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Registry No. **1a**, 73971-64-9; **1b**, 14271-37-5; **1c**, 73971-65-0; **3a**, 73971-66-1; **3c**, 73971-67-2; **4**, 73971-68-3; **5a**, 73985-91-8; **5b**, 73985-92-9; **6**, 26836-43-1; **7a**, 73971-69-4; **7b**, 73971-70-7; **8a**, 33143-54-3; **8b**, 73971-71-8; **8c**, 73971-72-9; **9**, 73971-73-0; **11a**, 73971-74-1; **11b**, 73971-75-2; **13**, 38458-58-1; **14a**, 24268-44-8; **14b**, 24268-45-9; **14c**, 35682-60-1.

Supplementary Material Available: Final atomic parameters (Table V), final anisotropic thermal parameters (Table VI), bond lengths (Table VII), and bond angles (Table VIII), for **14a** (4 pages). Ordering information is given on any current masthead page.

Phase-Transfer Alkylation of Heterocycles in the Presence of 18-Crown-6 and Potassium *tert*-Butoxide

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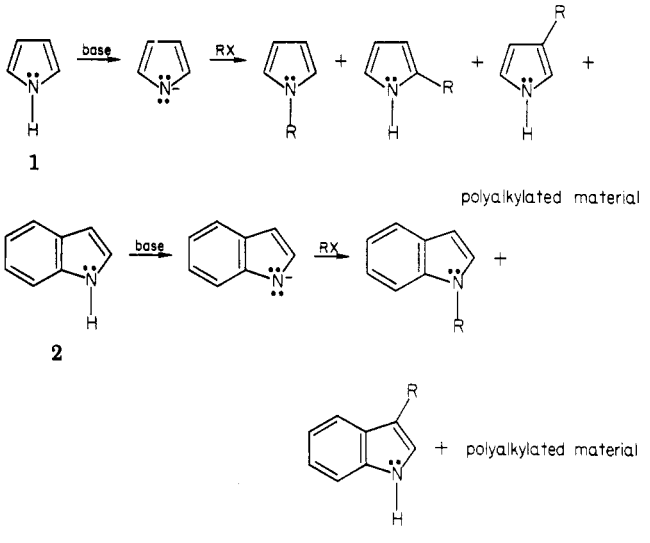
It has been found that the N-alkylation of heterocyclic compounds bearing an acidic hydrogen atom attached to nitrogen can be accomplished in diethyl ether via a phase-transfer process in which 18-crown-6 is employed as the catalyst and potassium *tert*-butoxide is employed as the base. In this manner, pyrrole (**1**), indole (**2**), pyrazole (**3**), imidazole (**4**), benzimidazole (**5**), benzotriazole (**6**), carbazole (**7**), and methyl indole-3-acetate (**8**) can be successfully alkylated. The procedure is convenient and mild and generally gives rise to exclusive N-alkylation.

The N-alkylation of heterocyclic compounds bearing an acidic hydrogen atom attached to nitrogen, like pyrrole (**1**) or indole (**2**), is generally accomplished by the treatment of these compounds with an appropriate base followed by the treatment of the resulting salt with an alkylating agent (Scheme I).[1] However, since the pyrrolyl and indolyl anions exhibit ambident behavior as nucleophiles, alkylation can occur at carbon as well as at nitrogen.[1,2] Thus, when these species are alkylated, substantial quantities of 2- and 3-alkylpyrrole or 3-alkylindole may contaminate the N-alkylated product along with some polyalkylated material. In many instances, the major products are those derived from C-alkylation.

