ziridine 1 in 2 mL of $CDCl_3$ or anisole and 0.091 g (0.000 50 mol) of bibenzyl as an internal NMR standard. After the solutions were heated for 72 h, the $CDCl_3$ sample showed that greater than 90% of 1 remained. In anisole, 1 was completely consumed under these conditions.

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Registry No. 1, 78377-89-6; ($PhSO_2N(O)$=CHC_6H_4-*p*-NO_2), 87586-25-2; anisole,, 100-66-3.

An Efficient Synthesis of Azidoindoles and Azidotryptophans

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Until 1979, when Scriven and co-workers[1] reported the synthesis of ethyl azidoindole-2-carboxylates, no azidoindoles had been described. Recently, azido analogues of several biologically significant indoles have been reported.[2-5] These compounds show great potential as photoaffinity labeling agents[6-11] for active sites of enzymes that manipulate indole and tryptophan[5] and for hormone receptors responsive to indole-3-acetic acid.[2,12,13]

Unfortunately, azidoindoles have proven difficult to make until now, and many of those reported have not been fully characterized. The azidotryptophans, for example, were prepared enzymatically from the corresponding azidoindoles, which were themselves obtained in low yield.[3,5] We now describe the efficient synthesis and complete characterization of 4-, 5-, and 6-azidoindole (**5a-c**) and of the representative 6-azido-L-tryptophan (**5d**) by a method that should be applicable to a wide variety of indole derivatives.

In all cases to date,[1-5] the azido group has been introduced into the benzene ring of the indole nucleus by diazotization of the corresponding amine followed by nucleophilic displacement by azide anion. The low yields[1,3,5] usually associated with this method of making azidoindoles result partly from the known sensitivity of indoles to acid, a necessary constituent of the diazotizing medium, and partly from the use of inefficient routes to the amine precursors.

We find that the problem of the acid sensitivity of the indole nucleus is easily circumvented by substituting aqueous 80% acetic acid for the dilute hydrochloric or sulfuric acid commonly employed in diazotizations. Previously applied in this Laboratory in preparing azido derivatives of the especially acid-labile indole-3-acetic acid,[2,4] the modification works as well or better for making azidoindoles (**5a-c**) and azidotryptophans (e.g., **5d**), as shown in Table I. With acetic acid, it is unnecessary to insert the azide moiety before introduction and elaboration of an alkyl side chain. This is fortunate, because the sensitivity of the azido group to elevated temperature, light, and strong acid makes its late introduction in a synthetic sequence highly desirable.

Table I. Yields for the Final Step and Overall Yields for Different Methods of Preparing Azidoindoles, Azidotryptophans, and Azidoindole-3-acetic Acids

compd	final step (diazotization) yield, % in HCl	final step (diazotization) yield, % in HOAc	overall yield, % literature	overall yield, % present
5a	*a*, *b*	47	0.5 [b,c]	30
5b	10 [b]	88	10 [b]	88
5c	10 [b]	58	3 [b]	49
5d	*b*, *d-f*	54	0.5 [b]	25
4-N_3IAA [g]	none [j]	42 [j]	1.4 [j]	*e*
5-N_3IAA [h]	none [j]	43 [j]	18 [j]-22 [k]	*e*
6-N_3IAA [i]	none [j]	80 [j]	20 [j]	*e*

[a] Not reported. [b] See ref 3. [c] Calculated from yields reported in ref 3 and 14. [d] See ref 5. [e] Not applicable. [f] Prepared enzymatically. [g] 4-Azidoindole-3-acetic acid. [h] 5-Azidoindole-3-acetic acid. [i] 6-Azidoindole-3-acetic acid. [j] See ref 2. [k] See ref 4.

