nmr (CCl_4) δ 8.09 (s, 1, NH), 3.70–3.25 (broad mound, 1, CH), 1.60–1.30 (m, 11, CH_2 and CH), 1.18 (d, J = 6.5 Hz, 3, CH_3), and 1.08 (s, 3, CH_3).

Anal. Calcd for $C_{11}H_{19}NO$: C, 72.88; H, 10.56; N, 7.72. Found: C, 72.76; H, 10.53; N, 7.84.

Registry No.—*cis*-**6**, 34387-94-5; *trans*-**6**, 34387-95-6; **7**, 34387-96-7; **8**, 34387-97-8; **9**, 34387-98-9; **10**, 34387-99-0; **11**, 34388-00-6; **14**, 34388-01-7; **15**, 34388-02-8; **17**, 34388-03-9; *cis*-**18**, 34388-04-0; *trans*-**18**, 34388-05-1; **19**, 34388-06-2.

Intramolecular Cyclization of *N*-Alkyl-3,3′,4,4′-tetrahydro-1,1′-biisoquinolinium Salts

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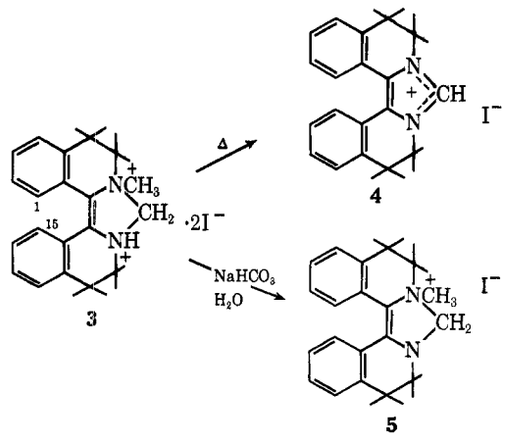
The preparation and chemiluminescence of 2,2′-dimethyl-3,3′,4,4′-tetrahydro-1,1′-biisoquinolinium diiodide (**1**) have recently been described.[1] Although 3,3′,4,4′-tetrahydro-1,1′-biisoquinoline (**2**) very readily forms a monomethiodide, its conversion to the dimethiodide requires more drastic reaction conditions. As a consequence, a competing, intramolecular cyclization, which will be described in this note, also occurs.

When **2** and excess methyl iodide were refluxed in acetonitrile for 18 hr, in addition to **1** (52% yield), there was recovered in approximately 10% yield an isomeric compound whose ^1H nmr spectrum and chemical behavior are consistent with those expected for 7-methyl-5,6,10,11-tetrahydro-8*H*-diisoquino[1,2-*c*:2′,1′-*e*]imidazolidiinium diiodide (**3**). The proton count on **3** indicated only one methyl group. The nmr spectrum was characterized by two other significant changes. One was the appearance of an AB quartet, which, although it is the chemical shift region assigned to 3 and 4 protons in 1,2-dihydroisoquinoline derivatives,[2] is due to the methylene in the imidazole ring, split because of the adjacent asymmetric nitrogen atom in the fused ring system. The other is a marked downfield shift of two of the aromatic ring protons, ascribed to an overlap of the 1,15 protons in the rigid, fused ring system of **3**.



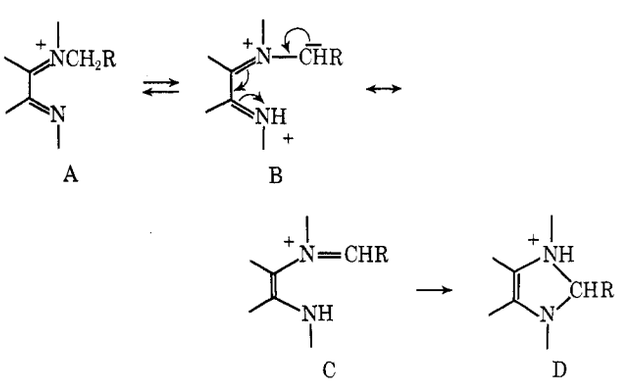
In **1**, rotation about the 1,1′ bond can still occur and the 8,8′ protons do not overlap.

