with Dowex 50 (H^+) (~1.5 g). Filtration of the resin and subsequent evaporation of the filtrate to dryness gave a white solid which crystallized from methanol to give **8** (0.9 g, 78%), mp 219°. An analytical sample was obtained by recrystallization from methanol to give white crystals, mp 222° dec. Physical properties of this material were identical with those of an authentic sample prepared previously.

Concentration of the mother liquor to about 10 ml afforded white crystals (0.20 g). Nmr, ir, and uv spectra, as well as the melting point of this material, are identical with those of lactone **4**.

Method D.—Compound **2** (0.3 g, 1 mmol) was dissolved in 10 ml of 0.5 *M* potassium hydroxide and the resulting solution was stirred at room temperature until the absorption above 240 nm was completely gone. Dilution with water (~50 ml), treatment with Dowex 50 (H^+), and subsequent evaporation of the solvent afforded a gel. This residue upon azeotropic distillation with absolute ethanol gave a syrup which crystallized from methanol after standing at ~4°. This material was shown (by ir, uv, nmr, and melting point) to be identical with compound **8**.

2′,6-Anhydro-1-β-D-arabinofuranosyl-5,6-dihydrouracil-6-carboxamide (**9**).—Compound **4** (0.2 g, 0.69 mmol) was stirred with 50 ml of methanol saturated with ammonia (0°). As soon as solution was effected, the solvent and excess ammonia were immediately evaporated. Addition of a small amount of methanol (~10 ml) furnished colorless crystals (0.19 g, 95%). Recrystallization from methanol (with a few drops of water) afforded pure **9**: mp 172–174° dec; $[\alpha]^{22}D$ +47.9° (*c* 1.0, DMF); nmr δ 10.35 (1, broad s, N^3H), 7.52 (2, broad s, CNH_2), 5.88 (1, d, H-1′, $J_{1',2'}$ = 4.4 Hz), 5.60 (1, broad peak, 3′-OH), 5.06 (1, broad s, 5′-OH), 4.65 (1, d, H-2′), 4.20 (1, broad peak, H-3′), ~3.64 (3, H-4′ at ~3.65 overlapped by the 2 H-5′ at ~3.64), 2.85 (2, q, H-5, $J_{5a,5b}$ = 18.5 Hz).

Anal. Calcd for $C_{10}H_{13}O_7N_3$: C, 41.81; H, 4.56; N, 14.63. Found: C, 41.67; H, 4.54; N, 14.54.

2,2′-Anhydro-3-β-D-arabinofuranosyluracil-6-carboxamide (**10**).—Compound **3a** (0.6 g, 0.002 mol) was suspended in 35 ml of trifluoroacetic acid saturated with hydrobromic acid (0°) and the resulting mixture was allowed to react at room temperature in a pressurized bottle overnight. Evaporation of the solvent and excess hydrobromic acid gave a foam which gradually crystallized from ethanol upon standing at ~4°. Filtration of the dark suspension afforded light gray crystals (400 mg, 67%); a second crop (~50 mg) was obtained from the mother liquor. Recrystallization from methanol with decolorization afforded white crystals (300 mg, 50%): mp 170° (sinters), 210° dec; $[\alpha]^{22}D$ −168.0° (*c* 0.4, DMF); $\lambda_{max}^{MeOH,\ pH\ 1\ and\ 11}$ 296 nm (ε 5000); nmr δ 7.85 (2, broad d, $CONH_2$), 6.58 (1, s, H-5), 6.45 (1, d, H-1′, $J_{1',2'}$ = 6 Hz), 5.91 (1, d, 3′-OH, $J_{3'\text{-OH}}$ = 5 Hz), 5.26 (1, d, H-2′), 4.95 (1, t, 5′-OH, $J_{5'\text{-OH}}$ = 5 Hz), ~4.45 (1, broad s, H-3′), ~4.14 (1, broad s, H-4′), 3.35 (2, broad t, H-5′, H-5″).

Anal. Calcd for $C_{10}H_{11}N_3O_6$: C, 44.61; H, 4.12; N, 15.61. Found: C, 44.45; H, 4.21; N, 15.35.