The problem of finding efficient routes to appropriate amine precursors must be solved for each target indole, as shown in Scheme I. For making 4-azidoindole (**5a**), we applied a modification of Kruse's[15] conversion of 2,6-dinitrotoluene (**1**) into 4-aminoindole (**4a**) via 2,6-dinitro-β-(dimethylamino)styrene (**2**) with dimethylformamide dimethyl acetal. In our hands, transformation of 2,6-dinitro-β-(dimethylamino)styrene (**2**) into the semicarbazone **3** before catalytic hydrogenation and ring closure provided a cleaner reaction. For 5-azidoindole (**5b**), we used commercially available 5-aminoindole (**4b**), as have others.[3,5] For 6-azidoindole (**5c**), we chose the same route as Saito and Rilling,[3] starting with 6-nitroindoline (**6**); but we used 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ) instead of chloranil to achieve aromatization to 6-nitroindole (**7a**) and Raney nickel with hydrogen at room temperature instead of Raney nickel with sodium hydroxide at 100 °C to effect reduction. For 6-azido-L-tryptophan (**5d**), we followed the procedure of Moriya and co-workers[16] for making 6-nitro-D-tryptophan (**7b**) and the method of Goodman and co-workers[17] for reducing the L enantiomer to the amine **4d**. Physical properties of the resulting azidoindoles agree reasonably well with available published values.[3,5] Melting points and UV extinction coefficients indicate that the present methods of synthesis and isolation produce compounds of higher purity than those previously obtained.

As shown in Table I, the use of aqueous 80% acetic acid as the diazotizing medium, together with the described modifications in the routes to the amine precursors, also dramatcally improves overall yields for making these

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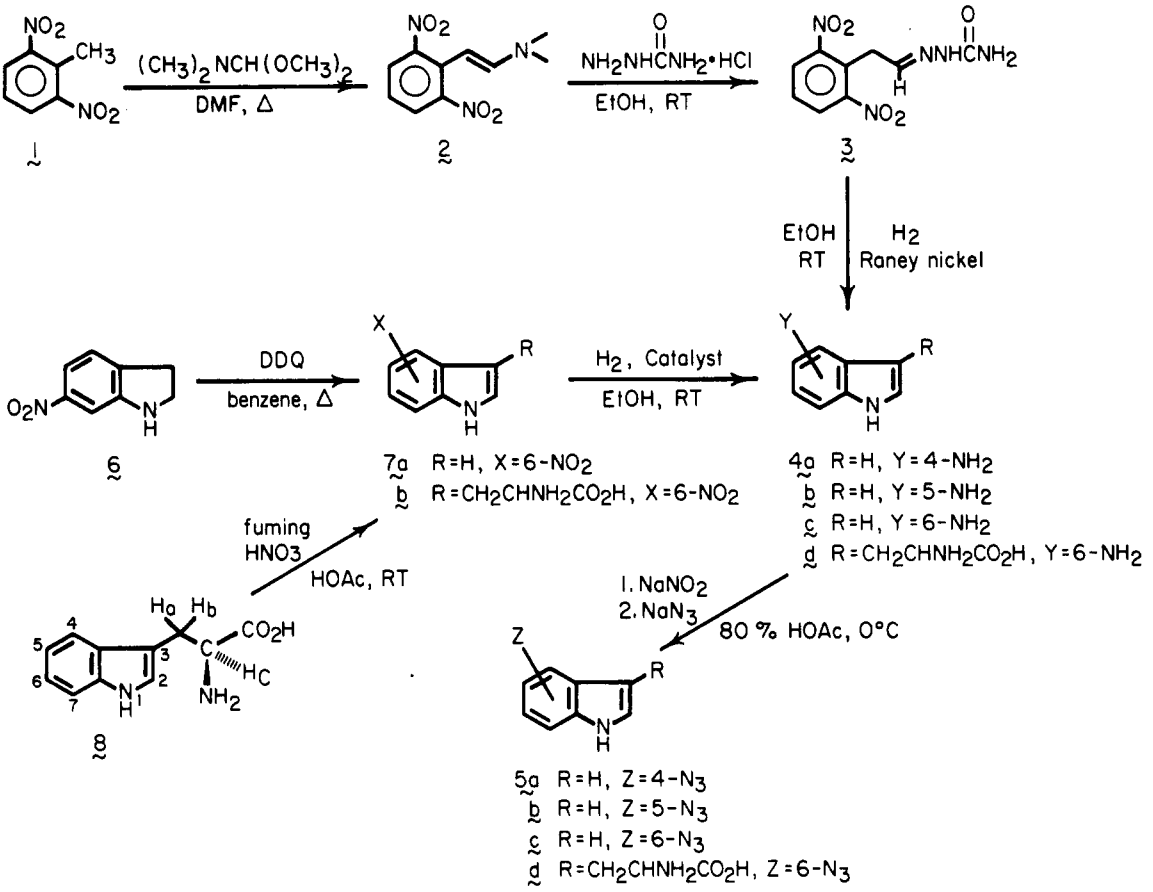
0022-3263/83/1948-5130$01.50/0