When **3** was heated to 165–170°, both loss of methyl iodide and oxidation occurred to give 5,6,10,11-tetrahydrodiisoquino[1,2-*c*:2′,1′-*e*]imidazolium iodide (**4**). Its ^1H nmr spectrum (see Experimental Section) reflected these changes. Heating an aqueous solution of **3** with sodium bicarbonate yielded the monoquaternary salt **5**, whose nmr spectrum, except for one less proton, was the same as that for **3**.

It appears that the cyclization which leads to **3** can occur in either of two ways. (1) The monomethiodide of the 1,1′-biisoquinoline cyclizes intramolecularly and the resulting product is further methylated. (2) The dimethiodide **1** is first formed and then undergoes cyclization. There is evidence for both routes. For example, when preformed monomethiodide was refluxed in dry acetonitrile for various lengths of time, the proton nmr spectra on the recovered mixture of salts showed decreasing methyl signals, increasing signals characteristic of a methylene group, and the downfield shift of two aromatic protons as a consequence of the 1,15 proton overlap which develops as the fused ring system forms. Similarly, when 2-benzyl-3,3′,4,4′-tetrahydro-1,1′-biisoquinolinium bromide was refluxed in acetonitrile, the benzyl methylene signal disappeared; in addition the generally complicated nmr spectrum of the starting compound (because of unsymmetrical substitution) became simpler and more symmetrical as the cyclization occurred. One of the products recovered from this latter reaction was the 8-phenyl-5,6,10,11-tetrahydrodiisoquino[1,2-*c*:2′,1′-*e*]imidazolium salt (as the perchlorate).

When purified dimethiodide **1** was refluxed in methanol, ethanol, or 2-propanol, the dark red-orange colored solutions gradually faded. Although the recovered pale yellow product was a difficultly separable mixture, one compound isolated and identified was **5**.

2-Benzyl-1,1′-biisoquinolinium bromide remains essentially unchanged under conditions which effect the complete loss of the corresponding 3,3′,4,4′-tetrahydro compound. This fact suggests that the greater basicity of the 3,4-dihydroisoquinoline moiety over that of the unreduced isoquinoline is an important factor in the cyclization process. One possible route for cyclization of a monoalkyl salt is depicted in the following simplified scheme.



Abstraction of a proton from the alkyl group on A leads to the ylide B, which through charge redistribution gives the immonium salt C. Intramolecular addition of the nucleophile to the latter in a manner

(1) R. A. Henry and C. A. Heller, *J. Luminescence*, **4**, 105 (1971).

(2) J. L. Neumeyer, M. McCarthy, K. K. Weinhardt, and P. L. Levins, *J. Org. Chem.*, **33**, 2890 (1968).

analogous to the formation of pseudobases from isoquinolinium salts furnishes D. Although proton abstraction from A has been written here as an intramolecular process, it could occur equally well as an intermolecular one. Cyclization by a similar sequence would then give unprotonated D. Only the cis configuration has been shown for C, since it would be the form to cyclize; any trans isomer would through the equilibrium revert to B and ultimately back to *cis*-C.

This reaction scheme is similar to one proposed for the reduction of bisquaternary 1,1′-biisoquinolinium salts by base to air-reactive olefins.[1,3]

Experimental Section

7-Methyl-5,6,10,11-tetrahydro-8*H*-diisoquino[1,2-*c*:2′,1′-*e*]imidazolidiinium Diiodide.—3,3′,4,4′-Tetrahydro-1,1′-biisoquinoline[1] (**2**, 5.2 g, 0.02 mol) and 8 ml of methyl iodide were refluxed in 100 ml of acetonitrile under a 0° condenser for 18 hr; after the solution had been chilled to 5°, the previously described,[1] dark red dimethiodide was removed, yield 5.7 g (52%).

Addition of ether to the above acetonitrile mother liquors and cooling gave 2.2 g of a mixture of materials. One of these (**3**), comprising about half of the mixture, was less soluble in 80% ethanol than either the monomethiodide or the dimethiodide (both of which were also present) and after several recrystallizations was obtained as pale purple needles with an orange-red hue. The melting point was very indefinite; partial melting, then resolidification at 160–165° with a change in color from purple to pale yellow. (This new solid decomposed at 240–265°.) When plunged into a hot bath at 190–195°, it completely melted; if plunged into a bath at 165°, it partially melted before resolidifying (see following experiment). This compound in methanol did not chemiluminesce in air when made basic: nmr (DMSO-d_6) τ 6.56 (s, 3, $-NCH_3$), 6.4–7.7 (m, 7), 5.8–6.3 (m, 2, H_6, H_6), 5.22 (d, 1, J = 7.0 Hz, H_8), 4.75 (d, 1, J = 7.0 Hz, H_5), 2.57–2.97 (m, 6, H_2, H_3, H_4, H_{12}, H_{13}, H_{14}), 2.10–2.57 (m, 2, H_1, H_{15}).

