

TABLE II  
CHEMICAL SHIFTS OF THE *N*-METHYL GROUPS OF  
2-SUBSTITUTED AND 2,6-DISUBSTITUTED  
*N*-METHYLPYRIDINIUM IODIDES IN DMSO<sup>a,b</sup>

Substituent	$\tau$	Substituent	$\tau$
H	5.51	Cl	5.55
CH <sub>3</sub>	5.63	Br	5.50
C <sub>2</sub> H <sub>5</sub>	5.58	CN	5.33
NH <sub>2</sub>	6.13	2'-C <sub>6</sub> H <sub>4</sub> N	5.63
NHCOCH <sub>3</sub>	5.70	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub>	5.55
CO <sub>2</sub> CH <sub>3</sub>	5.35	2,6-diCH <sub>3</sub>	5.88
		2-CH <sub>3</sub> -6-NH <sub>2</sub>	6.31

<sup>a</sup> The DMSO satellite peak at  $\tau$  6.23 served as a reference standard. <sup>b</sup> Value for 2-methylquinoline is  $\tau$  5.50.

Results for pyridine, 2-aminopyridine, and all alkylated compounds except 2-methylquinoline were obtained by a method reported earlier.<sup>16</sup> This method is based upon a determination of the relative amounts of *N*-methylated products after all the methyl iodide limiting reagent had been consumed.

Rate constant ratios for all other compounds were calculated from product ratios using eq 1 or from product concentrations using eq 2. In order to determine product concentrations, mesitylene (ring signals) was employed as an internal standard. Chemical shifts for the *N*-methyl peaks are listed in Table II.

**Registry No.**—Methyl iodide, 74-88-4; 1,6-dimethyl-2-aminopyridinium iodide, 32654-50-5; 2-methyl-6-trimethylammonio-pyridine iodide, 34314-77-7.

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## Formation of Triazabenzacephenanthrylium Salts. Their Solvolysis and Borohydride Reduction

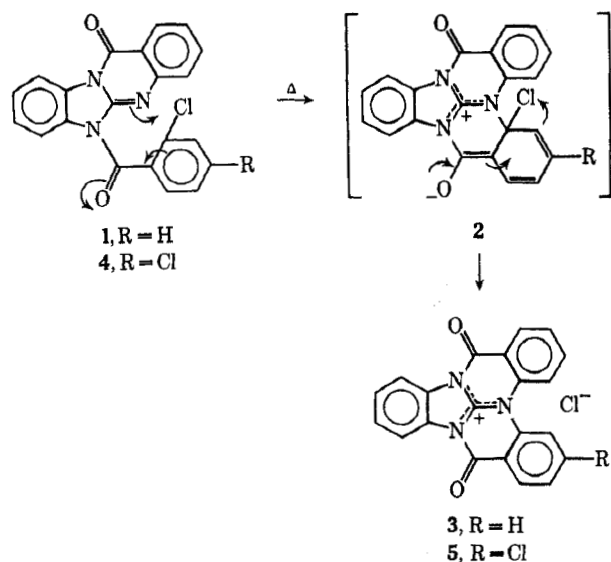
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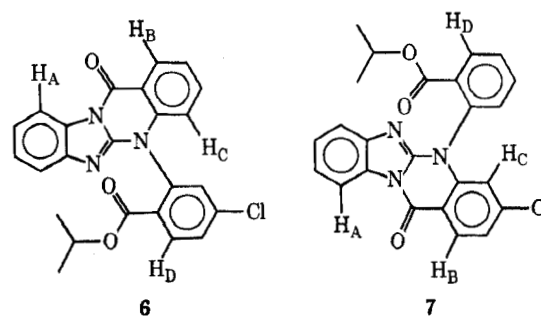
The preparation<sup>1</sup> of a series of benzimidazo[2,1-*b*]quinazolin-12-ones possessing potent immunosuppressive activity<sup>2</sup> has been described. A novel rearrangement of 6-(2-chlorobenzoyl)benzimidazo[2,1-*b*]quinazolin-12-ones is now discussed, together with the solvolytic cleavage of the resulting ionic pentacyclic salts. Borohydride reduction of this type of salt leads to unusual products containing the CH(N<)<sub>3</sub> unit.

The chlorobenzoyl compound 1 undergoes pyrolytic rearrangement which, we suggest, involves intermediate 2. The initial rearrangement product 3 was not identified directly but by means of the derivatives described later. Similarly, the corresponding 2,4-dichlorobenzoyl derivative 4 gives the ionic chloride 5.



The solvolysis of 5 on refluxing with isopropyl alcohol will be discussed first since this is the only case in which both of the two possible isomeric products were actually isolated in the pure state.

These isomers analyzed as C<sub>24</sub>H<sub>18</sub>N<sub>3</sub>O<sub>3</sub>Cl; and this, together with the infrared and nmr spectra, is consistent for the isopropyl esters 6 and 7.