Scheme I



azidoindoles. Since sodium nitrite in 80% aqueous acetic acid has now been shown to be a good diazotizing agent for unsubstituted aminoindoles, for aminoindoles carrying an acidic side chain,[2,4] and for those bearing both an acidic and a basic group on the side chain, these conditions appear to have broad applicability for preparation of azidoindoles. There is some indication that it may also be used to introduce other groups onto the indole nucleus,[16] and we are presently investigating the generality of this procedure. The availability of many nitro- and aminoindoles[18,19] makes such a route attractive.

Experimental Section

Melting points were determined on a Thomas-Hoover Uni-Melt or a Büchi capillary apparatus and are corrected. Optical rotations were measured on an Autopol III automatic polarimeter made by Rudolph Research, Fairfield, NJ. IR spectra were obtained in Nujol on a Perkin-Elmer Model 337 spectrophotometer. UV spectra were measured in 1-cm pathlength silica cells on a Beckman Acta Model MVI spectrophotometer. ^{1}H NMR spectra were recorded on a Varian EM 390 spectrometer. When the solvent was $(CD_3)_2SO$ or CD_3COCD_3, tetramethylsilane (Me_4Si) was used as an internal standard, but in D_2O–NaOD, sodium 2,2-dimethyl-2-silapentane-5-sulfonate (DSS) was the internal standard. Mass spectra were obtained by J. Carter Cook and his staff at the University of Illinois. Electron-impact mass spectra (EIMS) were recorded on a Varian-MAT CH-5 spectrometer coupled with a 620i computer and STATOS recorder. Low-resolution, field-desorption mass spectra (FDMS) were obtained on a Varian-MAT 731 spectrometer equipped with a Varian-MAT combination electron-impact–field-desorption ion source. Microanalyses were performed by Josef Nemeth and his staff at the University of Illinois, who also weighed samples for quantitative UV spectra. Neutral buffer (phosphate-based, pH 7.0) for quantitative UV spectra was prepared from Beckman packets. Except where noted, TLC was performed on Brinkmann silica gel plates with fluorescent indicator, elution with ethyl acetate–2-propanol–water (65:25:10), solvent A, or chloroform–methanol (9:1), solvent B. Unless stated otherwise, visualization was under 254-nm light or in iodine vapor. The adsorbent for column chromatography was Brinkmann silica gel, 0.2–0.05 mm. Platinum oxide, 2,6-dinitrotoluene, 5-aminoindole, and 6-nitroindoline were purchased from Aldrich, 10% palladium on charcoal from Engelhard, Raney nickel (molybdenum activated, no. 30) from W. R. Grace, semicarbazide hydrochloride from Eastman, and L-tryptophan from Sigma. Azides were stored as solids at room temperature in brown, foil-wrapped vials and showed no decomposition by TLC for 3–7 years. *All manipulations involving azides were carried out under red light.*

2,6-Dinitro-β-(dimethylamino)styrene (2). 2,6-Dinitrotoluene (1) was converted to 2,6-dinitro-β-(dimethylamino)styrene (2) with dimethylformamide dimethyl acetal in dimethylformamide, as previously described:[15] mp 91.5–93 °C (lit.[15] mp 90–93 °C); TLC, solvent A, R_f 0.77, iodine vapor.