The amount of N-alkylation relative to C-alkylation depends upon a number of factors, including the base employed for the deprotonation of the heterocycle, the solvent, and the alkylating agent. Thus, for salts derived from pyrrole or indole, the base (and hence, the cation associated with the pyrrolyl or indolyl anion) can influence the ratio of N to C alkylation.[2e-h] Although nitrogen alkylation generally predominates when the cation is a sodium or potassium ion, carbon alkylation usually predominates with harder[3] cations like lithium or magnesium

Scheme I



which are tightly bound to nitrogen.[4] The solvent can dramatically influence the ratio of N to C alkylation,[2e-h,5] and dipolar aprotic solvents can give rise to predominant N-alkylation of salts derived from pyrrole or indole even when magnesium is the counterion.[2e,f,5c] Finally, the alkylating agent can influence the ratio of N to C alkylation. For example, when compared to other alkylating agents, allylic or benzylic halides generally afford a greater proportion of C-alkylated material.[2e,5a,c,6]

During the past decade, several new procedures have been developed in which the N-alkylation of pyrrole or

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0022-3263/80/1945-3172$01.00/0

indole can be accomplished with little or no interference from C-alkylation.[5-7] Included in these procedures are those which rely on the use of dipolar aprotic solvents,[5a,b,7b,c] one in which the thallium salt of pyrrole is employed,[7a] and several procedures which rely on phase-transfer catalysis[8] by quaternary ammonium salts.[5c,6,7d,e]

The phase-transfer procedures appear to be the most useful in terms of mildness of conditions, yield, and convenience. Alkylation is effected by simply stirring a solution containing alkylating agent, heterocycle, and catalyst in the presence of concentrated aqueous sodium hydroxide. Exclusive N-alkylation is usually observed since the counterion is a quaternary ammonium ion and is therefore only loosely associated with the pyrrolyl or indolyl anion. However, some C-alkylation is observed when allylic or benzylic halides are employed as alkylating agents.[5c,6,7d]

In spite of the numerous advantages of the phase-transfer procedure described above, several disadvantages decrease the general applicability of this procedure. For example, when alkyl iodides are employed as alkylating agents, respectable yields of product can usually be obtained only when a stoichiometric amount of catalyst is employed.[5c,7e,9] In addition, there are a number of solvents in which the commonly employed quaternary ammonium salts are insoluble.[8] Consequently, the phase-transfer procedure employing quaternary ammonium salts as catalysts would be expected to fail when these solvents are used. For example, diethyl ether cannot be effectively utilized as a solvent for the quaternary ammonium salt catalyzed, phase-transfer alkylation of pyrrole.[10] Finally, functional groups attached to the pyrrole or indole nucleus which are labile to hydrolysis in the presence of hydroxide would not be expected to survive the phase-transfer alkylation procedure catalyzed by quaternary ammonium salts. In fact, hydrolysis of the carbomethoxy group of either methyl 2-methyl-5-methoxyindole-3-acetate[11] or methyl indole-3-acetate[10] accompanies N-alkylation under phase-transfer conditions with quaternary ammonium salts.

We sought to develop a general method for the N-alkylation of heterocycles possessing an acidic hydrogen. Such a method should retain the convenience of the phase-transfer procedure but should be free from the complications cited above. Therefore, we decided to explore the use of crown ethers as solid–liquid, phase-transfer catalysts[12] for the N-alkylation of heterocycles utilizing potassium *tert*-butoxide[13] as the base. We envisioned that N-alkylation would predominate with an appropriate alkylating agent since the crown-complexed potassium ion should only be loosely associated with the anion derived from the heterocycle. Furthermore, we envisioned that a variety of solvents and alkylating agents could be employed and that sensitive functionality would not undergo hydrolysis. We now describe the results of our studies.[14]

Table I. Phase-Transfer Methylation of Pyrrole and Indole[a]

heterocycle	solvent	product	% yield[b]
pyrrole (1)	pentane	*N*-methylpyrrole	88
	diethyl ether		86
	benzene		99[c,d]
indole (2)	pentane	*N*-methylindole	87
	diethyl ether		94
	benzene		82

[a] The reaction was carried out at room temperature for 1 h by utilizing potassium *tert*-butoxide (1.1 mol/mol of heterocycle), 18-crown-6 (0.1 mol/mol of heterocycle), and methyl iodide (1.1 mol/mol of heterocycle). [b] Products were purified by Kugelrohr distillation; unless otherwise noted, yields refer to isolated, analytically pure (>99% by GC) material. [c] Estimated by GC. [d] Difficulties were encountered in the separation of *N*-methylpyrrole from benzene by simple distillation techniques.

