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]

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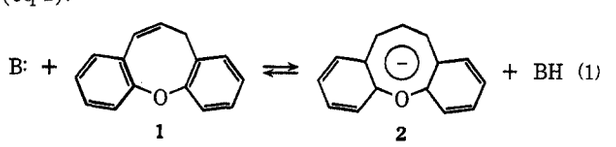
The synthesis of dibenz[b,g]oxocin is reported. It is a slightly stronger carbon acid than xanthene. This fact is interpreted as evidence for the aromaticity of the 10-π-electron oxocinyl anion.

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).

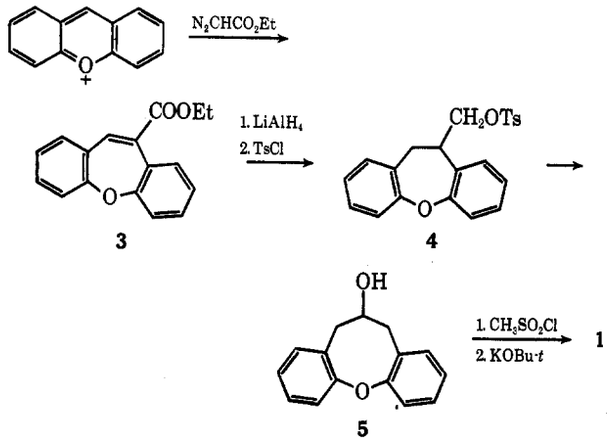
Addition of ethyl diazoacetate to xanthylium perchlorate in dry acetonitrile at 0° led to rapid gas evolution. Two major products were isolated: 9-carboethoxydibenz[b,f]oxepin (**3**) and 9-carboethoxy-10-acetylamino-9,10-dihydrodibenz[b,f]oxepin (**7**). The structure of **3** follows from analogy with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

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

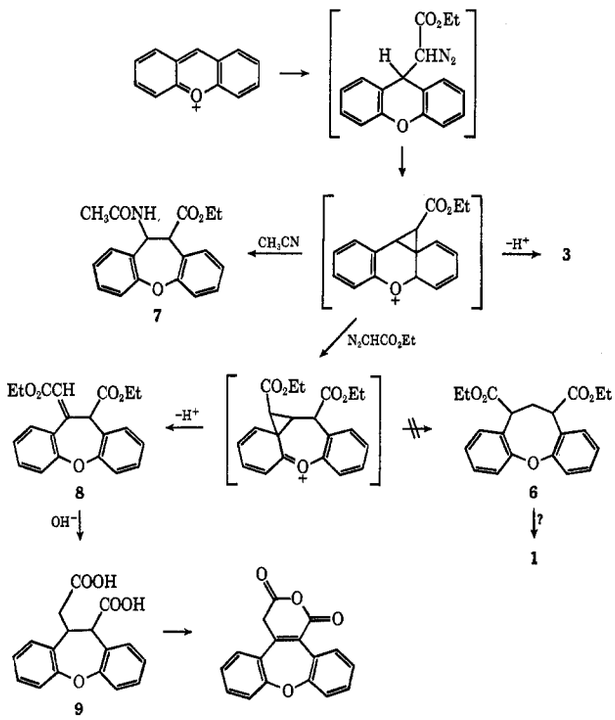
(2) (a) R. M. Coates and E. F. Johnson, *J. Amer. Chem. Soc.*, **93**, 4016 (1971), and references contained therein; (b) N. L. Allinger and G. A. Youngdale, *ibid.*, **84**, 1020 (1962); (c) R. Breslow and E. Mohacsi, *ibid.*, **85**, 431 (1963); (d) L. A. Paquette, T. Kakihana, J. F. Hansen, and J. 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).

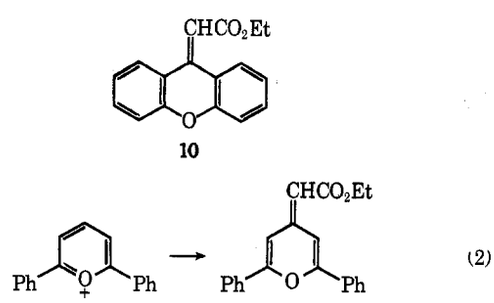
SCHEME I



SCHEME II



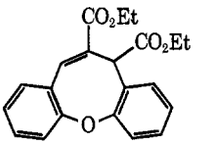
its oxidation[4] to (diphenyl ether)-2,2′-dicarboxylic acid.[5] The isolation of this acid rules out the alternative structure **10** for the ring expansion product. This type of structure was the exclusive product found in the homologation of the 2,6-diphenylpyrrylium cation[3c] (eq 2).