Inspection of Dreiding models of structures of type 8 (Figure 1) reveals that the likely conformation is as shown. The plane of the aroyl benzene ring is approximately at right angles to the plane of the tetracyclic system, while the position of the aroyl carbonyl group is, as will be seen later, dependent on the nature of R.

The nmr spectra of 6 and 7 each exhibit signals integrating for three protons between 8.9 and 8.4 ppm. These are due to H<sub>A</sub>, H<sub>B</sub>,<sup>3</sup> and presumably H<sub>D</sub> in the deshielding zones of the two carbonyl groups, with the aroyl carbonyl function in the position shown in the diagram. Also, both spectra contain a single proton signal, in the vicinity of 7 ppm; this arises from H<sub>C</sub> which is shielded by the aroyl benzene ring. In the case of 6 this signal is in the form of a broad doublet ( $J = 7.5$  cps) centered at 6.99 ppm; each of the peaks was widened by m and p coupling. In the spectrum of 7, however, a narrowly spaced doublet ( $J = 1.7$  cps) is evident (very small p coupling accounts for the sharpness of the doublet).

It was hoped that mass spectroscopy might confirm these assignments, but the mass spectra of 6 and 7

(1) W. H. W. Lunn and R. W. Harper, *J. Heterocycl. Chem.*, **8**, 141 (1971).

(2) W. H. W. Lunn and R. W. Harper, *J. Med. Chem.*, **14**, 1069 (1971).

(3) W. H. W. Lunn and R. W. Harper, *Tetrahedron*, **27**, 2079 (1971).

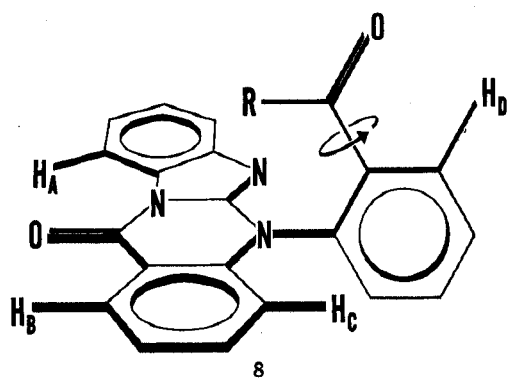
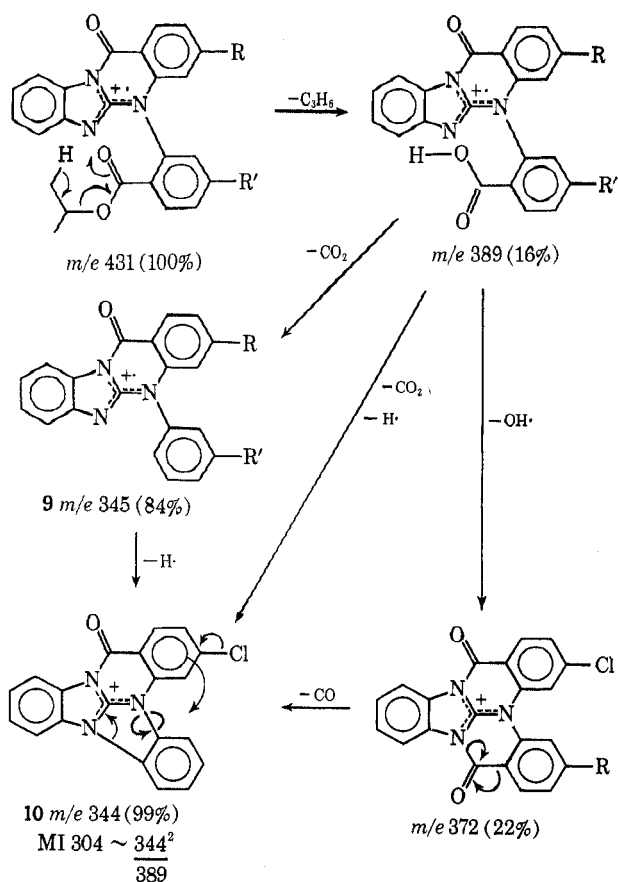


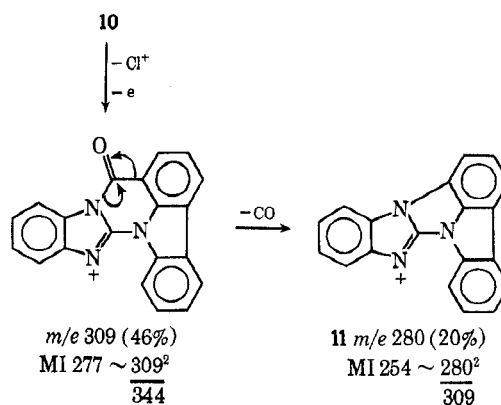
Figure 1.

proved to be extremely similar. This situation is quite reasonable if we presume that the first cleavage to occur with each compound is, predominantly, the well-established loss of alkoxide from esters.<sup>4</sup> This is probably the case since anchimeric assistance from the tetracyclic nucleus would give rise to the relatively stable common ion, namely, the cation of **5**, which would then result in similar spectra for both esters.