3-β-D-Arabinofuranosyluracil-6-carboxamide (**11**).—Compound **10** (0.5 g, 0.002 mol) was dissolved in 10 ml of 0.5 *M* potassium hydroxide and progress of the reaction at ambient temperature was followed by tlc on silica gel GF-254 using the solvent system ethyl acetate–1-propanol–water (4:1:2, upper phase). After about 4 hr the solution was treated with Dowex 50 (H^+) (~1 g). Evaporation of the solvent to dryness afforded a foam which crystallized upon addition of methanol (0.4 g, 80%). A small portion was recrystallized from ethanol to give colorless crystals: mp 172–174°; $[\alpha]^{22}D$ −59.5° (*c* 1.0, DMF); λ_{max}^{MeOH} 282 nm (ε 5500), $\lambda_{max}^{pH\ 1}$ 282 nm (ε 5900), $\lambda_{max}^{pH\ 11}$ 321 nm (ε 6400); nmr δ 10.77 (1, broad s, N^3H), 8.31 and 8.03 (2, broad s, $CONH_2$), 6.48 (1, d, H-1′, $J_{1',2'}$ = 7 Hz), 5.45–5.05 (2, m, 5′-OH), 4.00–4.50 (3, m, H-2′, H-3′, H-4′), 3.65 (2, broad s, H-5′, H-5″).

Anal. Calcd for $C_{10}H_{13}O_7N_3$: C, 41.81; H, 4.56; N, 14.64. Found: C, 42.02; H, 4.62; N, 14.42.

Registry No.—**2**, 33780-80-2; **3a**, 33780-81-3; **3b**, 33780-82-4; **4**, 33886-19-0; **5a**, 33886-20-3; **5b**, 33872-65-0; **6**, 33886-21-4; **7**, 33780-83-5; **8**, 33886-22-5; **9**, 33886-23-6; **10**, 33780-84-6; **11**, 33886-24-7.

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Mesoionic Compounds. XVI. 1,4-Dipolar Type Cycloaddition Reactions Utilizing Pyrimidinium Betaines[1]

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N,N′-Disubstituted amidines and carbon suboxide gave in excellent yield *anhydro*-4-hydroxy-6-oxo-1,2,3-trisubstituted pyrimidinium hydroxides which underwent 1,4-dipolar type cycloadditions with dimethyl acetylenedicarboxylate. In the case of *anhydro*-1,3-diphenyl-4-hydroxy-2-methyl-6-oxopyrimidinium hydroxide, the primary adduct, dimethyl 2,6-diaza-3,5-dioxo-2,6-diphenyl-1-methylbicyclo[2.2.2]oct-7-ene-7,8-dicarboxylate, was isolated; on heating, it lost phenyl isocyanate, forming dimethyl 6-methyl-2-oxo-1-phenylpyridine-4,5-dicarboxylate.

1,3-Dipolar cycloaddition reactions utilizing mesoionic ring systems as the source of the 1,3-dipole are well documented in the literature.[2] Both five-membered[2] and six-membered[3] ring systems have been utilized in these reactions. In most instances during the reaction the primary cycloadduct readily lost species such as carbon dioxide,[4] carbonyl sulfide,[5] isocyanates,[6,7] or sulfur[7] leading to substituted heterocycles often difficult to obtain by alternative routes. In other cases the primary cycloadduct was quite stable but, by standard procedures, could be converted into interesting ring systems.[3b,8]

In a recent communication[9] we showed how *anhydro*-

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TABLE I

CHEMICAL SHIFTS OF SOME PYRIMIDINE BETAINES (2)[a]

Compd	Solvent[b]	$\tau_{C_6H_5}$	τ_{C_5H}	τ_{CH_3}
$R^1 = R^2 = Ph$	A	2.50–3.13 (m)	5.01 (s)	
	B	2.50–2.9 (d)	3.55 (s, br)	
$R^1 = CH_3$; $R^2 = Ph$	A	2.40–2.96 (m)	5.13 (s)	6.97 (s)
	B	2.35–2.85 (d)	3.47 (s, br)	6.30 (s)
$R^1 = Ph$; $R^2 = CH_3$	A	2.25–2.78 (s, br)	5.21 (s)	8.1 (s)
	B	2.15–2.80 (m)	3.62 (s, br)	7.61 (s)