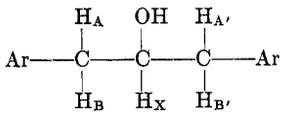
(2)

Amide **7** was isolated as a single stereosisomer of unknown configuration. It presumably arises from a Ritter-type capture of the intermediate cation by acetonitrile, and its structure follows from its pyrolysis at 230° to **3**. Small amounts of the 2:1 adduct **8** (see below) were also isolated. When dimethoxyethane was substituted as solvent for acetonitrile, no **7** was isolated and **3** could be obtained in up to 82% yield.

Inverse addition of xanthylium perchlorate to an excess of ethyl diazoacetate in dimethoxyethane afforded in addition to **3** a 2:1 diazo ester:cation adduct. That this adduct possesses the undesired seven-ring structure **8** rather than the sought-after oxocin **6** follows from these observations. Its nmr spectrum showed two singlets attributable to the aliphatic and vinyl hydrogens present. Brief treatment of **8** with alkali led to disappearance of its long-wavelength uv absorption at 313 mμ. Carried out preparatively, alkaline isomerization afforded as sole product an isomer **9** of **8** possessing a two-hydrogen singlet at δ 3.8 in its nmr spectrum. Its ultraviolet spectrum was consistent[6] with the presence of a dibenzo[*b*,*f*]oxepin chromophore. Saponification of **9** followed by treatment of the crude acid with acetic anhydride afforded a gummy material whose infrared spectrum (λ_{max} 5.58 and 5.76 μ) was consistent with its being a glutaconic anhydride.[7] These data rule out structure **6** and other unlikely alternatives such as



B. Conversion of 3 to Dibenz[*b*,*g*]oxocin.—Reduction of **3** with lithium aluminum hydride in refluxing tetrahydrofuran according to Jorgenson[8] resulted in reduction of the ester and double bond of **3**.[9] Solvolysis of toluenesulfonate **4** in refluxing acetic acid followed by lithium aluminum hydride reduction of the resulting acetate afforded a single alcohol **5**. Alcohol **5** was shown to be secondary and nonbenzylic by oxidation to a ketone, λ_{max} 5.82 μ. The nmr of **5**



indicated the part structure with coupling constants J_{AB} = 14, J_{AX} = 7, J_{BX} = 4.5 Hz. Dehydration of **5** was effected by treatment of its methanesulfonate with potassium *tert*-butoxide in refluxing *tert*-butyl alcohol. Attempted dehydration of **5** with *p*-toluenesulfonic acid in refluxing benzene afforded toluenesulfonate **4**. A compound having the expected spec-

(4) (a) E. v. Rudloff, *Can. J. Chem.*, **34**, 1413 (1956); (b) E. E. Koemmel, *Anal. Chem.*, **36**, 426 (1964).

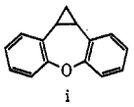
(5) (a) R. F. Manske and A. Ledingham, *J. Amer. Chem. Soc.*, **72**, 4797 (1950); (b) E. Bergman and M. Rabinowitz, *J. Org. Chem.*, **25**, 828 (1960); (c) O. V. Schickh, *Chem. Ber.*, **698**, 242 (1936); (d) F. Fujikawa and Y. Miyoshi, *J. Pharm. Soc. Jap.*, **8A**, 19 (1944).

(6) F. A. Anet and P. M. G. Bavin, *Can. J. Chem.*, **35**, 1084 (1957).

(7) K. Nakanishi, "Infrared Absorption Spectroscopy," Holden-Day, San Francisco, Calif., 1962, p 45.

(8) M. J. Jorgenson and A. W. Friend, *J. Amer. Chem. Soc.*, **87**, 1815 (1965).

(9) Extended reduction in refluxing dioxane afforded i, mp 55–56°, which



i

could also be prepared from dibenz[*b*,*f*]oxepin[3a] and iodomethylzinc iodide.

tral properties of the toluenesulfonate of **5** was detected on short reaction periods.