Apart from the parent peaks, the most intense peaks in the mass spectra of these two compounds lie at  $m/e$  345 and 344 which, we suggest, are due to ions **9** and **10**. These would be expected to be rather stable but would give rise to **11**,  $m/e$  280, as shown.



(4) H. Budzikiewicz, C. Djerassi, and D. H. Williams, "Interpretation of Mass Spectra of Organic Compounds," Holden-Day, San Francisco, Calif., 1964, pp 11-14.



MI = metastable ion

It is significant that the peaks corresponding to those cleavages leading to ions **5**, **9**, **10**, and **11** are important in the mass spectra of **12-17** inclusively.

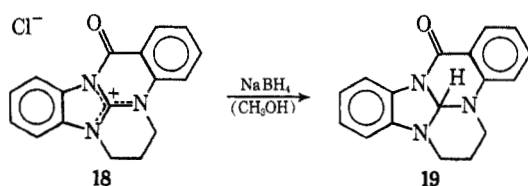
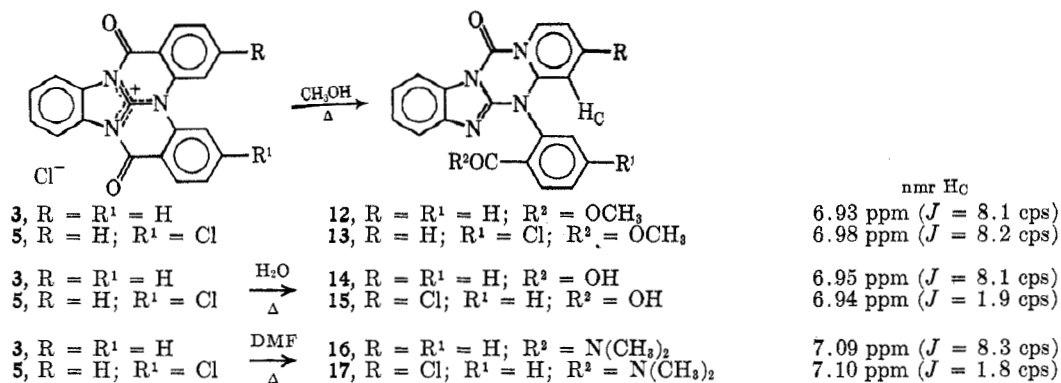
On heating in methanol, **3** gave methyl ester **12**, while **13** was isolated from **5**. When refluxed in water, **3** and **5** provided carboxylic acids **14** and **15**, respectively, the latter being a member of the series isomeric with **13**. Similarly, heating **3** and **5** in dimethylformamide led to the formation of **16** and **17**, respectively.

There is an interesting conformational difference between the dimethyl amides **16** and **17** and the rest of the rearrangement products. The nmr spectra of the four esters and the carboxylic acids all exhibit signals for three protons between 8.9 and 8.4 ppm, these arising from the protons  $H_A$ ,  $H_B$ , and  $H_D$  with the conformation shown in **8**. However, there are signals for only two protons in this region in the nmr spectra of the two amides. Since  $H_A$  and  $H_B$  are fixed in relation to the quinazolone carbonyl function, we must assume that in the amides the aroyl carbonyl group is not directed toward  $H_D$  as it is in the other compounds. The reason for this different conformation is probably largely steric hindrance.

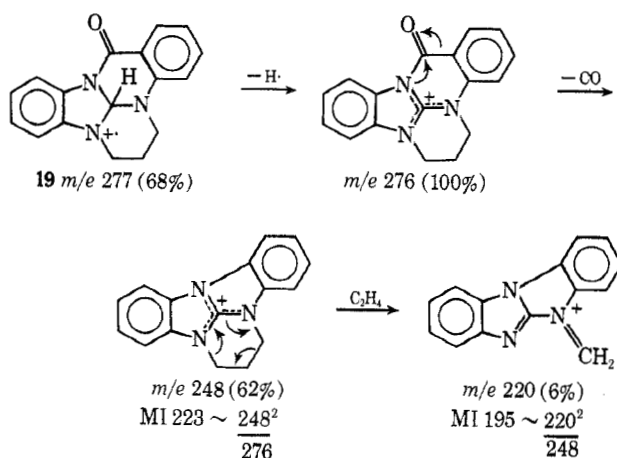
Reduction of the benzimidazo[2,1-*b*]azaquinolinium-12-one nucleus was then investigated. Treatment of **18**<sup>1</sup> with sodium borohydride in methanol gave a compound with an analysis indicating the addition of a hydrogen atom and loss of chloride; and the mass 277 of the parent ion, in its mass spectrum, confirmed this.

