tention time of this material were identical in every way with those of a sample isolated by gas–liquid chromatography of the product obtained from the vapor-phase chlorination of **3**.

Acknowledgment. We express our gratitude to Dr. A. R. Gilbert, Dr. D. M. White, and Dr. H. M. Relles for their many helpful discussions and to H. Grade, R. May, and P. Donahue for their spectroscopic analysis.

Registry No. 1, 85-44-9; 2, 118-45-6; 3, 117-21-5; 6, 942-06-3; 7, 51971-64-3; 4-chlorophthalic acid, 89-20-3; 3-nitrophthalic anhydride, 641-70-3; 4,5-dichlorophthalic acid, 56962-08-4; 5,5-dimethyl-1,3-cyclohexanedione, 126-81-8; 3,5-dichloro-*o*-xylene, 70172-92-8; 3,5-dichlorophthalic acid, 25641-98-9.

Ring–Chain Tautomerism in Anions Derived from Substituted (Arylideneamino)toluenes and (Arylideneamino)oxindoles

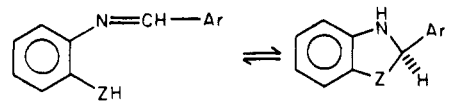
Frederick J. Goetz, Jerry A. Hirsch,* and Robert L. Augustine

Department of Chemistry, Seton Hall University, South Orange, New Jersey 07079

Received December 17, 1982

Intramolecular nucleophilic attack by carbon and nitrogen anions on imine and enone double bonds, respectively, has been investigated as a synthetic route to fused five-membered azacycles. In both (arylideneamino)toluenes and (arylideneamino)oxindoles, cyclization occurs only when a relatively localized anion attacks an electron-deficient double bond.

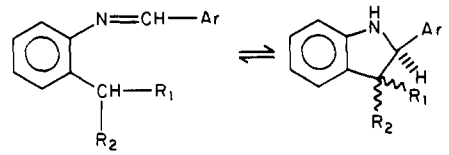
A recent report[1] of ring-chain tautomerism promoted by acids prompts us to report studies of ring-chain tautomerism catalyzed by bases. The tautomerism of 1-substituted 2-arylideneaminobenzenes (**1**, eq 1) have been ex-



(1)

1

tensively investigated.[2] In these systems the mobile hydrogen is attached to an electronegative atom in both the ring and chain tautomers. It was the intent of our study to evaluate the positions of these tautomeric equilibria in the 2-substituted 2-(arylideneamino)toluenes (**2**), where the tautomerism is generated by removal of an acidic benzylic hydrogen (eq 2).



(2)

2 **3**

a, R_1 = H; R_2 = $CON(CH_3)_2$
b, R_1 = H; R_2 = CO_2CH_3
c, R_1 = H; R_2 = CN
d, R_1 = CO_2CH_3; R_2 = CO_2CH_3

The required substituted 2-aminotoluenes were prepared by variations of literature methods and were rapidly treated with the desired aromatic aldehyde under acid catalysis to produce the desired chain tautomers **2a–d**. All compounds exhibited proton magnetic resonance, infrared, and ultraviolet spectra consistent with the chain tautomeric structures. The aldehydes utilized were 4-nitrobenzaldehyde, 2,4-dinitrobenzaldehyde, 2,4,6-trinitrobenzaldehyde, and 3,4,5-trimethoxybenzaldehyde. The nitroaldehydes were chosen because (a) the electron-withdrawing groups facilitate nucleophilic attack on the azomethine bond,[3] (b) the electron-withdrawing groups cause a downfield shift in the aromatic protons of the arylidene unit relative to those in the toluene aromatic groups and in any ring tautomer, and (c) the nitroarylideneanilines possess ultraviolet absorption maxima[4] at longer wavelengths than other arylideneanilines or in any ring tautomer. The 3,4,5-trimethoxybenzylidene system was chosen for ease of handling as a non-electron-withdrawing entity. The chemical shifts of the benzylic protons in **2a–d** also varied as expected with the electronegativity of the benzylic carbon substituents.

When each α-substituted 2-(arylideneamino)toluene (**2a–d**) was treated with a catalytic amount of potassium *tert*-butoxide in dimethyl sulfoxide (Me_2SO), no spectral changes were observed except with the malonates **2d**. Even upon being heated at temperatures up to 120 °C, systems **2a–c** did not produce the ring tautomer **3** on quenching with cold dilute acetic acid. The malonates **2d** were completely converted to ring tautomer **3d** as determined from spectral evidence and from isolation of **3d** as a crystalline solid. Tautomerization occurred readily with the *tert*-butoxide/Me_2SO system at room temperature or with the weaker base 1,5-diazabicyclo[5.4.0]undec-5-ene (DBU) in tetrahydrofuran with both electron-withdrawing and mild electron-donating arylidene groups. Since the benzylic hydrogen would be more acidic in the malonate than in the less substituted analogues, a stoichiometric amount of base was added to each substrate to confirm carbanion formation in each system.

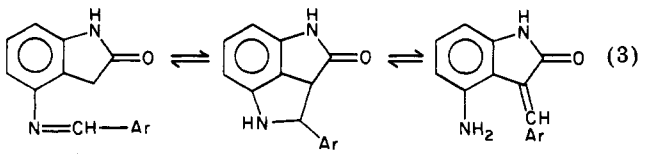
The observation of base-catalyzed tautomerism in the malonate **2d** and not in the other systems (**2a–c**) may have several explanations. The major factor probably is that the malonate carbanion for steric reasons assumes a geometry where the negative charge is not significantly delocalized into the benzene ring, while the other benzylic carbanions are effectively delocalized into the benzene–azomethine system. The malonate carbanion would then

(1) Lambert, J. B.; Majchrzak, M. W. *J. Am. Chem. Soc.* **1980**, *102*, 3588.
(2) For a literature survey, see: Goetz, F. J. Dissertation, Seton Hall University, 1974.
(3) McDonagh, A. F.; Smith, H. E. *J. Org. Chem* **1968**, *33*, 1, 8.
(4) The extinction coefficients in the 2,4,6-trinitro compounds were distinctly lower, presumably from steric distortion from coplanarity of the benzylideneamino chromophore. The 2,4-dinitro series were sensitive to visible light.