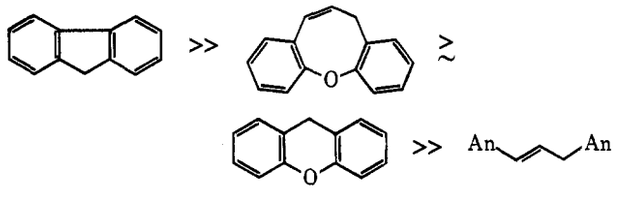
Acidity of Dibenzo[b,g]oxocin.—The acidity of **1** relative to xanthene, fluorene, and 1,3-bis(*p*-anisyl)propene was measured by equilibration of the butyllithium prepared salts in tetrahydrofuran.[10] It was initially shown that treatment of the above carbon acids with 1.05–1.1 equiv of *n*-butyllithium in tetrahydrofuran at −80° followed by 25° produced in good yield the monolithium salts (Table I). In all cases the nmr spectra of the deuterated species isolated on quenching of the anions with deuterium oxide showed the deuterium present to be localized on the allylic (or benzylic) carbons.

TABLE I
REACTION OF HYDROCARBONS WITH BUTYLLITHIUM IN TETRAHYDROFURAN FOLLOWED BY DEUTERIUM OXIDE QUENCHING

RH	BuLi:RH	Deuterium content, % d_0	% d_1	% d_2
Dibenz[b,g]-oxocin	1.05	11.5	82	6.5
Xanthene	1.05	5	92.5	2.5
Fluorene	1.05	8.5	86.5	5
Di(*p*-anisyl)-propene	1.09	9	88	3

Acid–base equilibration of pairs of the above carbon acids was performed by allowing a 1:1 mixture of one acid and the lithium salt of another to equilibrate followed by deuterium oxide quenching[1c] and low-voltage mass spectrometry of the deuterated acid mixture. Analysis by mass spectrometry of the separated components of the deuterated mixture was in agreement with that of the mixture itself, as was analysis by nmr. Where necessary (dibenz[b,g]oxocin–xanthene) equilibrium was approached from both directions.

The results (Table II) allow one to place the acidity of these four carbon acids in the order



From the data in Table II one may calculate that dibenz[b,g]oxocin is an approximately 1.90 pK units stronger acid than xanthene. Assuming the pK_a of xanthene to be 29,[11] this affords 27 as the pK_a of dibenz[b,g]oxocin. This number may be compared with the pK_a of fluorene, 23.[11] Employing the Streitwieser[12] correlation, pK_a = 48–15.5ΔM, where ΔM is the change in delocalization energy in units of β on ionization of a carbon acid, one calculates by simple Hückel theory a pK_a for dibenz[b,g]oxocin of 24.9 (ΔM = 1.4924β).

The significance of the acidity of dibenz[b,g]oxocin hinges on a number of imponderables, principal of which is the appreciable (but hard to evaluate) increase in strain energy on going from **1** to **2**. We feel that considering the ring strain involved in ionization of **1** (assuming that anion **2** is planar), the experimental pK_a is in satisfactory agreement with that calculated and hence the dibenz[b,g]oxocinyl anion shows a property consistent with "aromaticity."[13]

Experimental Section[14]

Xanthylium perchlorate[15] was prepared by reaction of xanthydrol with 60% perchloric acid in acetic acid at 5°, and was recrystallized from acetonitrile–ether, mp 230° dec (lit.[15] mp 235° dec).

Xanthylium fluoroborate, mp 179° dec, was prepared similarly from xanthydrol and 50% fluoroboric acid in acetic acid.

Xanthylium Perchlorate and Ethyl Diazoacetate in Acetonitrile.—Ethyl diazoacetate (1.95 g, 17 mmol) was added over 2 hr to a stirred solution of 3.10 g (11 mmol) of xanthylium perchlorate in 275 ml of acetonitrile maintained at 2°. At the end of addition, 455 ml (calculated, 381 ml) of gas had been evolved. The brown reaction mixture was poured into 1 l. of water and worked up to afford 3.33 g of a semicrystalline oil. Repeated chromatography of this oil on silica gel afforded the following substances in order of elution.

(1) 10-Carboethoxydibenz[b,f]oxepin (**3**), 330 mg (11.3% yield), had mp 72.5–73° (hexane); $\lambda_{max}^{CCl_4}$ 5.84 ($COOC_2H_5$), 6.19 μ (C=C); λ_{max}^{EtOH} 230 mμ (ϵ 2.3 × 10⁴), 293 (1.07 × 10⁴); nmr (CCl_4) δ 7.77 (singlet, 1 H, ArCH=C), 7.6–6.85 (multiplet, 8 H, ArH), 4.3 and 1.35 (quartet and triplet, 5 H, OCH_2CH_3); mass spectrum *m/e* 266 (parent, base).

Anal. Calcd for $C_{17}H_{14}O_3$: C, 76.67; H, 5.29. Found: C, 76.44; H, 5.26.

