27 (2 H), 6.65 (2 H), J = 12 Hz
2a[c]	8.08 (2 H, s)	7.37 (2 H), 6.52 (2 H), J = 12 Hz
3	8.24 (NH, 1 H, s)	7.60 (H_c, s),[d] 6.64 (H_d, s)
	7.80 (CH, 1 H, s)	6.90 (H_a, d),[e] 6.40 (H_b, d)[e]

[a] The cross-conjugated 1,2,3,3a,8a-pentahydroazulen-6-one exhibited absorptions at δ 6.21 and 5.87 (J = 12.5 Hz) for the olefinic doublets: O. L. Chapman and T. H. Kock, *J. Org. Chem.*, **31**, 1042 (1966). [b] Data taken from D. J. Bertelli, C. Golino, and D. L. Dreyer, *J. Amer. Chem. Soc.*, **86**, 3329 (1964), solvent CCl_4. [c] Taken from ref 4, solvent not reported. [d] *Cf.* Scheme I for H symbols. [e] J = 2 Hz, solvent DMSO-d_6.

Experimental Section

All melting points, taken on a Mel-Temp apparatus, are uncorrected. Infrared spectra were measured on a Perkin-Elmer Infracord Model 137 using the potassium bromide pellet technique. Nuclear magnetic resonance spectra were recorded on a Varian A-60A using tetramethylsilane as an internal standard. Ultraviolet spectra were obtained with a Bausch and Lomb 505 spectrophotometer. Combustion analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, N. Y., and Childers Microanalytical Laboratory, Milford, N. J.

Materials.—Diazomethane was prepared by Eistert's procedure,[10] and assayed by the method of Fieser.[11] The acetylenedialdehyde bis(diethyl acetal) was prepared according to the procedure of Wohl[12] and used in the procedure described by Henkel and Weygand[13] for the preparation of pyrazole-3(5),4-dicarboxyaldehyde, yield 81.8%, mp 202–203° (lit. 203–205°).

2,7-Dicarbethoxy[4,5-*c*(*d*)]pyrazolotropone.—To 4.96 g. (0.039 mol) of pyrazole-3(5),4-dicarboxaldehyde suspended in 55 ml of benzene was added 7.95 g (0.0044 mol) of diethyl acetonedicarboxylate and 0.5 ml of piperidine. The suspension was refluxed for 2 hr and cooled, and the solid was filtered and recrystallized from chloroform–pentane to yield 8.7 g (76.5%) of **6** as a white powder, mp 159–161°. Five preparations gave yields ranging from 43 to 77%: nmr ($CDCl_3$) δ 1.33 (t, 6, CH_3, J = 7 Hz), 4.38 (q, 4, CH_2), 8.22 (s, 2, tropone ring), 8.40 (s, 1, pyrazole CH), 12.80 (br, 1, NH).

Anal. Calcd for $C_{14}H_{14}N_2O_5$: C, 57.93; H, 4.86; N, 9.65. Found: C, 57.77; H, 4.97; N, 9.58.

2,7-Dicarboxy[4,5-*c*(*d*)]pyrazolotropone.—A suspension of the above dicarbethoxypyrazolotropone (16 g, 0.055 mol) in 200 ml of 20% sulfuric acid was refluxed for 1.5 hr and then stirred for 2 hr at room temperature. The cooled suspension was filtered and the residue was dried overnight in a desiccator at 100°. Recrystallization from absolute ethanol afforded 10 g (78%) of **7** as a tan solid, mp 259–261°. Five preparations gave the acid in 73–78% yields: uv λ_{max}^{MeOH} 213 nm (log ϵ 3.97), 272 (4.43), 333 (3.78); ir λ_{max} (KBr) 3226 (NH), 1709 (COOH), 1590 cm^{-1} (C=O tropone); nmr (DMSO-d_6) δ 8.00 (s, 1 H, pyrazole CH), 8.24 (s, 2 H, tropone), 10.25 (broad absorption, 3 H, NH and two COOH).

Anal. Calcd for $C_{10}H_6N_2O_5$: C, 51.29; H, 2.58; N, 11.96. Found: C, 51.72; H, 2.92; N, 11.65.

[4,5-*c*(*d*)]Pyrazolotropone.—To 4.6 g (0.0197 mol) of the above dicarboxypyrazolotropone was added 0.7 g of copper powder and 25 ml of quinoline. The solution was heated in an oil bath at 205° for 3.5 hr. The black suspension was poured into 30 ml of an ice-cold solution of 50% hydrochloric acid and the suspension was filtered. The filtrate was extracted with five 60-ml portions of ethyl acetate, and the extracts were dried ($MgSO_4$) and evaporated to a yellow solid. Solution in ethyl acetate and addition of pentane to the cloud point yielded 1.02 g (35.5%) of **3** as a light yellow solid, mp 223.5–225°. Eight preparations gave yields ranging from 10 to 36%. The product did not react with 2,4-dinitrophenylhydrazine reagent.

Anal. Calcd for $C_8H_6N_2O$: C, 65.74; H, 4.14; N, 19.17. Found: C, 65.70; H, 4.17; N, 19.25.

Registry No.—**3a**, 33015-60-0; **3b**, 33015-61-1; **3c**, 33015-62-2; **6a**, 33015-63-3; **6b**, 33015-64-4; **7a**, 33015-65-5; **7b**, 33015-66-6.

(9) O. L. Chapman and T. H. Kock, *J. Org. Chem.*, **31**, 1042 (1966).

(10) B. Eistert, "Organic Syntheses," Collect. Vol. II, A. H. Blatt, Ed., Wiley, New York, N. Y., 1967, p 165.

(11) L. F. Feiser and M. Feiser, "Reagents for Organic Synthesis," Wiley, New York, N. Y., 1967, p 191.

(12) A. Wohl, *Chem. Ber.*, **45**, 339 (1912).

(13) K. Henkel and F. Weygand, *Chem. Ber.*, **76**, 812 (1943).

The Electronic Effects of Oxygen in the 8-Oxabicyclo[4.3.0]non-3-ene Series

BRADFORD P. MUNDY* AND RODNEY D. OTZENBERGER

Department of Chemistry, Montana State University, Bozeman, Montana 59715

Received July 16, 1971

Replacement of a methylene group by an oxygen heteroatom has been shown to affect the chemistry of the molecule involved. A conformational effect has