0022-3263/83/1948-2468$01.50/0

have the greater electron density at the benzylic carbon and would also have its electron pair positioned for more efficient nucleophilic attack on the azomethine linkage. This combination of increased nucleophilicity and a better stereoelectronic relationship would then explain the enhanced 5-endo-trigonal[5] process in the malonate anion. Relative stabilities of the ring tautomers cannot be a significant factor since the ring tautomer from the malonate system would possess the most destabilizing steric interactions.

In an attempt to probe these phenomena further, we prepared several 4-(arylideneamino)oxindoles (**4**) and 3-arylidene-4-aminooxindoles (**5**) (eq 3). Reaction of 4-

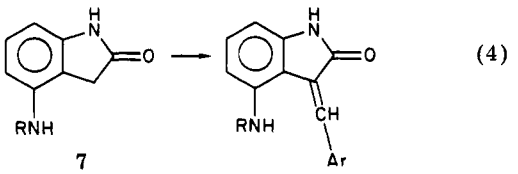


(3)

4 6 5

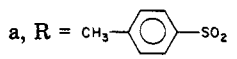
aminooxindole with 3,4,5-trimethoxybenzaldehyde or 4-nitrobenzaldehyde under acidic or neutral conditions produced the required azomethines **4**. Attempts to effect base-catalyzed cyclization to the ring tautomer **6** by using potassium *tert*-butoxide in dimethylsulfoxide or lithium diisopropylamide or *n*-butyllithium in hexane produced strongly colored solutions but no evidence that cyclization had taken place. These results are consistent with those obtained with **2a–c**, especially since the coplanarity of the oxindole ring system would promote maximum delocalization of the carbanion negative charge and minimize the possiblity of intramolecular nucleophilic attack.

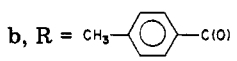
The 3-arylidene-4-aminooxindoles (**5**) were prepared by conversion of 4-aminooxindole to the *p*-toluenesulfonamido derivative **7a** and the *p*-toluamido derivative **7b**. Toluamide **7b** formed the desired 3-arylidene derivative **8b** (eq 4) on reaction with 4-nitrobenzaldehyde or 3,4,5-trimeth-



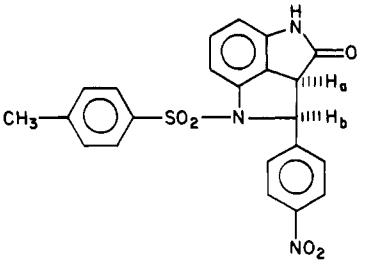
(4)

7 8

a, R = 

b, R = 

oxybenzaldehyde in the presence of piperidine. Similarly, sulfonamide **7a** reacts with 3,4,5-trimethoxybenzaldehyde to form the arylidene **8a**. However, reaction of **7a** with 4-nitrobenzaldehyde in the presence of piperidine produced the ring tautomer 3-(4-nitrophenyl)-4-(*p*-tolylsulfonyl)-2,2a,3,4-tetrahydro-1*H*-pyrrolo[4,3,2-*cd*]indol-2-one (**9**). The infrared spectrum of this material exhibits an oxindole N–H stretch near 3400 cm^{-1} but lacks the sulfonamide N–H stretch near 3200 cm^{-1}. Only one resonance appears below δ 3.88 as an AB pattern with J = 3.5 Hz, suggesting a cis orientation of these hydrogens. The downfield position of proton 2a is consistent with a deshielding influence of the oxindole carbonyl in such a cis arrangement. The cis orientation is consistent with protonation of tricyclic anion from the least hindered face

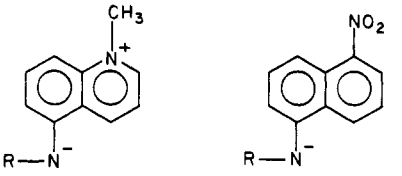


9

of the molecule. The ultraviolet spectrum of **9** closely resembles that of 4-(toluenesulfonamido)oxindole (**7b**) and is quite different from those of the 3-arylidene series **8**.

Attempts to cyclize **8a** or **8b** by using potassium *tert*-butoxide in dimethyl sulfoxide or lithium diisopropylamide or *n*-butyllithium in hexane failed. The cyclization of the sulfonamido-4-nitrobenzylidene system, where the chain tautomer **8a** could not be isolated, and the lack of cyclization of the three other 3-arylidene substrates (**8**) must involve a subtle interplay of the degree of double bond character and electronic effects in the 3-arylidene portion[6] and the degree of delocalization of the amidic anions obtained from the chain tautomers **8**. Electron donation from the 3,4,5-trimethoxyphenyl group to the oxindole group would lessen the chance of nucleophilic attacks on the 3-arylidene double bond. Attack on the *p*-nitrobenzylidene double bond should therefore be easier than attack on the 3,4,5-trimethoxybenzylidene double bond.

The question then is whether anionic delocalization should be greater in the amidic anion derived from the sulfonamide or the carboxamide. In an earlier study[7] of the visible spectroscopy of the amidic anions derived from 5-(N-substituted amino)-1-methylquinolinium ion (**10**) and



10 11

5-(N-substituted amino)-1-nitronaphthalene (**11**), it was found that N substituents influenced the longest wavelength absorptions in dipolar aprotic solvents in such a way that the sulfonamido-substituted anions absorbed at significantly shorter wavelengths than the benzoyl or acetyl substituted anions, which themselves absorbed at shorter wavelengths than the unsubstituted amidic anions. This would indicate less ana-conjugated character in the sulfonamido anions than in the carboxamido anions, suggesting that the sulfonamido anion would be less delocalized into the aromatic ring than a carboxamido anion. Since our results with the (arylideneamino)toluenes (**2**) suggest more nucleophilic attack and concomitant cyclization with the less delocalized anions, it is then quite consistent that sulfonamide **8a** would cyclize to **9** while carboxamide **8b** would not.

