The solution became yellow, and at the end of this time no starting material could be detected by t.l.c. Evaporation of the benzene gave a yellow oil which was sublimed onto a Dry Ice cooled finger. A 50-μl. sample of the sublimate, m.p. *ca.* 0°, was injected onto a 25-in. Silicone SF-96 column at 140°. A single major peak was eluted, retention time 55 min. The spectra suggested that this material was 2,3-dimethyl-4-phenylfuran: ν 1625, 1575, 1140 cm.$^{-1}$; n.m.r. 2.03 (s, 3), 2.27 (s, 3), 7.35 p.p.m. (s, 6, slight shoulder).

The sublimation residue was triturated with ether and a pale yellow solid, m.p. 125–130°, was obtained. Recrystallization from methylene chloride–ether gave cream-colored plates: m.p. 135–136°; ν^{KBr} 3400, 1610, 1150 cm.$^{-1}$; λ_{max}^{EtOH} 305 mμ; n.m.r. 2.7 (d, 3, J = 3 c.p.s.), 4.42 (s, 1), 7.35 p.p.m. (m, 6).

Anal. Calcd. for $C_{11}H_{11}NO$: C, 76.27; H, 6.40; N, 8.09. Found: C, 76.35; H, 5.89; N, 7.99.

Hydrolysis of 10.—A suspension of 600 mg. of the hydrochloride **10**·HCl in 12 ml. of concentrated HCl was heated for 5 min. at 85°. The hot mixture was filtered to give 250 mg. of black solid. A 32-mg. sample of this cinder-like material was extracted with hot water and the clear aqueous solution was treated with 1 drop of benzaldehyde. On chilling, 6 mg. of yellow prisms of benzalazine separated, m.p. and m.m.p. 88–90°.

The aqueous acidic filtrate from the original mixture was neutralized with $NaHCO_3$ and extracted with methylene chloride. Evaporation of the methylene chloride solution gave 210 mg. of the butenolide **20**, m.p. 42–44°. Recrystallization from aqueous ethanol or sublimation gave colorless needles, m.p. 53–54°; for spectra, see discussion.

Anal. Calcd. for $C_{12}H_{12}O_2$: C, 76.57; H, 6.43. Found: C, 76.79; H, 6.33.

Hypoiodite Degradation of 20.—A solution of 200 mg. of **20** in 5 ml. of dioxane containing 4 ml. of 10% NaOH was treated at 60° with KI_3 solution. After a permanent brown color was present, a few more drops of NaOH solution were added, the solution was chilled, and the precipited iodoform, 173 mg. (42%), m.p. 120–121°, was collected. The aqueous filtrate was acidified and the iodine was reduced with $NaHSO_3$. The solution was again made alkaline, extracted with ether to remove impurities, and finally acidified and chilled to give 85 mg. (40%) of light yellow crystals of methylphenylmaleic anhydride, m.p. 90°. Recrystallization from acetone–hexane gave cream-colored needles, m.p. and m.m.p. (with an authentic sample[16]) 95°.

(16) J. A. Moore and F. J. Marascia, *J. Am. Chem. Soc.*, **81**, 6049 (1959).

Aziridines. XIV. 3-Oxa-6-azabicyclo[3.1.0]hexane[1]