Results and Discussion

Our initial study revealed that exclusive N-methylation of pyrrole or indole could indeed be accomplished by employing potassium *tert*-butoxide as the base, 18-crown-6 as the catalyst, and methyl iodide as the alkylating agent. N-Methylation can be effected by stirring a suspension of potassium *tert*-butoxide, 18-crown-6, and the heterocycle in an appropriate solvent for several minutes. Subsequent introduction of methyl iodide with continued stirring for 1 h results in the production of either *N*-methylpyrrole or *N*-methylindole in excellent yield (see Table I).

In order to explore the generality of the procedure developed for the N-methylation of pyrrole and indole, we conducted experiments in which other alkylating agents and other heterocycles were employed. The results presented in Table I suggest that a variety of solvents can be utilized in this procedure. However, diethyl ether was chosen as a solvent for subsequent studies since its low boiling point facilitates workup of the reaction mixture and since it is readily available in anhydrous form. The latter property is desirable for the alkylation of heterocycles bearing functionality labile to hydrolysis in the presence of hydroxide ion.

The results presented in Table II indicate that a variety of alkylating agents can be substituted for methyl iodide in the crown ether catalyzed, phase-transfer procedure described above. However, longer reaction times are required with the less reactive alkylating agents. With the exception of allyl bromide, all of the alkylating agents employed give rise to exclusive N-alkylation of both pyrrole and indole. Even when allyl bromide is employed as the alkylating agent, substantial quantities of either *N*-allylpyrrole or *N*-allylindole can be produced. These results should be contrasted with the results obtained when allyl

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(9) Similar results have been observed for other phase-transfer processes involving quaternary ammonium salts and are due to the fact that the quaternary ammonium iodides produced in these reactions are ineffective as phase-transfer catalysts. See, for example: Dockx, J. *Synthesis* **1973**, 441.

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(14) During the preparation of this manuscript we became aware of a procedure which employs 18-crown-6 as a phase-transfer catalyst for the alkylation of pyrrole and indole in the presence of solid potassium hydroxide: Santaniello, E.; Farachi, C.; Ponti, F. *Synthesis* **1979**, 617. It is not clear whether this procedure possesses any distinct advantages over the quaternary ammonium salt, phase-transfer procedure although alkyl iodides can be used as alkylating agents. Nonetheless, this procedure possesses the disadvantage of requiring harsher conditions (i.e., refluxing benzene) than either the quaternary ammonium salt, phase-transfer procedure or the procedure described in this work.

Table II. Phase-Transfer Alkylation of Pyrrole and Indole[a]

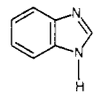
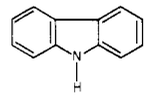
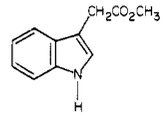
heterocycle	alkylating agent	T, h	product	% yield[b] (% unreacted heterocycle)
pyrrole (1)	ethyl bromide	18	N-ethylpyrrole	76
	ethyl iodide	1	N-ethylpyrrole	83
	n-propyl bromide	18	N-propylpyrrole	78
	n-propyl iodide	18	N-propylpyrrole	91
	isopropyl iodide	18	N-isopropylpyrrole	34[c] (66)[c]
	n-butyl iodide	18	N-butylpyrrole	92
	tert-butyl bromide	18	pyrrole	(100)[c]
	benzyl bromide	1	N-benzylpyrrole	83
	allyl bromide	1	N-allylpyrrole	70[d]
indole (2)	ethyl bromide	18	N-ethylindole	88
	ethyl iodide	1	N-ethylindole	80
	n-propyl bromide	18	N-propylindole	93
	n-propyl iodide	18	N-propylindole	93
	isopropyl iodide	18	N-isopropylindole	38[c] (62)[c]
	n-butyl iodide	18	N-butylindole	83
	tert-butyl bromide	18	indole	(100)[c]
	benzyl bromide	1	N-benzylindole	90
	allyl bromide	1	N-allylindole	78[e]