(2,6-Dinitrophenyl)acetaldehyde Semicarbazone (3). To a slurry of 3.00 g (1.27 mmol) of 2,6-dinitro-β-(dimethylamino)-styrene (2) in 50 mL of absolute ethanol was added a solution containing 1.42 g (1.27 mmol) of semicarbazide hydrochloride, 1 mL of concentrated HCl, and 10 mL of water. After the mixture was stirred at room temperature for 1 h, it was chilled in ice and filtered. On drying in air, the tan solid weighed 2.808 g (83%), mp 196 °C (blackens and foams). Recrystallization from ethanol gave white needles (85% recovery): mp 199.5 °C; TLC, solvent A, R_f 0.67, iodine vapor; ^{1}H NMR [$(CD_3)_2SO$] δ 3.83 (d, 2, J_{CH_2-CH} = 3.6 Hz, CH_2), 5.82 (br s, 2, NH_2, exchanges with D_2O), 7.25 (t, 1, J_{CH-CH_2} = 3.6 Hz, CH), 7.85 (dd, 1, $J_{4,5} = J_{4,3}$ = 7.8 Hz, 4-H), 8.26 (d, 2, $J_{3,4} = J_{5,4}$ = 7.8 Hz, 3-H and 5-H), 9.87 (br s, 1, NH, exchanges with D_2O); FDMS, *m/e* 267 (M^+), 195 (M^+ – $NNHCONH_2$).

Anal. Calcd for $C_9H_9N_5O_5$: C, 40.46; H, 3.39; N, 26.21. Found: C, 40.65; H, 3.22; N, 26.19.

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4-Aminoindole (4a). In a 500-mL hydrogenation bottle were placed 0.500 g (1.87 mmol) of crude (2,6-dinitrophenyl)acetaldehyde semicarbazone (**3**) and 50 mL of absolute ethanol. After the flask was flushed with nitrogen, 0.100 g of 10% palladium on charcoal was added and the mixture was shaken on a Parr apparatus for 2 h at 45 psi under hydrogen. The catalyst was removed by filtration and washed twice with 20 mL of absolute ethanol. The combined filtrate and washings were evaporated to dryness at 20 °C under reduced pressure, giving a white solid, which was washed five times with 15 mL of anhydrous diethyl ether. The washings were evaporated to dryness as before, giving white crystals weighing 0.208 g (81%): mp 100–102 °C (lit. mp 108 °C,[20] 106–108 °C,[15] 105–107 °C[21]); TLC,[22] solvent A, R_f 0.74, iodine vapor, Van Urk's reagent,[23] Prochazka's reagent;[24] EIMS (10 eV), m/e (relative intensity) 132 (M^+, 100) 133 ($M^+ + 1$, 10.2) implying $C_8H_8N_2$.

6-Nitroindole (7a). 6-Nitroindoline (**6**) was converted to 6-nitroindole (**7a**) with DDQ in refluxing benzene, as previously described[4] for oxidation of 7-bromo-5-nitroindoline to 7-bromo-5-nitroindole. From 5.00 g (30.5 mmol) of 6-nitroindoline (**6**) was obtained 4.27 g of 6-nitroindole (**7a**) in 86% yield: mp 142.5–143 °C (lit. mp 139–140.5 °C,[25] 141–142 °C[26]); TLC, solvent A, R_f 0.77, visualization under 254-nm light.

6-Aminoindole (4c). 6-Aminoindole (**4c**) was prepared from 6-nitroindole (**7a**) by a modification of the procedure of Brown and Nelson.[27] In a 500-mL hydrogenation bottle was dissolved 0.500 g (3.09 mmol) of 6-nitroindole in 50 mL of absolute ethanol. The bottle was flushed with nitrogen and Raney nickel (~0.25 tsp) was added. The mixture was shaken on a Parr apparatus for 5 h at room temperature under 45 psi of hydrogen. The catalyst was removed by suction filtration and washed with absolute ethanol, and the combined filtrate and washings were evaporated to a yellow oil under reduced pressure at 30 °C. Crystallization was achieved by prolonged trituration under petroleum ether. The grey crystals were collected by filtration and air-dried, weighing 0.405 g (99%): mp 68–70 °C (lit. mp 68–70 °C,[21] 66–67 °C[27]); TLC, solvent A, R_f 0.65.