A mixture of 104 mg (0.39 mmol) of **3** and 0.4 g of potassium permanganate in 8 ml of water and 0.1 ml of 10% sodium hydroxide was refluxed with stirring for 4.5 hr. The mixture was cooled and acidified, and sufficient sodium bisulfite was added to dissolve the manganese dioxide. Xanthone, 15 mg, mp 177–178°, was removed by filtration and the filtrate was extracted with ether to afford 40 mg (40% yield) of (diphenyl ether)-2,2′-dicarboxylic acid, mp 232–233° (lit.[5a] mp 231°), identical with a sample prepared from dibenz[b,f]oxepin. Oxidation by the procedure of Kuemmel[5b] afforded (diphenyl ether)-2,2′-dicarboxylic acid only, in 63% yield.

(2) Xanthone, 65 mg (3% yield), was identified by comparison with an authentic sample.

(3) Diester **8**, 241 mg (6.3% yield), was obtained as cubes: mp 105–106.5° (benzene–hexane); $\lambda_{max}^{CHCl_3}$ 5.78, 5.85 ($COOC_2H_5$), 6.16 μ (C=C); λ_{max}^{EtOH} 234 mμ (ϵ 1.67 × 10⁴), 273 (1.32 × 10⁴), 313 (8.35 × 10³); nmr ($CDCl_3$) δ 7.7–6.93 (multiplet, 8 H, ArH), 6.9 (singlet, 1 H, C=C**H**$CO_2C_2H_5$), 6.23 (singlet, 1 H, C=C**H**Ar$CO_2C_2H_5$), 4.27 and 4.04 (quartets, 2 H each, OCH_2CH_3), 1.32 and 0.94 (triplets, 3 H each, OCH_2CH_3); mass spectrum *m/e* 352 (parent), 250 [base, parent − (C_2H_5OH + CO + C_2H_4)].

Anal. Calcd for $C_{21}H_{20}O_5$: C, 71.56; H, 5.72. Found: C, 71.22; H, 5.63.

Base-Catalyzed Isomerization of 8.—A solution of 100 mg of **8** and 0.5 g of sodium in 20 ml of dry ethanol was allowed to stand at room temperature. There was rapid (~1 min) loss of the absorption at 313 mμ characteristic of **8**. After 2 hr the reaction mixture was worked up to afford 75 mg of **9**: mp 156–158° (benzene–hexane); λ_{max}^{EtOH} 226 mμ (ϵ 1.29 × 10⁴), 278 (6.58 × 10³); $\lambda_{max}^{CHCl_3}$ 5.82 ($COOC_2H_5$), 6.22 μ (C=C); nmr ($CDCl_3$) δ 7.23 (8 H, multiplet, ArH), 4.34 and 4.16 (quartets, 2 H each,

(10) *I.e.*, as the solvent separated ion pairs: T. E. Hogen-Esch and J. Smid, *J. Amer. Chem. Soc.*, **88**, 207 (1966).

(11) (a) W. K. McEwen, *ibid.*, **58**, 1124 (1936); (b) D. J. Cram, "Fundamentals of Carbanion Chemistry," Academic Press, New York, N. Y., 1965, p 4.

(12) A. Streitwieser, *Tetrahedron Lett.*, 23 (1960).

(13) A number of attempts to observe the nmr spectrum of **2** were unsuccessful.

(14) "Work-up" entailed: (1) partitioning diluted reaction mixtures between water and ether; (2) washing the ether layer with saturated sodium bicarbonate solution and then with saturated salt solution; (3) drying of the ether layer over anhydrous sodium sulfate followed by filtration and evaporation. Isotopic analyses of deuterated compounds were performed at 7 eV nominal ionization voltage on a CEC-103C mass spectrometer.

(15) K. A. Hofmann, R. Roth, K. Hobold, and A. Hetzler, *Chem. Ber.*, **43**, 2624 (1910).

TABLE II

ADDITION OF 1.0 EQUIV OF RH TO R'Li (PREPARED FROM R'H AND n-C_4H_9Li) IN TETRAHYDROFURAN

$$R'Li + RH \rightleftharpoons R'H + RLi$$

R'H derived R'Li	RH	Recovered R'H			Recovered RH		
		% d_0	% d_1	% d_2	% d_0	% d_1	% d_2
Dibenz[b,g]oxocin[a]	Xanthene	18.5	78.5	3	92	8	e
Xanthene[b,c]	Dibenz[b,g]oxocin	91	9	e	16	81.5	2.5
Xanthene[b,d]	Dibenz[b,g]oxocin	91.5	8.5	e	20	77.5	2.5
Fluorene[b]	Dibenz[b,g]oxocin	10	86	4	98.5	1.5	
1,3-Bis(p-anisyl)-propene[b]	Dibenz[b,g]oxocin	97	3		26.5	71.5	2