[a] With the exception of reaction times, the reaction conditions were the same as those listed in Table I; diethyl ether was used as the solvent. [b] Products were purified by either Kugelrohr distillation or recrystallization; unless otherwise noted, yields refer to isolated, analytically pure (>99% by GC) material. [c] Estimated by GC. [d] Purity was 82% by GC; contaminated with unreacted pyrrole (7%), 2-allylpyrrole (6%), and three unidentified components (5% total). [e] Purity was 97% by GC; contaminated with 3-allylindole (3%).

halides are used in the quaternary ammonium salt, phase-transfer alkylation of pyrrole or indole.[5c,6] In these procedures, C-alkylated material predominates over N-alkylated material in a 4:1 ratio when pyrrole is utilized as the substrate.[5c] Furthermore, in contrast to the results obtained with the quaternary ammonium salt, phase-transfer procedure,[6,7d] the results presented in Table II demonstrate that exclusive N-benzylation of both pyrrole and indole occurs when benzyl bromide is employed as the alkylating agent. Finally, as expected,[12] incomplete conversion of the heterocycle to the product is observed when isopropyl iodide is used as the alkylating agent; the reaction fails altogether with *tert*-butyl bromide.

As is demonstrated in Table III, a number of heterocyclic compounds bearing an acidic hydrogen atom attached to nitrogen can be alkylated by using our procedure. Thus, the N-methylations of pyrazole (**3**), imidazole (**4**), benzimidazole (**5**), benzotriazole (**6**), carbazole (**7**), and methyl indole-3-acetate (**8**) proceed smoothly with yields ranging from good to excellent. It is noteworthy that methyl indole-3-acetate undergoes N-methylation to form methyl *N*-methylindole-3-acetate. Thus, hydrolysis of the carbomethoxy group by hydroxide does not accompany

Table III. Phase-Transfer Methylation of Heterocyclic Compounds[a]

heterocycle	product	% yield[b]
 **3**	*N*-methylpyrazole	86[c]
 **4**	*N*-methylimidazole	86
 **5**	*N*-methylbenzimidazole	61
 **6**	1-methylbenzotriazole	70
 **7**	*N*-methylcarbazole	91
 **8**	methyl *N*-methylindole-3-acetate	85

[a] The reaction conditions were the same as those listed in Table I; diethyl ether was employed as the solvent. [b] Products were purified by either Kugelrohr distillation or by recrystallization; unless otherwise noted, yields refer to isolated, analytically pure (>99% by GC) material. [c] Purity was 95% by GC; contaminated with *tert*-butyl alcohol (5%).

N-alkylation even though hydroxide ion may be present in small amounts since rigorous precautions were not taken for the exclusion of moisture from the reaction mixture.

As expected,[12] only a catalytic amount of crown ether was required in order to obtain the yields of N-alkylated product reported in Tables I–III. In order to demonstrate that the crown ether is actually necessary to obtain these yields, we conducted several experiments in which the crown ether was omitted. Diethyl ether was chosen as the solvent; all other reaction conditions were identical with those described in the tables. Thus, only unreacted starting material was obtained when pyrrole was allowed to react with either methyl iodide, ethyl iodide, or *n*-propyl bromide. Interestingly, the attempted N-methylation of indole with methyl iodide in the absence of crown ether resulted in the formation of a substantial amount of *N*-methylindole (62% by GC) along with unreacted starting material (36%) and C-alkylated material [3-methylindole (1%) and 1,3-dimethylindole (1%)]. However, when ethyl iodide was used as the alkylating agent, only a small amount (9% by GC) of *N*-ethylindole was obtained along with unreacted indole (91%). With *n*-propyl bromide, unreacted indole (85% by GC) and *N*-propylindole (15%) were obtained.

In summary, we believe that the phase-transfer alkylation of relatively acidic, nitrogen-containing, heterocyclic compounds in the presence of potassium *tert*-butoxide and 18-crown-6 is a superior method for the formation of *N*-alkyl heterocycles. The procedure is mild and convenient, and exclusive N-alkylation is generally observed. Alkyl

iodides can be used as alkylating agents, and diethyl ether can be utilized as the solvent. Futhermore, since hydroxide is not employed as the base, complications due to its presence are avoided.