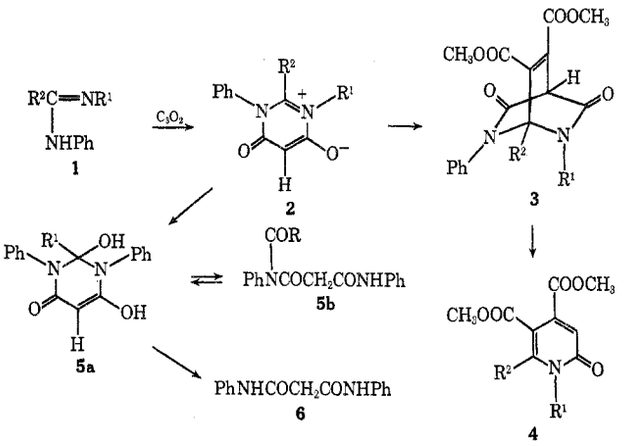
[a] In parts per million from internal TMS. [b] A = DMSO-d_6, B = CF_3COOH.

2-hydroxy-1-methyl-4-oxopyrido[1,2-*a*]pyrimidinium hydroxide underwent a ready cycloaddition reaction with acetylenic dipolarophiles to yield 1,2-disubstituted 4*H*-quinolizin-4-ones, with extrusion of methyl isocyanate. In contrast to the reactions of the six-membered ring systems already reported, this cycloaddition may be interpreted in terms of the intermediacy of a 1,4-dipole.[10] This present communication describes the extension of this concept to a series of pyrimidinium betaines.

The betaines (2) were synthesized in excellent yields by condensation of the *N*,*N*′-disubstituted amidines (1) with carbon suboxide. They were characterized by analytical and spectral data, especially by the presence of molecular ions in their mass spectra and by two carbonyl absorptions at *ca.* 1700 and 1665 cm^{-1}. Hydrolysis experiments also supported the assigned structures. *anhydro*-4-Hydroxy-6-oxo-1,2,3-triphenylpyrimidinium hydroxide (2, $R^1 = R^2 = Ph$), when treated with 2% sodium hydroxide at room temperature for 1 min, gave 2,4-dihydroxy-6-oxo-1,2,3-triphenyl-1,2,3,6-tetrahydropyrimidine (**5a**, $R^1 = Ph$) which, in this case, existed in the carbinolamine form rather than the open chain amino aldehyde form (**5b**). Infrared absorptions (ν_{OH} 3280, ν_{CO} 1698, 1652 cm^{-1}) together with nmr data showing two exchangeable protons (D_2O) at $-\tau$ 0.2, an exchangeable singlet at τ 4.2, and the absence of a methylene group, support structure **5a**. Replacement of the 2-phenyl substituent in 2 with a hydrogen atom greatly increased the susceptibility of the ring system to hydrolysis. *anhydro*-1,3-Diphenyl-4-hydroxy-6-oxopyrimidinium hydroxide (2, $R^1 = Ph$; $R^2 = H$), on dissolution in acetonitrile containing small amounts of water, gave *N*-formylmalonanilide (**5b**, R = H). The existence of the hydrolysis product in this case in the amino aldehyde form was indicated by the spectral data (ν_{NH} 3300, 3200; ν_{CO} 1695, 1655; ν_{CHO} 1725 cm^{-1}), particularly the nmr data, which showed absorptions at τ 6.65 (s, 2, $COCH_2CO$, exchanged with D_2O), 1.56 (broad s, 1, NH, exchanged with D_2O), 0.5 (s, 1, CHO), and aromatic protons. When 2 ($R^1 = Ph$; $R^2 = H$) was heated in aqueous acetone hydrolysis was complete, the product isolated being malonanilide (**6**) which was also obtained from 2 ($R^1 = R^2 = Ph$) and warm sodium hydroxide solution. Reaction of aniline with carbon suboxide gave **6**, whose physical constants were identical with those already described.[11]

Table I lists the nmr data for the pyrimidinium betaines and shows that in trifluoroacetic acid they are to a large extent protonated on the exocyclic oxygen atom. In trifluoroacetic acid the proton attached to C-5 of the nucleus, and also the methyl group at C-2, undergo appreciable downfield shifts of *ca.* 1.5 and 0.5 ppm, respectively, from their resonances observed in DMSO-d_6. No OH proton signal was observed due to the rapid exchange with the solvent. The substantial downfield shift of the C_5 H is attributable to an increase in the heteroatom ring current caused by protonation and is analogous to the results observed on protonation of 3-phenylsydnone and its derivatives.[12] In most of the spectra the singlet due to the C-5 methine hydrogen is invariably broadened in trifluoroacetic acid in comparison to that observed in DMSO-d_6.