[a] 0.5 mM R'H and 0.5 mM n-C_4H_9Li. [b] 1.0 mM R'H and 1.05 mM n-C_4H_9Li. [c] 30 min equilibration time. [d] 75 min equilibration time. [e] The low voltage mass spectrum of dibenz[b,g]oxocin exhibits weak fragment peaks at m/e 181–183 (xanthylium cations). As a result these peaks were corrected for both isotopic natural abundance and contribution from the deuterated oxocin.

OCH_2CH_3), 3.83 (singlet, 2 H, $C{=}CCH_2COOC_2H_5$), 1.31 and 1.2 (triplets, 3 H each, OCH_2CH_3); mass spectrum m/e 352 (parent).

Saponification of 80 mg of **9** in refluxing aqueous ethanolic sodium hydroxide afforded 78 mg of an acidic material: λ_{max}^{EtOH} 227 mμ (ϵ 1.33 × 10^4), 278 (6.82 × 10^3); $\lambda_{max}^{CHCl_3}$ 5.85 μ; mp 154–157°. A solution of this material in 2 ml of acetic anhydride was heated under reflux for 1.5 hr, and solvent was removed *in vacuo* to afford 50 mg of a gum: $\lambda_{max}^{CHCl_3}$ 5.58, 5.76 μ (cyclic anhydride[7]); mass spectrum m/e 278 (parent).

(4) **Acetamide 7**, 1.44 g (40.3% yield), was obtained as needles: mp 171–172.5° (benzene–hexane); $\lambda_{max}^{CHCl_3}$ 2.92 (NH), 5.77 ($COOC_2H_5$), 5.98 μ (CONHR); λ_{max}^{EtOH} 270 mμ (ϵ 1650); mass spectrum m/e 325 (parent), 2.66 (base, parent − CH_3CONH_2); nmr ($CDCl_3$) δ 7.18 (multiplet, 8 H, ArH), 5.82 (doublet, J = 5 Hz, superimposed on a broad singlet, 2 H, NH and $CHCO_2C_2H_5$), 4.26 (triplet, J = 5 Hz, 1 H, CHNHAc), 4.03 (quartet, 2 H, OCH_2CH_3), 1.82 (singlet, 3 H, CH_3CONH–), 1.06 (triplet, 3 H, OCH_2CH_3). Addition of deuterium oxide to the nmr sample led to slow exchange of the NH to produce ϵ 4.24 (doublet, J = 5 Hz, 1 H) and 5.84 (doublet, J = 5 Hz, 1 H).

Anal. Calcd for $C_{19}H_{19}O_4N$: C, 70.12; H, 5.98; N, 4.30. Found: C, 69.91; H, 5.88; N, 4.38.

Pyrolysis of 150 mg of **7** at 250° under nitrogen followed by sublimation and chromatography of the sublimate afforded 23 mg of **3**, identified by comparison with an authentic sample, and 89 mg (60% recovery) of **7**.

Addition of xanthylium perchlorate to a threefold excess of ethyl diazoacetate in acetonitrile afforded a 31% yield of the 2:1 adduct **8** and a 39% yield of the Ritter product **7**.

Xanthylium Perchlorate and Ethyl Diazoacetate in Dimethoxyethane.—To a stirred slurry of 3 g (10.7 mmol) of xanthylium perchlorate in 50 ml of dry dimethoxyethane at 0° was added over 1.5 hr a solution of 1.35 ml (1.46 g, 12.8 mmol) of ethyl diazoacetate in 20 ml of dimethoxyethane. Gas (360 ml, calculated 336 ml) was evolved. The brown-red reaction mixture was poured into water and worked up to afford 3.27 g of a dark solid. Chromatography of this on silica gel afforded, in order of elution, 40 mg (2% yield) of xanthene, 1.37 g (48% yield) of 9-carbethoxydibenz[b,f]oxepin (**3**), mp 70–71.5°, and 453 mg (22% yield) of xanthone, identified by comparison with an authentic sample.

Xanthylium Fluoroborate and Ethyl Diazoacetate.—Addition of ethyl diazoacetate (16.74 g, 0.165 mol) over 4 hr to xanthylium fluoroborate (33.5 g, 0.125 mol) in dimethoxyethane (300 ml) containing γ-collidine (9.17 g, 0.76 mol) at −13° afforded on chromatography 27.2 g (82% yield) of oxepin **3**, mp 71–72°.