Anal. Calcd for $C_{20}H_{22}N_2I_2$: C, 44.15; H, 4.07; N, 5.15; I, 46.64. Found: C, 44.38; H, 3.80; N, 5.10; I, 46.75.

When some of **3** was dissolved in a minimum volume of boiling water and treated with excess sodium bicarbonate, cooling gave a pale yellow solid **5**. Recrystallization from water furnished coarse yellow needles or prisms, mp 177–178° dec; an aqueous solution had an intense blue fluorescence. The ^1H nmr spectrum in DMSO-d_6 was almost identical with that for **3** except that the total proton count was one less. Surprisingly, a mass spectrum showed a small parent peak, m/e 416, with the base peak at m/e 290. The presence of a parent peak suggests opening of the imidazole ring by the nucleophile, iodide ion, to give an iodomethylene derivative.

Anal. Calcd for $C_{20}H_{21}N_2I$: C, 57.70; H, 5.08; N, 6.73; I, 30.49. Found: C, 57.85, 57.80; H, 5.03, 5.08; N, 6.62, 6.73; I, 30.64, 30.35.

The monopicrate from **5** melted at 170–171° after two recrystallizations from absolute ethanol.

Anal. Calcd for $C_{26}H_{23}N_5O_7$: N, 13.53. Found: N, 13.61.

Decomposition of 3.—When **3** was heated for 10 min at 155–165°, there was a 22% loss in weight (theory, 26% for one CH_3I); further heating caused very little more loss. Even when heated at 94° (25 mm) there was an 18% loss of weight in 5 days. The crude product decomposed at 240–260°. Recrystallization from 2-propanol gave yellow blades of 5,6,10,11-tetrahydroiisoquino[1,2-*c*:2′,1′-*e*]imidazolium iodide (**4**): mp 296–298° dec; nmr (DMSO-d_6) τ 6.83 (t, 4, J = 6.0 Hz, H_5, H_{11}), 5.67 (t, 4, J = 6.0 Hz, H_6, H_{10}), 2.5–2.9 (m, 6, H_2 H_3, H_4, H_{12}, H_{13}, H_{14}), 2.05–2.36 (m, 2, H_1, H_{15}), 0.70 (s, 1, CH in imidazolium ring, H_8).

Anal. Calcd for $C_{19}H_{17}N_2I$: C, 57.01; H, 4.28; N, 7.00; I, 31.71. Found: C, 56.80; H, 4.36; N, 6.93; I, 32.10.

The picrate decomposed at 241–242°.

Anal. Calcd for $C_{25}H_{19}N_5O_7$: N, 13.97. Found: N, 14.00.

Decomposition of 1 in Methanol.—A solution of 0.86 g of **1** in 100 ml of absolute methanol was refluxed for 26.5 hr while protected from moisture. The initially dark red-orange solution became pale orange in color. Cooling for 2 days at 5° deposited 0.36 g of starting compound, mp 208–209° dec; an additional 0.15 g was recovered by evaporating the mother liquors to 20 ml and cooling. Further evaporation to 4–5 ml and cooling gave a mixture of **1** and yellow needles, mp *ca.* 150°, which were separated mechanically. Additional amounts of the latter compound can be isolated by reworking the mother liquors. Recrystallization from 2-propanol gave pale yellow needles, mp 166–167°; the ^1H nmr indicated a mono-2-propanolate. A sample was desolvated at 70° (25 mm) for 24 hr prior to analysis. The nmr spectrum and the analytical data agree with those for **5**.

Anal. Calcd for $C_{20}H_{21}N_2I$: C, 57.70; H, 5.08; N, 6.73; I, 30.49. Found: C, 57.46; H, 5.05; N, 6.67; I, 30.56.

