H; 1.31 g, 69%) as approximately a 1:1.5 mixture of *Z*:*E* isomers (by NMR) after column chromatography [SiO_2, light petroleum (bp 60–80 °C)]: R_f 0.4; IR ν_{max} (film) 1595 (Ar C=C), 1260 ($SiMe_3$); NMR (CCl_4, CH_2Cl_2 as internal standard) δ 7.3 (5 H, m, Ph), 6.62 (0.5 H, q, $J = 1.5$ Hz, CH=C), 1.90 (3 H, dd, $J = 1.5$ Hz, CMe), 0.13 and 0.00 (9 H, 2 s in ratio 1.5:1, SiMe); MS, m/z 190 (36, M^+), 135 (100), 73 (89, $SiMe_3$).

Registry No. **2** (R^1 = Me), 67373-67-5; **2** (R^1 = *n*-Bu), 87739-07-9; **2** (R^1 = Ph), 87739-08-0; **3**, 28830-22-0; **4** (R^1 = H), 30536-77-7; **4** (R^1 = Me), 87729-74-6; **4** (R^1 = *n*-Bu), 87729-75-7; **5**, 62762-44-1; **6**, 62761-90-4; **7**, 41823-71-6; **8** (R^1 = H; R^2 = $SiMe_3$; R^3 = Ph; R^4 = H), 18001-47-3; **8** (R^1 = H; R^2 = $SiMe_3$; R^3 = R^4 = Ph), 51318-07-1; (*Z*)-**8** (R^1 = Me; R^2 = $SiMe_3$; R^3 = Ph; R^4 = H), 57266-91-8; (*E*)-**8** (R^1 = Me; R^2 = $SiMe_3$; R^3 = Ph; R^4 = H), 57266-92-9; **8** (R^1 = Me; R^2 = $SiMe_3$; R^3 = R^4 = Ph), 87729-76-8; **8** (R^1 = Me; R^2 = $SiMe_3$; R^3 = R^4 = H), 18163-07-0; **8** (R^1 = *n*-Bu; R^2 = $SiMe_3$; R^3 = Ph; R^4 = H), 87729-77-9; **8** (R^1 = *n*-Bu; R^2 = $SiMe_3$; R^3 = R^4 = Ph), 71814-13-6; **8** (R^1 = *n*-Bu; R^2 = $SiMe_3$; R^3 = R^4 = H), 59549-81-4; **8** (R^1 = Ph; R^2 = $SiMe_3$; R^3 = R^4 = H), 1923-01-9; **9** (R^1 = Me), 87739-09-1; **9** (R^1 = *n*-Bu), 87729-78-0; **9** (R^1 = Ph), 87729-79-1; **10**, 87729-80-4; **11** (R^1 = H), 37891-39-7; **11** (R^1 = Me), 87729-81-5; **11** (R^1 = *n*-Bu), 87729-82-6; **12** (R^1 = R^2 = $SiMe_3$; R^3 = Ph; R^4 = H), 18415-23-1; **12** (R^1 = R^2 = $SiMe_3$; R^3 = R^4 = Ph), 78375-55-0; **12** (R^1 = R^2 = $SiMe_3$; R^3 = R^4 = H), 5654-07-9; **13** (R^1 = H; R^2 = SPh; R^3 = Ph; R^4 = H), 16619-61-7; **13** (R^1 = H; R^2 = SPh; R^3 = R^4 = Ph), 13112-46-4; **13** (R^1 = H; R^2 = SPh; R^3 = R^4 = $(CH_2)_5$), 33521-88-9; **13** (R^1 Me; R^2 = SPh; R^3 = Ph; R^4 = H), 16158-83-1; **13** (R^1 = *n*-Bu; R^2 = SPh; R^3 = Ph; R^4 = H), 87729-83-7; **13** (R^1 = *n*-Bu; R^2 = SPh; R^3 = R^4 = Ph), 87729-84-8; **13** (R^1 = *n*-Bu; R^2 = SPh; R^3 = R^4 = H), 86887-88-9; **13** (R^1 = *n*-Bu; R^2 = SPh; R^3 = R^4 = $(CH_2)_5$), 87729-85-9; **14**, 87729-86-0; **15** (R^1 = $SiMe_3$; R^2 = SPh; R^3 = Ph; R^4 = H), 59176-57-7; **15** (R^1 = $SiMe_3$; R^2 = SPh; R^3 = R^4 = Ph), 87729-87-1; **15** (R^1 = $SiMe_3$; R^2 = SPh; R^3 = R^4 = H), 62762-20-3; (phenylthio)(trimethylsilyl)methane, 17873-08-4; chlorotrimethylsilane, 75-77-4; bis(phenylthio)(trimethylsilyl)methane, 37891-39-7; [bis(phenylthio)(trimethylsilyl)methyl]lithium, 87729-88-2; diphenyl disulfide, 882-33-7; [bis(trimethylsilyl)(phenylthio)methyl]lithium, 62762-44-1; benzaldehyde, 100-52-7; diphenyl ketone, 119-61-9; cyclohexanone, 108-94-1.

