Reaction of **2** with morpholine: 2.85 g (42%); mp 64–65 °C; IR (CCl_4) 3060, 2960, 2850, 1580, 1460, 1440, 1250, 1130, 1115, 1010, 905, 860, 690 cm^{-1}; NMR ($CDCl_3$) δ 1.3 (d, 3 H, J = 7 Hz, CH_3), 2.45 (m, 4 H), 3.4 (dq, 1 H, $J_{2,3}$ = 2.5 Hz, C_3-H), 3.6 (m, 4 H), 4.65 (d, 1 H, C_2-H), 7.1 (m, 4 H, aromatic H); mass spectrum, *m/e* (relative intensity) 235 (M^+, 36), 202 (4), 149 (100), 148 (92), 147 (60), 135 (28), 134 (64), 114 (16), 115 (24), 105 (16), 103 (16), 100 (34), 91 (25), 77 (28).

Anal. Calcd for $C_{13}H_{17}NOS$: C, 66.34; H, 7.28; N, 5.95; O, 6.80; S, 13.62. Found: C, 66.35; H, 7.16; N, 6.16; O, 6.99; S, 13.74.

Reaction of Piperidine and Benzo[*b*]thiophene by Means of *n*-Butyllithium. *n*-Butyllithium (0.15 M, 20% solution in hexane) was added to 60 mL of piperidine under nitrogen. The temperature of the mixture was maintained at 40 °C, and a solution of 4 g (0.03 M) of benzo[*b*]thiophene in 10 mL of amine was added. Reaction and isolation were performed as previously described. 2-Piperidino-2,3-dihydrobenzo[*b*]thiophene (**4**) was purified by chromatography, 3 g (46%).

Reaction of Morpholine and Benzo[*b*]thiophene by Means of Sodium Hydride. A mixture of 60 mL of morpholine and 3.6 g (0.15 M) of NaH was refluxed under nitrogen until the evolution of hydrogen ceased and was cooled to 40 °C. The addition of benzo[*b*]-thiophene and the reaction procedure were as previously described. 2-Morpholino-2,3-dihydrobenzo[*b*]thiophene (**5**) was recrystallized from heptane–toluene, 2.7 g (41%).

2-Morpholinobenzo[*b*]thiophene (12). A 1.1-g (0.005 mol) amount of **5** and 0.16 g (0.005 mol) of sulfur were heated at 250 °C until the evolution of H_2S ceased (5 min). The reaction mixture was taken into benzene and decolorized with Norit. Evaporation of benzene and recrystallization from toluene–heptane gave a colorless solid: 0.65 g (60%); mp 179–180 °C; IR (CCl_4) 3060, 2960, 2900, 2855, 2815, 1530, 1440, 1120, 1030, 930, 900, 870, 650 cm^{-1}; NMR (CCl_4) δ 3.2 (m, 4 H), 3.9 (m, 4 H), 6.2 (s, 1 H, C_3-H), 7.3 (m, 4 H, aromatic H); mass spectrum, *m/e* (relative intensity) 219 (M^+, 100), 204 (6), 162 (23), 161 (93), 160 (38), 147 (14), 135 (8), 134 (26), 133 (9), 89 (20), 80 (12).

Anal. Calcd for $C_{12}H_{13}NOS$: C, 65.72; H, 5.97; N, 6.39; O, 7.30; S, 14.62. Found: C, 65.71; H, 5.95; N, 6.35; O, 7.55; S, 14.58.

2-Morpholino-3-methylbenzo[*b*]thiophene (13). From aromatization of 100 mg of **9** with 15 mg of sulfur: 65 mg (65%); mp 79–80 °C; IR (CCl_4) 3060, 2960, 2900, 2855, 2820, 1575, 1435, 1190, 1120, 1045, 1015, 980, 880 cm^{-1}; NMR (CCl_4) δ 2.3 (s, 3 H, CH_3), 3.0 (m, 4 H), 3.9 (m, 4 H), 7.4 (m, 4 H, aromatic H); mass spectrum, *m/e* (relative intensity) 234 (18), 233 (M^+, 100), 232 (27), 218 (5), 188 (5), 176 (11), 175 (50), 174 (58), 173 (16), 161 (12), 160 (30), 159 (10), 147 (30), 134 (11).

Anal. Calcd for $C_{13}H_{15}NOS$: mol wt 233.0874. Found (high-resolution mass spectrum): mol wt 233.0876.

