tallized from ethanol-water as colorless plates, m.p. 50.8–52.4°, reported m.p. 57°,[14] 54–55°.[15] IIa was converted to the acetyl derivative, m.p. 131.4–131.9°, reported, m.p. 130–131°[15]; and to the phenylthiourea derivative, m.p. from ethanol, 157.8–158.1°, reported, m.p. 163–164°,[15] 157–158°.[16]

2-Aminophenylcyclohexane (IIb). An ethanolic solution of 0.475 g. of Ib was catalytically reduced with Adams catalyst and absorbed four mole equivalents of hydrogen to furnish 0.39 g. (95%) of the crude amine, IIb. The amine was characterized as the acetyl derivative, colorless needles, m.p. 101.2–102°, reported, m.p. 101°,[14] 102–103°[15]; and as the benzoyl derivative, felted needles from hexane, m.p. 153.8–154.4°, reported, m.p. 154°.[14]

3-Aminophenylcyclohexane (IIc). Reduction of 3.0 g. of the *meta-* adduct Ic proceeded rapidly and quantitatively over Adams catalyst to furnish 75% of the purified amine, IIc, b.p. 123–125° at 1.5 mm. IIc was converted to the benzenesulfonamide in the usual way. Recrystallization from ethanol afforded colorless crystals, m.p. 128.0–128.2°.

Anal. Calcd. for $C_{18}H_{21}NO_2S$: C, 68.5: H, 6.7; N, 4.4. Found: C, 68.6; H, 6.6; N, 4.3.

Stability of the adducts. The thermal stability of the adducts, Ia, Ib, and Ic was established by heating them alone at 125° or higher for 40 hr. in sealed tubes. In each case, the adduct could be recovered essentially unchanged.

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Ultraviolet Spectra of 2-Substituted Furans and 5-Substituted Methyl Furoates

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The recent synthesis of many furan compounds containing furan to heteroatom bonds[2] together with the few compounds for which spectra have been recorded has permitted a fairly complete compilation of ultraviolet spectral data for simple furan derivatives. The wave length maxima, log ϵ, and $\Delta\lambda$[3] values are recorded in Table I for the 2-substituted furans and in Table II for the methyl 5-substituted-2-furoates. In each table the corresponding benzene or methyl *p*-substituted benzoate $\Delta\lambda$ values are included and are designated as $\Delta\lambda_{Ph}$.

TABLE I

$x(C_4H_3O)$

x	λ_{max}(mμ)	log ϵ	$\Delta\lambda^a$	$\Delta\lambda_{Ph}{}^b$
H—	(208)	(3.9)	0	0
Br—	215.5	3.99	7.5	6.5^c
MeO—	221.0	3.82	13.0	13.5^c
C_6H_5O—	222.0	4.06	14.0	23.2
C_6H_5S—	241.5	4.21	33.5	28.3
$C_6H_5SO_2$—	249.5	4.13	41.5	32.8
MeOOC—	252.1	4.13	44.1	26.3

^{a} $\lambda_{max} - \lambda$ where $\lambda = 208$. ^{b} $\lambda_{max} - \lambda$ where $\lambda = 203.5$.

TABLE II

$x(C_4H_2O)COOMe$

x	λ_{max} (mμ)	log ϵ	$\Delta\lambda^a$	$\Delta\lambda_{Ph}{}^b$
H—	252.1	4.13	44.1	26.3
Cl—	260.5	4.23	52.5	37.5^c
$C_6H_5SO_2$—	261.7	4.33	53.7	39.0
Br—	264.1	4.23	56.1	41.5
MeOOC—	264.6^d	4.19	56.6	38.5
C_6H_5O—	275.0	4.25	67.0	54.5
MeO—	279.0	4.10	71.5	53.0
C_6H_5S—	291.8	4.33	83.8	89.7
O_2N—	295.4	4.08	87.4	55.0

^{a} $\lambda_{max} - \lambda$ where $\lambda = 208$. ^{b} $\lambda_{max} - \lambda$ where $\lambda = 203.5$. ^{c} Taken from Doub and Vandenbelt, ref. 3. ^{d} Taken from ref. 4.

To calculate $\Delta\lambda$ values it was necessary to assume a wave length maximum for furan of 208 which was obtained by extrapolation of the experimental curve. The extrapolation of the solvent spectrum appears to be valid since a vapor spectrum (max = 222) was obtained of almost identical shape.

The $\Delta\lambda$ value is a measure of the electronic interaction of the group with the aromatic system to which it is attached and may provide information of a sort not obtainable from a study of reaction rates, for example, since it does not involve polarization by a reagent. By first separating the substituents into those which are "*ortho-para*" directing and those which are "*meta*" directing and then arranging each group in order of increasing $\Delta\lambda$ the following series are obtained:

$$C_6H_5S > C_6H_5O \geq MeO > Br > Cl > H$$

$$NO_2 > MeOOC > C_6H_5SO_2 > H$$

These results agree qualitatively with the degree of directing power observed in various aromatic electrophilic substitution reactions.

In Table I the most significant differences in $\Delta\lambda$ and $\Delta\lambda_{Ph}$ are to be found in cases where the substituents are of the markedly electrophilic type (ϕ-SO_2— and MeO—CO—). These differences require the furan ring to be a stronger nucleophile than the benzene ring. The same conclusion is required by the fact that for the phenoxy group

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$\Delta\lambda_{Ph} > \Delta\lambda$. Table II demonstrates the conjugative interaction of the rings with the common carbomethoxy substituent, as modified by the substituents of Table I. In general, it is clear that the furan ring is more nucleophilic and less electrophilic than the benzene ring.

