method by means of a computer program written by Maddox and Maddox.[18] These values were used to calculate phases by the symbolic addition procedure.[19] Origin determining signs were chosen for (058), (173), and (871) as all positive. Their E values are 3.38, 3.20, and 2.66, respectively. The 16 possible combinations of signs of four additional reflections were used to calculate probable phases for the remaining 110 reflections whose $|E|$ values were equal to or greater than 1.50. One combination of signs was clearly superior to the others. The four reflections chosen for iteration, their E values and correct phases are as follows (51 phases are plus and 66 are negative).

3	12	1	+2.72
3	2	1	−2.25
1	3	3	−2.46
1	6	1	−2.33

(18) H. S. Maddox and M. L. Maddox, private communication, 1965.
(19) J. Karle and I. L. Karle, *Acta Crystallogr.*, **21**, 849 (1966).

An E Fourier synthesis revealed the position of the heavy atoms. The positional parameters and an isotropic temperature factor for each of the 11 atoms were least-squares refined and resulted in an R index of 0.16, where R is defined as $\Sigma||F_o| - |F_c||/\Sigma|F_o|$. With anisotropic temperature factors, R was reduced to 0.060. A Fourier difference calculation revealed the approximate position of the nine hydrogen atoms. Three additional cycles of least-squares refinement, with anisotropic temperature factors for the heavy atoms, and isotropic temperature factors for the hydrogen atoms, gave a final R index of 0.046.[12]

Registry No.—**1c**, 34454-53-0; **2a**, 34454-54-1; **2b**, 34454-55-2; HSCN, 463-56-9.

Acknowledgment.—The authors wish to thank Miss Leila Wing for technical assistance and Dr. Alan Zalkin for use of his computer programs.

1-Acyl-2,4,5-triphenyl-3-imidazolines[1]

J. N. WELLS,* O. REED TARWATER, AND P. E. MANNI

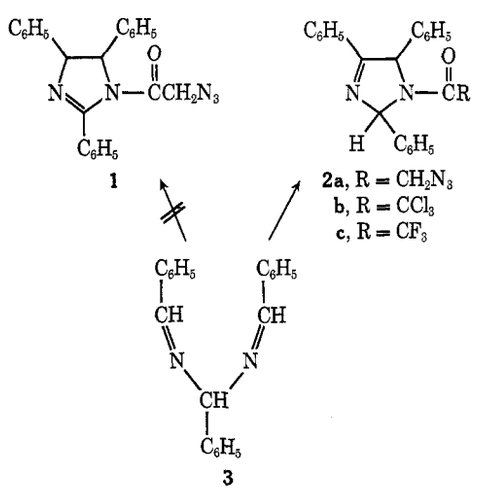
Department of Medicinal Chemistry and Pharmacognosy, School of Pharmacy and Pharmacal Sciences, Purdue University, Lafayette, Indiana 47907

Received October 13, 1971

Condensation of hydrobenzamide with acid chlorides in the presence of triethylamine is shown to give 1-acyl-2,4,5-triphenyl-3-imidazolines. Synthesis of the isomeric 1-acyl-2-imidazolines and the hydrolysis of 1-acyl-2- and -3-imidazolines is also discussed.

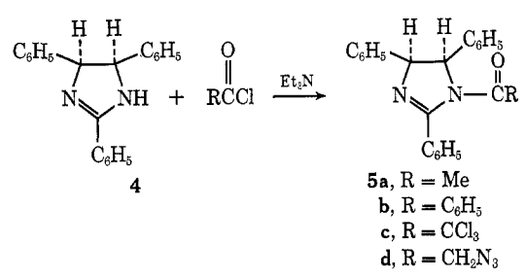
A recent publication from these laboratories[2] reported the isolation of a compound postulated to be 1-azidoacetyl-2,4,5-triphenyl-2-imidazoline (**1**). We now wish to report further work which indicates that this compound is instead a mixture of *cis*- and *trans*-azidoacetyl-2,4,5-triphenyl-3-imidazoline (**2a**). We have also expanded the cyclization to other acid chlorides and trifluoroacetic anhydride.