These pyrimidinium betaines are derivatives of 4,6-dihydroxypyrimidine and several have been prepared[13] from 5-substituted 4,6-dimethoxypyrimidine in poor yield by reaction with methyl iodide in a sealed tube at 120°. Preparation by this route restricts the substituents on the nitrogen atoms to methyl groups and, in contrast to the betaines described in this current study, those betaines unsubstituted in the five position underwent an interesting dimerization involving positions two and five of the nucleus.



The betaines 2 readily underwent 1,4-dipolar type cycloaddition reactions with dimethyl acetylenedicarboxylate. With *anhydro*-4-hydroxy-1,3-diphenyl-2-methyl-6-oxopyrimidinium betaine (2, $R^1 = Ph$; $R^2 = CH_3$), the primary 1:1 adduct dimethyl 2,6-diaza-3,5-dioxo-2,6-diphenyl-1-methylbicyclo[2.2.2]oct-7-ene-7,8-dicarboxylate (**3**, $R^1 = Ph$; $R^2 = CH_3$) was isolated in 94% yield as colorless needles, mp 188–189°. This structural assignment is based on analytical and spectral data, especially infrared absorptions (ν_{COOCH_3} 1720 cm^{-1}, $\nu_{CON<}$ 1690 cm^{-1}) and nmr data [($CDCl_3$) τ 8.82 (s, 3, C_1 CH_3), 6.11 (s, 3, $C_{7(8)}$ $COOCH_3$), 6.09 (s, 3, $C_{8(7)}$ $COOCH_3$), 5.02 (s, 1, C_4 H), 3.0–2.7 (m, 10,

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aromatics] in which the resonance of the C_4 bridgehead proton is consistent with that found in other [2.2.2] bicyclic ring systems.[14] Thermolysis of **3** resulted in elimination of phenyl isocyanate and the formation of dimethyl 6-methyl-2-oxo-1-phenylpyridine-4,5-dicarboxylate (**4**, R^1 = Ph; R^2 = CH_3). With the other betaines **2**, the intermediate **3** was not isolated, the isocyanate being eliminated during the course of the reaction and the pyridone **4** being obtained directly. It is interesting to note that it is phenyl isocyanate which is eliminated in preference to methyl isocyanate from the intermediate adduct **3** when both possibilities are present. Spectral data of the pyridones **4** were consistent with such a representation and dimethyl 1,6-diphenyl-2-oxopyridine-4,5-dicarboxylate (**4**, R^1 = R^2 = Ph) obtained from **2** (R^1 = R^2 = Ph) was identical with a sample prepared from *anhydro*-2,3-diphenyl-4-hydroxythiazolium hydroxide and dimethyl acetylenedicarboxylate.[7]

Ethyl propiolate and *N*,*N*-diethylaminophenylacetylene as well as olefinic dipolarophiles such as dimethyl maleate did not form well-defined products with the pyrimidinium betaines.

Experimental Section[15]

The following preparation illustrates the method used for the synthesis of the pyrimidinium betaines.

anhydro-**4-Hydroxy-6-oxo-1,2,3-triphenylpyrimidinium Hydroxide** (**2**, R^1 = R^2 = Ph).—*N*,*N*-Diphenylbenzamidine[16] (1.9 g, 0.007 mol), dissolved in anhydrous ether (70 ml) with a catalytic amount of anhydrous $AlCl_3$, was added slowly to a stirred, ethereal solution of carbon suboxide[17] (*ca.* 0.7 g, 0.01 mol). A crystalline product separated toward the end of this addition. After stirring the reaction mixture at room temperature for 12 hr, the product was collected, washed with anhydrous ether, and recrystallized from absolute ethanol, from which it separated as colorless prisms: yield 1.8 g (76%); mp 255–257° dec; ir (KBr) 3060, 3040 (CH), 1700, 1665 cm^{-1} (CO); $\lambda_{max}^{CH_3OH}$ 350–270 nm (plateau), 253 sh (log ϵ 3.96), 235 sh (4.25), 215 (4.62); nmr (DMSO-d_6) τ 5.01 (s, 1, H_5), 3.13–2.50 (m, 15, aromatic); mass spectrum $M^{+\cdot}$, *m*/*e* (rel intensity) 340 (5).