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Condensation of 2,3,3-Trimethyl-3*H*-indole with Methylene Iodide and Oxidative Coupling

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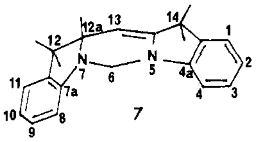
Received May 18, 1983

2,3,3-Trimethyl-3*H*-indole (**1**) has been coupled through the nitrogens with dihalides to give open-chain species.[1] In the case of 1,2-dihaloethane, a five-ring heterocyclic system was observed by NMR but not isolated.[2] We now describe the reaction of diiodomethane with **1** and potassium hydroxide to give the pyrimido diindole **6**, a previously unreported heterocyclic system.

The mass spectrum of **6** shows sequential loss of methyl radicals from the 12-, 12a-, and 14-positions to give an ion conjugated between the aromatic rings. Its UV spectrum is essentially identical with that of 1,3,3-trimethyl-2-methyleneindoline, confirming the presence of a similar chromophore in **6**. The indoline was also used in assigning the ^{13}C and ^{1}H NMR spectra of **6**.[3]

The nonequivalence of the methylene protons suggested the fused ring structure, and the proposed structure fit the ^{13}C and ^{1}H NMR very well. The final question was the conformation of the rings, particularly the nitrogen atoms. The nitrogens could be sp^3 or have some sp^2 character. The enamine nitrogen would be most likely to have sp^2 character. Studies of similar systems with only sp^3 nitrogens showed that cis electron pairs on the nitrogens gave large chemical shift differences between the methylenes similar to those in **6**; however, if the pairs were trans, the chemical shift differences were negligible, eliminating this possibility.

Further clarification was obtained from an evaluation of the C–H coupling constants in the ^{13}C NMR. The peaks of interest were for the 4a- (δ 144.8) and 7a- (δ 148.4) carbons. These are the aromatic carbons bonded to nitrogen. The 4a-carbon has two 8-Hz coupling constants due to coupling with the meta protons in the aromatic ring; however, the 7a-carbon has a third 8-Hz coupling, in addition to the two meta couplings, which was decoupled by irradiation of the protons at δ 4.71. It is very unlikely that the vinyl proton would have an 8-Hz coupling to either of those carbons since they would be four-bond couplings, which seldom exceed 4 Hz.[5] The third constant must therefore be due to coupling to one of the methylene protons. Lemieux's Karpus plot of $^3J_{C-N-C-H}$ vs. dihedral angle shows that an 8-Hz coupling constant would be observed for an angle of about 180°.[6] Although he has no measurements for 0° angles, one would assume that similar sized coupling constants would be observed. Of the possible conformations, (1) sp^3 nitrogens with cis electron pairs, (2) sp^2 nitrogens, and (3) an sp^2 nitrogen at position 5, with the 7-nitrogen sp^3, only in case 3 with the electron pair on the sp^3 nitrogen cis to the 12a-methyl is an 8-Hz coupling constant predicted. In this case there is an angle of about 0° between the methylene hydrogen trans to the 12a-methyl and the 7a-carbon. In cases 1 and 2 all constants are predicted to be about 1 Hz. Therefore the structure must be as shown in **7** with the hydrogen trans to the 12a-methyl absorbing at δ 4.71. The coupling of the methylene protons to the vinyl carbon at δ 151.3 is consistent with this structure. The δ 4.71 proton will be at about a 100° angle, giving neglibible coupling, while the δ 5.36 proton will be at about a 120° angle, which predicts about a 2-Hz coupling constant.