6-Nitro-L-tryptophan (7b). 6-Nitro-L-tryptophan (**7b**) was made by nitration of L-tryptophan and conversion of the resulting nitrate salt to the free amino acid according to the method of DeFazi et al.[28] as modified by Moriya et al.[16] for preparation of the D isomer: mp 253–254 °C dec (lit. mp 250 °C dec,[28] 252 °C dec[16] for 6-nitro-D-tryptophan).

6-Amino-L-tryptophan (4d). 6-Amino-L-tryptophan (**4d**) was obtained by hydrogenation of 6-nitro-L-tryptophan (**7b**) over platinum oxide as previously described:[17] mp 252–255 °C dec (lit. mp 210–212 °C[17] for 0.125 hydrate, 252 °C dec[16] for 6-amino-D-tryptophan hydrate); $[\alpha]^{25}_D$ +12.9° (1% in 1 N HCl) [lit. $[\alpha]^{25}_D$ +10° (1% in 1 N HCl)[17] for 0.125 hydrate, −13.1° (1% in 1 N HCl)[16] for 6-amino-D-tryptophan hydrate]. A hydrate containing approximately 2.5 mol of H_2O/mol of **4d** was used in the diazotization (see below).

General Procedure for Azidoindoles and Azidotryptophan (5a–d). In a 200-mL flask, about 0.5 g of the appropriate aminoindole or aminotryptophan (**4a–d**) dissolved in 40 mL of 80% (v/v) aqueous acetic acid was cooled to 0 °C by immersion in an ice–salt bath. To this was first added dropwise, with stirring, sodium nitrite and, after 5 min, sodium azide, each 1.1 equiv dissolved in 1 mL of ice-cold water. Stirring and cooling were continued for 2.5 h. The mixture was evaporated to dryness at 30 °C under reduced pressure. The usual safety precautions for handling armoatic azides should be followed. Purification of the resulting residues is described below for each compound (**5a–d**).

4-Azidoindole (5a). From 0.506 g (3.83 mmol) of 4-aminoindole (**4a**) was obtained a black tar to which was added 25 mL each of water and diethyl ether. The layers were separated, and the aqueous layer was extracted three times with 25-mL portions of diethyl ether. The combined organic extracts were evaporated to dryness at room temperature, and the resulting tar was purified by column chromatography (3.0 cm × 20 cm) with chloroform as eluant, giving 0.283 g of 4-azidoindole (**5a**) as an orange solid (47%): mp 68–69 °C; TLC, chloroform, R_f 0.43; solvent A, R_f 0.83, ^{1}H NMR [$(CD_3)_2CO$] δ 6.54 [m (collapses to dd with CD_3CD_2OH), 1, $J_{3,2}$ = 3.3 Hz, $J_{3,7}$ = 1.2 Hz, 3-H], 6.76 (dd, 1, $J_{5,6}$ = 7.2 Hz, $J_{5,7}$ = 1.2 Hz, 5-H), 7.12 (t, 1, $J_{6,5}$ = $J_{6,7}$ = 7.2 Hz, 6-H), 7.28–7.35 [2 m (collapse to overlapping dt and d with CD_3CD_2OH), 2, $J_{7,6}$ = 7.2 Hz, $J_{7,5}$ = $J_{7,3}$ = 1.2 Hz and $J_{2,3}$ = 3.3 Hz, 7-H and 3-H], 10.40 (br s, 1, NH, exchanges with CD_3CD_2OH); IR 2111 (N_3) cm^{-1}; UV (absolute ethanol) λ_{max} 223 nm (log ϵ 4.81), 292 (4.33); FDMS, m/e 158 (M^+).

