Formation of 2-Oxazolines by a Cyclization Involving the Displacement of Mercury

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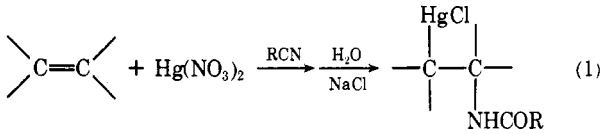
A series of *N*-acyl-2-aminoalkylmercuric chlorides has been synthesized by the reaction of olefins with mercuric nitrate monohydrate and nitriles followed by treatment with aqueous NaCl. This acylaminomercuration reaction was demonstrated to take place by way of trans addition. Thermal decomposition of the resulting *N*-acyl-2-aminoalkylmercuric chlorides at 180–240° in vacuo resulted in an intramolecular displacement of the chloromercury group with inversion of configuration to give the corresponding 2-oxazolines.

The facile reaction of olefins with mercuric nitrate and nitriles has recently been demonstrated to result in the formation of *N*-acyl-2-aminoalkylmercuric salts, which are conveniently isolated as the chlorides (eq 1).[2]



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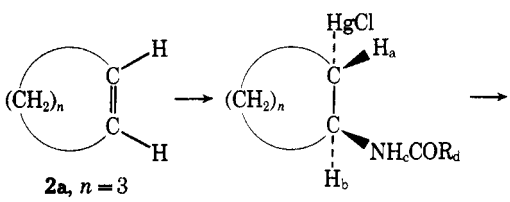
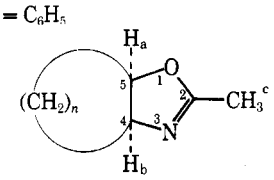
As a consequence of our interest in the synthetic potential of the organic compounds of mercury, we have undertaken the preparation of a series of these little-studied *N*-acyl-2-aminoalkylmercuric salts 1 in order to examine their chemical properties. It was felt that these salts might serve as a convenient and efficient source of 2-oxazolines.

A series of olefins was allowed to react at 0° with a mercuric nitrate monohydrate–nitrile system and the resulting mixture was treated with aqueous sodium chloride solution. In each case, a single *N*-acyl-2-aminoalkylmercuric chloride 1 was isolated. Cyclopentene (**2a**), cyclohexene (**2b**), and cycloheptene (**2c**) afforded the corresponding trans adducts **3a, 3b, 3c,** and **3d.** Similarly, trans-4-octene



2a, $n = 3$
b, $n = 4$
c, $n = 5$

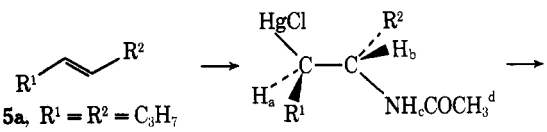
3a, $n = 3$; R = CH_3
b, $n = 4$; R = CH_3
c, $n = 5$; R = CH_3
d, $n = 4$; R = C_6H_5



4a, $n = 3$
b, $n = 4$
c, $n = 5$

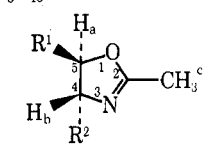
(**5a**) was converted to the erythro compound **6a,** and 1-octene (**5b**) was converted to **6b.**

The formation of *N*-acyl-2-aminoalkylmercuric salts 1 in the acylaminomercuration reaction (eq 1) has been rationalized in terms of nucleophilic attack by the nitrile on an intermediate mercurinium ion 8 (eq 2).[3] This, in turn, leads to a prediction that acylaminomercuration proceeds by way of trans addition. This prediction has not yet been adequately verified, however. The only experimental support



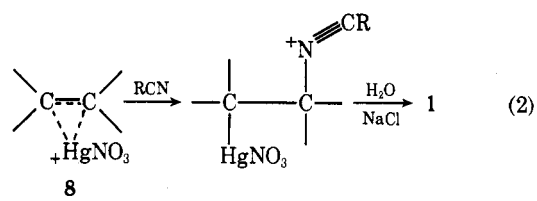
5a, $R^1 = R^2 = C_3H_7$
b, $R^1 = H$; $R^2 = C_6H_{13}$

6a, $R^1 = R^2 = C_3H_7$
b, $R^1 = H$; $R^2 = C_6H_{13}$



7a, $R^1 = R^2 = C_3H_7$
b, $R^1 = H$; $R^2 = C_6H_{13}$

for this prediction consists of a demonstration that halogen cleavage of the carbon–mercury bond in a series of *N*-acyl-