The imidazoline **2a** was produced by the reaction of hydrobenzamide (**3**) and azidoacetyl chloride in the



presence of triethylamine. Although other imines have been treated with acid chlorides or ketenes to give cycloaddition products,[3-5] there seem to have been no reports of related electrophilic substitutions of hydrobenzamide in the literature. It was reported that the order of addition of the reactants played an important role in the course of this reaction. When **3** and triethylamine were combined and a solution of azidoacetyl chloride was added dropwise, 3-azido-4-phenyl-2-azetidinone was produced. If the order of addition was reversed, *i.e.*, if **3** and azidoacetyl chloride were combined and triethylamine was added, the imidazoline was obtained. Although **3** cyclizes on heating to 2-*cis*-4,5-triphenyl-2-imidazoline (**4**),[6] no reaction was observed with **3** and triethylamine in methylene chloride solution in the absence of acid chloride.

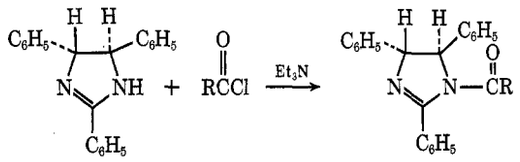
The two geometrical isomers of **1** have been prepared by an alternate method. 2-*cis*-4,5-Triphenyl-2-imidazoline (**4**) with acetyl chloride and trichloroacetyl chloride gave the corresponding 1-acyl-2-*cis*-4,5-triphenyl-2-imidazolines (**5**). Acylation with benzoyl chloride gave a compound whose physical data agreed with those of authentic 1-benzoyl-2-*cis*-4,5-triphenyl-2-imidazoline (**5b**).[7] Reaction with azidoacetyl chloride gave 1-azidoacetyl-2-*cis*-4,5-triphenyl-2-imidazoline (**5d**).



Conversion of **4** to 2-*trans*-4,5-triphenyl-2-imidazoline (**6**) occurs on heating to 170° in the presence of metallic

(1) Abstracted from the Ph.D. Thesis of O. Reed Tarwater, Purdue University, Aug 1970.
(2) J. N. Wells and R. E. Lee, *J. Org. Chem.*, **34**, 1477 (1969).
(3) J. C. Sheehan and J. J. Ryan, *J. Amer. Chem. Soc.*, **73**, 1204 (1951).
(4) A. K. Bose, B. Anjaneyulu, S. K. Bhattacharya, and M. S. Manhas, *Tetrahedron*, **23**, 4769 (1967).
(5) J. C. Martin, K. C. Brannock, R. D. Burpitt, P. G. Gott, and V. A. Hoyle, Jr., *J. Org. Chem.*, **36**, 2211 (1971).
(6) R. J. Ferm and J. L. Riebsomer, *Chem. Rev.*, **54**, 593 (1954).
(7) A. Claus and L. Scherbel, *Ber.*, **18**, 3077 (1885).

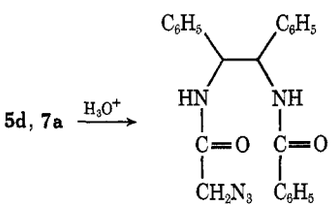
sodium.[8] By this method **6** was prepared and treated with azidoacetyl chloride to give 1-azidoacetyl-2-*trans*-4,5-triphenyl-2-imidazoline (**7a**). Reaction of **6** with trichloroacetyl chloride gave 1-trichloroacetyl-2-*trans*-4,5-triphenyl-2-imidazoline (**7b**).



6 **7a**, R = CH_2N_3; **b**, R = CCl_3

The imidazoline **2a** had a melting point of 218–219°.[2] Compounds **5d** and **7a** had melting points of 169–171 and 120.5–121.5°, respectively.

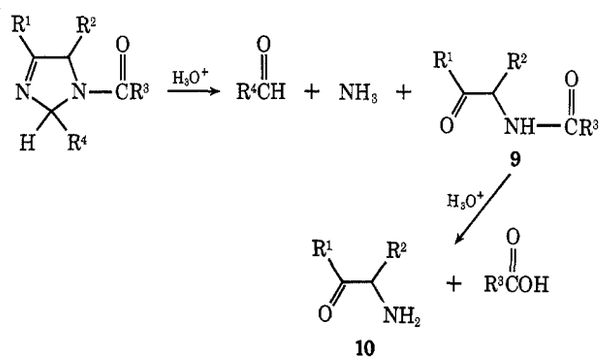
The hydrolysis of acylated 2-imidazolines has been shown to occur with cleavage at the 1,2 bond to give the corresponding diamide.[5] Hydrolysis of **5d** and **7a** produced *erythro*- and *threo*-*N*-benzoyl-*N'*-azidoacetyl-1,2-diphenylethylenediamine, respectively (**8**). Therefore, both **5d** and **7a** are confirmed to be the 2-imidazolines.