Anal. Calcd for $C_{22}H_{16}N_2O_2$: C, 77.63; H, 4.74; N, 8.23. Found: C, 77.59; H, 4.76; N, 8.23.

anhydro-**1,2-Diphenyl-4-hydroxy-3-methyl-6-oxopyrimidinium hydroxide** (**2**, R^1 = CH_3; R^2 = Ph) prepared from *N*-methyl-*N*′-phenylbenzamidine[18] separated from ethanol as colorless prisms: mp 206–208° (100%); ir (KBr) 3050, 2950 (CH), 1695, 1670 cm^{-1} (CO); $\lambda_{max}^{CH_3OH}$ 350–275 nm (plateau), 255 (log ϵ 3.39), 217 (4.27); nmr (DMSO-d_6) τ 6.97 (s, 3, NCH_3), 5.13 (s, 1, H_5), 2.96–2.40 (m, 10, aromatic); mass spectrum $M^{+\cdot}$, *m*/*e* (rel intensity) 278 (17).

Anal. Calcd for $C_{17}H_{14}N_2O_2$: C, 73.44; H, 5.07; N, 10.06. Found: C, 73.04; H, 5.12; N, 9.93.

anhydro-**1,3-Diphenyl-4-hydroxy-6-oxopyrimidinium hydroxide** (**2**, R^1 = Ph; R^2 = H) was obtained from *N*,*N*′-diphenylformamidine[19] as colorless, irregular prisms on trituration of the reaction product with anhydrous acetone: mp 193–195° (78%); ir (KBr) 3035 (CH), 1680, 1670 cm^{-1} (CO); $\lambda_{max}^{CH_2Cl_2}$ 360–315 nm (plateau), 280 sh (log ϵ 3.65), 243 (4.36); nmr (DMSO-d_6) τ 5.25 (s, 1, H_5), 2.67–2.55 (broad s, 10, aromatic), 0.68 (s, 1, H_2). Trace amounts of water present in recrystallization solvents caused sufficient hydrolysis to result in incorrect analytical values.

anhydro-**1,3-Diphenyl-4-hydroxy-2-methyl-6-oxopyrimidinium hydroxide** (**2**, R^1 = Ph; R^2 = CH_3) was prepared from *N*,*N*′-diphenylacetamidine[20] and crystallized from absolute ethanol as colorless prisms: yield 71%; mp 260–261°; ir (KBr) 3045, 3000, 2900 (CH), 1699, 1665 cm^{-1} (CO); $\lambda_{max}^{CH_3OH}$ 370–345 nm (plateau), 252 (log ϵ 3.82), 208 (4.66); nmr (DMSO-d_6) τ 8.1 (s, 3, C_2CH_3), 5.21 (s, 1, H_5), 2.00 (s, 10, aromatics); mass spectrum $M^{+\cdot}$ *m*/*e* (rel intensity) 278 (9).

Anal. Calcd for $C_{17}H_{14}N_2O_2$: C, 73.44; H, 5.07; N, 10.06. Found: C, 73.18; H, 4.98; N, 9.73.

Hydrolysis of *anhydro*-**1,3-Diphenyl-4-hydroxy-6-oxopyrimidinium Hydroxide** (**2**, R^1 = Ph; R^2 = H).—The betaine (0.39 g, 0.001 mol), acetone (10 ml), and H_2O (1 ml) were refluxed for 30 min. The solvent was evaporated *in vacuo* and the residue was recrystallized from ethanol, affording colorless flakes of *N*,*N*′-diphenylmalonamide, mp 223–225° (lit.[11] mp 223–224°) (92%). The mixture melting point with an authentic sample was not depressed and their ir spectra were identical.