10-p-Toluenesulfonyloxymethyl-10,11-dihydrodibenz[b,f]oxepin (4).—A mixture of 300 mg (1.13 mmol) of **3** and 400 mg of lithium aluminum hydride in 50 ml of dry tetrahydrofuran was refluxed with stirring under nitrogen for 16 hr.[8] Excess hydride was decomposed with water and the reaction mixture was worked up to afford 250 mg (98% yield) of 9-hydroxymethyl-9,10-dihydrodibenz[b,f]oxepin as an oil: λ_{max}^{EtOH} 270 mμ (ϵ 1580); nmr (CCl_4) δ 7.0 (multiplet, 8 H, ArH), 3.76–2.9 (multiplet, 5 H, $ArCH_2CHArCH_2OH$), 2.8 (broad singlet, D_2O-exchangeable, 1 H, OH). The same compound (nmr, ir, conversion to p-toluenesulfonate **4** below) was obtained by sequential hydrogenation (Pd/C, atmospheric pressure) and lithium aluminum hydride reduction of **3**. The crude alcohol was converted to its toluenesulfonate **4** by the procedure of Tipson[16] in 72% yield as needles: mp 76–77° (hexane–benzene); λ_{max}^{EtOH} 269 mμ (ϵ 1360); nmr ($CDCl_3$) δ 7.7 and 7.23 (AB quartet, J = 8 Hz, 4 H, sulfonate ring protons), 7.05 (multiplet, 8 H, oxepine ring protons), 4.37–2.73 (multiplet, 5 H, CH_2CHCH_2OTs), 2.41 (singlet, 3 H, CH_3Ar).

Anal. Calcd for $C_{22}H_{20}O_4S$: C, 69.46; H, 5.30; S, 8.41. Found: C, 69.27; H, 5.33; S, 8.43.

Acetolysis of 4. 11-Hydroxydibenzoxocin (5).—A solution of 8.05 g of **4** in 150 ml of dry acetic acid was refluxed under nitrogen for 15 hr. The reaction mixture was worked up and the crude product was allowed to react with a solution of 1 g of lithium aluminum hydride in 50 ml of ether at 25° for 2 hr. Excess hydride was destroyed with water and the reaction mixture was worked up to afford 4.0 g (85% yield) of **5** as needles: mp 104–105° (benzene–hexane); $\lambda_{max}^{CHCl_3}$ 2.79 and 2.90 μ (OH); nmr ($CDCl_3$) δ 7.14 (multiplet, 8 H, ArH), 4.05 [broad singlet, 1 H, $(ArCH_2)_2CHOH$], 2.83 (AB part of ABX, J_{AB} = 14 Hz, J_{AX} = 7 Hz, J_{BX} = 4.5 Hz, 4 H, $ArCH_2CHOH$), 1.57 (singlet, 1 H, OH); λ_{max}^{EtOH} 237 mμ (ϵ 6353), 272 (1732).

Anal. Calcd for $C_{15}H_{14}O_2$: C, 69.71; H, 6.24. Found: C, 79.75; H, 6.23.

Oxidation of **5** with Jones[17] reagent afforded a 63% yield of the ketone 10-oxo-9,10-dihydrodibenz[b,g]oxocin: mp 74–75° (hexane); $\lambda_{max}^{CHCl_3}$ 5.82 μ; nmr ($CDCl_3$) δ 7.2 (multiplet, 8 H, ArH), 3.65 (singlet, 4 H, $ArCH_2CO$). Reaction of **5** with methanesulfonyl chloride in pyridine at 5° afforded the corresponding methanesulfonate as unstable needles: mp 124–126.5° dec (ether); nmr ($CDCl_3$) δ 7.13 (multiplet, 8 H, ArH), 5.06 [pentet, J = 6 Hz, 1 H, $(ArCH_2)_2CHOMs$], 3.05 (doublet, J = 7 Hz, 4 H, $ArCH_2$), 3.0 (singlet, 3 H, CH_2SO_2).