8 (erythro, threo)

Hydrolysis of acylated 3-imidazolines has been shown[9] to occur as follows.

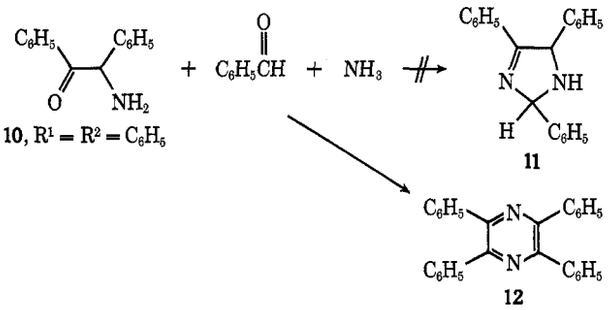
Hydrolysis of **2a** gave two identifiable products. An aldehyde was isolated which was shown by comparison of ir spectra to be benzaldehyde (**9**, $R^4 = C_6H_5$). An amino ketone was isolated whose mass spectrum was consistent with **10** ($R^1 = R^2 = C_6H_5$); the ir spectrum



9 **10**

was identical with that of authentic **10** ($R^1 = R^2 = C_6H_5$).[10] Treatment of **2c** with potassium hydroxide in ethanol removed the trifluoroacetyl group. Migration of the double bond then gave the more stable amidine system, 2-*trans*-4,5-triphenyl-2-imidazoline (**6**).

Several attempts were made to prepare 2,4,5-triphenyl-3-imidazoline (**11**) so that it could be acylated and provide an independent synthesis of the 1-acyl-3-imidazolines. α-Aminodeoxybenzoin[10] was treated with benzaldehyde in the presence of ammonia. The only product isolated was tetraphenylpyrazine (**12**) formed by reaction of 2 mol of **10**.[11,12]



10, $R^1 = R^2 = C_6H_5$ **11** **12**

Spectral evidence strongly supports the 3-imidazoline assignment. The infrared spectra of the proposed 3-imidazolines (**2a–c**) showed a strong band between 5.95 and 6.02 μ assigned to a tertiary amide,[13] and a band of moderate intensity between 6.12 and 6.18 μ indicative of a conjugated C=N linkage.[14,15] These assignments are reinforced by the presence of similar bands in authentic 2-imidazolines (**4**, **6**) and the C–N absorption at 6.16 μ in hydrobenzamide.

The ultraviolet spectrum of **2c** was measured in neutral and acidic solution. A solution in ethanol–hexane (8:2) exhibited λ_{max} 248 nm. This value compares favorably with those of other compounds containing the ArC=NR chromophore.[16] Addition of H_2SO_4 produces a bathochromic displacement of absorption to 268 nm. Protonation of the azomethine nitrogen is known to give similar shifts.[16,17] Similarly, the ultraviolet spectra of *cis*- and *trans*-2,4,5-triphenyl-2-imidazolines show a peak near 220 nm which is shifted to 245 nm upon acidification. A compound having the 4-imidazoline structure should show absorption characteristics of enamines, in which case a hypsochromic rather than bathochromic shift would be observed upon acidification.[18]

Confirmation of the structural assignment made from degradation studies and uv and ir spectra was sought from nmr studies of the 2- and 3-imidazolines. Both types show a two-proton multiplet near δ 7.75 which we assign to phenyl protons ortho to the point of attachment to the azine group. In the 2-imidazolines the chemical shift of this multiplet changes with the nature of the acyl groups; the most significant changes occur when the acyl group is trichloroacetyl (δ 7.91) or benzoyl (δ 7.68). In the 3-imidazolines (**2a–c**) this resonance is insensitive to acyl substitution, suggesting that the carbon bearing the phenyl group is not attached to the acyl-substituted nitrogen.