Experimental Section

Melting points were determined on a Fisher-Johns melting point apparatus and were not corrected. Infrared spectra were recorded on a Perkin-Elmer Model 457 grating infrared spectrophotometer. Nuclear magnetic resonance spectra were recorded on a Varian Model EM-360 spectrometer, and chemical shifts are reported in parts per million downfield from Me_4Si. Gas chromatographic analyses were performed either on a Beckman Model GC-2A gas chromatograph equipped with a thermal conductivity detector and a 5 ft × 0.25 in. (o.d.) column packed with 10% FFAP on Chromosorb W or on a Varian Model 3700 gas chromatograph equipped with flame-ionization detectors and 5 ft × 0.125 in. (o.d.) columns packed with 3% OV-17 on Chromosorb W.

Benzimidazole, benzotriazole, benzyl bromide, carbazole, imidazole, indole, potassium *tert*-butoxide, pyrazole, and pyrrole were obtained commercially and used without subsequent purification. Allyl bromide, *tert*-butyl bromide, *n*-butyl iodide, ethyl bromide, ethyl iodide, methyl iodide, *n*-propyl bromide, *n*-propyl iodide, and isopropyl iodide were obtained commericially, dried over anhydrous sodium sulfate, distilled, and stored over Linde 4-Å molecular sieves prior to use. Anhydrous diethyl ether (Mallinckrodt) was used as received. Opened cans were stored in a desiccator over Drierite. Benzene (Baker) and Pentane (Eastman) were distilled and then stored over sodium metal prior to use. 18-Crown-6 was prepared according to a procedure reported in the literature.[15] Methyl indole-3-acetate was prepared from commercial indole-3-acetic acid by using a general esterification procedure reported in the literature.[16]

The general procedure which follows was used to prepare all of the N-alkylated heterocyclic compounds reported in Tables I–III. The physical properties (boiling and/or melting point) of *N*-methylpyrrole,[17] *N*-ethylpyrrole,[17] *N*-propylpyrrole,[17] *N*-butylpyrrole,[17] *N*-benzylpyrrole,[17] *N*-allylpyrrole,[2a] *N*-methylindole,[18] *N*-ethylindole,[7c] *N*-propylindole,[19] *N*-butylindole,[7d] *N*-benzylindole,[5b] *N*-allylindole,[7c] *N*-methylpyrazole,[18] *N*-methylimidazole,[18] *N*-methylbenzimidazole,[17] *N*-methylbenzotriazole,[20] *N*-methylcarbazole,[17] and methyl *N*-methylindole-3-acetate[21] were in agreement with those reported in the literature.[2a,5b,7c,d,17–21] *N*-Isopropylpyrrole[7a] and *N*-isopropylindole[2e] were not isolated and were identified by comparison (GC) with authentic samples prepared via literature procedures.[2e,7a]

The IR spectra of the N-alkylated heterocycles were consistent with the assigned structures in that the N–H absorption (ca. 3400 cm^{-1}) present in the starting material was absent in the product. The NMR spectra of *N*-methylpyrrole,[22] *N*-ethylpyrrole,[7a] *N*-propylpyrrole,[7a] *N*-butylpyrrole,[7a] *N*-benzylpyrrole,[7a] *N*-methylindole,[22] *N*-ethylindole,[2e] *N*-propylindole,[2e] *N*-butylindole,[14] *N*-benzylindole,[2e] *N*-allylindole,[2e] *N*-methylpyrazole,[23] *N*-methylimidazole,[22] *N*-methylbenzimidazole,[24] and *N*-methylbenzotriazole[20] were in agreement with those reported in the literature.[2e,7a,14,20,22–24] The NMR data listed below are for compounds for which no comparison with published spectra could be made. Also listed below are procedures for those compounds which exhibited anomalous behavior when the general procedure was followed.