Anal. Calcd for $C_8H_6N_4$: C, 60.75; H, 3.83; N, 35.42. Found: C, 60.78; H, 3.78; N, 35.75.

5-Azidoindole (5b). From 0.500 g (3.79 mmol) of 5-aminoindole (**4b**) was obtained a dark solid, which was collected by suction filtration after the addition of 10 mL of water. The crude product was washed with water and recrystallized by dissolving it in a minimum volume of absolute ethanol at room temperature, treating with activated charcoal, filtering through Celite, adding water to the filtrate, refrigerating, and collecting the solid by filtration. The product was washed with water and dried at room temperature under reduced pressure for 10 h, giving 0.527 g of 5-azidoindole (**5b**) as orange plates (88%): mp 84–85 °C (lit. mp 82–84 °C,[3] 81–82 °C[5]); TLC, solvent B, R_f 0.68; ^{1}H NMR [$(CD_3)_2CO$] δ 6.43 [m (collapses to dd with CD_3CD_2OD), 1, $J_{3,2}$ = 3.0 Hz, $J_{3,7}$ = 0.9 Hz, 3-H], 6.80 (dd, 1, $J_{6,7}$ = 8.3 Hz, $J_{6,4}$ = 2.1 Hz, 6-H), 7.25 (dd, 1, $J_{4,6}$ = 2.1 Hz, $J_{4,7}$ = 0.9 Hz, 4-H), 7.33 [m (collapses to d with CD_3CD_2OD), 1, $J_{2,3}$ = 3.0 Hz, 2-H], 7.43 (dt, 1, $J_{7,6}$ = 8.3 Hz, $J_{7,4}$ = $J_{7,3}$ = 0.9 Hz, 7-H), 10.33 (br s, 1, NH, exchanges with CD_3CD_2OD; IR 2100 (N_3) cm^{-1}; UV (absolute ethanol) λ_{max} 244 nm (log ϵ 4.38), 300 (3.60), 311 (3.43); EIMS (10 eV), m/e (relative intensity) 158 (M^+, 60), 130 ($M^+ - N_2$, 100).

6-Azidoindole (5c). From 0.500 g (3.79 mmol) of 6-aminoindole (**4c**) was obtained 0.592 g of tan solid as crude product (99%), which was purified by dissolving it in hot ethanol, treating with activated charcoal, filtering through Celite, and cooling to room temperature. Addition of water and refrigeration gave tan crystals, which were collected by filtration. After the purification procedure was repeated, the resulting solid was washed with water and air-dried, giving 6-azidoindole (**5c**) as 0.345 g of off-white crystals (58%): mp 83–83.5 °C (lit. 79.5 °C[3]); TLC, solvent B, R_f 0.68; ^{1}H NMR [$(CD_3)_2CO$] δ 6.43 [m (collapses to dd with CD_3CD_2OD), 1, $J_{3,2}$ = 3.3 Hz, $J_{3,7}$ = 1.0 Hz, 3-H], 6.76 (dd, 1, $J_{5,4}$ = 8.4 Hz, $J_{5,7}$ = 2.3 Hz, 5-H), 7.14 (dd, $J_{7,5}$ = 2.3 Hz, $J_{7,3}$ = 1.0 Hz), 7.30 [m (collapses to d with CD_3CD_2OD), 1, $J_{2,3}$ = 3.3 Hz, 2-H], 7.56 (d, 1, $J_{4,5}$ = 8.4 Hz, 4-H), 10.20 (br s, 1, NH, exchanges with CD_3CD_2OD); IR 2104 (N_3) cm^{-1}; UV (absolute ethanol) λ_{max} 214 nm (log ϵ 4.70), 243 (4.61), 285 (4.40); EIMS (10 eV), m/e (relative intensity), 158 (M^+, 60), 130 ($M^+ - N_2$, 100).

Anal. Calcd for $C_8H_6N_4$: C, 60.75, H, 3.83; N, 35.42. Found: C, 60.37, H, 3.70; N, 35.42.