The outstanding features of the nmr spectrum ( $CDCl_2$ ) of the reduction product are two single-proton quartets centered at 8.05 and 7.88 ppm and a sharp single-proton signal at 5.59 ppm. Two low-field quartets are found in the nmr spectra of benzimidazo[2,1-*b*]azaquinolizin-12-ones,<sup>3</sup> albeit at somewhat lower field, about 8.6 and 8.5 ppm, and have been shown to arise from H-1 and H-10 (see structure **21**), which are in the deshielding zone of the carbonyl group. Thus, it would seem that the pentacyclic nucleus has been retained on reduction, but the completely planar character of the system may have been lost. These various data conform to structure **19**, the sharp uniproton signal being due to the new NNCHN unit.

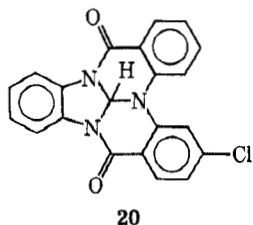
Details of the mass spectrum of **19** further support this structure. The most intense peak lies at  $m/e$  276, with other strong peaks at  $m/e$  values of 277, 248,



and 220. These could be accounted for very well by the following processes.



In a similar fashion the ionic chloride **5** was reduced with sodium borohydride to **20**.

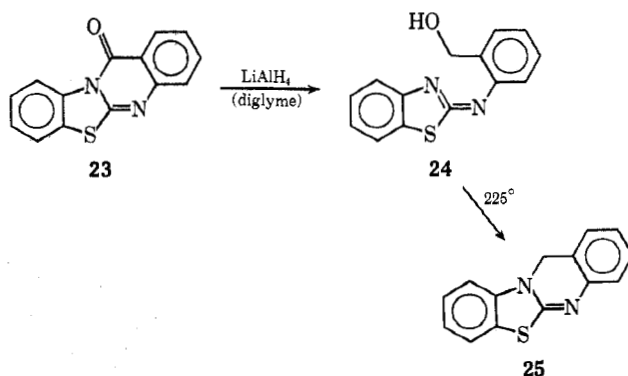
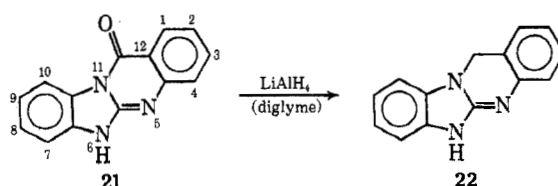


The NNCHN proton of **20** gives rise to a sharp nmr signal at 7.01 ppm, and the principal peaks in the mass spectrum of **20** can be assigned to the anticipated cleavages: *m/e* 372 (*M* - H), 344 (*M* - H - CO), 337 (*M* - H - Cl), and 309 (*M* - H - CO - Cl).

At this point we will describe some reductions of the related, but nonionic tetracyclic compounds **21** and **23**.

Compound **21** was reduced by lithium aluminum hydride to the deoxy compound **22**, whereas **23** afforded the hydroxy compound **24** under the same conditions. Pyrolysis of **24** produced the deoxy compound

**25**. The position of the C=N double bond shown in **22** is presumed because of the similarity of the ultra-violet spectra of **22** and **25**.



The action of zinc on **23** in refluxing acetic acid resulted in cleavage and rearrangement to give 2-(2-aminophenyl)benzothiazole (**26**), identified as its *N*-acetyl derivative. It is suggested that intermediate **27**, formed first, is cleaved to **28**, which is reduced to **29**. Hydrolysis of **29** would lead to loss of the NCH<sub>2</sub>N methylene group as formaldehyde and dehydration of the resulting product would afford **26**.

The corresponding benzimidazo compound **21** proved resistant to this treatment and was recovered unchanged.

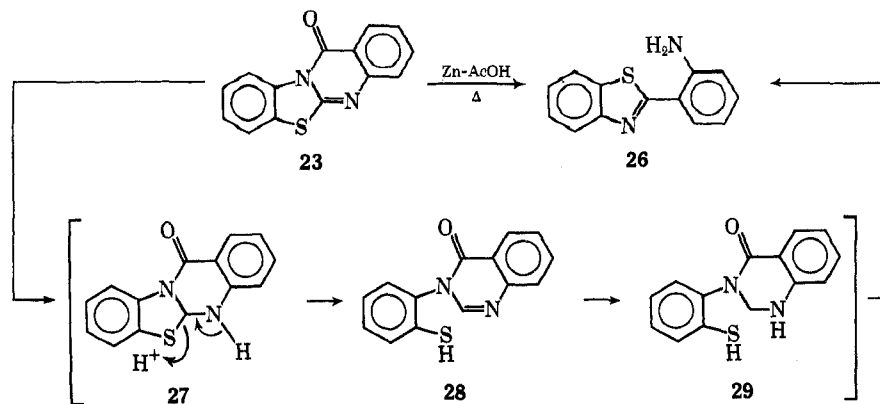
### Experimental Section

Unless otherwise stated, all the nmr spectra were run in a solution in trifluoroacetic acid-*d*<sub>4</sub>.