The 100-MHz spectrum of 1-azidoacetyl-2,4,5-triphenyl-3-imidazoline (**2a**) indicates the presence of cis and trans isomers. Two methylene signals of unequal

(8) F. R. Japp and J. Moir, *J. Chem. Soc.*, **77**, 608 (1900).
(9) F. Asinger, M. Thiel, and R. Sowada, *Monatsh. Chem.*, **90**, 402 (1959).
(10) R. Pschorr and F. Bruggeman, *Ber.*, **35**, 2740 (1902).
(11) E. Jassman and H. Schultz, *Pharmazie*, **18**, 461 (1963).
(12) G. Kirchner, *Justus Liebigs Ann. Chem.*, **625**, 98 (1959).
(13) A. D. Cross and R. A. Jones, "An Introduction to Practical Infra-red Spectroscopy," 3rd ed, Plenum Press, New York, N. Y., 1969, p 89.
(14) J. Fabian, V. Delaroff, and M. Legrand, *Bull. Soc. Chim. Fr.*, 287 (1956).
(15) J. Fabian, M. Legrand, and P. Poirier, *ibid.*, 1499 (1956).
(16) M. A. El-Bayoumi, M. El-Asser, and F. Abdel-Halin, *J. Amer. Chem. Soc.*, **93**, 586 (1971).
(17) A. I. Scott, "Interpretation of the Ultraviolet Spectra of Natural Products," Macmillan, New York, N. Y., 1964, p 39.
(18) J. L. Johnson, M. E. Herr, J. C. Babcock, A. E. Fonken, J. E. Stafford, and F. W. Heyl, *J. Amer. Chem. Soc.*, **78**, 430 (1956).

intensity are noted for the azidoacetyl group, a singlet at δ 3.35 and an apparent doublet (separation 1 Hz) at δ 3.45, which corresponds to the inner lines of an AB quartet produced from nearly equivalent nuclei. The ratio of integrals of the "doublet" to the singlet is 3:4. The resonances of the C-2 and C-5 protons appear as two pairs of doublets located near δ 7.0 and 6.5, respectively. The ratio of integrals of the weaker pair of doublets (δ 6.32 and 7.15) to the stronger pair is the same as calculated for the azidoacetyl methylene signals. The resonances of the ring methine protons in **2b** and **2c** show a pattern similar to that described above in that a pair of doublets is located near δ 6.5. However, the multiplicity of the downfield signals is obscured by overlapping phenyl absorption. Chromatographic analysis of **2a–c** failed to show two isomers. The compounds were homogeneous by tlc. Glc of **2c** yielded one peak, while data for **2a,b** were equivocal. If the samples are homogeneous the nmr data are consistent with either a system undergoing slow (on the nmr time scale) inversion at the acylated nitrogen or one in which rotation about the nitrogen–carbonyl bond is restricted. It is noteworthy that for aziridines, in which nitrogen is substituted with acyl groups or bulky substituents, nonequivalence due to slow inversion is seen only at low temperatures.[19] This behavior need not be shown by **2a–c**, although they are acylated and molecular models indicate significant steric interaction among the 3- and 5-phenyl groups and the acyl group. The same steric interaction inhibits free rotation of the acyl group. Our data cannot exclude either the possibility of slow inversion or hindered rotation.

The coupling of 3.5–4 Hz between methine protons on C-2 and C-5 in **2a–c** indicates significant long-range interaction between these protons. Homoallylic coupling of this magnitude has been observed in other systems.[20] Recent studies[21] have shown long-range coupling (J = 0.3 Hz) between the same protons in imidazolidines.

Direct evidence against a 4-imidazoline structure was obtained from a deuterium-exchange experiment. The nmr spectrum (60 Hz) of **2a** was unchanged after shaking the sample with D_2O.

Experimental Section[22]

Acylation of 2-*cis*-4,5-Triphenyl-2-imidazoline (4) and 2-*trans*-4,5-Triphenyl-2-imidazoline (6).—2-*cis*-4,5-Triphenyl-2-imidazoline (**4**) or 2-*trans*-4,5-triphenyl-2-imidazoline (**6**) (5.0 g, 16.7 mmol) and triethylamine (1.7 g, 16.7 mmol) were combined in 150 ml of dry CH_2Cl_2 and stirred at 0° while 16.7 mmol of the appropriate acid chloride in 50 ml of CH_2Cl_2 was added over 1–2 hr. The reaction mixture was allowed to warm to room temperature and refluxed for 4 hr. After cooling to room temperature the reaction mixture was poured into 300 ml of water. The CH_2Cl_2 phase was separated and the aqueous phase was then extracted several times with $CHCl_3$. The CH_2Cl_2 and $CHCl_3$ extracts were combined and washed with cold dilute HCl and then with water. The organic extracts were dried and the solvent was removed *in vacuo*. The residue was recrystallized from EtOH.