Dibenz[b,g]oxocin.—A solution of the above methanesulfonate, 265 mg (0.90 mmol), and 0.5 g of potassium in 15 ml of *tert*-butyl alcohol was refluxed under nitrogen for 8 hr. The reaction mixture was worked up to afford 150 mg (93% yield) of an oil shown by glpc (20% SE-30 on Chromosorb P at 235°) to be an 80:20 mixture of two compounds. Two evaporative distillations afforded 106 mg (66% yield) of the more abundant compound (pure by glpc) as a colorless oil: $\lambda_{max}^{CHCl_3}$ 6.14, 14.03, 14.48 μ (cis CH=CH); λ_{max}^{EtOH} 261 mμ (ϵ 5350); nmr ($CDCl_3$) δ 7.15 (multiplet, 8 H, ArH), 6.55 (A part of ABX_2, J_{AB} = 11, J_{AX} = 1 Hz, 1 H, $ArCH{=}CHCH_2$), 5.99 (B part of ABX_2, J_{BA} = 11, J_{BX} = 7 Hz, 1 H, $ArCH{=}CHCH_2Ar$), 3.34 (X part of ABX_2, J_{BX} = 7 Hz, 2 H, $ArCH{=}CHCH_2Ar$); mass spectrum m/e 208 (parent), 181 (base, parent − C_2H_3, xanthylium cation).

Anal. Calcd for $C_{15}H_{12}O$: C, 86.50; H, 5.81. Found: C, 86.47; H, 5.81.

The minor component was isolated by glpc and identified as 10-methylene-10,11-dihydrodibenz[b,f]oxepin by comparison with a sample prepared by treatment of toluenesulfonate **4** with refluxing collidine.

Attempted dehydration of 5 with p-toluenesulfonic acid in benzene at 25° afforded a mixture of **4** and an unstable toluenesulfonate whose nmr spectrum [($CDCl_3$) δ 4.81 (pentet, J = 5.5 Hz, 1 H relative to the toluenesulfonate methyl singlet, $ArCH_2CHOTsCH_2Ar$)] was consistent with the presence of 11-toluenesulfonyloxydibenz[b,g]oxocin. The proportion of the two depended on the toluenesulfonic acid:**5** ratio and reaction time. On reflux with toluenesulfonic acid in benzene the unstable tosylate disappeared and **4**, mp 72–74°, mmp 72.5–74°, was isolated in 70% yield.

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1,3-Bis(*p*-anisyl)propene.—1,3-Bis(*p*-anisyl)-2-propanone was prepared from *p*-anisylacetic acid and lead carbonate.[18] Reduction of the above ketone with lithium aluminum hydride in tetrahydrofuran at 25° afforded 1,3-bis(*p*-anisyl)-2-propanol in 91% yield as needles, mp 56.5–57.5°.

Anal. Calcd for $C_{17}H_{20}O_3$: C, 74.96; H, 7.41. Found: C, 74.60; H, 7.24.

Reaction of the above alcohol with *p*-toluenesulfonyl chloride in pyridine[16] afforded 1,3-bis(*p*-anisyl)-2-propanol *p*-toluenesulfonate in 85% yield as needles, mp 99–99.5° (methanol).

Anal. Calcd for $C_{24}H_{26}O_5S$: C, 67.59; H, 6.15; S, 7.50. Found: C, 67.85; H, 6.19; S, 6.48.

The above toluenesulfonate was refluxed in *tert*-butyl alcohol containing excess potassium *tert*-butoxide to afford 1,3-bis(*p*-anisyl)propene in 84% yield as needles: mp 66.5–67° (methanol); nmr ($CDCl_3$) δ 6.4 (A part of ABX_2, J_{AB} = 15.5 Hz, 1 H, ArC**H**=CHCH$_2$Ar), 6.18 (B part of ABX_2, J_{AB} = 15.5 Hz, J_{BX} = 5.5 Hz, 1 H, ArCH=C**H**CH$_2$Ar), 3.4 (X part of ABX_2, J_{BX} = 5.5 Hz, 2 H, ArCH=CHC**H**$_2$Ar).

Anal. Calcd for $C_{17}H_{18}O_2$: C, 80.27; H, 7.14. Found: C, 80.29; H, 6.90.

Formation of Lithium Salts of Carbon Acids.—The following procedure is typical. To a stirred solution of 208 mg (1.0 mmol) of dibenz[*b*,*g*]oxocin in 5 ml of dry tetrahydrofuran at −80° (Dry Ice–acetone) under nitrogen was added 0.5 ml (1.05 mmol) of 2.1 *M* butyllithium in hexane. A red precipitate was formed. The mixture was stirred for 10 min, the cooling bath was removed, and the now homogeneous solution was allowed to stand at 25° for 4.5 hr. The red solution was added dropwise to a rapidly stirred solution of 4 ml of deuterium oxide (99.77% isotopic purity) in 2.5 ml of tetrahydrofuran. Work-up afforded 204 mg of an oil that was distilled at 55° (0.5 mm) to afford 177 mg of a clear oil. Low-voltage mass spectrometry afforded the isotopic content: 12% d_0, 82% d_1, 6% d_2. The area of the nmr peak at ε 3.34 corresponded to 1 H and the splitting pattern to the part structure ArCH=CHCHDAr.