Registry No.—**1**, 95-15-8; **2**, 1455-18-1; *cis*-**7**, 66902-28-1; *trans*-**7**, 66902-27-0; *cis*-**8**, 66902-26-9; *trans*-**8**, 66902-22-5; *cis*-**9**, 66902-21-4; *trans*-**9**, 66902-20-3; **12**, 18774-55-5; **13**, 66902-25-8.

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(6) When the reaction is performed with *n*-butyllithium and a primary amine, no reduction products are formed but the yield of adduct remains disappointingly low.
(7) Cis and trans isomers of adducts **7**, **8**, and **9** cannot be separated, even at an analytical scale. The assumption that the major product is the trans isomer is based on literature data assuming that the chemical shift of H_2 should be higher in the cis isomer than in the trans isomer and that $J_{2,3}$ is higher when H_2 and H_3 are cis than when they are trans.[8]
(8) (a) L. M. Jackman and S. Sternhell, "Application of NMR Spectroscopy in Organic Chemistry", 2nd ed, Pergamon Press, Oxford, 1969, p 233; (b) J. J. Christol, T. W. Russel, J. R. Mohrig, and D. C. Plorde, *J. Org. Chem.*, **31**, 581 (1966).
(9) The yield is less than 1% based on consumed benzo[*b*]thiophene.
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Facile Synthesis of 2-Substituted Imidazoles

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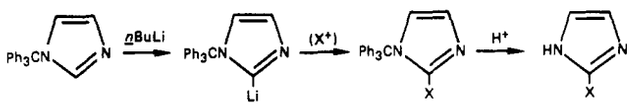
Continuing studies in the biochemistry and pharmacology of ring-fluorinated imidazoles have revealed striking differences in behavior between 2- and 4-fluoro isomers in each series.[1] For example, 2-fluorohistidine displays a wide range of biological activities[2] while 4-fluorohistidine shows little or no activity in the same systems. As part of our efforts to elucidate the causes of these differences, we wished to extend our testing to isomer pairs of the other haloimidazoles—particularly the halohistidines. The 4 (or 5)-halo derivatives can be obtained by direct electrophilic substitution,[3] but no methods are available for preparation of the 2-halo isomers. While 2-fluoro-[4] and 2-chloroimidazoles[5] have been prepared by photochemical decomposition of 2-diazoniumimidazoles, the method fails for bromine or iodine, and there exists no obvious procedure for the introduction of the latter halogens.[6] We have now developed a general synthesis, not only for 2-haloimidazoles, but for a variety of other 2-substituted imidazoles.

In 1-alkyl or 1-arylimidazoles (methyl, benzyl, phenyl), H-2 is the most acidic hydrogen and a carbanion is readily generated at C-2 by reaction with *n*-butyllithium; this carbanion has been used for addition to carbonyl groups[7] as well as to other electrophilic reagents.[8] Unfortunately, the 1-substituent is not easily removed from the product in these cases. *N*-Benzylimidazole can be debenzylated with sodium in liquid ammonia,[9] but bromine or iodine at C-2 undoubtedly would be removed at the same time. We have found that 1-tritylimidazole[10] also forms a carbanion (**1**) with *n*-butyllithium,



1 **2** **3**

that the carbanion reacts readily with various electrophiles to form 1-trityl-2-X-imidazoles (**2**), and that the trityl group is easily removed by mild acid hydrolysis to give 2-X-imidazoles (**3**).

Tables I and II describe compounds prepared by this general method. Yields of **2** are consistently high,[11] except where X is halogen. Attempts to improve yields in the halogenation steps by variation in conditions or source of halogen were unsuccessful. Unreacted tritylimidazole accounted for most of the material loss in these cases. The presence of a single imidazole proton resonance in the NMR spectrum of each **3** supports assignment of the substituent to the 2-position. For **3c**, **3d**, and **3g**, structural assignments were confirmed by comparison with authentic samples. In no case was there formed a detectable quantity of the isomeric 4(5)-X-imidazole, based on NMR and chromatographic evidence.

The preparation of 2-aminoimidazole through the phenyltriazene (**2g**), based on a procedure for the preparation of 1-alkyl-2-aminoimidazoles,[12] has special significance in that it allows a nonreductive introduction of the 2-amino function into a preformed imidazole ring. (In our hands, the catalytic reduction of 2-arylazo-4-X-imidazoles often results in simultaneous loss of the 4-X substituent.[5]) Consistent with the results of others,[12] our attempts to aminate **1** with methoxyamine,[13] *O*-mesitylenesulfonylhydroxylamine,[14] or *O*-2,4-dinitrophenylhydroxylamine[15] were unsuccessful.