Experimental Section

Microanalyses were performed by Alfred Benhardt Mikroanalytisches Laboratorium, Elback uber Engelskirchen, West Germany, or Micro-Analysis, Inc., Wilmington, DE. Ultraviolet

(5) Baldwin, J. E. *J. Chem. Soc., Chem. Commun.* **1976**, 734. Baldwin, J. E.; Cutting, J.; Dupont, W.; Kruse, L.; Silberman, L.; Thomas, R. C. *Ibid.* **1976**, 736.

(6) Iacconi, G.; Maggi, L. D.; Righetti, P.; Desimoni, G.; Azzolina, O.; Ghislandi, V. *J. Chem. Soc., Perkin Trans. 2* **1976**, 150.

(7) Goetz, F. J.; Bailey, W. J. "Abstracts of Papers", 4th Middle Atlantic Regional Meeting of the American Chemical Society, Washington, DC, 1969; American Chemical Society: Washington, DC, 1969, p 78.

and visible spectra were determined on a Cary 15 spectrophotometer by using 1-cm quartz cells. Infrared spectra were recorded on a Beckman IR-10 spectrometer as deuteriochloroform solutions ($CDCl_3$) or as potassium bromide (KBr) disks. Nuclear magnetic resonance spectra were obtained on a Varian Associates Model A-60A spectrometer in deuteriochloroform ($CDCl_3$) or dimethyl-d_6 sulfoxide (Me_2SO), and all chemical shifts are reported in parts permillion relative to internal tetramethylsilane.

***N,N*-Dimethyl(2-nitrophenyl)acetamide.** To a suspension of 36 g (0.20 mol) of (2-nitrophenyl)acetic acid (Aldrich) in 200 mL of benzene was added 48 g (0.04 mol) of thionyl chloride with rapid magnetic stirring. After 24 h of stirring, the volume was concentrated to 50 mL by distillation, and then 200 mL of benzene and 2 g of charcoal were added. Filtration and concentration in vacuo gave the crude acid chloride as a brownish oil. This was dissolved in 500 mL of anhydrous ether, cooled to −20 °C, and combined with 100 mL of 25% anhydrous dimethylamine in benzene over a 30-min period with stirring. The resulting mixture was warmed to 25 °C and filtered, and the filtrate was extracted with water, 5% HCl, 5% $NaHCO_3$, water, and saturated brine. The solvent was removed to give 33.5 g (80% yield) of large yellow prisms. Further treatment with activated charcoal in benzene, recrystallization from benzene, and subsequent recrystallization from methanol resulted in light yellow prisms: mp 72–73 °C; IR ($CDCl_3$) 3075, 2935, 1642 cm^{-1}; NMR ($CDCl_3$) 2.97 (s, 3, NCH_3), 3.12 (s, 3, NCH_3), 4.05 (s, 2, CH_2CO), 7.43 (m, 3, Ar H), 9.70 (m, 1, Ar H). Anal. Calcd for $C_{10}H_{12}N_2O_3$: C, 57.69; H, 5.77; N, 13.46. Found: C, 57.57; H, 5.94; N, 13.31.

(2-Nitrophenyl)acetonitrile was prepared by the method of Pschorr[8] from (2-nitrophenyl)acetic acid. The crude acid chloride (see above) was converted into the (2-nitrophenyl)acetamide [75% yield; mp 160–161 °C (lit.[8] mp 160 °C)], and this was converted into (2-nitrophenyl)acetonitrile: 66% yield; mp 84 °C. The resulting nitrile was refluxed for 16 h as a methanolic solution with a catalytic amount of 30% palladium on carbon, concentrated, filtered, and precipitated to remove an impurity interfering with the subsequent hydrogenation. However, the melting point was unchanged.

Methyl (2-nitrophenyl)acetate was prepared by a literature procedure.[9]

Dimethyl (2-Nitrophenyl)malonate. A solution of 29 g (0.21 mol) of dimethyl malonate in 200 mL of anhydrous dimethylformamide (DMF) was treated with 22.6 g of (0.20 mol) of potassium *tert*-butoxide for 10 min at 90 °C with stirring. The resulting mixture was cooled to 20 °C, and 14 g (0.01 mol) of 2-fluoronitrobenzene was added. The mixture was heated at 90 °C for 2 h, stored for 16 h at 25 °C, poured into 1 kg of ice-cold 5% HCl, and extracted with benzene (2 × 200 mL). The benzene extract was dried ($MgSO_4$) and filtered, and the solvent was removed. The residue was distilled, bp 169–171 °C (0.35 mm). This fraction solidified and was recrystallized from benzene–hexane to give 16.4 g (65% yield) of light yellow prisms: mp 53–55 °C; NMR ($CDCl_3$) 3.74 (s, 6, OCH_3), 5.30 (s, 1, CH), 7.55 (m, 3, Ar H), 8.00 (m, 1, Ar H). Anal. Calcd for $C_{11}H_{11}NO_6$: C, 52.17; H, 4.35; N, 5.53. Found: C, 52.17; H, 4.24; N, 5.62.

General Synthesis of Derivatives of [2-(Benzylideneamino)phenyl]acetic Acid. A solution of 0.01 mol of one of the above four compounds in 50 mL of absolute methanol containing 1 mL of glacial acetic acid was cooled to 0 °C in a Pyrex hydrogenation vessel. After addition of 0.5 g of 10% palladium on carbon, hydrogenation (Parr apparatus) was performed until a pressure drop corresponding to the absorption of the theoretical amount of hydrogen was noted. The vessel was removed, cooled in ice, and rapidly filtered into an ice-cooled filtering flask. To the filtrate was added 0.009 mol of the appropriate aromatic aldehyde in 5 mL of warm glacial acetic acid. After being allowed to stand at room temperature for 16 h; the mixture was cooled while water was carefully added to precipitate the product.

2a (Ar = 4-nitrophenyl): 91% yield; mp 151–152 °C; NMR ($CDCl_3$) 3.88 (CHCO), 8.68 (1, =CH); NMR (Me_2SO) 3.70 (2, CHCO), 7.02 (m, 4, Ar H), 7.98 (m, 4, Ar H) 8.43 (1, =CH); UV ($CHCl_3$) 346 nm (ϵ 1.04 × 10^4). Anal. Calcd for $C_{17}H_{17}N_3O_3$: C, 65.59; H, 5.46; N, 13.55. Found: C, 65.37; H, 5.44; N, 13.47.