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2-aminocyclohexylmercuric chlorides yields the corresponding *N*-acyl derivatives of *trans*-2-bromo- and *trans*-2-chlorocyclohexylamine.[2c] An assignment of stereochemistry to the *N*-acyl-2-aminocyclohexylmercuric chloride substrates, which is founded on this evidence, requires an assumption that the halogen cleavage is a stereospecific electrophilic process which takes place with retention of configuration. Unfortunately, this assumption may be incorrect as a consequence of possible competition by a nonstereospecific radical cleavage process.[4] In addition, the very real possibility exists that the presence of a neighboring acylamino group may alter the stereochemical result of the halogenation reaction.[5] Consequently, it was of interest to obtain direct physical evidence that the acylaminomercuration of olefins does, in fact, take place by way of trans addition.

The NMR data set forth in Table I provide such direct physical evidence that the acylaminomercuration of cyclohexene (**2b**) and cycloheptene (**2c**) proceeds by way of trans addition. *N*-Acetyl-2-aminocyclohexylmercuric chloride (**3b**) and *N*-benzoyl-2-aminocyclohexylmercuric chloride (**3d**) have vicinal coupling constants J_{ab} of 9.6 and ca. 11 Hz, respectively. These values are of the magnitude expected for the coupling between two axial protons and are indicative of trans addition.[6] Similarly, *N*-acetyl-2-aminocycloheptylmercuric chloride (**3c**) has a vicinal coupling constant J_{ab} of 8.9 Hz which is also consistent with trans addition and a dihedral angle between the vicinal hydrogens of about 180°.[6a,7] First-order analysis of the H_a sextet

Table I
Physical Properties and NMR Spectra of *N*-Acyl-2-aminoalkylmercuric Chlorides

N-Acryl-2-aminoalkylmercuric Chloride	Yield, %	Mp, °C	Chemical shift, δ[a]			
			H_a	H_b	H_c	H_d
3a[b]	32	139–140[c]	*d*	4.17–4.80 (m) J_{ab} = ca. 7.7[e]	8.62 (d) J_{bc} = 6.2	1.99 (s)
3b	93	201–202[g]	2.48[h]	3.67–4.60 (br) J_{ab} = 9.6[f]	8.49 (d) J_{bc} = 6.6	1.94 (s)
3c	3.2[i]	185–186 dec[j]	2.79[k]	4.27–4.80 (br) J_{ab} = 8.9[f]	8.63 (d) J_{bc} = 6.8	1.99 (s)
3d	50	238–240 dec[l]	2.72[m] J_{ab} = ca. 11[n]	4.43–5.07 (br)	ca. 9.3[o]	7.37–7.78 (3 H, m), 8.23–8.75 (2 H, m)
6a	65	169–170[p]	2.67–3.37 (m)	4.37–4.93 (br)	8.88 (d) J_{bc} = 7.8	2.13 (s)
6b[b]	22	101–102[q]	1.97–2.60 (m)	4.33–4.93 (br)	8.84 (d) J_{bc} = 7.5	2.10 (s)

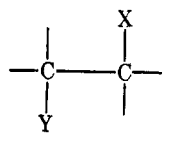
[a] In pyridine-d_5 with Me_4Si as internal standard. *J* values expressed in hertz. [b] Satisfactory elemental analyses and mass spectra were obtained for all new compounds. [c] Recrystallized from 50% aqueous ethanol. [d] Not measured. [e] Exchange of H_c with deuterium afforded a quartet of lines for H_b with J = 7.7 Hz. [f] Determined by exchange of H_c with deuterium followed by spin decoupling of the methylene protons coupled to H_b. [g] Lit.[2a] 201.5–202°. [h] Sextet. First-order analysis indicates coupling of ca. 10 Hz with two protons and ca. 4 Hz with a third. [i] After two recrystallizations from 95% ethanol. A 3.2% yield of elemental mercury was also obtained. [j] Lit.[2c] 172–175°. [k] Sextet. First-order analysis indicates coupling of ca. 9 Hz with two protons and ca. 3 Hz with a third. [l] Lit.[2c] 243°. [m] Sextet. [n] First-order analysis indicates coupling of ca. 11 Hz with two protons and ca. 4 Hz with a third. [o] Partially obscured by solvent. [p] Lit.[2c] 164–165°. [q] Recrystallized from 95% ethanol.

in the NMR spectrum of **3c** supports this conclusion. In view of the stereochemical results for cyclohexene (**2b**) and cycloheptene (**2c**), the stereochemistry of **3a** and **6a** has been assigned on the basis of an anticipated trans addition to the double bond of cyclopentene (**2a**)[8] and *trans*-4-octene (**5a**), respectively.