Table I. Products of the Reaction of 1-Trityl-2-lithioimidazole with Electrophilic Agents

registry no.	cpd[a]	electrophilic agent	registry no.	X	yield, %	mp, °C	NMR, ppm (J, Hz)[b]
67478-46-0	**2a**	*N*-iodosuccinimide[c]	516-121	I	40	170–172	6.81 (d) (*J* = 1.5), 6.98 (d) (*J* = 1.5), 7.05–7.38 (m)
	2a	I_2[c]	7553-56-2	I	41		
67478-47-1	**2b**	*N*-bromosuccinimide[c]	128-08-5	Br	35	208–209	6.82 (d) (*J* = 1.5), 6.99 (d) (*J* = 1.5), 7.08–7.40 (m)
67478-48-2	**2c**	*N*-chlorosuccinimide[c]	128-09-6	Cl	<5	208–210	6.87 (d) (*J* = 1.5), 7.01 (d) (*J* = 1.5), 7.15–7.65 (m)
	2c	*tert*-butyl hypochlorite[d]	507-40-4	Cl	39		
23593-68-2	**2d**	CH_3I[e]	74-88-4	CH_3	95	217–218.5	1.64 (s), 6.69 (d) (*J* = 1.4), 6.89 (d) (*J* = 1.4), 7.05–7.40 (m)
67478-49-3	**2e**	$ClCO_2C_2H_5$[d]	541-41-3	$CO_2C_2H_5$	90	204.5–206.5	0.94 (t) (*J* = 7), 3.84 (q) (*J* = 7), 7.09 (d) (*J* = 1.5), 7.1–7.5 (m)
67478-50-6	**2f**	$HCON(CH_3)_2$[e]	68-12-2	CHO	98	189–190	7.07 (d) (*J* = 1.5), 7.20–7.50 (m), 9.40 (s)
67478-51-7	**2g**	PhN_3[d]	622-37-7	N=NNHPh	95	124–135 (d)	6.82 (d) (*J* = 1.5), 7.08 (d) (*J* = 1.5), 7.13–7.48 (m)

[a] Identity and purity of all compounds were confirmed by chemical ionization mass spectrometry and by combustion analysis. (Satisfactory analytical data (C, H, N) were submitted.) Purifications were effected by recrystallization from ethyl acetate/cyclohexane mixtures. [b] Spectra measured in $CDCl_3$ on a Varian A60 spectrometer. [c] Added in 5 mL of tetrahydrofuran. [d] Added neat. [e] Added neat, threefold excess.

Table II. Preparation of 2-X-imidazoles by Acid Catalyzed Cleavage of 1-Trityl-2-X-imidazoles

registry no.	cpd[a]	X	cleavage[b]	yield, %	mp, °C	purification	NMR, ppm in Me_2SO-d_6 (*J*, Hz)[c]
3034-62-6	**3a**	I	A	99	190–192	sublimation	7.08 (s)
16681-56-4	**3b**	Br	A	>99	197–198[d]	sublimation	7.08 (s)
16265-04-6	**3c**	Cl	A	98	166–167[e]	sublimation	7.07 (s)
693-98-1	**3d**	CH_3	B	97	130–133[f]	sublimation	2.29 (s), 6.89 (s)
33543-78-1	**3e**	$CO_2C_2H_5$	A	>99	178–179	ethanol	1.30 (t) (*J* = 7), 3.35 (q) (*J* = 7), 7.32 (s)
10111-08-7	**3f**	CHO	C	99	190–196[g]	ethyl acetate	7.41 (s), 9.63 (s)
52737-40-3	**3g**	$NH_2 \cdot HCl$	D	73	144–146[h]	ethanol	6.88 (s)

[a] All new compounds had satisfactory elemental analyses. Identity of all compounds was checked by mass spectrometry. [b] (A) 1 mmol refluxed 30 min in 5 mL of 5% acetic acid in methanol; (B) 1 mmol refluxed 4 h in 1 mL of 1 N HCl and 0.5 mL of ethanol; (C) 1 mmol refluxed for 1 h in 5 mL of 5% acetic acid in methanol; (D) 1 mmol refluxed for 3 h in 10 mL of methanol and 0.2 mL of concentrated HCl. [c] NMR spectra were measured on a JEOL Model FX 100 spectrometer. [d] Lit. mp 207 °C: H. King and W. O. Murch, *J. Chem. Soc.*, **123**, 621 (1923). [e] Lit.[6] mp 165–166 °C. [f] Lit. mp 137 °C: O. Wallach, *Justus Liebigs Ann. Chem.*, **214**, 257 (1882). [g] Lit. mp 204 °C: H. Shubert and H.-D. Rudolf, *Angew. Chem. Int. Edit. Engl.*, **5**, 674 (1966). [h] Lit. mp 152 °C: R. G. Fargher and F. L. Pyman, *J. Chem. Soc.*, **115**, 217 (1919).