General Procedure for the N-Alkylation of Heterocycles. To a solution of 0.8 g (3 mmol) of 18-crown-6 in 50 mL of solvent was added 3.9 g (35 mmol) of potassium *tert*-butoxide. The mixture was stirred magnetically while 30 mmol of the heterocycle was introduced in a single portion. The reaction vessel was then fitted with a drying tube containing anhydrous $CaCl_2$ in order to prevent exposure to atmospheric moisture, and stirring was continued for 15 min. The alkylating agent (35 mmol) dissolved in 20 mL of solvent was added dropwise to the reaction mixture. With the more reactive alkylating agents, it was necessary to cool the reaction mixture in an ice bath during the addition. The reaction vessel was then stoppered, and stirring was continued for 1–18 h (reaction times given in Tables I–III). Water (20 mL) was added to the reaction mixture, the layers were separated, and the aqueous layer was extracted with Et_2O (2 × 20 mL). Alternatively, the reaction mixture could be filtered and the inorganic salts washed with Et_2O (2 × 20 mL). The combined organic solution was extracted with 50 mL of saturated NaCl and then dried over anhydrous Na_2SO_4. The solvent was removed by evaporation under reduced pressure, and the residue was purified by short-path (Kugelrohr) distillation or by recrystallization.

***N*-Allylpyrrole.** The general procedure afforded 2.2 g (70% based on *N*-allylpyrrole as the sole product) of an oil. The purity of the product was 82% by GC. The major component was separated from the mixture by preparative gas chromatography and was identified as *N*-allylpyrrole. GC analysis indicated that the mixture also contained pyrrole (7%) and 2-allylpyrrole (6%) identified by comparison with authentic samples (2-allylpyrrole was prepared from the lithium salt of pyrrole and allyl bromide[2h]). Three unidentified components (5% total) were also present in the mixture.

***N*-Allylindole.** The general procedure afforded *N*-allylindole (78%) with a purity of 97% by GC. The IR spectrum showed a very weak absorption in the region 3300–3400 cm^{-1}, and GC analysis indicated that the product also contained 3-allylindole (3%), identified by comparison with an authentic sample (prepared via the method of Cardillo et al.[2e]).

1-Methylbenzotriazole. The general procedure afforded 1-methylbenzotriazole (70%) with a purity of >99% by GC after recrystallization from ethanol. However, the crude product (prior to recrystallization) exhibited an additional component by GC (15%, probably 2-methylbenzotriazole[20]).

Attempted N-Alkylation of Pyrrole and Indole in the Absence of 18-Crown-6. The general procedure was followed with the exception that the crown ether was omitted (Et_2O solvent; reaction times given in Tables I and II). Methyl iodide, ethyl iodide, and *n*-propyl iodide were employed as the alkylating agents. The products were not isolated and yields were estimated by GC. Authentic samples of 3-methylindole and 1,3-dimethylindole (for GC comparison) were prepared via literature procedures.[2e,f]

NMR Data. *N*-Allylpyrrole: ($CDCl_3$) δ 4.4 (m, 2 H), 4.8–5.3 (m, 2 H), 5.6–6.1 (m, 1 H), 6.1 (m, 2 H), 6.5 (m, 2 H). *N*-Methylcarbazole ($CDCl_3$) δ 3.6 (s, 3 H), 7.2 (m, 6 H), 8.0 (m, 2 H). Methyl *N*-methylindole-3-acetate ($CDCl_3$) δ 3.5 (s, 3 H), 3.6 (s, 3 H), 3.7 (s, 2 H), 6.8 (s, 1 H), 7.0 (m, 3 H), 7.5 (m, 1 H).

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Registry No. 1, 109-97-7; 2, 120-72-9; 3, 288-13-1; 4, 288-32-4; 5, 51-17-2; 6, 95-14-7; 7, 86-74-8; 8, 1912-33-0; *N*-methylpyrrole, 96-54-8; *N*-methylindole, 603-76-9; *N*-ethylpyrrole, 617-92-5; *N*-propylpyrrole, 5145-64-2; *N*-isopropylpyrrole, 7057-97-8; *N*-butylpyrrole, 589-33-3;

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Comparative Study of Reactions of 2-Benzylisoquinolinium and 3,4-Dihydro-2-benzylisoquinolinium Salts with Carbon Disulfide in Two Base-Solvent Environments