5,6,10,11-Tetrahydro-8-phenyldiisoquino[1,2-*c*:2′,1′-*e*]imidazolium Perchlorate.—2-Benzyl-3,3′,4,4′-tetrahydro-1,1′-biisoquinolinium bromide[1,4] (0.76 g) in 25 ml of acetonitrile was refluxed for 72 hr. The cooled solution was diluted with a large volume of ether to precipitate a hygroscopic, amorphous solid which was filtered and dried, mp 110–150°; the ^1H nmr spectrum in either $CDCl_3$ or DMSO-d_6 revealed the complete disappearance of the benzyl methylene signal. Since attempts to recrystallize this product were unsatisfactory, it was dissolved in a small volume of water, filtered from insoluble material, and converted to the perchlorate by adding excess sodium perchlorate. This salt, when dry, was easily recrystallized from 2-propanol. The cream-colored crystals turned dark at *ca.* 270° and decomposed at 283–285°: nmr ($CDCl_3$) τ 6.87 (t, 4, J = 6.5 Hz, H_5, H_{11}), 5.83 (t, 4, J = 6.5 Hz, H_6, H_{10}), 2.60 (s, 5, phenyl), 2.16–2.70 (m, 6, H_2, H_3, H_4, H_{12}, H_{13}, H_{14}), 1.94–2.16 (m, 2, H_1, H_{15}).

Anal. Calcd for $C_{25}H_{21}ClN_2O_4$: Cl, 7.89; N, 6.24. Found: Cl, 7.50; N, 6.11.

2-Benzyl-1,1′-biisoquinolinium Bromide.—1,1′-Biisoquinoline (0.6 g) and benzyl bromide (0.4 g) (equimolar ratio) in 10 ml of dry acetonitrile stood at room temperature for 6 days. The former compound gradually dissolved as benzylation occurred. Addition of ether precipitated the monoquaternary salt, which was recrystallized twice from 2-propanol as needles, mp 136–137° dec. The nmr spectrum indicated one propanol of crystallization. The desolvated compound decomposed at 195–197°: nmr (DMSO-d_6) τ 4.18 (s, 2, benzyl CH_2), 2.35–3.22 (complex multiplet, 9, benzyl C_6H_5, H_5', H_6', H_7', H_8'), 2.67 (d, 1, J = 7.0 Hz, H_5), 2.14 (t, 1, J = 7.0 Hz, H_6), 1.73 (t, 1, J = 7.0 Hz, H_7), 1.64 (d, 1, J = 5.5 Hz, H_4'), 1.37 (d, 1, J = 7.0 Hz, H_8), 1.11 (d, 1, J = 5.5 Hz, H_3'), 0.97 (d, 1, J = 7.0 Hz, H_4), 0.62 (d, 1, J = 7.0 Hz, H_3).

Anal. Calcd for $C_{25}H_{19}BrN_2 \cdot C_3H_8O$: C, 68.99; H, 5.58; Br, 16.39; N, 5.75. Found: C, 69.11; H, 5.40; Br, 16.55; N, 5.77.

Refluxing some of the desolvated salt in dry acetonitrile for 72 hr caused no change; the recovered product melted at 194.5–196° and its nmr spectrum was the same as that of the starting material.

Registry No.—**1**, 34414-11-4; **3**, 34410-07-6; **4**, 34414-12-5; **4** monopicrate, 34414-13-6; **5**, 34414-14-7; **5** monopicrate, 34414-15-8; 5,6,10,11-tetrahydro-8-phenyldiisoquino[1,2-*c*:2′,1′-*e*]imidazolium perchlorate, 34414-16-9; 2-benzyl-1,1′-biisoquinolinium bromide, 34414-17-0.

(3) C. A. Heller and R. A. Henry, unpublished work.

(4) Nmr (DMSO-d_6) τ 6.90 (t, 2, J = 7.5 Hz, H_4'), 6.25–6.72 (m, 2, H_{4eq}, H_{4ax}), 6.10 (t, 1, J = 10.0 Hz, H_{3ax}), 5.82 (doubled triplet, 2, J_t = 7.5 Hz, J_d = 3.0 Hz, H_3'), 5.60 (m, 1, H_{3eq}), 4.55 (s, 2, benzyl CH_2), 2.08–2.70 (m, 5, benzyl C_6H_5).

An Improved Synthesis of *N*-Amino Imides

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Depending upon reaction conditions, the reaction of five-membered ring anhydrides with hydrazine can proceed with formation of the cyclic hydrazide, the bis-