The procedure described in this report is now being applied to the preparation of 2,4-disubstituted imidazoles and to 2-substituted histidines and histamines. The variety of X groups introduced is also being expanded.

Experimental Section

Preparation of 1-Trityl-2-X-imidazoles (2). The preparation of 1-trityl-2-iodoimidazole (**2a**) illustrates the general procedure. 1-Trityl-2-lithioimidazole (I) was prepared by the addition of 1.5 mL of 1.6 M *n*-butyllithium in hexane (Aldrich) to a solution of 620 mg (2 mmol) of 1-tritylimidazole in 25 mL of tetrahydrofuran (freshly distilled from lithium aluminum hydride) at 0 °C under a nitrogen atmosphere. The solution, which gradually turned red, was stirred at room temperature for 1.5 h, was then cooled to 0 °C, and 508 mg (2 mmol) of iodine in 5 mL of tetrahydrofuran was added dropwise over 5 min. After an additional 10 min at 0 °C, the reaction mixture was poured into 25 mL of water. After concentration of the solution by rotary evaporation, ether extraction, and silica gel chromatography (1:1 ether–petroleum ether), **2a** was obtained in 40% yield.

Products described in Table I were prepared from 2 mmol of tritylimidazole. No problems are encountered when the reaction is carried out on a larger scale.

Preparation of 2-X-Imidazoles (3). 2-Iodoimidazole[16] (**3a**) was prepared from **2a** by refluxing a solution of 350 mg (0.80 mmol) of **2a** in 5 mL of 5% acetic acid in methanol for 30 min. After evaporation of the solvent, water was added to the residue. After chilling, the solution was filtered and the filtrate evaporated to give 155 mg of crystalline **3a** (99%), the homogeneity of which was demonstrated by thin-layer chromatography and chemical ionization mass spectrometry.

Variations in hydrolysis condition are given in Table II. The course of the reaction in each case was monitored by silica gel thin-layer chromatography.

Registry No.—**1**, 67478-52-8; 1-tritylimidazole, 15469-97-3.

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(16) The material originally identified as 2-iodoimidazole [H. Pauly and E. Arauner, *J. Prakt. Chem.*, **118**, 33 (1928)] was shown later to be 4-iodoimidazole (ref 3). Authentic 2-iodoimidazole has been obtained in 5% yield by reaction of iodine with 1-benzenesulfonyl-2-lithioimidazole [R. J. Sundberg, *J. Heterocycl. Chem.*, **14**, 517 (1977)]; this N-protecting group was found unsuitable for general use in the preparation of 2-X-imidazoles, a conclusion we had also reached from early studies.

Reactivity of Oxoindole-$\Delta^{3,\alpha}$-acrylates toward Diazoalkanes: An Unusual Ring Expansion

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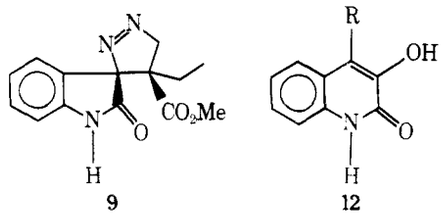
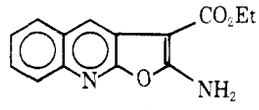
As part of our work on the regiospecific behavior of enedicarbonyl compounds[1a] we decided to examine the reaction of diazoalkanes[1b] with oxoindol-$\Delta^{3,\alpha}$-acrylates (**1**). With diazomethane acrylate **1** (X = H)[2] provided pyrazoline **3a** (X = H). The observed NMR coupling of the pyrazoline methylene and methine protons was sufficient evidence to assign structure **3a** and not **2a** to the product. Steric (tertiary vs. secondary carbon) as well as electronic (polarization of the C–C double bond) effects are such that the [1,3]-dipolar addition of diazomethane involves initial C–C bond formation α to the ester, with the reaction proceeding via a nonsynchronous intermediate such as **4** and not **5**.[3] When heated above its melting point or in refluxing xylene, pyrazoline **3a** (X = H) underwent N_2 loss giving spirocyclopropane **7a** (X = H). Reaction of acrylate **1**, X = H, with phenyldiazomethane provided the corresponding spirocyclopropane **7b** (X = H) as a single diastereomer.