Hydrolysis of *anhydro*-**4-Hydroxy-6-oxo-1,2,3-triphenylpyrimidinium Hydroxide** (**2**, R^1 = R^2 = Ph).—The betaine (0.4 g) was treated with aqueous sodium hydroxide (20 ml of 2% solution) for 1 min. After filtration, the reaction mixture was acidified with dilute HCl and the product which separated was collected and dried. It crystallized from ethanol as colorless prisms of 2,4-dihydroxy-6-oxo-1,2,3-triphenyl-1,2,3,6-tetrahydropyrimidine (**5a**): 84%; mp 208–210°; ir (KBr) 2980 (OH), 3140–3010 (CH), 1698 cm^{-1} (CO); $\lambda_{max}^{CH_3OH}$ 310 nm sh (log ϵ 4.07), 267 sh (4.82), 256 (4.85), 201 (5.06); nmr (DMSO-d_6) τ 4.20 (s, 1, H_5, exchanged with D_2O), 1.9–2.95 (m, 15, aromatic), −0.2 (s, 2, OH, exchanged with D_2O); mass spectrm $M^{+\cdot}$, *m*/*e* (rel intensity) 358 (1).

Anal. Calcd for $C_{22}H_{18}N_2O_3$: C, 73.81; H, 5.05; N, 7.31. Found: C, 73.51; H, 5.07; N, 7.73.

Hydrolysis of *anhydro*-**1,3-Diphenyl-4-hydroxy-6-oxopyrimidinium Hydroxide** (**2**, R^1 = Ph; R^2 = H).—The above betaine, on dissolution in wet acetonitrile, gave a small amount of *N*-formylmalonanilide (**5b**, R = H) as colorless rhombs: mp 122–123°; ir (KBr) 3300, 3200 (NH), 3150, 3055, 2940 (CH), 1725 (CO), 1695, 1655 cm^{-1} (CON<); nmr ($CDCl_3$) τ 6.65 (s, 2, CH_2, exchanged with D_2O), 2.42–3.00 (m, 10, aromatic), 1.56 (broad s, 1, NH, exchanged with D_2O), 0.5 (s, 1, CHO); mass spectrum, $M^{+\cdot}$, *m*/*e* (rel intensity) 282 (3).

Anal. Calcd for $C_{16}H_{14}N_2O_3$: C, 68.01; H, 5.00; N, 9.93. Found: C, 67.97; H, 4.94; N, 9.86.

Dimethyl 1,6-Diphenyl-2-oxopyridine-4,5-dicarboxylate (**4**, R^1 = R^2 = Ph).—The betaine **2** (R^1 = R^2 = Ph) (0.34 g, 0.001 mol), dimethyl acetylenedicarboxylate (0.568 g, 0.004 mol), and acetone (15 ml) were refluxed for 24 hr. Acetone was then removed *in vacuo* and the residue was chromatographed on silica gel (Fluorsil F-100) with benzene–ether (2:1) as eluent. The product was recrystallized from chloroform–ether, giving colorless prisms, mp 180–182° (82%) (lit.[7] mp 180–181°).

In a similar manner, **dimethyl 1-methyl-2-oxo-6-phenylpyridine-4,5-dicarboxylate** (**4**, R^1 = CH_3; R^2 = Ph) was prepared from **2** (R^1 = CH_3; R^2 = Ph) and dimethyl acetylenedicarboxylate in 55% yield. In this case the reaction mixture was refluxed for 48 hr, chromatographed on silica gel, and eluted with benzene–ether (1:1). The product recrystallized from benzene–petroleum ether (bp 30–60°) forming colorless prisms: mp 102–103°; ir (KBr) 3060, 2950 (CH), 1735, 1650 cm^{-1} (CO); $\lambda_{max}^{CH_3OH}$ 330 nm (log ϵ 3.82), 250 (3.95); nmr ($CDCl_3$) τ 6.77 (s, 3, C_5COOCH_3), 6.57 (s, 3, C_6COOCH_3), 6.15 (s, 3, NCH_3), 2.95 (s, 1, H_3), 2.4–2.85 (m, 5, aromatic); mass spectrum, $M^{+\cdot}$, *m*/*e* (rel intensity) 301 (100).