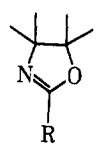
Jensen and Ouellette have demonstrated that the mercury of simple alkylmercuric salts can function as a leaving group under solvolytic conditions and have postulated that solvolysis involves ionization of the salt followed by loss of mercury to form a carbonium ion (eq 3).[9] In view of this,

$$RHgX \rightleftharpoons RHg^+ + X^- \qquad (3)$$
$$\searrow$$
$$R^+ + X^-$$

the interesting possibility exists that a chloromercury group might have value as a synthetically useful leaving group which is subject to displacement by an internal nucleophile. This prediction has been verified, in part, by the recent observation that 2-hydroxyalkylmercuric chlorides **9a** can be converted to epoxides in high yield under basic conditions.[10] In an effort to further extend the scope of this observation, we have examined a series of *N*-acyl-2-aminoalkylmercuric halides **1** in the expectation that they might possess chemical properties analogous to those of the corresponding *N*-acyl-2-aminoalkyl halides **9b.** The conversion of *N*-acyl-2-aminoalkyl halides **9b** to 2-oxazolines **10** is a facile and well-documented reaction[11] which is ordi-



9a, X = HgCl; Y = OH
b, X = Br or Cl; Y = RCONH



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narily carried out under basic conditions and proceeds via an internal displacement of halide ion with inversion of configuration.[12] Consequently, it appeared possible that *N*-acyl-2-aminoalkylmercuric chlorides **1** might also undergo decomposition to yield 2-oxazolines **10.**

Reaction of *trans*-*N*-acetyl-2-aminocyclohexylmercuric chloride (**3b**) with potassium *tert*-butoxide or sodium carbonate in inert solvents afforded oxazoline in only trace amounts. It was found, however, that with one exception, all of the *N*-acyl-2-aminoalkylmercuric chlorides **1** examined could be converted to 2-oxazolines in 10–30% yield by thermal decomposition at 180–240° under reduced pressure. Thus, **3a, 3b,** and **3c** afforded the *cis*-2-oxazolines **4a, 4b,** and **4c,** respectively, whereas **6a** yielded the corresponding *trans*-2-oxazoline **7a** and **6b** afforded **7b.** In all cases, deacylaminomercuration also took place as a major side reaction to give substantial amounts of the corresponding olefin. These results are set forth in Tables II and III. The stereospecificity of oxazoline formation was demonstrated by the fact that the resulting 2-oxazolines were found to be homogeneous both by gas chromatography and on the basis of their NMR spectra.

Table II
Pyrolysis of *N*-Acyl-2-aminoalkylmercuric Chlorides

N-Acyl-2-aminoalkylmercuric chloride	Pyrolysis temp, °C	Pyrolysis pressure, mm	Product yield, %[a]		
			Oxazoline	Olefin	Acetamide
3a[b]	178	9	31	60[c]	1.2
3b	240	3	25	60[d]	15
3c	200	0.2	11	*e*	*e*
3d	235	0.3	0	*e*	*e*
6a	180	9	16	*e*	*e*
6b	180	8	21	*e*	*e*

[a] Isolated yield unless otherwise specified. The formation of small amounts of elemental mercury could be detected visually in each case. [b] Treatment of the pyrolysis residue with aqueous ammonia resulted in a black coloration indicative of the presence of mercurous ion. [c] Cyclopentene determined by quantitative gas chromatography on a 15 ft × 0.25 in. column of 10% Silicone QF-1 on 60/80 Chromosorb P. [d] Cyclohexene determined by quantitative gas chromatography on a 15 ft × 0.25 in. column of 10% Silicone QF-1 on 60/80 Chromosorb P. [e] Not measured.