2a (Ar = 2,4-dinitrophenyl): 87% yield; mp 126–127 °C; NMR (Me_2SO) 3.78 (2, CHCO), 7.03 (m, 4, Ar H), 8.25 (m, 3, Ar H), 8.69 (1, =CH); UV ($CHCl_3$) 363 nm (ϵ 1.32 × 10^4). Anal. Calcd for $C_{17}H_{16}N_4O_5$: C, 57.30; H, 4.49; N, 15.73. Found: C, 57.20; H, 4.70; N, 15.56.

2a (Ar = 2,4,6-trinitrophenyl): 82% yield; mp 193–194 °C; NMR (Me_iSO) 3.52 (2, CHCO), 7.03 (m, 4, Ar H), 8.85 (m, 2, Ar H), 8.64 (1, =CH); UV ($CHCl_3$) 376 nm (ϵ 2.49 × 10^3). Anal. Calcd for $C_{17}H_{15}N_5O_7$: C, 50.87; H, 3.74; N, 17.45. Found: C, 51.01; H, 3.90; N, 17.56.

2b (Ar = 4-nitrophenyl): 80% yield; mp 106–107 °C (lit.[10] mp 105–107); IR ($CDCl_3$) 1632 cm^{-1}; NMR ($CDCl_3$) 3.85 (CHCO), 8.51 (1, =CH); NMR (Me_2SO) 3.82 (2, CHCO), 3.52 (3, OCH_3), 7.30 (m, 4, Ar H), 8.73 (1, =CH), UV ($CHCl_3$) 343 nm (ϵ 1.02 × 10^4).

2b (Ar = 2,4-dinitrophenyl): 72% yield; mp 117–118 °C; NMR (Me_2SO) 3.84 (2, CHCO), 3.58 (s, 3, OCH_3), 7.30 (m, 4, Ar H), 8.60 (m, 3, Ar H), 8.90 (1, =CH); UV ($CHCl_3$) 350 nm (ϵ 1.41 × 10^4). Anal. Calcd for $C_{16}H_{13}N_3O_6$: C, 55.98; H, 3.79; N, 12.24. Found: C, 55.80; H, 3.63; N, 12.21.

2b (Ar = 2,4,6-trinitrophenyl): 87% yield; mp 151–152 °C; NMR (Me_2SO) 3.63 (2, CHCO), 3.52 (s, 3, OCH_3), 7.25 (m, 4, Ar H), 9.10 (m, 2, Ar H), 8.92 (1, =CH); UV 365 nm (ϵ 2.40 × 10^3). Anal. Calcd for $C_{16}H_{12}N_4O_8$: C, 49.48; H, 3.09: N, 14.43. Found: C, 49.28, H, 3.14; N, 14.57.

2c (Ar = 4-nitrophenyl): 85% yield; mp 163–164 °C; IR ($CDCl_3$) 1630 cm^{-1}; NMR ($CDCl_3$) 3.93 (2, CHCN), 8.68 (1, =CH); NMR (Me_2SO) 4.17 (2, CHCN), 7.50 (m, 4, Ar H), 8.33 (m, 4, Ar H), 8.90 (1, =CH); UV ($CHCl_3$) 333 nm (ϵ 1 × 10^4). Anal. Calcd for $C_{15}H_{11}N_3O_2$: C, 67.92; H, 4.02; N, 15.85. Found: C, 67.86; H, 3.99; N, 15.85.

2c (Ar = 2,4-dinitrophenyl): 70% yield; mp 160–161 °C; NMR (Me_2SO) 4.21 (2, CHCN), 7.54 (m, 4, Ar H), 8.85 (m, 3, Ar H), 9.15 (1, =CH); UV ($CHCl_3$) 350 nm (ϵ 1.0 × 10^4). Anal. Calcd for $C_{15}H_{10}N_4O_4$: C, 58.06; H, 3.23; N, 18.16. Found: C, 58.05; H, 3.34; N, 18.23.

2c (Ar = 2,4,6-trinitrophenyl): 91% yield; mp 212–213 °C; NMR (Me_2SO) 4.01 (2, CHCN), 7.60 (m, 4, Ar H), 9.35 (m, 2, Ar H), 9.20 (1, =CH); UV ($CHCl_3$) 353 nm (ϵ 2.98 × 10^3). Anal. Calcd for $C_{15}H_9N_5O_6$: C, 50.70; H, 2.54; N, 19.72. Found: C, 50.86; H, 2.51; N, 19.90.

2d (Ar = 4-nitrophenyl): 82% yield; mp 120–122 °C; IR ($CDCl_3$) 1632 cm^{-1}; NMR ($CDCl_3$) 5.39 (1, CHCO), 8.52 (1, =CH); NMR (Me_2SO) 5.42 (1, CHCO), 3.67 (s, 6, OCH_3), 7.38 (m, 4, Ar H), 8.56 (m, 4, Ar H), 8.80 (1, =CH); UV ($CHCl_3$) 337 nm (ϵ 1.01 × 10^4). Anal. Calcd for $C_{18}H_{17}N_2O_6$: C, 60.67; H, 4.49; N, 7.86. Found: C, 60.51; H, 4.62; N, 7.99.

2d (Ar = 2,4-dinitrophenyl): 80% yield; mp 136–137 °C; NMR (Me_2SO) 5.37 (1, CHCO), 3.69 (s, 6, OCH_3), 7.37 (m, 4, Ar H), 8.60 (m, 3, Ar H), 8.69 (1, =CH); UV ($CHCl_3$) 355 nm (ϵ 1.32 × 10^4). Anal. Calcd for $C_{18}H_{15}N_3O_8$: C, 53.87; H, 3.74; N, 10.47. Found: C, 54.02; H, 3.81; N, 10.58.