**Pyrolysis of 6-(2-Chlorobenzoyl)benzimidazo[2,1-*b*]quinazolin-12-one (1) and the 6-(2,4-Dichloro) Analog (4).**—Chlorobenzoyl compound **1**<sup>1</sup> (5.5 g) was heated at 245° for 50 min. It slowly melted; then, after about 20 min, it commenced to resolidify. Solidification was complete after 40 min. The material, crude **3**, was collected and ground in a mortar and pestle in preparation for further reactions.

Dichlorobenzoyl compound **4**<sup>1</sup> was treated as described above to yield crude **5**.

**Treatment of 6-Chloro-9,14-dioxo-9*H*,14*H*-4*b*,9*a*,13*b*-triazabenz[*a,e*]acephenanthrylium Chloride (5) with Isopropyl Alcohol.**—Crude **5** (1.0 g) was refluxed with stirring in dry *i*-PrOH (20 ml) for 14 hr; the mixture was allowed to cool and then was evapo-



rated to dryness under reduced pressure. The residue was slurried in  $\text{CH}_2\text{Cl}_2$  (10 ml) and filtered. Evaporation to dryness under reduced pressure and fractional recrystallization of the residue from  $\text{CHCl}_3$ -*i*-PrOH gave two crops of **7** (265 and 37 mg), mp 278–279° and 277–279°, respectively.

*Anal.* Calcd for  $\text{C}_{24}\text{H}_{18}\text{N}_4\text{O}_3\text{Cl}$ : C, 66.74; H, 4.20; N, 9.73; Cl, 8.21. Found: C, 66.88; H, 4.12; N, 9.98; Cl, 8.41.

The mother liquors afforded two crops of **6** (293 and 69 mg), mp 188–190° and 186–188°, respectively.

*Anal.* Calcd for  $\text{C}_{24}\text{H}_{18}\text{N}_4\text{O}_3\text{Cl}$ : C, 66.74; H, 4.20; N, 9.73; Cl, 8.21. Found: C, 66.93; H, 4.48; N, 9.87; Cl, 8.09.

**5-(2-Carbomethoxyphenyl)benzimidazo[2,1-*b*]quinazolin-12(5H)-one (12).**—Crude **3** (1.0 g) was refluxed with stirring in dry  $\text{CH}_3\text{OH}$  (20 ml) for 14 hr and then treated as **5** above. Recrystallization from the same solvent mixture gave **12** (278 mg), mp 232–234°.

*Anal.* Calcd for  $\text{C}_{22}\text{H}_{15}\text{N}_3\text{O}_3$ : C, 71.53; H, 4.09; N, 11.38. Found: C, 71.63; H, 4.08; N, 11.05.

**5-(5-Chloro-2-carbomethoxyphenyl)benzimidazo[2,1-*b*]quinazolin-12(5H)-one (13).**—Crude **5** (1.0 g) was refluxed in dry  $\text{CH}_3\text{OH}$  (20 ml) for 14 hr, allowed to cool, and evaporated to dryness under reduced pressure. The residue was slurried in  $(\text{CH}_3)_2\text{CO}$  (10 ml) and filtered. Evaporation of the filtrate under reduced pressure yielded a solid which, after three recrystallizations from  $\text{CH}_3\text{OH}$ -*i*-PrOH, gave **13** (273 mg), mp 208–210°.

*Anal.* Calcd for  $\text{C}_{22}\text{H}_{14}\text{N}_3\text{O}_3\text{Cl}$ : C, 65.43; H, 3.49; N, 10.41; Cl, 8.78. Found: C, 65.27; H, 3.74; N, 10.14; Cl, 8.99.

**5-(2-Carboxyphenyl)benzimidazo[2,1-*b*]quinazolin-12(5H)-one (14).**—Crude **3** (1.0 g) was refluxed in diglyme (5 ml) containing  $\text{H}_2\text{O}$  (1 ml) for 4 hr; the mixture was allowed to cool and then was evaporated to dryness under reduced pressure. The residue was slurried in DMF (6 ml) and filtered. Concentration of the filtrate and addition of  $\text{CH}_3\text{OH}$  provided crystals from which pure **14** (149 mg), mp 287–289°, was obtained by one recrystallization from DMF- $\text{CH}_3\text{OH}$ .

*Anal.* Calcd for  $\text{C}_{21}\text{H}_{13}\text{N}_3\text{O}_3$ : C, 70.99; H, 3.69; N, 11.82. Found: C, 70.70; H, 3.64; N, 11.62.

**3-Chloro-5-(2-carboxyphenyl)benzimidazo[2,1-*b*]quinazolin-12(5H)-one (15).**—Crude **5** (1.0 g) was refluxed in diglyme (5 ml) containing  $\text{H}_2\text{O}$  (1 ml) for 4 hr. The mixture was allowed to cool and was evaporated to dryness under reduced pressure. Pure **15** (374 mg), mp 302–304°, was obtained after recrystallization of the residue from DMF.