The assignment of cis and trans configurations to oxazolines **4c** and **7a,** respectively, is based on their NMR spectra (Table III). In a series of 4,5-dimethyl- and 4,5-diethyl-2-oxazolines of established configuration the coupling constant J_{ab} between the C-4 and C-5 protons is from 8.0 to

Table III
Physical Properties and NMR Spectra of 2-Oxazolines

Oxazoline[a]	Bp, °C (mm)	Chemical shift, δ[b] H_a	H_b	H_c
4a	47.5–48.0 (9)[c]			
4b	52.0–56.0 (2)[d]			
4c[e]	23.5–24.0 (0.1)	4.45–4.93 (m) J_{ab} = 9.8	3.93–4.47 (br) J_{ab} = 9.8	1.96 (d) J_{bc} = 1.5
7a	48.0–49.0 (3)	3.87–4.27 (m) J_{ab} = 6.0	3.37–3.83 (br) J_{ab} = 6.0	1.95 (d) J_{bc} = 1.2
7b	25.0–26.0 (0.02)	3.60–4.50 (m)		1.98 (s) $W_{1/2}$ = 2.4

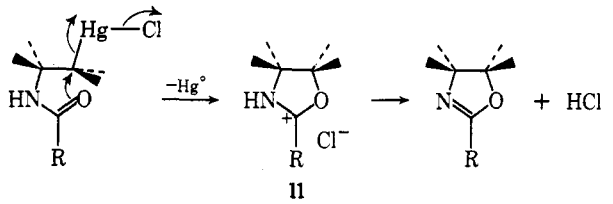
[a] Satisfactory elemental analyses and mass spectra were obtained for all compounds except where indicated. [b] In $CDCl_3$ with J values expressed in hertz. Values for J_{ab} determined by spin decoupling of the coupled methylene protons. [c] Lit.[13] 57.0–57.5° (13 mm). [d] Lit.[13] 75.5–76.5 (13 mm). [e] Satisfactory mass spectrum. Elemental analysis not carried out.

9.0 Hz for the cis compounds.[14] It has generally been observed that in five-membered rings which cannot deviate appreciably from planarity, such as the 2-oxazolines, J_{cis} is always appreciably larger than J_{trans}.[15] On this basis, **7a**, with a coupling constant J_{ab} of 6.0 Hz, may be unambiguously assigned a trans configuration. In the bicyclic oxazoline **4c**, the coupling constant J_{ab} is less definitive, however, as a result of the distortions introduced by the fused ring system. Nevertheless, the observed coupling constant J_{ab} for this bicyclic compound is consistent, on the basis of the Karplus relationship,[6a] with a cis configuration.

The assignment of configuration to oxazolines **4c** and **7a** finds further support in a consideration of the chemical shifts of the C-4 and C-5 hydrogen signals in the NMR spectra (Table III). It has been found in a series of 4,5-dimethyl- and 4,5-diethyl-2-oxazolines that the C-4 and C-5 hydrogens appear at about 0.5 ppm lower field in the cis compounds than in the trans isomers.[14] Specifically, in trans compounds the C-4 hydrogen is found in the range of δ 3.4–3.8 and the C-5 hydrogen is found at δ 4.0–4.2. In the cis compounds, the C-4 proton signal is observed at δ 4.0–4.1 and the C-5 proton is found at δ 4.4–4.7. This difference in chemical shift of the C-4 and C-5 protons in *cis*- and *trans*-2-oxazolines has been attributed to the shielding effect of the alkyl groups attached to the adjacent carbon atoms in the trans isomers, and has been found in many cis/trans isomer pairs of five-membered ring compounds.[16] The relatively flexible cycloheptyl ring associated with **4c** would be expected to produce similar shielding effects.[17] Comparison of these expected values with those set forth in Table III for **4c** and **7a** serves to confirm the assignment of stereochemistry to each of these compounds.

The formation of 2-oxazolines upon thermal decomposition of the *N*-acetyl-2-aminoalkylmercuric chlorides can be rationalized in terms of the mechanism set forth in Scheme I. A back-side displacement of mercury by the oxygen