2d (Ar = 3,4,5-trimethoxyphenyl): 70% yield; mp 112–113 °C; IR ($CDCl_3$) 1630 cm^{-1}; NMR ($CDCl_3$) 5.33 (1, CHCO), 8.50 (1, =CH); NMR (Me_2SO) 5.33 (1, CHCO), 3.64 (s, 6, OCH_3), 3.76 (s, 6, OCH_3) 3.86 (s, 3, OCH_3), 7.34 (m, 6, Ar H) 8.50 (1, =CH); UV ($CHCl_3$) 304 nm (ϵ 6.22 × 10^4). Anal. Calcd for $C_{21}H_{23}NO_7$: C, 62.84; H, 5.74; N, 3.49. Found: C, 62.61; H, 5.55; N, 3.63.

Cyclization with Potassium *tert*-Butoxide. A solution of 60 mg of the substrate in 0.5 mL of freshly dried dimethyl-d_6 sulfoxide was prepared. Fresh doubly sublimed potassium *tert*-butoxide (1 mg) was added with swirling. The product was isolated by cooling the reaction mixture and quenching the reaction with ice-cold acetic acid. In most instances, the reaction vessel was a carefully dried NMR tube.

Cyclization with DBU. A solution of 200 mg of substrate in 2.0 mL of a 1 × 10^{-2} M solution of 1-5-diazabicyclo[5.4.0]undec-5-ene in dry tetrahydrofuran was heated at 65 °C for 4 h. The product was crystallized by careful addition of hexane on cooling to room temperature.

3d (Ar = 4-nitrophenyl): 82% yield; mp 174–175 °C; IR ($CDCl_3$) 3399 cm^{-1}; IR (KBr) 3342 cm^{-1}; NMR ($CDCl_3$) 3.20 (s, 3, OCH_3), 3.87 (s, 3, OCH_3), 5.90 (s, 1, ArCHN), 7.25 (m, 4, Ar H), 7.90 (m, 4, Ar H); UV ($CHCl_3$) 255 nm. Anal. Calcd for $C_{18}H_{11}N_2O_6$: C, 60.67; H, 4.49; N, 7.86. Found: C, 60.88; H, 4.37; N, 7.98.

(8) Pschorr, R.; Hoppe, G. *Ber.* **1910**, *43*, 2543.
(9) Walker, G. N. *J. Am. Chem. Soc.*, **1955**, *77*, 3844. Schulenberg, J. W.; Archer, S. *Ibid.* **1961**, *83*, 3091.
(10) Neber, P. W. *Ber.* **1922**, *55*, 826.

3d (Ar = 2,4-dinitrophenyl): 54%[11] yield; mp 132–133 °C; IR ($CDCl_3$) 3398 cm^{-1}; NMR ($CDCl_3$) 3.30 (s, 3, OCH_3), 3.81 (s, 3, OCH_3), 7.00 (m, 5, Ar H and ArCHN), 8.00 (m, 3, Ar H). Anal. Calcd for $C_{18}H_{15}N_3O_8$: C, 53.87; H, 3.74; N, 10.47. Found: C, 53.98; H, 3.84; N, 10.38.

3d (Ar = 3,4,5-trimethoxyphenyl): 80% yield; mp 150–151 °C; IR ($CDCl_3$) 3399 cm^{-1}; NMR ($CDCl_3$) 3.22 (s, 3, OCH_3), 3.78 (s, 3, OCH_3), 5.70 (s, 1, Ar CHN), 7.10 (m, 6, Ar H). Anal. Calcd for $C_{21}H_{23}NO_7$: C, 62.84; H, 5.74; N, 3.49. Found: C, 62.96; H, 5.75; N, 3.71.

Dimethyl (2,6-Dinitrophenyl)malonate. A solution of 29.0 g (0.21 mol) of dimethyl malonate in 200 mL dimethylformamide was treated with 22.6 g (0.20 mol) of potassium *tert*-butoxide, and the *tert*-butyl alcohol was removed by distillation. The resulting mixture was cooled to 20 °C, and 0.1 mol of 2,6-dinitrochlorobenzene was added. The mixture was heated at 90 °C with stirring for 2 h, stirred for 16 h at 25 °C, cooled to 10 °C, and poured into 600 mL of ice-cold 1% sodium hydroxide solution containing 100 g of ice. The resulting mixture was extracted with ether (3 × 300 mL). The aqueous layer was treated with 400 mL of 0.1 M nitric acid and extracted with ether (3 × 200 mL). The latter ether extracts were washed with water (4 × 400 mL) and saturated brine (2 × 400 mL) and dried ($MgSO_4$). After filtration and removal of the ether in vacuo, the residue was recrystallized from methanol: yield 82%; mp 159–160 °C. Anal. Calcd for $C_{11}H_{10}N_2O_8$: C, 44.27; H, 3.36; N, 9.39. Found: C, 44.24; H, 3.46; N, 9.51.

Methyl (2,6-Dinitrophenyl)acetate. A solution of 14.9 g (0.05 mol) of the above malonate in 100 mL of glacial acetic acid containing 5.0 mL of 70% perchloric acid was refluxed while the methyl acetate formed was removed by distillation until 4.2 g of distillate was collected over 1 h. The reaction mixture was poured into 30 mL of ice–water and extracted with dichloromethane (3 × 200 mL). The organic layer was extracted with 10% $NaHCO_3$ (3 × 200 mL) and saturated brine (2 × 100 mL) and dried ($MgSO_4$). After filtration and solvent removal, recrystallization from ether produced 8.4 g (70% yield) of methyl (2,6-dinitrophenyl)acetate, mp 58–59 °C (lit.[12] mp 57 °C).

The combined sodium bicarbonate extracts were acidified to give 2.6 g (23% yield) of (2,6-dinitrophenyl)acetic acid, mp 200–21 °C (lit.[12] mp 202 °C). Longer reaction times with collections of more methyl acetate distillate favored production of this acid over the desired methyl ester. The (2,6-dinitrophenyl)acetic acid was converted to methyl (2,6-dinitrophenyl)acetate by reaction[13] with boron trifluoride–methanol complex.