*Anal.* Calcd for  $\text{C}_{21}\text{H}_{12}\text{N}_3\text{O}_3\text{Cl}$ : C, 64.71; H, 3.10; N, 10.78; Cl, 9.10. Found: 63.26; H, 3.29; N, 10.38; Cl, 8.80.

**5-(2-Dimethylcarbamoylphenyl)benzimidazo[2,1-*b*]quinazolin-12(5H)-one (16).**—Crude **3** (1.0 g) was refluxed in dry DMF (7 ml) for 2 hr. The resulting solution was concentrated to about 3 ml and allowed to cool. Crude **16** crystallized and was collected by filtration. The filtrate was concentrated to about 1.5 ml and, after cooling, diluted with  $\text{C}_6\text{H}_6$  (10 ml). This led to the deposition of colorless plates of dimethylamine hydrochloride, which were removed by filtration. The mother liquors from the amine hydrochloride were evaporated to dryness under reduced pressure, and the residue, bulked with the above crystals of **16** and recrystallized from  $\text{CHCl}_3$ -*i*-PrOH, afforded pure **16** (216 mg), mp 255–256°.

*Anal.* Calcd for  $\text{C}_{23}\text{H}_{18}\text{N}_4\text{O}_2$ : C, 72.23; H, 4.74; N, 14.65. Found: C, 71.93; H, 4.49; N, 14.66.

**3-Chloro-5-(dimethylcarbamoylphenyl)benzimidazo[2,1-*b*]quinazolin-12(5H)-one (17).**—Crude **5** (1.0 g) was treated as described in the preparation of **16**. Recrystallization of crude **17** from DMF-*i*-PrOH provided pure material (470 mg), mp 216–218°.

*Anal.* Calcd for  $\text{C}_{23}\text{H}_{17}\text{N}_4\text{O}_2\text{Cl}$ : C, 66.26; H, 4.11; N, 13.44; Cl, 8.50. Found: C, 66.39; H, 4.11; N, 13.29; Cl, 8.74.

**2,3-Dihydro-1H,8H-3a,7b,12b-triazobenz[c]acephenanthrylene-8-one (19).**—Salt **18** (5.0 g) was stirred in aqueous  $\text{CH}_3\text{OH}$  (250 ml, 80%) and  $\text{NaBH}_4$  (0.83 g) was added portionwise, the temperature being maintained at 20–25° by intermittent cooling. The mixture effervesced, and a yellow material precipitated during the borohydride addition. The mixture was stirred at room temperature for 0.5 hr, cooled in an ice bath, and acidified to pH 1.5 with 10% HCl; then a solution of  $\text{Na}_2\text{CO}_3$  (3 g) in  $\text{H}_2\text{O}$  (300 ml) was added. The resulting suspension was filtered to give crude product **19** (4.1 g), mp 139–143°.

*Anal.* Calcd for  $\text{C}_{17}\text{H}_{13}\text{N}_3\text{O}$ : C, 73.63; H, 5.45; N, 15.15; O, 5.77. Found: C, 74.03; H, 5.53; N, 15.15; O, 6.10.

**6-Chloro-9H,14H-4b,9a,13b-triazadibenz[*a*,*c*]acephenanthrylene-9,14-dione (20).**—Finely divided ionic chloride **5** (1.0 g) was stirred in  $\text{CH}_3\text{OH}$  (5 ml) while  $\text{NaBH}_4$  (1.2 g) was added slowly in small portions; 0.5 hr after the addition, the mixture was processed as in the above borohydride reduction. Compound **20** (0.27 g), mp 205–207°, was obtained on recrystallization of the crude product from DMF.

*Anal.* Calcd for  $\text{C}_{21}\text{H}_{12}\text{N}_3\text{O}_2\text{Cl}$ : C, 67.47; H, 3.24; N, 11.24; Cl, 9.49. Found: C, 67.23; H, 2.98; N, 11.46; Cl, 9.69.

**Reduction of Benzimidazo[2,1-*b*]quinazolin-12(6H)-one (21) with  $\text{LiAlH}_4$ .**—The parent nitrogen tetracyclic **21** (7.05 g) was stirred, in an ice bath, in dry diglyme (250 ml);  $\text{LiAlH}_4$  (2.28 g) was added in portions. The mixture was stirred at room temperature for 24 hr and then was cooled in an ice-water bath while  $\text{H}_2\text{O}$  (4.6 ml) and then aqueous NaOH (4.0 ml, 10%), was added dropwise.  $\text{CHCl}_3$  (200 ml) was added to make the inorganic precipitate more granular; after stirring for 2 hr at room temperature, the mixture was filtered; the solid on the filter was washed with diglyme (50 ml). The filtrate was evaporated to dryness at reduced pressure, and the residue was recrystallized twice from  $\text{CHCl}_3$  to give **22** (2.03 g): mp 363–366° dec;  $\lambda_{\text{max}}^{\text{EtOH}}$  212 m $\mu$  ( $\epsilon$  29,000), 265 (10,800), 295 (20,400), and 304 (19,300).