6-Azido-L-tryptophan (5d). From 0.500 g (1.89 mmol) of 6-amino-L-tryptophan (**4d**) 2.5 hydrate was obtained a dark residue to which was added 10 mL of water. The dark solid was collected by filtration, washed three times with 5-mL portions of water, and allowed to dry in air overnight, giving 0.425 g of grey-brown solid (92%). The crude product (**5d**) was purified by dissolving it in hot water, treating with charcoal, filtering through Celite, and evaporating nearly to dryness at 30 °C under reduced pressure. The resulting slurry was filtered and the solid washed three times with 5-mL portions of water. After drying in air overnight, the tan crystals of 6-azido-L-tryptophan (**5d**) weighed 0.248 g (54%): mp ~190 °C dec (evacuated, sealed tube); TLC, Eastman cellulose, 1-butanol–acetic acid–water, 3:1:1, R_f 0.76; ^{1}H NMR (NaOD–D_2O) δ 3.04 and 3.32 (2 overlapping dd, 2, $J_{a,b}$ = 14.4 Hz, $J_{a,c}$ = 7.7 Hz, and $J_{b,a}$ = 14.4 Hz, $J_{b,c}$ = 5.2 Hz, CH_aH_b), 3.69 (dd, 1, $J_{a,c}$ = 7.7 Hz, $J_{b,c}$ = 5.2 Hz, CH_c), 6.75 (dd, 1, $J_{5,4}$ = 9.6 Hz, $J_{5,7}$ = 2.3 Hz, 5-H), 6.95 (d, 1, $J_{7,5}$ = 2.3 Hz, 7-H), 7.27

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(s, 1, 2-H), 7.61 (d, 1, $J_{4,5}$ = 9.6 Hz, 4-H); IR 2110 (N_3) cm^{-1}; UV (95% ethanol) λ_{max} 214 nm (log ϵ 4.31), 247 (4.34), 289 (3.99); UV (0.1 N HCl) λ_{max} 210 nm (log ϵ 4.30), 244 (4.34), 285 (3.99); UV (pH 7.0 buffer) λ_{max} 210 nm (log ϵ 4.28), 242 (4.35), 287 (4.00); UV (0.1 N NaOH) λ_{max} 220 nm (log ϵ 4.12), 245 (4.29), 289 (3.92); FDMS, m/e 245 (M^+).

Anal. Calcd for $C_{11}H_{11}N_5O_2$: C, 53.87; H, 4.52; N, 28.56. Found: C, 53.70; H, 4.57; N, 28.40.

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Registry No. **1**, 606-20-2; **2**, 79476-53-2; **3**, 87586-68-3; **4a**, 5192-23-4; **4b**, 5192-03-0; **4c**, 5318-27-4; **4d**, 2462-30-8; **5a**, 81524-73-4; **5b**, 81524-74-5; **5c**, 81524-75-6; **5d**, 81524-70-1; **6**, 19727-83-4; **7a**, 4769-96-4; **7b**, 46885-76-1; **8**, 73-22-3; $(CH_3)_2NCH(OCH_3)_2$, 4637-24-5; $NH_2NHCONH_2$·HCl, 563-41-7.

Reaction of Dimethyloxosulfonium Methylide with Epoxides. Preparation of Oxetanes

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Methods for the preparation of oxetanes include the cyclization of 1,3-halohydrins with alkali, the light-catalyzed 1,2-cycloaddition of olefins and carbonyl compounds,[1] the thermal decomposition of tributyltin derivatives,[2] and the reaction of sulfoximide anion with carbonyl compounds.[3] The analogous azetidines have been prepared by reaction of dimethyloxosulfonium methylide with aziridines.[4] We now report on a convenient synthesis of oxetanes by reaction of dimethyloxosulfonium methylide (1) with epoxides and with carbonyl compounds.