Exposure of acrylate **1** (X = CN)[6] to diazomethane did not afford either a pyrazoline (**2** or **3**) or a spirocyclopropane (**7**). Instead, only quinolone **11a** (X = CN) could be isolated (92%). Rearrangement of the intermediate resulting from loss of N_2, **8**, and isomerization of the resulting exocyclic double bond out of conjugation with the cyanoester and into aromatization would account for the observed product.[7] The addition of a cyano group[8] has thus reversed the polarization of the C–C double bond while equalizing the steric effects of substitution such that the diazomethane addition now involves initial C–C bond formation β to the ester moiety (**5**). The rearrangement of isatins to quinolones has precedent in the literature.[9] Eistert and coworkers had reported that the reaction of isatin and *N*-methylisatin with diazoalkanes ($RCHN_2$) led in good yield to 4-R-substituted 3-hydroxycarbostyrils (**12**).

An equilibrium mixture of **11a** (X = CN) and tricyclic **13** was established after only 12 h in Me_2SO at ambient temperature. Dissolution of either **11a** or **13** in Me_2SO resulted in the same mixture. The ^{13}C chemical shifts for compounds **11a** (X = CN) and **13** were consistent with structural assignments made on the basis of other spectral data.[10] The ^{13}C NMR spectrum of **11a** displayed a single aliphatic, methine carbon which disappeared on isomerization in Me_2SO to **13**. In addition the A ring aromatic carbons β to N shifted downfield on isomerization, an indication of the imino ether tautomeric form. The rather high-field (80.2 ppm) absorption of the furan ring C α to the ester in **13** is consistent with a high-electron density resulting from mesomeric O and NH_2 participation. Furthermore, hydrolysis of **11a** (X = CN) followed by decarboxylation provided the known quinolone-3-acetic acid (**11a**, X = H), identical in all respects[11a] with the compound prepared by literature techniques.[11b]



9 **12**



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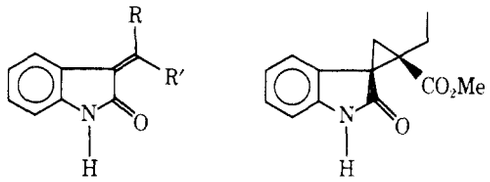

14a, R = Et; R′ = CO_2Me
b, R = CO_2Me; R′ = Et

15

In a similar manner, reaction of **1** (X = CN) with $PhCHN_2$[12] provided the corresponding rearrangement product **11b** (X = CN) mp >325 °C in a yield of 42%. Reaction of **14a**[9c] with diazomethane, on the other hand, provided pyrazoline **9** resulting from C–C bond formation α to the ester. When heated in refluxing xylene this pyrazoline underwent smooth conversion to spirocyclopropane **15**. The double bond carbons of compound **14a** are more sterically equivalent (tertiary vs. tertiary) than in the case where X = H and yet initial C–C bond formation has still occurred α to the ester. This result lends support to the argument that only when C–C double bond polarization of the oxoindol-$\Delta^{3,\alpha}$-acrylates has been reversed (as in the case where X = CN)[13] such that dipolar species react initially at the carbon β to the ester will rearrangement to the quinolone ring system occur. Furthermore, the sequence provides an efficient procedure for the synthesis of quinolone-3-acetates. Additional work relating to this rearrangement and the regioselectivity of such dipolar addition reactions is now in process.

Experimental Section

The IR spectra were recorded on a Perkin-Elmer Model 257 or 457 grating spectrophotometer and NMR spectra were recorded using either a Varian T-60 or EM-360 spectrometer. ^{13}C NMR spectra were recorded using a Varian XLFT-100 spectrometer. Chemical shifts (δ) are recorded relative to Me_4Si; coupling constants (J) are given in hertz. Mass spectra were recorded using either an LKB 9000 or an AEI MS-30-D5-50 spectrometer. Melting points were obtained on a Thomas-Hoover capillary melting point apparatus and are uncorrected. In all workup procedures, the drying process involved swirling over $MgSO_4$ and filtering prior to evaporation.

Ethyl 4′,5′-Dihydro-2-oxospiro(3*H*-indole-3,3′-pyrazole)-4′-carboxylate (3a, X = H). To a solution of acrylate **1**[2] (X = H) (21.9 g, 0.1 mol) in anhydrous Et_2O (700 mL) at 0 °C was added CH_2N_2 (ca. 5.1 g, 0.12 mol) (from 36 g of Diazald).[20] After an additional 18 h at ambient temperature, the excess CH_2N_2 was quenched with HOAc and the solution was washed with aqueous $NaHCO_3$, dried, and

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