*Anal.* Calcd for  $\text{C}_{14}\text{H}_{11}\text{N}_3$ : C, 75.99; H, 5.01; N, 18.99. Found: C, 75.83; H, 5.35; N, 19.20.

**Reduction of Benzothiazolo[2,3-*b*]quinazolin-12-one (23) with  $\text{LiAlH}_4$ .**—Quinazolinone **23** (7.56 g) was treated with  $\text{LiAlH}_4$  (1.70 g) in diglyme (150 ml) and processed in the manner described above. Recrystallization from  $\text{CHCl}_3$  provided **24** (0.83 g), mp 155–157°.

*Anal.* Calcd for  $\text{C}_{14}\text{H}_{12}\text{N}_3\text{OS}$ : C, 66.13; H, 3.96; N, 11.02; S, 12.61. Found: C, 65.82; H, 4.19; N, 11.06; S, 12.59.

**Benzothiazolo[2,3-*b*]quinazolinone (25).**—Benzimidazole **8** (1.50 g) was heated in a nitrogen atmosphere at 265° for 15 min. The resulting glass was twice recrystallized from  $(\text{CH}_3)_2\text{CO}$  at the temperature of a  $(\text{CH}_3)_2\text{CO}$ -solid  $\text{CO}_2$  bath to give pure **25** (0.28 g): mp 155–157°;  $\lambda_{\text{max}}^{\text{EtOH}}$  219 m $\mu$  ( $\epsilon$  27,000), 231 (25,300), 322 (19,300), 334 (20,700), and 350 (11,700).

*Anal.* Calcd for  $\text{C}_{14}\text{H}_{10}\text{N}_2\text{S}$ : C, 70.58; H, 4.23; N, 11.76; S, 13.43. Found: C, 70.32; H, 4.50; N, 11.63; S, 13.19.

**Reduction of Benzothiazolo[2,3-*b*]quinazolin-12-one (23) with Zinc in AcOH.**—The tetracyclic benzothiazoloquinazolinone (5.04

g) was refluxed vigorously with zinc dust (12 g) in glacial AcOH (70 ml) for 3.5 hr. After cooling to room temperature, the mixture was filtered, and the filtrate was evaporated under reduced pressure until the AcOH was removed. The residue, a thick oil containing some solids, was stirred with  $(\text{CH}_3)_2\text{CO}$  (150 ml) and filtered to remove the last traces of zinc acetate. The resulting solution was evaporated to dryness, leaving a thick oil (3.37 g).

A portion (1.0 g) of this oil was dissolved with  $\text{Ac}_2\text{O}$  (2 ml) in dry pyridine (7 ml). After 16 hr the mixture was poured into ice-water, and the resulting mixture was extracted with ether. The ether extract was dried over anhydrous  $\text{MgSO}_4$ , filtered, and evaporated under reduced pressure to give an oil which slowly crystallized on standing. Recrystallization from  $\text{CH}_3\text{OH}$  gave the product (0.53 g), mp 115–118°. Another recrystallization from  $\text{CH}_3\text{OH}$  provided an analytical sample, mp 120–121°, of 2-(2-acetylamino-phenyl)benzothiazole.

*Anal.* Calcd for  $\text{C}_{16}\text{H}_{12}\text{N}_2\text{OS}$ : C, 67.14; H, 4.51; N, 10.44; S, 11.95. Found: C, 67.05; H, 4.29; N, 10.22; S, 11.89.

**Registry No.**—3, 32612-56-9; 5, 32612-57-0; 6, 32827-40-0; 7, 32675-27-7; 12, 32722-78-4; 13, 32675-28-8; 14, 32722-79-5; 15, 32675-29-9; 16, 32675-30-2; 17, 32675-31-3; 19, 32675-32-4; 20, 32675-33-5; 22, 32675-34-6; 24, 32675-35-7; 25, 243-95-8; 2-(2-acetylamino-phenyl)benzothiazole, 32675-37-9.

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## Synthesis of 2-Methoxyallyl Chloride, Bromide, and Iodide by Two Independent Routes. The Reaction of *N*-Halosuccinimides with 2-Methoxypropene and the Pyrolysis of 1-Halo-2,2-dimethoxypropanes