Acylation of **4** with acetyl chloride gave 4.1 g (75% yield) of 1-acetyl-2-*cis*-4,5-triphenyl-2-imidazoline (**5a**): mp 153.5–154.5°; nmr δ 7.75 (m, 2, ArC=N), 7.40 (m, 3, Ar), 6.95 (s, 10, Ar), 5.63 (s, 2, C-4 and C-5), 1.85 (s, 3, $COCH_3$); ir 5.92 (C=O), and 6.15 μ (C=N); mass spectrum m/e 340 (M^+).

Acylation of **4** with benzoyl chloride gave 2.40 g (36% yield) of 1-benozyl-2-*cis*-4,5-triphenyl-2-imidazoline (**5b**): mp 181–183° (lit.[8] mp 180°); nmr δ 7.68 (m, 2, ArC=N), 6.67–7.50 (m, 18, Ar), 5.63 (AB quartet, J_{AB} = 8 Hz, 2, C-4 and C-5); ir 6.0 μ (C=O).

Acylation of **4** with trichloroacetyl chloride gave 6.55 g (88.5% yield) of 1-trichloroacetyl-2-*cis*-4,5-triphenyl-2-imidazoline (**5c**): mp 220–221°; nmr δ 7.91 (m, 1, ArC=N), 7.58 (m, 3, Ar), 7.05 (m, 10, Ar), 5.97 (AB quartet, J_{AB} = 7 Hz, 2, C-4 and C-5); ir 5.88 (C=O) and 6.12 μ (C=N); mass spectrum m/e 442 (M^+).

Acylation of **4** with azidoacetyl chloride gave 4.30 g (68% yield) of 1-azidoacetyl-2-*cis*-4,5-triphenyl-2-imidazoline (**5d**): mp 169–171°; nmr δ 7.78 (m, 2, ArC=N), 7.51 (m, 3, Ar), 6.98 (s, 10, Ar), 5.67 (s, 2, C-4 and C-5), 3.60 (AB quartet, J_{AB} = 16 Hz, 2, CH_2N_3); ir (KBr) 4.75 (N_3), 5.9 (C=O), and 6.15 μ (C=N); mass spectrum m/e 381 (M^+).

Acylation of 2-*trans*-4,5-triphenyl-2-imidazoline (**6**) with azidoacetyl chloride gave 6.3 g (98% yield) of 1-azidoacetyl-2-*trans*-4,5-triphenyl-2-imidazoline (**7a**): mp 120.5–121.5°; nmr δ 7.75 (m, 2, ArC=N), 7.2–7.6 (m, 13, Ar), 5.17 (s, 2, C-4 and C-5), 3.5 (AB quartet, J_{AB} = 17 Hz, 2, CH_2N_3); ir 4.75 (N_3), 5.9 (C=O), and 6.15 μ (C=N); mass spectrum m/e 381 (M^+).

Acylation of **6** with trichloroacetyl chloride gave 6.9 g (92% yield) of 1-trichloroacetyl-2-*trans*-4,5-triphenyl-2-imidazoline (**7b**): mp 191–192°; nmr δ 7.96 (m, 2, ArC=N), 7.17–7.67 (m, 13, Ar), 5.80 (s, broad, 1, C-5), 5.30 (s, broad, 1, C-4); ir 5.85 (C=O) and 6.12 μ (C=N); mass spectrum m/e 442 (M^+).

Anal. Calcd for $C_{23}H_{17}N_2OCl_3$: C, 62.25; H, 3.86. Found: C, 62.12; H, 4.10.

Hydrolysis of 1-Azidoacetyl-2-*cis*-4,5-triphenyl-2-imidazoline (5d).—1-Azidoacetyl-2-*cis*-4,5-triphenyl-2-imidazoline (**5d**) (1.0 g, 2.63 mmol) was dissolved in 80 ml of 95% EtOH, 2 ml of 3 *N* HCl was added, and the reaction mixture was refluxed for 16 hr. The reaction mixture was allowed to cool to room temperature and the white solid was removed by filtration. *erythro*-*N*-Benzoyl-*N'*-azidoacetyl-1,2-diphenylethylenediamine (**8**) (0.79 g, 75% yield) was obtained and was recrystallized from EtOH: mp 260–262°; nmr (DMSO-d_6) δ 8.7 (s, broad, 1, NH) 7.0–7.67 (m, 1, Ar and NH), 5.38 (apparent d, separation 4 Hz, C-1 and C-2), 3.43 (apparent d, separation 2 Hz, 2, CH_2N_3); ir 4.75 (N_3) and 6.1 μ (C=O); mass spectrum m/e 399 (M^+), 342 (1), 300 (2), 236 (2), 210 (74), 105 (100), 77 (30).