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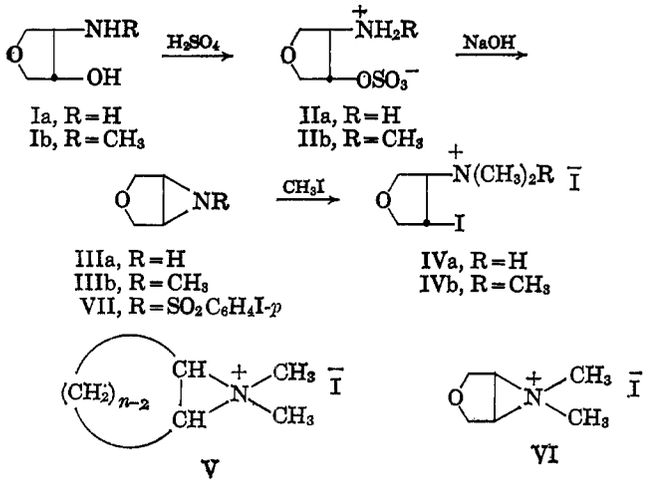
The fused, bicyclic aziridine 3-oxa-6-azabicyclo[3.1.0]hexane and its 6-methyl homolog were prepared by conventional Wenker syntheses. Both aziridines gave only ring-opened products on treatment with methyl iodide. Pyrolysis of the 6-benzoyl derivative gave the isomeric *cis*-fused bicyclic oxazoline, rather than the anticipated unsaturated amide. The same isomerization occurred on treatment of the benzoyl derivative with sodium iodide in acetone or acetonitrile.

As part of our continuing study of the chemistry of fused, bicyclic aziridines, we have now prepared 2,5-dihydrofuranimine or 3-oxa-6-azabicyclo[3.1.0]hexane, IIIa. The new aziridine was made by the conventional Wenker synthesis from the known *dl-trans*-3-amino-4-hydroxytetrahydrofuran (Ia) *via* the sulfate ester IIa. The N-methyl homolog IIIb was prepared in a similar manner from the amino alcohol Ib. The structures assigned to the aziridines IIIa and b are fully supported by the n.m.r. spectra, as shown in Figure 1.



In previous work, it had been found that the quaternary methiodides of the series of cycloalkenimines represented by V, where n = 7, 8, 10, and in *cis* and *trans* 12, are stable, crystalline compounds.[2] Three of these substances were found to be particularly suitable for the determination of the molecular structure by the three-dimensional X-ray diffraction technique.[3] On the other hand, attempts to prepare the quaternary derivative of cyclohexenimine (V, n = 6) gave only ring-opened products.[4] Similarly, the attempted preparation of the quaternary derivative VI by the treatment of IIIa or b with methyl iodide gave only the ring-opened iodides IVa and b, respectively. Therefore, the heavy element *p*-iodobenzenesulfonyl derivative VII was prepared in the conventional way, and its crystal and molecular structure is now under investigation in the laboratory of Dr. L. M. Trefonas. The n.m.r. spectrum of compound VII indicated that no isomerization of the bicyclic skeleton occurred in the course of preparation of the derivative.

In previous work, it has been found that the pyrolytic rearrangement of an N-acyl aziridine follows one of two courses.[5] At 125° N-benzoylaziridine rearranges rapidly to 2-phenyl-2-oxazoline,[6] and a similar rearrangement of other acyl derivatives of ethylenimine was observed during attempted distillation.[7] The mechanism

(1) This investigation was supported in part by Public Health Service Grant No. GM-11883 from the National Institute of General Medical Sciences.

(2) P. E. Fanta, R. Golden, and H.-J. Hsu, *J. Chem. Eng. Data*, **9**, 246 (1964), and preceeding papers.

(3) L. M. Trefonas and R. Towns, *J. Heterocyclic Chem.*, **1**, 19 (1964), and preceeding papers.

(4) (a) T. Taguchi and M. Eto, *J. Am. Chem. Soc.*, **80**, 4075 (1958); (b) P. E. Fanta and E. N. Walsh, *J. Org. Chem.*, **30**, 3574 (1965).

(5) H. W. Heine, *Angew. Chem. Intern. Ed. Engl.*, **1**, 528 (1962).

(6) A. A. Goldberg and W. Kelley, *J. Chem. Soc.*, 1919 (1948).

(7) C. W. Woods, A. B. Borkovec, and F. M. Hart, *J. Med. Chem.*, **7**, 371 (1964).