Equilibration of Anions.—The following experiment is typical. To a solution of 127 mg (0.50 mmol) of 1,3-bis(*p*-anisyl)propene in 2.5 ml of dry tetrahydrofuran at −80° was added 0.235 ml (0.50 mmol) of 2.13 *M* butyllithium in hexane. The pink reaction mixture was stirred at −80° for 10 min and allowed to stand at 25° for 3.5 hr. A solution of 104 mg (0.50 mmol) of dibenz[*b*,*g*]oxocin in 1.5 ml of tetrahydrofuran was added, and the mixture was stirred for 25 min and then added to a mixture of 3 ml of deuterium oxide and 2.5 ml of tetrahydrofuran. Work-up afforded 227 mg of a sticky solid. Low-voltage mass spectrometry of this mixture afforded the following results: dianisylpropene (*m/e* 254–256), 97% d_0, 3% d_1; dibenzoxocin (*m/e* 208–212), 24% d_0, 74% d_1, 2% d_2. Recrystallization and distillation of this mixture allowed separation of the two olefins, low-voltage mass spectra of which indicated the same isotopic distribution as above. The results for the series of experiments are in Table II.

Registry No.—**1**, 24974-26-3; **3**, 34414-43-2; **4**, 34414-44-3; **5**, 34414-45-4; **5** methanesulfonate, 34414-50-1; **7**, 34414-46-5; **8**, 34414-47-6; **9**, 34414-48-7; 10-oxo-9,10-dihydrodibenz[*b*,*g*]oxocin, 34414-49-8; 1,3-bis(*p*-anisyl)-2-propanol, 34414-51-2; 1,3-bis(*p*-anisyl)-2-propanol *p*-toluenesulfonate, 24573-54-4; 1,3-bis(*p*-anisyl)propene, 34414-53-4.

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Aminoethylation of Some Pyrimidine Derivatives[1]

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Ethylenimine alkylated readily and exclusively the N^1 and N^3 positions of 2,4-dioxopyrimidine derivatives. Substitution of ethylenimine by 2-chloroethylamine produced lower yields. The reactivity of several other nucleic acid building blocks was investigated. The structures were assigned on the basis of spectral data and on the results of hydrolysis.

In aqueous ethylenimine, $HN(CH_2)_2$, 4-thiouridine is the most readily modified base[2] at pH 8 but the modification is not absolutely specific in that a slower alkylation of guanine residues in *E. coli* B tRNA is also detectable.[3]

This paper presents the evidence that under more drastic conditions $HN(CH_2)_2$ alkylates readily and exclusively the N^1 and N^3 positions of 2,4-dioxopyrimidine derivatives. The highest yields were obtained when pyrimidines were directly dissolved in $HN(CH_2)_2$; dilution with water or with organic solvents decreased yields considerably.

Compounds 3-(2-aminoethyl)uridine (**5**) and 3-(2-aminoethyl)thymidine (**9**) were isolated from the reaction mixture of uridine (**1**) or thymidine (**3**) in yields of over 70%; less than 10% of nucleosides were recovered unchanged; the rest comprised a mixture of higher alkylated derivatives.

The presence of alkyl at the N^3 position of **5** and **9** was indicated by the uv spectra; comparison was made with spectra of known 3-alkyl nucleosides. The presence of two strong bands in the carbonyl region in the ir spectra of aminoethylated derivatives excluded O-alkylation. The assigned structures were confirmed by acidic hydrolysis of **5** and **9** to 3-(2-aminoethyl)-uracil (**6**) and 3-(2-aminoethyl)thymine (**10**), respectively. No unsubstituted pyrimidines were obtained after hydrolysis. This would have been the case if the O-alkylation of sugar moiety or the acid-labile O-alkylation on the heterocyclic ring had occurred.[4]

Deoxyuridine, 2′,3′-*O*-isopropylideneuridine, and 5′-*O*-tritylthymidine reacted like the corresponding parent compounds, whereas 3-methyluridine and 3-methylthymidine were, as expected, quantitatively recovered from the reaction mixture.

A small amount of higher alkylated derivatives was present in all reaction products. It was proven by chemical and spectroscopic means that these compounds are oligomers of $HN(CH_2)_2$ attached to the N^3 position of nucleosides. Some polymerization of $HN(CH_2)_2$

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