7

The size of the bridge between the nitrogens determines the type of product obtained. When the bridge is four or more carbons, coupling takes place, but no ring formation occurs.[1] A three-carbon chain does not give coupling. Instead the chain attaches to the 2-methyl on the indole ring.[7] With a two-carbon bridge an equilibrium between

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(1) Delzenne, G. A.; Smelts, G. J.; Hoefnagels, J. A. British Patent 1 278 775, 1972; *Chem. Abstr.* 1973, 78, 65312h.

(2) Mushkalo, I. L.; Turova, L. S.; Turov, A. V.; Kornilov, M. Yu. *Khim. Geterosikl. Soedin. Riga* 1980, 122–3; *Chem. Abstr.* 1980, 93, 7938r.

(3) Sadtler Research Laboratories, Inc. Spectra, UV 6747, ^1H NMR 16082M and ^{13}C NMR 3615C.

(4) (a) Chivers, P. J.; Crabb, T. A.; Williams, R. O. *Tetrahedron* 1968, 24, 6625–42. (b) Chivers, P. J.; Crabb, T. A.; Williams, R. O. *Ibid.* 1969, 25, 2921–38. (c) Crabb, T. A.; Newton, R. F. *Ibid.* 1968, 24, 6327–38.

(5) Hanson, P. E. *Prog. NMR Spectrosc.* 1981, 14, 175–295.

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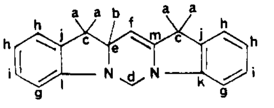
0022-3263/84/1949-0170$01.50/0

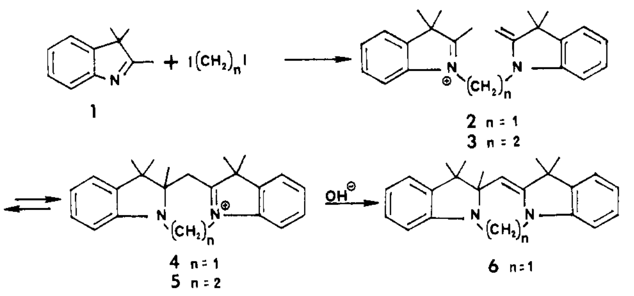
Table I. ^{13}C NMR Data for 6[a]