Anal. Calcd for $C_{16}H_{15}NO_5$: C, 63.78; H, 5.02; N, 4.65. Found: C, 63.46; H, 5.02; N, 4.53.

Dimethyl 2,6-Diaza-3,5-dioxo-2,6-diphenyl-1-methylbicyclo[2.2.2]oct-7-ene-7,8-dicarboxylate (**3**, R^1 = Ph; R^2 = CH_3).—The betaine **2** (R^1 = Ph; R^2 = CH_3) (0.6 g, 0.0022 mol), dimethyl acetylenedicarboxylate (0.612 g, 0.0043 mol), and benzene (50 ml) were refluxed for 24 hr. The solvent was evaporated *in vacuo* and the residue, after trituration with ether, was recrystallized

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(15) Spectral characterization of products was carried out on the following instrumentation: ir, Perkin-Elmer Model 337 spectrophotometer; uv, Cary Model 14 spectrophotometer; nmr, Varian A-60 nmr spectrometer using TMS as internal standard; mass spectra, Hitachi Perkin-Elmer RMU-6E mass spectrometer, 70 eV, using the direct inlet probe at a source of temperature of *ca.* 100°. All evaporations were done under reduced pressure using a rotatory evaporator and melting points were taken in capillaries. Chromatographic columns utilized a length:width ratio of 10:1. Microanalyses were by Instranal Laboratories, Rensselaer, N. Y.

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from ethanol, affording colorless needles: mp 188–189° (94%); ir (KBr) 3045, 3010, 2960 (CH), 1720, 1690 cm^{-1} (CO); $\lambda_{max}^{CH_3OH}$ 235 nm sh (log ϵ 3.00), 2.00 (4.69); nmr ($CDCl_3$) τ 8.82 (s, 3, C_1 CH_3), 6.11 (s, 3, C_6 $COOCH_3$), 6.09 (s, 3, C_5 $COOCH_3$), 5.02 (s, 1, H_4), 3.0–2.4 (m, 10, aromatic); mass spectrum, identical with that of **4** (R^1 = Ph; R^2 = CH_3).

Anal. Calcd for $C_{28}H_{20}N_2O_6$: C, 65.70; H, 4.80; N, 6.66. Found: C, 65.62; H, 4.78; N, 6.62.

Thermal Elimination of Phenyl Isocyanate from 3 (R^1 = Ph; R^2 = CH_3).—The primary adduct **3** (R^1 = Ph; R^2 = CH_3) (0.42 g, 0.001 mol) was heated for 20 min above its melting point at about 0.5 mm. After cooling and trituration with ether, the product crystallized from benzene–cyclohexane as colorless prisms of dimethyl 6-methyl-2-oxo-1-phenylpyridine-4,5-dicarboxylate (**4**, R^1 = Ph; R^2 = CH_3): 90%; mp 155–158°; ir (KBr) 3001, 2950 (CH), 1740, 1725, 1660 cm^{-1} (CO); $\lambda_{max}^{CH_3OH}$ 328 nm (log ϵ 3.74), 251 (4.08), 203 (4.68); nmr ($CDCl_3$) τ 7.90 (s, 3, C_6 CH_3), 6.17 (s, 3, C_4 $COOCH_3$), 6.10 (s, 3, C_5 $COOCH_3$), 3.09 (s, 1, H_3), 2.32–2.90 (m, 10, aromatic); mass spectrum, $M^{+\cdot}$, m/e (rel intensity) 301 (100).

Anal. Calcd for $C_{16}H_{15}NO_5$: C, 63.78; H, 5.02; N, 4.65. Found: C, 63.50; H, 4.98; N, 4.52.

Registry No.—**2** (R^1 = R^2 = Ph), 33821-84-0; **2** (R^1 = CH_3; R^2 = Ph), 33821-85-1; **2** (R^1 = Ph; R^2 = H), 33821-86-2; **2** (R^1 = Ph; R^2 = CH_3), 33821-87-3; **3** (R^1 = Ph; R^2 = CH_3), 33821-88-4; **4** (R^1 = CH_3; R^2 = Ph), 33821-89-5; **4** (R^1 = Ph; R^2 = CH_3), 33821-90-8; **5a** (R^1 = Ph), 33821-91-9; **5b** (R = H), 33821-92-0.