Scheme I



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atom of the amide carbonyl group would result in formation of the corresponding 2-oxazoline hydrochloride **11**, which could then undergo thermal decomposition to oxazoline and HCl. Such a reaction path would serve to explain the inversion of configuration observed during oxazoline formation. Inversion of configuration is also consistent with the related observation that epoxides can be generated by base treatment of both *trans*-2-hydroxycyclopentylmercuric chloride and *trans*-2-hydroxycyclohexylmercuric chloride.[10a] Such a stereochemical result, however, is at variance with the retention of configuration ordinarily observed in the electrophilic cleavage reactions of organomercurials.[18] Although 2-oxazolines form stable, isolable salts,[13,19] it has been demonstrated that 2-propyl-2-oxazolines can be distilled at 1 mm pressure and 185° from a reaction system that also produces phosphoric acid.[20] Consequently, it is not unreasonable to expect the oxazoline hydrochloride **11** to exist in equilibrium with HCl and free oxazoline at elevated temperatures. The HCl is then subject to removal by distillation in vacuo.[21]

The failure of *trans*-*N*-benzoyl-2-aminocyclohexylmercuric chloride (**3d**) to yield an oxazoline upon pyrolysis is surprising. The failure of potassium *tert*-butoxide and sodium carbonate to exert a favorable effect on the conversion of *trans*-*N*-acetyl-2-aminocyclohexylmercuric chloride (**3b**) to the corresponding 2-oxazoline is also unexpected. Although the analogous *N*-acyl-2-aminoalkyl halides **9b** are known to undergo thermal decomposition to yield 2-oxazoline salts,[19] these compounds are most conveniently converted to oxazolines in the presence of basic reagents.[11]

Experimental Section

All melting points and boiling points are uncorrected. Infrared spectra were determined either with a Beckman IR-8 or a Perkin-Elmer 257 infrared spectrophotometer. NMR spectra were recorded on a Varian T-60 spectrometer equipped with a T-6057 lock-decoupler. The mass spectra were obtained with a Varian MAT CH7 mass spectrometer. GLC analyses were carried out with either an Aerograph Model A-90-P or a Carle Model 8000 gas chromatograph. Microanalyses were performed by M-H-W Laboratories, Garden City, Mich.

***trans*-*N*-Acetyl-2-aminocyclohexylmercuric Chloride (3b).** The following procedure is representative of the general procedure employed for the preparation of the *N*-acyl-2-aminoalkylmercuric chlorides set forth in Table I. To a suspension of 137.0 g (0.40 mol) of mercuric nitrate monohydrate in 300 ml of acetonitrile at ice-bath temperature was added dropwise with mechanical stirring over a period of 27 min a solution of 32.8 g (0.40 mol) of cyclohexene (**2b**) in 100 ml of acetonitrile to give a clear, colorless solution. Stirring was continued at room temperature for 1 hr. The resulting clear yellow solution was poured into a mixture of 1 l. of water and 200 ml of saturated NaCl solution. The resulting white precipitate was separated by filtration, washed with 1 l. of water, and dried in vacuo to give 139.5 g (93%) of **3b**, mp 200.0–201.0°. Recrystallization from 2 l. of 95% ethanol afforded 100.0 g of **3b** as white, fibrous needles, mp 201.0–202.0° (lit.[2a] mp 201.5–202).

***cis*-2-Methyl-4,5-tetramethylene-2-oxazoline (4b).** The following procedure is representative of the general procedure employed for preparation of the 2-oxazolines set forth in Table III. *trans*-*N*-Acetyl-2-aminocyclohexylmercuric chloride (**3b**, 5.004 g, 13.29 mmol) was heated at an oil-bath temperature of 240° and a

pressure of 2.85 mm under a 10-cm Vigreux column, and the volatile product collected at dry ice–acetone bath temperature. The resulting volatile product consisted of 1.300 g of a colorless liquid which contained a suspended white solid. Crystallization of the crude product from ether afforded 0.116 g (15%)of acetamide as white needles, mp 81.5–82.5°. The filtrate was concentrated and the residual colorless oil subjected to short-path distillation (2.75 mm and 65° bath) to give 0.467 g (25%) of oxazoline **4b** as a colorless liquid.

Oxazoline **4b**, obtained from a large-scale preparative experiment, bp 52.0–56.0° (1.75–2.10 mm) [lit.[13] 75.5–76.5° (13 mm)], was homogeneous by gas chromatography on a 6 ft × 0.094 in. column packed with 8% Carbowax 1540 on 60–80 mesh calcined diatomite support. It was further characterized by conversion to its picrate, mp 165–169°.

Anal. Calcd for $C_{14}H_{16}N_4O_8$: C, 45.66; H, 4.38; N, 15.21. Found: C, 45.36; H, 4.18; N, 14.98.