EXPERIMENTAL

Furan (Du Pont) on redistillation boiled at 31.5°.

2-Substituted furans were prepared by the methods previously reported.[2]

Methyl 5-chloro-2-furoate was prepared in 42% yield (m.p. 40–41°) by passing chlorine through rapidly stirred methyl 2-furoate at 150° for 3 hr.

Methyl 5-bromo-2-furoate and *methyl 5-methoxy-2-furoate* were prepared as previously reported.[2]

Methyl 5-nitro-2-furoate (m.p. 79–80°) was prepared by the usual method.[4]

Methyl 5-phenoxy-2-furoate was prepared by reaction of the acid[2] with diazomethane in 98% yield; b.p. 133–135°/0.3 mm.

Anal. Calcd. for $C_{12}H_{10}O_4$: C, 66.1; H, 4.62. Found: C, 66.1; H, 4.63.

Methyl 5-thiophenoxy-2-furoate was prepared by reaction of the acid[2] with diazomethane in 98% yield; b.p. 146–148°/0.5 mm. m.p. 39–40°.

Anal. Calcd. for $C_{12}H_{10}O_2S$: C, 61.5; H, 4.30. Found: C, 61.5; H, 4.36.

Phenyl 5-carbomethoxy-2-furyl sulfone was obtained in quantitative yield by reaction of methyl 5-thiophenoxy-2-furoate with excess 30% hydrogen peroxide in glacial acetic acid. Recrystallization from methanol-water gave white needles melting at 102–103°.

Anal. Calcd. for $C_{12}H_{10}O_5S$: C, 54.1; H, 3.79. Found: C, 54.1; H, 3.90.

Methyl benzoate b.p. 85°/15 mm. 220.8 mμ (4.08).

Methyl p-bromobenzoate m.p. 77–78°. 245.0 mμ (4.26).

Methyl p-anisate m.p. 47–48°. 256.5 mμ (4.43).

Methyl p-nitrobenzoate m.p. 95–96°. 259.0 mμ (4.12).

Dimethyl terephthalate m.p. 139–140°. 242.0 mμ (4.47).

Diphenyl sulfone m.p. 128–130°. 236.3 mμ (4.17).

Diphenyl sulfide b.p. 151–153°/15 mm. 231.8 (3.80), 250.4 (4.07), 275.0 (3.28).

Diphenyl ether b.p. 129.5°/12 mm. 226.7 mμ (4.01).

Methyl p-phenoxybenzoate. The *p*-phenoxy acid[5] (m.p. 158–159°) was prepared by carbonation of the Grignard reagent from *p*-bromophenyl phenyl ether (Eastman). Direct esterification of the acid followed by recrystallization from 95% ethanol gave the product m.p. 56–57°, 258.0 mμ (4.26).

Anal. Calcd. for $C_{14}H_{12}O_3$: C, 73.7; H, 5.30. Found: C, 73.5; H, 5.05.

Methyl p-thiophenoxybenzoate. p-Thiophenoxybenzoic acid[6] was prepared by adding a cold solution of diazotized *p*-aminobenzoic acid to a solution of thiophenol in dilute sodium hydroxide. A poor yield of the product was obtained which after several recrystallizations from 95% ethanol melted at 170–174°. Direct esterification followed by recrystallization from 95% ethanol gave the ester, m.p. 69–70°, 293.2 mμ (4.23).

Anal. Calcd. for $C_{14}H_{12}O_2S$: C, 69.0; H, 4.57. Found: C, 68.9; H, 4.74.

Phenyl p-carbomethoxyphenyl sulfone was prepared by the action of hydrogen peroxide on methyl *p*-thiophenoxybenzoate. The product was recrystallized from 95% ethanol, m.p. 145–146°, 242.5 mμ (4.29).

Anal. Calcd. for $C_{14}H_{12}O_4S$: C, 60.9; H, 4.38. Found: C, 60.8; H, 4.26.

Spectra were taken in 95% ethanol at a concentration of 10 mg./l. on a Warren Recording Spectrophotometer.

The vapor spectrum of furan was obtained by placing one drop of furan in the bottom of the dry cell and allowing about 10 min. for the vapor to reach equilibrium.

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Synthesis of Xanthurenic Acid-4-C^{14}

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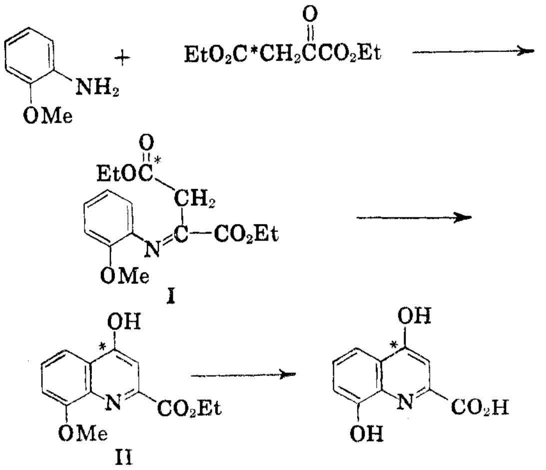
Xanthurenic acid has been known for some time as a tryptophan metabolite in mammals. In order to study the metabolism of this compound, it was desirable to incorporate a radioactive carbon atom into the molecule. A small scale synthesis (7mM) of xanthurenic acid-4-C^{14} was therefore undertaken utilizing the general procedure of Furst and Olsen[2]:



Numerous changes in the original procedure had to be made in order to provide a simple, continuous synthetic pathway starting from relatively inexpensive sodium acetate-1-C^{14}. These changes have more than doubled the over-all yield of xanthurenic

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