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2-Methoxyallyl chloride (**3a**), the corresponding bromide **3b**, and iodide **3c** have been synthesized by two independent routes, and like the series of previously unknown 1-halo-2-methoxypropenes **4a-c** are now readily available for the first time. Our first route is the reaction of 2-methoxypropene (**1**) with the *N*-halosuccinimides (**2a-c**), especially *N*-chlorosuccinimide (**2a**) and *N*-bromosuccinimide (**2b**), to give a series of five products, namely, in the case of **2b**, the desired 2-methoxyallyl bromide (**3b**), 1-bromo-2-methoxypropene (**4b**), 1-bromo-2-methoxy-2-succinimidopropane (**7b**), as well as minor amounts of 1-bromo-2,2-dimethoxypropane (**5b**) and bromoacetone (**6b**). The reaction of *N*-bromosuccinimide (**2b**) and **1** is completely ionic, being insensitive to free-radical donors and inhibitors, and represents the first thoroughly studied example of the reaction of *N*-bromosuccinimide with an enol ether. A second entry into the 2-methoxyallyl system has been provided by the pyrolysis of 1-chloro-2,2-dimethoxypropane (**5a**) above 180° in the presence of Lewis acids. As in the reaction of 2-methoxypropene (**1**) with *N*-chlorosuccinimide (**2a**), not only 2-methoxyallyl chloride (**3a**) is formed in this pyrolysis but also the isomeric 1-chloro-2-methoxypropene (**4a**). Interestingly, even the ratio of **3a:4a** is similar to that obtained in the first route. Thermolysis of 1-bromo-2,2-dimethoxypropane (**5b**) proceeds in milder conditions and again produces **3b** as well as **4b**. 2-Methoxyallyl iodide (**3c**) is most readily available from the corresponding bromide **3b** by treatment with NaI in acetone.

2-Alkoxyallyl halides represent a simple class of bifunctional compounds which aside from having intrinsic interest deserve attention in synthesis. For example, we have used **3b** as a precursor in  $4 + 3 \rightarrow 7$  cycloadditions,<sup>1,2</sup> and one may easily envisage further applications, for example, in the realm of organometallic chemistry. Curiously, apart from a claim in a dated patent<sup>3</sup> which we have reinvestigated, there is to our knowledge nowhere in the chemical literature any mention of these simple compounds, be it as the parent, *i.e.*, **3a-c**, or more highly substituted, say as part of a

ring. As enol ethers<sup>4</sup> and alkyl halides the desired compounds are expected to be electron rich and electron deficient at the same time. Naturally, the confrontation of two such sites within one molecule will not only present problems in synthesis but also new properties, and it seemed to us from the very beginning that neither strongly acidic nor strongly basic conditions could be part of any satisfactory approach and that also some care would be required in working up any potentially interesting reaction mixture.

We now wish to record the synthesis of 2-methoxyallyl chloride (**3a**), bromide **3b**, and iodide **3c** by two efficient routes.

### Results

**A. Product Analysis and Structural Assignments.**—Generally, *N*-halosuccinimides (**2a-c**) have been found to react with 2-methoxypropene (**1**) to give succinimide and five other products as exemplified in Scheme I for the reaction with *N*-bromosuccinimide (**2b**).

(4) For reviews of enol ethers, see (a) H. Meerwein, "Methoden der Organischen Chemie," Houben-Weyl-Müller, Ed., Vol. 6/3, Thieme, Stuttgart, 1965, p 97; (b) F. Effenberger, *Angew. Chem., Int. Ed. Engl.*, **8**, 295 (1969); (c) M. F. Shostakovskii, A. V. Bogdanova, and G. I. Plotnikova, *Russ. Chem. Rev.*, **33**, 66 (1964); see also M. F. Shostakovskii, B. A. Trofimov, A. S. Atavin, and V. I. Lavrov, *ibid.*, **37**, 907 (1968).

(1) (a) H. M. R. Hoffmann, D. R. Joy, and A. K. Suter, *J. Chem. Soc. B*, 57 (1968); (b) H. M. R. Hoffmann and D. R. Joy, *ibid.*, 1182 (1968); (c) H. M. R. Hoffmann and N. F. Janes, *J. Chem. Soc. C*, 1456 (1969); (d) H. M. R. Hoffmann, G. F. P. Kernaghan, and G. Greenwood, *J. Chem. Soc. B*, 2257 (1971); (e) H. M. R. Hoffmann, K. E. Clemens, and R. H. Smithers, *J. Amer. Chem. Soc.*, in press; (f) G. Greenwood, A. E. Hill, and H. M. R. Hoffmann, unpublished work.

(2) Cycloadditions classified according to the ring-size criterion; see R. Huisgen, *Angew. Chem., Int. Ed. Engl.*, **7**, 321 (1968). For  $4 + 3 \rightarrow 7$  cycloadditions involving oxyallyl, see N. J. Turro, S. S. Edelson, J. R. Williams, T. R. Darling, and W. B. Hammond, *J. Amer. Chem. Soc.*, **91**, 2283 (1969); R. C. Cookson, M. J. Nye, and G. Subrahmanyam, *J. Chem. Soc. C*, 473 (1967), 2009 (1965); A. W. Fort, *J. Amer. Chem. Soc.*, **84**, 2620, 2625, 4979 (1962).

(3) K. Westphal and H. Klös, German Patent 614,462 [*Chem. Abstr.*, **29**, 5994<sup>4</sup> (1935)]; U. S. Patent 2,119,802 (1938).