4-Aminooxindole. A solution of 12.0 g (0.05 mol) of methyl (2,6-dinitrophenyl)acetate in 400 mL of methanol was prepared in a Pyrex hydrogenation vessel, 1.0 g of 10% palladium on carbon was added, and the hydrogenation was performed in a Parr apparatus until absorption of the theoretical quantity of hydrogen was complete. The catalyst was removed by filtration and the filtrate concentrated to 200 mL. The residue was refluxed for 72 h under nitrogen with stirring. Concentration produced 6.8 g (94% yield) of 4-aminooxindole: mp 182–183 °C (lit.[14] mp 180–182 °C; UV ($CHCl_3$) 295 nm (ϵ 1.93 × 10^3).

4-(Arylideneamino)oxindoles. A solution of 0.01 mol of 4-aminooxindole in 10 mL of methanol containing 1 mL of glacial acetic acid was treated with 0.009 mol of the aromatic aldehyde in 5 mL of warm acetic acid. The crystalline product which separated on cooling was removed by filtration, washed with 5 mL of methanol, and recrystallized from toluene–hexane mixtures before being dried in vacuo at 58 °C.

4 (Ar = 4-nitrophenyl): 99% yield; mp 247–248 °C; IR (KBr) 330, 1750, 1700, 1500, 1480 cm^{-1}; NMR (Me_2SO) 3.30 (s, CH_2), 7.00 (m, Ar H), 8.30 (m, Ar H), 8.83 (s, =CH), 10.39 (s, CONH); UV ($CHCl_3$) 346 nm (ϵ 8.79 × 10^3). Anal. Calcd for $C_{15}H_{11}N_3O_5$: C, 64.05; H, 3.92; N, 14.95. Found: C 63.82; H, 4.08; N, 15.03.

4 (Ar = 3,4,5-trimethoxyphenyl): 96% yield; mp 175–176 °C; IR (KBr) 3200, 1710, 1640 cm^{-1}; NMR (Me_2SO) 3.33 (s, 2, CH_2), 3.37 (s, 3, OCH_3), 3.94 (s, 6, OCH_3), 6.70 (m, 3, Ar H), 7.25 (s, 2, Ar H), 8.56 (s, 1, =CH), 10.37 (s, 1, CONH); UV ($CHCl_3$) 314 nm (ϵ 14.2 × 10^3). Anal. Calcd for $C_{18}H_{18}N_2O_4$: C, 66.25; H, 5.52; N, 8.59. Found: C, 66.04; H, 5.69; N, 8.40.

4-Toluenesulfonamidooxindole (7a). A solution of 1.48 g (0.010 mol) of 4-aminooxindole in 50 mL of anhydrous pyridine was cooled to 0 °C under nitrogen, and 2.09 g (0.011 mol) of *p*-toluenesulfonyl chloride was added with stirring. After 24 h at room temperature under nitrogen, the mixture was concentrated to 10 mL, and 10 mL of absolute methanol was added. The resulting mixture was poured into a stirred solution of 100 mL of water and 20 mL of glacial acetic acid. The solid which separated was treated with charcoal during recrystallization from 95% ethanol and then recrystallized from absolute methanol to give a solid: 82% yield; mp 254–255 °C; NMR (Me_2SO) 2.32 (s, 3, CH_3), 3.20 (s, 2, CH_2), 7.10 (m, 7, Ar H), 9.78 (s, 1, SO_2NH), 10.32 (s, 1, CONH). Anal. Calcd for $C_{15}H_{14}N_2O_3S$: C, 59.60; H, 4.64; N, 9.27. Found: C, 59.83; H, 4.66; N, 9.01.

4-Toluamidooxindole (7b). A solution of 1.48 g (0.010 mol) of 4-aminooxindole in 50 mL of anhydrous pyridine was cooled to 0 °C under nitrogen as 1.70 g (0.011 mol) of *p*-toluyl chloride in 5 mL of anhydrous dioxane was added with stirring over 30 min. After 24 h at room temperature under nitrogen, the mixture was concentrated in vacuo to 10 mL, and 10 mL of anhydrous dioxane was added. The mixture was poured with stirring into 100 mL of water containing 20 mL of glacial acetic acid. The resulting precipitate was removed, washed with 200 mL of water, and stirred with 100 mL of 2% $NaHCO_3$ solution for 24 h. This mixture was filtered, and the solid was washed with 200 mL of water, air-dried, and recrystallized from ethanol: mp 292–293 °C; yield 88%; NMR (Me_2SO) 2.38 (s, 3, CH_3), 3.37 (s, 2, CH_2), 7.20 (m, 7, Ar H), 9.90 (s, 1, CONH), 10.36 (s, 1, CONH). Anal. Calcd for $C_{16}H_{14}N_2O_2$: C, 72.18; H, 5.26; N, 10.53. Found: C, 71.99; H, 5.20; N, 10.06.

General Method for Formation of 3-Arylidene-4-(N-substituted amino)oxindoles. A solution of 0.0020 mol of the oxindole and 0.0025 mol of the aromatic aldehyde were combined in 60 mL of absolute ethanol in the presence of 50 mg of piperidine and refluxed under nitrogen for 24 h with stirring. Concentration and cooling produced the crystalline products, which were recrystallized from methanol.

8b (Ar = 4-nitrophenyl): 93% yield; mp 288–289 °C; IR (KBr) 3058, 1724, 1639 cm^{-1}; NMR ($CDCl_3$) 225 (s, 3, CH_3O), 7.10 (m, 7, Ar H), 7.65 (m, 4, Ar H), 9.50 (s, 1, CONH), 10.78 (s, 1, =CH); UV ($CHCl_3$) 375 nm (ϵ 7.19 × 10^3). Anal. Calcd for $C_{23}H_{17}N_3O_4$: C, 69.17; H, 4.26; N, 10.53. Found: C, 69.02; H, 4.17; N, 10.41.

8b (Ar = 3,4,5-trimethoxyphenyl): 95% yield; mp 298–299 °C; IR (KBr) 3058, 1724, 1642; NMR ($CDCl_3$) 2.38 (s, 3, CH_3), 3.65 (d, 9, OCH_3), 7.40 (m, 9, Ar H), 9.95 (s, 1, CONH), 10.40 (s, 1, =CH); UV ($CHCl_3$) 374 nm (ϵ 2.78 × 10^3). Anal. Calcd for $C_{26}H_{24}N_2O_5$: C, 70.27; H, 5.41; N, 6.31. Found: C, 69.97; H, 5.37; N, 6.21.