Anal. Calcd for $C_{23}H_{21}N_5O_2$: C, 69.16; H, 5.30. Found: C, 69.00; H, 5.54.

Hydrolysis of 1-Azidoacetyl-2-*trans*-4,5-triphenyl-2-imidazoline (7a).—1-Azidoacetyl-2-*trans*-4,5-triphenyl-2-imidazoline (**7a**) (0.75 g, 1.97 mmol) was dissolved in 75 ml of 95% EtOH, 6 ml of 3 *N* HCl was added, and the mixture was refluxed for 24 hr. Upon cooling in an ice bath 0.45 g (57.5% yield) of *threo*-*N*-benzoyl-*N'*-azidoacetyl-1,2-diphenylethylenediamine (**8**) precipitated, which was isolated by filtration and recrystallized from EtOH: mp 234–234.5°; nmr (DMSO-d_6) δ 8.72 (s, broad, 1, NH), 6.8–7.8 (m, 16, Ar and NH), 5.4 (m, 2, C-1 and C-2), 3.75 (apparent d, separation 1 cps, 2, CH_2N_3); ir (KBr) 4.75 (N_3) and 6.11 μ (C=O); mass spectrum m/e 399 (M^+), 342 (1), 300 (2), 236 (2), 210 (74), 105 (100), 77 (30).

Anal. Calcd for $C_{23}H_{21}N_5O_2$: C, 69.16; H, 5.30. Found: C, 68.93; H, 5.37.

Hydrolysis of 1-Azidoacetyl-2,4,5-triphenyl-3-imidazoline (2a).—1-Azidoacetyl-2,4,5-triphenyl-3-imidazoline (**2a**) (0.70 g, 1.84 mmol) was combined with 75 ml of 3 *N* HCl and refluxed for 20 hr. The reaction mixture was then allowed to cool to room temperature and extracted with chloroform to remove any nonbasic products. After drying, the chloroform was removed *in vacuo* to give an oil which was shown by ir to be benzaldehyde.

(19) F. A. L. Anet and J. M. Osyany, *J. Amer. Chem. Soc.*, **89**, 352 (1967).

(20) P. Bladon, *Annu. Rev. NMR (Nucl. Magn. Resonance) Spectrosc.*, **2**, 11 (1969).

(21) J. P. Albrand, A. Cogne, D. Gagnaire and J. B. Robert, *Tetrahedron*, **27**, 2453 (1971).

(22) Melting points were determined using a Buchi Capillary Melting Point Apparatus with open capillary tubes and are uncorrected. Infrared spectra were obtained with a Perkin-Elmer 21 or Model 237-B infrared spectrophotometer. Mass spectral data were obtained on a Perkin-Elmer Hitachi RMU-6-A mass spectrometer. A Varian Associates A-60A spectrometer was used at a sweep width of 500 cps using TMS as an internal standard to determine nmr spectra. Gas chromatographic data were obtained from a Beckman GC-5 instrument equipped with a hydrogen flame ionization detector. The column used was 3% OV-1 on Chromosorb G (AW-DMCS), 6 ft × 0.125 in., and helium carrier flow was 75 ml/min. Unless otherwise noted samples were dissolved in $CDCl_3$ (nmr) or $CHCl_3$ (ir). The high-resolution nmr spectra were determined on a Varian Associates HA-100 spectrometer. Elemental analysis were determined by Midwest Microlabs, Inc., Indianapolis, Ind. 46226.

The aqueous phase was made basic with aqueous NaOH and then extracted with chloroform. Removal of the dried chloroform *in vacuo* gave a yellow oil, ir (neat) 5.95 μ (aryl ketone). This ir was identical with that of authentic α-aminodeoxybenzoin.[10] The hydrochloride was formed and recrystallized from EtOH–Et_2O: mp 240–244° (lit.[7] mp 244°); mass spectrum (as the free base) *m/e* 211 (M^+, 3), 210 (7), 106 (11), 105 (100), 77 (44).