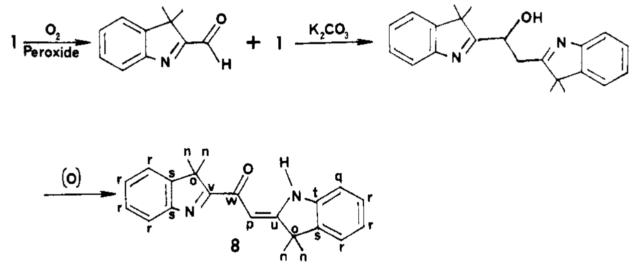
δ	J_{C-H} (mult)	$J_{long-range}$ (mult)	assignment	ν of protons coupled to
22.0	126 (q)	4 (q)	a	1.51
22.1	126 (q)		b	1.49
26.5	127 (q)	4 (q)	a	1.30
27.7	128 (q)	4 (q)	a	1.38
30.3	127 (q)	4 (q)	a	1.07
43.2		?	c	1.07-1.51
45.7		?	c	1.07-1.51
52.1	147, 152 (d of d)		d	4.71-5.36
69.9		4, 4, & ? (d of d of q)	e	1.38, 4.71, 5.36
94.6	160 (d)	3 (q)	f	4.71
104.4	158 (d)	8 (d)	g	6.7
109.1	158 (d)	8 (d)	g	6.7
118.4	~160 (d)	7 (d)	h	6.8
119.8	161 (d)	7 (d)	h	6.8
121.8	~160 (d)	~8 (d)	h	7.1
121.9	~160 (d)	~8 (d)	h	7.1
126.5	161 (d)	7 (d)	i	7.1
127.4	160 (d)	8 (d)	i	7.24
137.2		6, 6, 3, & 3 (d of d of q of q)	j	6.8
140.3		6, 6, 3, & 3 (d of d of q of q)	j	6.8
144.8		8 & 8 (d of d)	k	7.08-7.24
148.4		8, 8, & 8 (d of d of d)	l	7.08-7.24 & 4.71
151.3		2, 2, & 2 (d of q of q)	m	1.07-1.51, 5.36

[a] CDCl$_3$ solution.

the open, **3**, and closed, **5**, forms was observed in the monoprotonated state in solution, but only the open form, **3**, was isolated as the monoperchlorate salt.[2] In the case of the one-carbon bridge, we believe **2** is formed as an intermediate. Rearrangement of **2** to **4** is followed by reaction with base to give **6**.



Scheme I



If oxygen is not excluded from the reaction, the oxidative condensation product **8** is formed. Although oxidation of indole derivatives has been studied extensively,[8] little work has been done in basic solution. The yield of **8** was improved by eliminating the CH$_2$I$_2$, bubbling in oxygen or air, using potassium carbonate as base, and adding benzoyl peroxide to initiate the reaction.

Chemical and spectral considerations led to the skeletal structure with extended conjugation. The major question was whether the low-field hydrogen (δ 11.5) was attached to a nitrogen or the oxygen. The absorbtion at 1600 cm^{-1} is reasonable for a strongly hydrogen bonded carbonyl group,[9] the presence of which is also born out by ^{13}C NMR data. Selective irradiation of the δ 11.7 proton produced a marked change at C$_t$ (δ 142) from a complicated multiplet in the fully coupled spectrum to an overlapping doublet of doublets resulting from the two residual meta couplings in the aromatic ring. Consequently the hydrogen must be attached to a nitrogen to be close enough to couple into an aromatic system. This is only the second example of a $^2J_{C-N-H}$ coupling in amines, the other being in an aminotriazine,[5] suggesting the hydrogen bonding is very strong. A nuclear Overhauser effect difference spectroscopy (NOEDS) experiment showed C$_t$ (δ 142), C$_u$ (δ 175), and C$_w$ (δ 185), to be in the proximity of the δ 11.5 proton, further supporting the N–H assignment as well as those of C$_u$ and C$_w$.

To complete the assignment of the carbons of interest, C$_v$ (δ 183) was identified by selectively irradiating the methyls and thus simplifying the farthest downfield ^{13}C resonances of C$_u$ (δ 175, d), C$_v$ (δ 183, s) and C$_w$ (δ 185, d). The doublets probably arise from coupling to the vinylic proton for both carbons C$_u$ and C$_w$. The sharp singlet at δ 183 corresponds to C$_v$ with no nearby protons with which to couple. The NOEDS experiment described above supports this assignment. C$_v$ is a sharp singlet in the

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(7) Mushkalo, I. L.; Turova, L. S.; Murovanaya, N. V. *Dopov. Akad. Nauk. Ukr. RSR, Ser B*: *Geol., Khim Biol. Nauki* **1979**, 1022–5; Chem. Abstr. **1980**, *92* 182554p.