The crude volatile product from a comparable experiment was found to contain 60% of cyclohexene (**2b**) by quantitative gas chromatography on a 15 ft × 0.25 in. column packed with 10% silicone (Fluro) QF-1 on 60–80 Chromosorb using *n*-octane as an internal standard.

Reaction of *trans*-*N*-Acetyl-2-aminocyclohexylmercuric Chloride (3b) with Potassium *tert*-Butoxide. A mixture of 5.001 g (13.3 mmol) of *trans*-*N*-acetyl-2-aminocyclohexylmercuric chloride (**3b**) and 1.490 g (13.3 mmol) of potassium *tert*-butoxide in 15 ml of diglyme (distilled from CaH_2) was heated at relfux in a nitrogen atmosphere for 3.5 hr. After cooling, the resulting brown solution was found to contain less than a 1% yield of *cis*-2-methyl-4,5-tetramethylene-2-oxazoline (**4b**) by quantitative gas chromatography on a 6 ft × 0.094 in. column packed with 8% Carbowax 1540 on 60–80, acid washed, silane treated, calcined diatomite support using 0.437 g of *o*-xylene as an internal standard.

Reaction of *trans*-*N*-Acetyl-2-aminocyclohexylmercuric Chloride (3b) with Sodium Carbonate. A mixture of 2.500 g (6.64 mmol) of *trans*-*N*-acetyl-2-aminocyclohexylmercuric chloride (**3b**) and 0.800 g (7.55 mmol) of anhydrous sodium carbonate in 50 ml of benzene was heated with shaking in a high-pressure steel reaction vessel at 250° for 2 hr. After cooling, the mixture was filtered and the filtrate concentrated to yield 0.213 g of dark brown oil. The infrared spectrum of this material indicated that little or no 2-oxazoline **4b** was present.

Registry No.—**2a**, 142-29-0; **2b**, 110-83-8; **2c**, 628-92-2; **3a**, 56943-31-8; **3b**, 31718-62-4; **3c**, 56943-32-9; **3d**, 19907-98-3; **4a**, 56943-33-0; **4b**, 23236-44-4; **4b** picrate, 56943-34-1; **4c**, 56943-35-2; **5a**, 14850-23-8; **5b**, 111-66-0; **6a**, 56943-36-3; **6b**, 56943-37-4; **7a**, 56943-38-5; **7b**, 56994-88-8; mercuric nitrate, 10045-94-0; NaCl, 7647-14-5; potassium *tert*-butoxide, 865-47-4; sodium carbonate, 497-19-8.

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Ring Expansion Reaction of 1,2-Dihydroquinolines to 1-Benzazepines

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When 1-methyl-2,3-dialkyl-1,2-dihydroquinolines (**1a–c**) were treated with ethyl azidoformate, 1-methyl-2-ethoxycarbonylimino-3,4-dialkyl-2,3-dihydro-1*H*-1-benzazepines (**2a–c**) were produced in 30–80% yields. These benzazepines (**2a–c**) were obtained in 91–99% yields under a similar reaction condition from 1-methyl-2-alkylidene-3-alkyl-1,2-dihydroquinolines (**16a–c**) prepared from the corresponding 1,2,3-trialkylquinolinium chlorides (**18a–c**).

Attempts to expand smaller rings into a heterocyclic ring of 1-benzazepines have been achieved by many investigators; e.g., by the reaction of indoles with dimethyl acetylenedicarboxylate[1] or ethyl cyanoacetate,[2] by the Beckman[3] or Schmidt[4] rearrangement of tetralones, and by the treatment of 1,2-dihydroquinoline with dibromocarbene followed by the treatment of 1,2-dihydroquinoline with dibromocarbene followed by dehydrobromination.[5] The utility of azides in the azepine formation is well known.[6] This paper describes a new ring expansion reaction by ethyl azidoformate from 1-methyl-2,3-dialkyl-1,2-dihydroquinolines (**1**) to 1-methyl-2-ethoxycarbonylimino-3,4-dialkyl-2,3-dihydro-1*H*-1-benzazepines (**2**) via 1-methyl-2-alkylidene-3-alkyl-1,2-dihydroquinolines (**16**).

In a recent publication[7] we have reported that *N*-alkylanilinomagnesium bromides reacted with aliphatic aldehydes to give 1,2,3-trialkyl-1,2-dihydroquinolines in good yields. When the reaction of 1,3-dimethyl-2-ethyl-1,2-di-