8a (Ar = 3,4,5-trimethoxyphenyl): 94% yield; 248–249 °C; IR (KBr) 3049, 1709, 1351, 1333 cm^{-1}; NMR ($CDCl_3$) 2.30 (s, 3, CH_3), 3.82 (d, 9, OCH_3), 7.30 (m, 9, Ar H), 9.95 (s, 1, SO_2NH), 10.60 (s, 1, =CH); UV ($CHCl_3$) 636 nm (ϵ 10.5 × 10^3). Anal. Calcd for $C_{25}H_{24}N_2O_6S$: C, 62.50; H, 5.00; N, 5.83. Found: C, 62.27; H, 5.01; N, 5.82.

3-(4-Nitrophenyl)-4-(*p*-tolylsulfonyl)-2,2a,3,4-tetrahydro-1*H*-pyrrolo[4,3,2-*cd*]indol-2-one (9). By use of the above method for 3-arylideneoxindoles, a light yellow product was obtained which was recrystallized from tetrahydrofuran–hexane after charcoal treatment to give 0.44 g (50% yield) of colorless prisms: mp 282–283 °C dec; IR (KBr) 3400 cm^{-1}; NMR ($CDCl_3$) 2.36 (s, 3, CH_3O), 3.88 (d, 1, J = 3.5 Hz), 5.52 (d, 1, J = 3.5 Hz) 6.9–7.5 (m, 7, Ar H), 7.7–8.1 (m, 4, Ar H), 10.32 (s, 1, CONH); UV ($CHCl_3$) 256 nm (ϵ 16.6 × 10^3). Anal. Calcd for $C_{22}H_{17}N_3SO_5$: C, 60.95; H, 3.91; N, 9.66. Found: C, 61.24; H, 4.17; N, 9.40.

Registry No. **2a** (Ar = 4-nitrophenyl), 86162-62-1; **2a** (Ar = 2,4-dinitrophenyl), 86162-63-2; **2a** (Ar = 2,4,6-trinitrophenyl), 86162-64-3; **2a** (Ar = 4-nitrophenyl) anion, 86162-74-5; **2a** (Ar = 2,4-dinitrophenyl) anion, 86162-75-6; **2a** (Ar = 2,4,6-trinitrophenyl) anion, 86162-76-7; **2b** (Ar = 4-nitrophenyl), 86162-65-4; **2b** (Ar = 2,4-dinitrophenyl), 86162-66-5; **2b** (Ar = 2,4,6-trinitrophenyl), 86162-67-6; **2b** (Ar = 4-nitrophenyl) anion, 86162-77-8;

(11) This cyclization produced the highest yield of crude product, but the presence of a small amount of contaminant (not the chain tautomer) required additional recrystallizations.

(12) Borsche, W.; Rantscheff, D. *Justus Liebigs Ann. Chem.* **1911**, *379*, 152.

(13) Goetz, F. J. Dissertation, Seton Hall University, 1974.

(14) Hull, R. U.S. Patent 282372, 1959.

2b (Ar = 2,4-dinitrophenyl) anion, 86162-78-9; **2b** (Ar = 2,4,6-trinitrophenyl) anion, 86162-79-0; **2c** (Ar = 4-nitrophenyl), 86162-68-7; **2c** (Ar = 2,4-dinitrophenyl), 86162-69-8; **2c** (Ar = 2,4,6-trinitrophenyl), 86162-70-1; **2c** (Ar = 4-nitrophenyl) anion, 86162-80-3; **2c** (Ar = 2,4-dinitrophenyl) anion, 86162-81-4; **2c** (Ar = 2,4,6-trinitrophenyl) anion, 86162-82-5; **2d** (Ar = 4-nitrophenyl), 86162-71-2; **2d** (Ar = 2,4-dinitrophenyl), 86162-72-3; **2d** (Ar = 3,4,5-trimethoxyphenyl), 86162-73-4; **2d** (Ar = 4-nitrophenyl) anion, 86162-83-6; **2d** (Ar = 2,4-dinitrophenyl) anion, 86162-84-7; **2d** (Ar = 3,4,5-trimethoxyphenyl) anion, 86162-85-8; **3d** (Ar = 4-nitrophenyl), 86162-86-9; **3d** (Ar = 2,4-dinitrophenyl), 86162-87-0; **3d** (Ar = 3,4,5-trimethoxyphenyl), 86162-88-1; **4** (Ar = 4-nitrophenyl), 86162-91-6; **4** (Ar = 3,4,5-trimethoxyphenyl), 86162-92-7; **7a**, 86162-93-8; **7b**, 86162-94-9; **8a** (Ar = 3,4,5-trimethoxyphenyl), 86162-97-2; **8b** (Ar = 4-nitrophenyl), 86162-95-0; **8b** (Ar = 3,4,5-trimthoxyphenyl), 86162-96-1; **9**, 86162-98-3; *N*,*N*-dimethyl(2-nitrophenyl)acetamide, 76016-34-7; (2-nitrophenyl)acetic acid, 3740-52-1; (2-nitrophenyl)acetyl chloride, 22751-23-1; dimethylamine, 124-40-3; (2-nitrophenyl)acetonitrile, 610-66-2; (2-nitrophenyl)acetamide, 31142-60-6; dimethyl (2-nitrophenyl)malonate, 26465-37-2; dimethyl malonate, 108-59-8; 2-fluoronitrobenzene, 1493-27-2; methyl (2-nitrophenyl)acetate, 30095-98-8; *N*,*N*-dimethyl(2-aminophenyl)acetamide, 86162-60-9; (2-aminophenyl)acetonitrile, 2973-50-4; methyl (2-aminophenyl)acetate, 35613-44-6; dimethyl (2-aminophenyl)malonate, 86162-61-0; 4-nitrobenzaldehyde, 555-16-8; 2,4-dinitrobenzaldehyde, 528-75-6; 2,4,6-trinitrobenzaldehyde, 606-34-8; 3,4,5-trimethoxybenzaldehyde, 86-81-7; dimethyl (2,6-dinitrophenyl)-malonate, 86162-89-2; 2,6-dinitrochlorobenzene, 606-21-3; methyl (2,6-dinitrophenyl)acetate, 86162-90-5; (2,6-dinitrophenyl)acetic acid, 37777-63-2; 4-aminooxindole, 54523-76-1; *p*-toluenesulfonyl chloride, 98-59-9; *p*-toluyl chloride, 874-60-2.