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Table II. ^{13}C NMR Data for 8[a]

δ	J_{C-H} (mult)	$J_{long-range}$ (mult)	assignment[b]
23.3	129.5 (q)	4.5 (q)	n
27.2	129.5 (q)	5.2 (q)	n
48.0		<2 (m)	o
53.8		<2 (m)	o
88.8	164.5 (d)		p
110.5	162.3 (d)	8.2 (d)	q
121.2	158.5 (d)	7.4 (d)	r
122.3	158.5 (d)	?	r
122.5	158.5 (d)	?	r
122.7	158.5 (d)	?	r
127.5	160.8 (d)	?	r
127.7	160.8 (d)	?	r
128.0	160.8 (d)	?	r
138.4		? (m)	s
142.2		6 & 6 & ? (m) d of d of d	t
148.6		? (m)	s
152.8		? (m)	s
174.6		1.5 & ~2 (m) d of hep	u
182.6		~2 (m) heptet	v
184.5		1.5 (d)	w

[a] $CDCl_3$ solution. [b] See structure 8.

selective methyl decoupling experiment, which is consistent with a cis relationship between C_v and the vinylic proton.[5] The sizable downfield shift of the N–H due to hydrogen bonding and the NOE between the N–H and carbonyl carbon are also supportive of the cis conformation. Spectra of model compounds[10] suggest that C_q absorbs at δ 110 and the proton at δ 7.8 is ortho to the imino nitrogen.

A possible mechanism for the formation of 8 is shown in Scheme I. Oxidation of the 2-methyl in 1 to an aldehyde is similar to the photooxidation of methylenes observed by Kanaoka et al.; however, they did not observe the oxidation of 2-methyl-3*H*-indoles under their conditions.[8a,b] Aldehydes have been formed from 2-methylindoles in this way.[8c,d] The aldehyde undergoes an aldol-like condensation with another molecule of 1, and the dimer is oxidized to the fully conjugated system, which rearranges to the ketone 8.

Experimental Section

^{1}H NMR and ^{13}C NMR spectra were taken on Bruker 200-MHz Supercon (FT) and Bruker UM 360-MHz spectrometers in $CDCl_3$ solution, using Me_4Si as an internal standard. Mass spectra were determined on an AEI MS 902 instrument.

12,12,12a,14,14-Pentamethyl-6*H*,12*H*,12a*H*,14*H*-pyrimido[1,6-*a*:3,4-*a*′]diindole (6). A mixture of methylene iodide (25 g) and 1 (30 g) was stirred with pulverized KOH (16 g) for 18 h at 80 °C under nitrogen. The KOH was filtered off and the reaction mixture chromatographed on silica gel (CH_2Cl_2 solvent). Compound **6** was obtained in the early fractions, while 1 (5 g impure) was found in the last fraction that was eluted with 1–2% methanol. Compound **6** was recrystallized from ethanol: 3.42 g (11%); mp 124–127 °C; mass spectrum, *m*/*e* (relative intensity) 330 (29), 315 (100), 300 (6), 285 (15); UV (95% EtOH) 280 nm (ϵ 23 000), 244 (12 000), 206 (36 000); IR (CCl_4 solvent) 1605 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.24 (t of d, J = 8, 1.3 Hz, 1 H), 7.11 (d of t, J = 8, 1.3 Hz, 2), 7.08 (t of d, J = 8, 1.3 Hz, 1), 6.86 (t of d, J = 8, 0.9 Hz, 1), 6.84 (t of d, J = 8, 0.9 Hz, 1), 6.73 (d of t, J = 8, 0.9 Hz, 1), 6.71 (d of t, J = 8, 0.9 Hz, 1), 5.36 (d, J = 12 Hz, 1), 4.71 (d, J = 12 Hz, 1), 4.71 (s, 1), 1.51 (s, 3), 1.49 (s, 3), 1.38 (s, 3), 1.30 (s, 3), 1.07 (s, 3); see Table I for ^{13}C NMR data; exact mass calcd for $C_{23}H_{26}N_2$ 330.2096, found 330.2084 (M^+).