1-Trichloroacetyl-2,4,5-triphenyl-3-imidazoline (2b).—Hydrobenzamide (5.5 g, 18.5 mmol) and 1.87 g (18.5 mmol) of triethylamine were combined in 200 ml of CH_2Cl_2 at 0° and stirred while 3.4 g (18.5 mmol) of trichloroacetyl chloride dissolved in 50 ml of CH_2Cl_2 was added over a 2-hr period. The reaction mixture was allowed to warm to room temperature and stirred for 12 hr. The reaction mixture was treated with 100 ml of 1.5 *N* HCl, the CH_2Cl_2 phase was separated, and the aqueous phase was extracted several times with chloroform. The CH_2Cl_2 and $CHCl_3$ extracts were combined and washed twice with H_2O. After drying, the organic solvents were removed *in vacuo* to give a thick yellow oil which crystallized upon washing with Et_2O to give 1.77 g (21.6% yield) of white solid. Recrystallization from ethanol gave a solid: mp 207–209° dec; nmr δ 7.75 (m, 2, ArC=N), 7.16–7.55 (m, 14, Ar and C-2), 6.75 (d, J = 3.5 Hz, 1, C-5); ir 5.97 (C=O) and 6.12 μ (C=N); mass spectrum *m/e* 442 (M^+). The nmr signal due to the C-5 proton was weak, and the presence of a small amount of a second isomer could not be ruled out on the basis of nmr integration alone. Glc analysis of **2b** (column 228°, inlet 265°) showed two peaks, retention time 17.5 and 23.5 min. The major component always eluted first, but the ratio of minor to major peak varied from 0.05 to 0.40.

Anal. Calcd for $C_{23}H_{17}OCl_3N_2$: C, 62.25; H, 3.86. Found: C, 62.17; H, 4.11.

1-Trifluoroacetyl-2,4,5-triphenyl-3-imidazoline (2c).—Following the foregoing procedure, 18.5 mmol of hydrobenzamide was treated with 3.9 g (18.5 mmol) of trifluoroacetic anhydride to give 1.5 g (25% yield) of white solid: mp 192–193°; nmr δ 7.75 (m, 2, ArC=N), 7.2 (m, 14 Ar and C-2), 6.45 and 6.55 (two doublets, J = 3.5 Hz, 1 H, C-5); ir (KBr) 5.95 (C=O), and 6.18 μ (C=N). Glc of **2c** (column 210°, inlet 265°) gave one peak, retention time 12 min.

Anal. Calcd for $C_{23}H_{17}N_2OF_3$: C, 70.06; H, 4.34. Found: C, 70.46; H, 7.58.

Reaction of 1-Trifluoroacetyl-2,4,5-triphenyl-3-imidazoline (2c) with Alcoholic Potassium Hydroxide.—A mixture of 1-trifluoroacetyl-2,4,5-triphenyl-3-imidazoline (93 mg, 13.2 mmol), potassium hydroxide (132 mg, 13.2 mmol), and 25 ml of absolute ethanol was heated at reflux for 30 min. The ethanol was removed *in vacuo*, and 50 ml of water was added to the residue. The aqueous mixture was extracted with ether. Evaporation of the dried ether gave a solid which was recrystallized from aqueous ethanol to give 47.4 mg of white, crystalline solid, mp 201–203°. A mixture melting point with 2-*trans*-4,5-triphenyl-2-imidazoline was undepressed and the ir spectra were identical.

Nmr spectrum (100 MHz) of 1-azidoacetyl-2,4,5-triphenyl-3-imidazoline (2a)[2] showed peaks at δ 3.35 (s) and 3.44 (d, separation 1 Hz), total integration 2 H, CH_2N_3, 6.32 (d, J = 4 Hz) and 6.58 (d, J = 4 Hz), total integration 1 H, C-2, 6.90 (d, J = 4 Hz) and 7.15 (d, J = 4 Hz), C-5, 7.40 (m, 13 H, Ar), 7.80 (m, 2 H, ArC=N). Glc analysis (column 220°, inlet 265°) showed a major peak, retention time 25 min, and three minor ones, retention times 16, 17.5, and 32.5 min. The intensity of the minor peaks varied greatly; *e.g.*, repeated injections gave area ratios of retention times 16/25 that ranged from 0.07 to 0.17. To check for possible decomposition of the sample in the injection port the temperature was reduced to 235°. However, the sample was poorly vaporized at this temperature, and an extremely broad peak of low intensity was seen. Thin layer chromatography using several solvent systems indicated that **2a** was homogeneous.