Dimerization of Cyclopropanecarboxylic Acid Dianion and Thermal Decarboxylative Rearrangement of the Dimer to 2-Cyclopropyl-4,5-dihydrofuran

Edwin G. E. Jahngen,*[†] Douglas Phillips,[†] Robert J. Kobelski,[‡] and Donald M. Demko[†]

Department of Chemistry, Wilkes College, Wilkes-Barre, Pennsylvania 18766, and the Process Research and Development Department, Buffalo Color Corporation, Buffalo, New York 14240

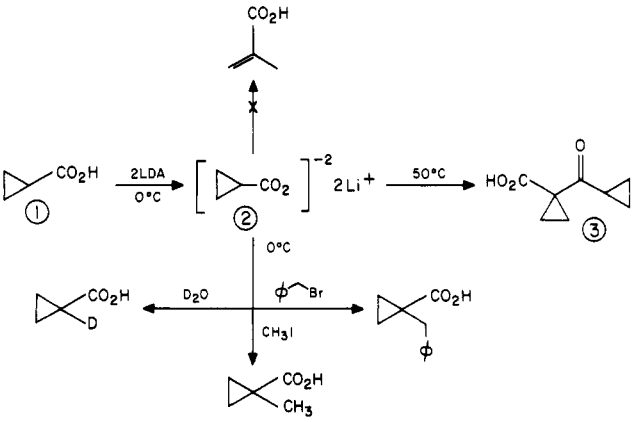
Received November 16, 1982

The dianion of cyclopropanecarboxylic acid (**2**) reacted with alkyl halides and deuterated water at temperatures below 0 °C; however, self-condensation to the β-keto acid **3** was the only observed product at elevated temperatures. This observation contrasts the self-condensation of the ethyl ester where a trimeric diester alcohol is the product. Attempted mixed condensations of the dianion **2** and carboxylic acids without acidic α-protons did not proceed as well, **3** being the major product. Thermal decarboxylation of **3** did not yield the expected dicyclopropyl ketone; rather, a facile rearrangement in a sealed tube at 120 °C occurred, giving rise to 2-cyclopropyl-4,5-dihydrofuran. This "vinyl–cyclopropyl" type rearrangement does not occur through dicyclopropyl ketone or its enolate.

Previous reports have demonstrated that the dianions of carboxylic acids undergo nucleophilic attack at electron-deficient centers.[1] These centers include alkyl halides[2] and the carbonyl carbons of aldehydes, ketones, esters, and acid chlorides.[3,4] An exception we reported previously was cyclopropanecarboxylic acid.[5] Upon dianion formation at 50 °C, followed by treatment with an electrophilic trapping agent, the only observed product appeared to be a dimer of the cyclopropanecarboxylic acid. This dimerization was in apparent conflict with experiments already completed by Ainsworth[6] and Ford[7] that demonstrated the incorporation of trimethylsilyl and deuterium, respectively, into the α-position of cyclopropanecarboxylates, using lithium diisopropyl amide (LDA) as a hindered base in THF. Concurrent with our own investigations, work by Pinnick[8] and Warner[9] have shed light on this "anomalous" reaction of the dianion of cyclopropanecarboxylic acid, and this has prompted us to report our work on the facile rearrangement of the dimeric product into 2-substituted 4,5-dihydrofurans.

The α-proton of a substituted cyclopropane may be rendered acidic by the attachment of a heteroatom such as phosphorus[10] or sulfur,[11] and in the ylide form, these substituted cyclopropyl anions act as good nucleophiles, attacking ketones and alkyl halides. The attachment of a carboxylate function to a cyclopropane ring should also cause the α-proton to be labile, and by analogy to our previous reports[3] on the formation of β-hydroxy acids from

Scheme I



*Address correspondence to: Department of Oral Biology, University of Connecticut Health Center, Farmington, Connecticut 06032.
[†]Wilkes College.
[‡]Buffalo Color Corp.

(1) (a) Krapcho, A. P.; Jahngen, E. G. E. *J. Org. Chem.* **1974**, *39*, 1322. (b) Adam, W.; Baeaza, J.; Liu, J. C. *J. Am. Chem. Soc.* **1972**, *94*, 2000. (c) Moersch, G. W.; Burkett, A. R. *J. Org. Chem.* **1971**, *36*, 1149.
(2) (a) Creger, P. L. *J. Am. Chem. Soc.* **1967**, *89*, 2500. (b) Pfeffer, P. E.; Sibert, L. S.; Kinsel, E. *Tetrahedron Lett.* **1973**, 1163.
(3) (a) Olofson, R. A.; Dougherty, C. M. *J. Am. Chem. Soc.* **1973**, *95*, 582. (b) Krapcho, A. P.; Jahngen, E. G. E.; Kashdan, D. S. *Tetrahedron Lett.* **1974**, 2721.
(4) (a) Rathke, M. W.; Deitch, J. *Tetrahedron Lett.* **1971**, 2953. (b) Logue, M. W. *J. Org. Chem.* **1974**, *39*, 3455. (c) Krapcho, A. P.; Kashdan, D. S.; Jahngen, E. G. E. *Ibid.* **1977**, *42*, 1189.
(5) Krapcho, A. P.; Jahngen, E. G. E. *J. Org. Chem.* **1974**, *39*, 1650.
(6) (a) Ainsworth, C.; Cheir, F.; Kuo, Y.-N. *J. Organomet. Chem.* **1972**, *46*, 59. (b) Ainsworth, C.; Cheir, F.; Kuo, Y.-N. *Ibid.* **1973**, *47*, 73.

0022-3263/83/1948-2472$01.50/0