(3,3-Dimethyl-2-indolinylidene)methyl 3,3-Dimethyl-3*H*-indol-2-yl Ketone (8). Oxygen was bubbled into a suspension of K_2CO_3 (3.0 g) in 1 (25.0 g) and benzoyl peroxide (1.0 g) at 140 °C for 4 h. After filtration, the reaction mixture was chromatographed on silica gel (CH_2Cl_2 solvent). The early fractions were recrystallized from ethanol to give 6.96 g (27%): mp 203–204 °C; mass spectrum, *m*/*e* (relative intensity) 330 (18), 315 (8), 186 (16), 171 (6), 159 (5), 145 (91), 144 (100), 130 (41), 115 (24), 77 (17); UV (95% EtOH) 415 nm (ϵ 25 000), 275 (11 600), 247 (11 400), 243 (10 800), 206 (31 000); IR (thin film) 3240 (NH), 1600 (C=O) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 11.5 (br, 1), 7.79 (m, 1), 7.44–6.98 (m, 7), 6.69 (s, 1), 1.61 (s, 6), 1.50 (s, 6); see Table II for ^{13}C NMR data; exact mass calcd for $C_{22}H_{22}N_2O$ 330.1732, found 330.1727 (M^+).

Acknowledgment. We thank The Pennsylvania State University for their financial support, Dr. R. Minard for taking the mass spectrum, and Dr. L. Jackman, Dr. R. Olofson, Dr. S. Benkovic, and Dr. J. Weiss for their very helpful discussions.

Registry No. 1, 1640-39-7; **6**, 87697-25-4; **8**, 87697-26-5; methylene iodide, 75-11-6.

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[10] Sadtler Research Laboratories, Inc. Spectra, ^{1}H NMR 9761M and 16082M; ^{13}C NMR 3167 and 3615.

Facile One-Pot Synthesis of Bromo Homoallyl Alcohols and 1,3-Keto Acetates via Allyltin Intermediates

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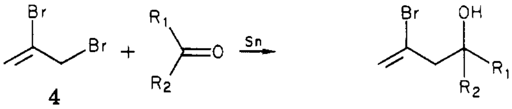
Received July 5, 1983

Allylation of carbonyl compounds by means of allyltin intermediates has been the subject of current interest, and we have previously disclosed that the reaction is extensively accelerated by the presence of water.[1]

Bromo homoallyl alcohols 1, useful intermediates for α-methylene γ-lactones, can be prepared from [1-(trimethylsilyl)vinyl]magnesium bromide and epoxy compounds as reported first by Matsuda[2] and later by Stille et al.[3] More recently, Trost et al. have reported the preparation from 2-bromo-3-(trimethylsilyl)propene.[4] These papers prompted us to describe here our own synthetic method of 1 by the allyltin method. Furthermore, acetonylation of the carbonyl compounds leading to 1,3-keto acetates 3 will also be described.

When 2,3-dibromoprop-1-ene (4) was subjected to the reaction with carbonyl compounds in the presence of metallic tin in a 1:1 ether–water mixture (eq 1), 1 was obtained in good yields as shown in Table I. The notable features of the present method consist of the following aspects. (1) The reaction is a one-pot synthesis, and yields are high. (2) Operations are simple and do not need an inert atmosphere. (3) 2,3-Dibromoprop-1-ene is readily or commercially available. (4) Masked aldehydes such as acetals or ketals are employable without deblocking pro-



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(1)

1a, $R_1 = n\text{-}C_4H_9$; R_2 = H
b, $R_1 = PhS(CH_2)_2$; R_2 = H
c, R_1 = Ph; R_2 = H
d, $R_1 = EtO_2C(CH_2)_8$; R_2 = H
e, $R_1 = NC(CH_2)_2$; R_2 = H
f, $R_1,R_2 = (CH_2)_5$

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