Liquid Crystals. II. Unsymmetrical *p*-Phenylene Di-*p*-*n*-alkoxybenzoates[1]

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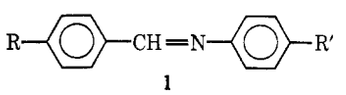
Nematic mesophases that exist at low temperatures are desirable in several applications, but compounds which exhibit nematic mesomorphism tend also to have high melting points. Schiff bases (**1**), the best materials for these applications until recently, are relatively unstable chemically. Esters are more stable and the symmetrical *p*-phenylene di-*p*-*n*-alkoxybenzoates (**2**, R = R′) are nematogenic. However, no compound in this series melts to a nematic mesophase below 122°. The possibility of obtaining lower melting nematic esters by introducing molecular dissymmetry was explored. Twenty-eight unsymmetrical esters (**2**, R ≠ R′), providing all possible combinations of terminal *n*-alkyl groups from methyl through *n*-octyl, were synthesized and their phase transition temperatures determined. The nematic–isotropic transition point is high, even for the most unsymmetrical esters, while the melting point is depressed. The lowest melting products are the hexyl–octyl and pentyl–heptyl esters, which are nematic at 107–202 and 108–210°, respectively. The high nematic–isotropic transition temperatures of these compounds suggest that much lower melting points can be achieved in this system, without losing nematic mesomorphism, by introducing even more molecular dissymmetry. In addition to the 28 unsymmetrical esters of type **2**, seven new *p*-hydroxyphenyl *p*-*n*-alkoxybenzoates (**3**) and the previously unreported **2** (R = R′ = n-C_5H_{11}) were also prepared. Similar studies of other chemically stable nematic compounds are reviewed briefly.

Nematic liquid crystallinity (mesomorphism)[2,3] is exhibited by certain compounds with relatively rigid, polar, rod-shaped molecules that tend to be oriented with their long axes parallel because of mutual attractive forces. When such a compound is heated, the crystalline solid melts to a birefringent, anisotropic liquid (nematic mesophase) in which adjoining molecules lie parallel to one another. At a higher temperature, the mesophase undergoes transition to isotropic liquid.

For practical applications, such as optical and display devices[4] and gas–liquid chromatography,[5] nematic mesophases which exist at or near room temperature are desirable. This is a difficult criterion to meet because the molecular characteristics that are necessary for nematic mesomorphism also produce stable crystalline lattices. Accordingly, nematic compounds generally have high melting points. Success in meeting the requirement has been achieved with nematic substances having a relatively high degree of molecular dissymmetry and their mixtures. The dissymmetry and the mixing depress the solid–nematic melting point without necessarily lowering the nematic–isotopic transition temperature. Accordingly, by proper selection of compounds, low melting points are obtainable with retention of nematic mesomorphism.

At the time our investigation was begun, the outstanding examples of these successes involved Schiff bases (**1**). A ternary mixture of **1** (R = CH_3O; R′ = n-C_3H_7COO), **1** (R = n-C_4H_9O; R′ = CH_3COO), and **1** (R = CH_3O; R′ = CH_3COO) has a nematic range[6] of 22–105°.[7] The compound **1** (R = CH_3O; R′ = n-C_4H_9) is nematic at 22–48°.[8] The trouble with Schiff bases is their hydrolytic, oxidative, and thermal instability. Aromatic esters are much more stable, and symmetrical *p*-phenylene di-*p*-*n*-alkoxybenzoates (**2**, R = R′) are known to have long nematic ranges.[9,10] However, no compound in the series undergoes transi-



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(1) (a) Presented at the 162nd National Meeting of the American Chemical Society, Washington, D. C., Sept 1971. (b) From the M.S. thesis of S. A. H., The University of North Carolina at Greensboro, 1971. (c) This work was supported in part by a grant-in-aid from The University of North Carolina at Greensboro Research Council. (d) Previous paper in this series: J. P. Schroeder and Dorothy C. Schroeder, *J. Org. Chem.*, **33**, 591 (1968).

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