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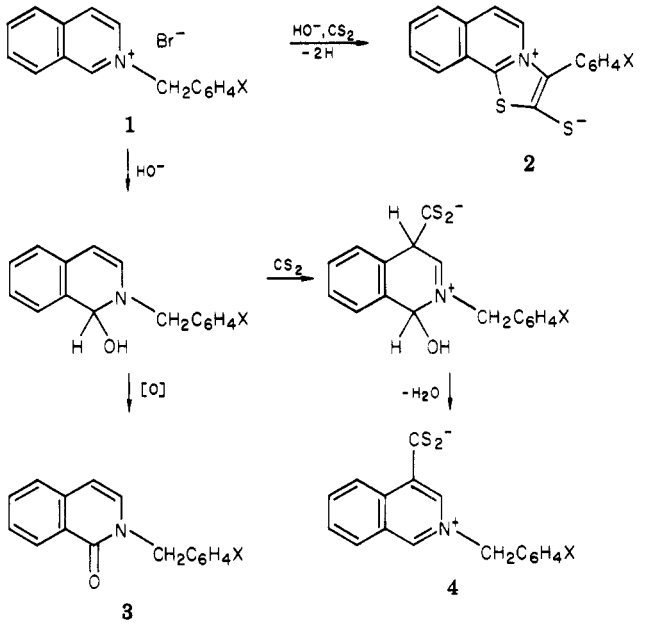
3,4-Dihydro-2-(*p*-nitrobenzyl)isoquinolinium bromide (**9a**) reacts with carbon disulfide in both aqueous hydroxide–dioxane and triethylamine–pyridine to afford the expected 5,6-dihydro-3-(*p*-nitrophenyl)thiazolo[2,3-*a*]isoquinolinium-2-thiolate (**12**) and a new product identified as 1,2,3,4-tetrahydro-2-(*p*-nitrobenzyl)isoquinoline (**13a**). Deuterium-labeling studies reveal that **13a** is formed in a process by which adduct **12** is obtained from intermediate **11a**; a different pathway is followed in each base–solvent system. In contrast, 2-(*p*-nitrobenzyl)-isoquinolinium bromide (**1**, X = *p*-NO_2) gives only the thiolate product **2** (X = *p*-NO_2) in both base–solvent environments. Substrates **1** and **9a** undergo no hydrogen–deuterium exchange at C_α in either base–solvent system; only **1** sustains exchange at C_1 and then only in aqueous hydroxide–dioxane. The implications of these results concerning the mechanisms for the **1** to **2** and **9a** to **12** transformations are discussed. A convenient direct reduction of **9** with ammonium formate, initiated to confirm the structural assignment of **13**, is described.

We have reported[2,3] on the reaction of 2-benzylisoquinolinium bromides (**1**) with carbon disulfide in aqueous hydroxide–dioxane. In addition to 2-benzylisoquinolone side products (**3**), these reactions afforded 3-phenylthiazolo[2,3-*a*]isoquinolinium-2-thiolates[4] (**2**) and 2-benzylisoquinolinium-4-dithiocarboxylate adducts[5] (**4**) as the only isolable products[6] (Scheme I). By an isotopic dilution method, we estimated[3] the Hammett ρ value for the **1** → **2** conversion to be +2.3 and by deuterium-labeling experiments[2] on **1** (X = *p*-Br), determined that its most accessible conjugate base is **6** (X = *p*-Br) (Scheme II). These results raised logical questions about the accuracy of earlier mechanistic formulations[7,8] for this conversion that implicate the azomethine ylide 1,3-dipolar intermediate **5**, which through cycloaddition with carbon disulfide would produce **7** and then **2** by oxidation. We hypothesized an alternative scheme[3] leading to adduct **2** through **7** and involving nucleophilic attack on **1** by dithiocarbonate (or hydrogen dithiocarbonate) at C_1 to give intermediate **8**. The fate of the hydrogens lost in the alleged **7** → **2** conversion has not been determined.

Scheme I



In earlier work, Huisgen[9] had reported, without experimental detail, the isolation of 5,6-dihydro-3-(*p*-nitrophenyl)thiazolo[2,3-*a*]isoquinolinium-2-thiolate (**12**) in 65% yield from a reaction that treated 3,4-dihydro-2-(*p*-nitrobenzyl)isoquinolinium bromide (**9a**) with carbon disulfide in triethylamine–pyridine (Scheme III). No other

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