Results and Disscussion

The ylide 1 is an efficient methylene-transfer reagent in reactions with epoxides **3a–e**, affording the corresponding oxetanes **3a–e** in yields of 83–97% on standing at 50 °C for 3 days (Table I). We propose the following pathway for the reaction:

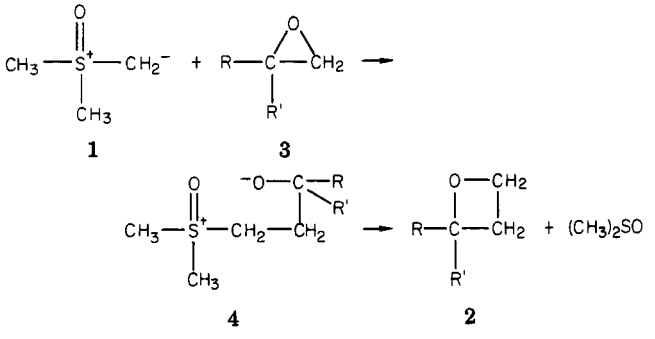


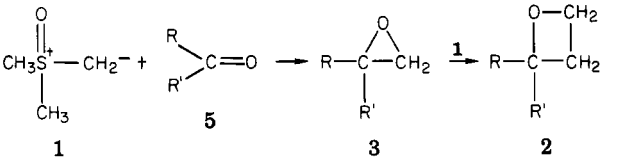
Table I. Preparation of Oxetanes from Epoxides

compd	R	R′	compd	yield,[a] %	yield,[b] %
3a	H	C_6H_5	**2a**	65	94
3b	C_6H_5	C_6H_5	**2b**	55[c]	99
3c	H	*p*-ClC_6H_4	**2c**	23[c]	88
3d	CH_3	C_6H_5	**2d**	24[c]	85
3e	cyclohexanone		**2e**	81	83

[a] 10 mol % excess ylide; reflux 4 h. [b] 100 mol % excess ylide; 50 °C, 3 days. [c] Unreacted epoxide recovered in yields of 25%, 45%, and 50%, respectively.

The reaction of epoxides with 1 differs from those reported with related reagents. Thus, anions of *N*-(*p*-tolylsulfonyl)sulfoximines are nucleophilic alkylidene transfer reagents in reactions with ketones, imines, and α,β-unsaturated ketones, affording epoxides, aziridines, and cyclopropanes, respectively.[5] However, reaction of this anion with epoxides yields only the corresponding γ-hydroxy sulfoximines. Likewise, reaction of epoxides with α-lithio *tert*-butyl sulfoxide gives γ-hydroxy sulfoxides.[6]

Since oxosulfonium ylides are practical reagents for the synthesis of epoxides from carbonyl compounds, we explored the reaction of 2 equiv of 1 with carbonyl compounds. As shown in Table II, oxetanes **2** were obtained in 80–97% yields by carrying out the reaction at 50 °C for 3 days.



The reported synthesis of oxetanes by reaction of *N*-(*P*-tolylsulfonyl)sulfoximide anion with carbonyl compounds is quite sensitive to temperature.[3] For example, oxetane **2i** was obtained in 69% yield at a reaction temperature of 40 ± 2 °C. However, at a reaction temperature of 45 ± 2 °C, 2-(4-*tert*-butylcyclohexenyl)ethanol was formed as a byproduct in 17% yield. The reaction with 1 does not require such rigidly controlled reaction conditions; reaction with benzophenone gave **2b** in yields of 97% (50 °C, 3 days) or 88% (reflux, 1 day).

The use of dimethyloxosulfonium methylide as a nucleophilic methylene-transfer reagent to epoxides has advantages over most known oxetane synthesis methods: the reaction conditions are mild and convenient; yields of the products are much higher than those reported by the procedures of Deric (40%),[1] Biggs (20–40%),[2] and Welch (46–96%).[3]

Experimental Section

The aldehydes and ketones used as starting materials were reagent grade (>95% pure) and were used as received unless otherwise specified. Epoxides were prepared by the reaction of dimethylsulfonium methylide with carbonyl compounds.[7,8] ^1H

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