Registry No.—*cis*-**2a**, 34454-36-9; *trans*-**2a**, 34493-25-9; **2b**, 34454-37-0; **2c**, 34454-38-1; **5a**, 34454-39-2; **5b**, 34454-40-5; **5c**, 34454-41-6; **5d**, 34454-42-7; **7a**, 34454-43-8; **7b**, 34454-44-9; *erythro*-**8**, 34454-45-0; *threo*-**8**, 34454-46-1.

Synthesis and Thermodynamic Acidity of Dibenz[b,g]oxocin[1]

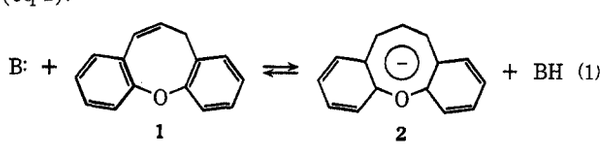
H. S. KASMAI AND H. W. WHITLOCK, JR.*

Department of Chemistry, University of Wisconsin, Madison, Wisconsin 53706

Received December 17, 1971

The synthesis of dibenz[b,g]oxocin is reported. It is a slightly stronger carbon acid than xanthene. This fact is interpreted as evidence for the aromaticity of the 10-π-electron oxocinyl anion.

The influence of heteroatoms on potentially aromatic 10-π-electron systems has been the source of considerable interest.[2] Despite predictions of simple Hückel theory, there is little evidence that neutral or mononegatively charged heterocyclic π systems possess substantial resonance stabilization and a diamagnetic ring current. We report here the synthesis of dibenz[b,g]oxocin (**1**) and measurement of its acidity as a test of the aromaticity of the 10-π-electron oxocinyl anion **2** (eq 1).



1 **2**

Results and Discussion

The synthesis of **1** is outlined in Scheme I.

A. Homologation of Xanthylium Cation.—We have shown[3] that the reaction of diazoalkanes and their derivatives with stable carbonium ions is a useful method for preparing homoallyl and benzyl cations as transient intermediates. It was initially felt that reaction of xanthylium cation with excess ethyl diazoacetate should afford a direct entry into the dibenzoxocin ring systems *via* **6** (Scheme II).

Addition of ethyl diazoacetate to xanthylium perchlorate in dry acetonitrile at 0° led to rapid gas evolution. Two major products were isolated: 9-carboethoxydibenz[b,f]oxepin (**3**) and 9-carboethoxy-10-acetylamino-9,10-dihydrodibenz[b,f]oxepin (**7**). The structure of **3** follows from analogy with the diazomethane ring expansion of xanthylium perchlorate[3a] and from

(1) Abstracted from the Ph.D. thesis of H. S. K., 1969.

(2) (a) R. M. Coates and E. F. Johnson, *J. Amer. Chem. Soc.*, **93**, 4016 (1971), and references contained therein; (b) N. L. Allinger and G. A. Youngdale, *ibid.*, **84**, 1020 (1962); (c) R. Breslow and E. Mohacsi, *ibid.*, **85**, 431 (1963); (d) L. A. Paquette, T. Kakihana, J. F. Hansen, and J. C. Phillips, *ibid.*, **93**, 152 (1971); (e) L. B. Anderson, J. F. Hansesen, T. Kakihana, and L. A. Paquette, *ibid.*, **93**, 161 (1971); (f) A. P. Bindra, J. A. Elix, P. T. Garratt, and R. H. Mitchell, *ibid.*, **90**, 7372 (1968); (g) A. G. Anastassiou and J. H. Gebrian, *Tetrahedron Lett.*, 825 (1970); (h) A. G. Anastassiou and R. P. Cellura, *Chem. Commun.*, 903, 1521 (1969).

(3) (a) H. W. Whitlock, *Tetrahedron Lett.*, 593 (1961); (b) *J. Amer. Chem. Soc.*, **84**, 2807 (1962); (c) H. W. Whitlock and N. A. Carlson, *Tetrahedron*, **20**, 2101 (1964); (d) H. W. Whitlock and M. R. Pesce, *Tetrahedron Lett.*, 743 (1964).