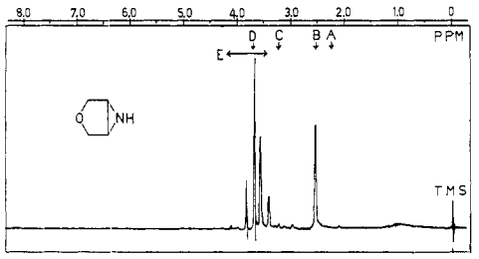


Figure 1.—Nuclear magnetic resonance spectrum of 3-oxa-6-azabicyclo[3.1.0]hexane. The capital letters indicate the location of the singlet due to the bridgehead protons in the following N-substituted derivatives: A, methyl (compound IIIb); B, hydrogen (the parent compound, IIIa); C, trichloromethylmercapto; D, *p*-iodobenzenesulfonyl (compound VII). In all cases the multiplet due to the ring methylene protons fell into the range indicated by the line E. The very broad band at 1.0 is due to the proton on nitrogen and is absent from the spectra of the derivatives.

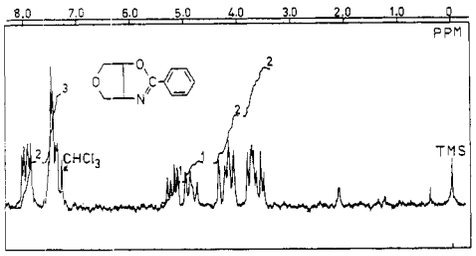
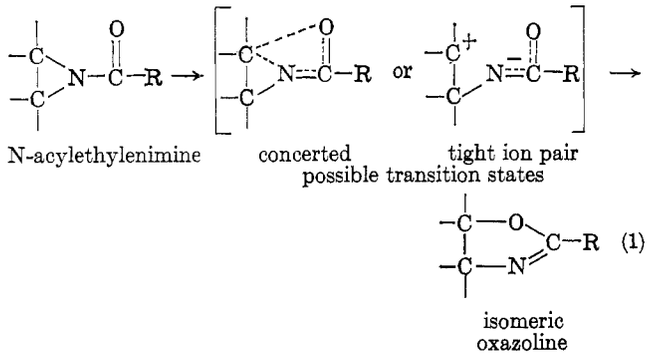


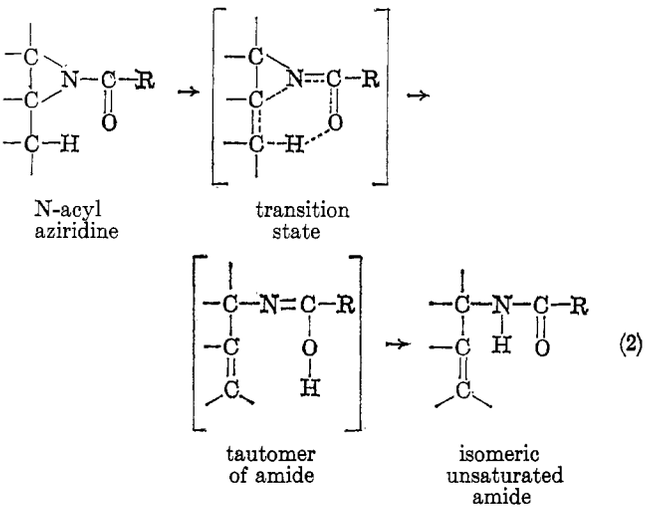
Figure 2.—Nuclear magnetic resonance spectrum of 2-phenyl-*cis*-tetrahydrofuro[3,4-*d*]oxazoline (compound XI) in deuteriochloroform. Numerals indicate relative heights of the integration curves shown.

of this reaction may either be concerted, involving a rather strained, four-center transition state,[5] or it may possibly involve an intermediate tight ion pair as illustrated in eq. 1.[8]



(1)

On the other hand, the pyrolysis of N-acylaziridines having the necessary side-chain proton results in a rearrangement to the isomeric unsaturated amide, as illustrated by the part-structure formulas of eq. 2.[5] Stereochemical[9] and kinetic[10] evidence has been presented in support of the view that this reaction is an intramolecular rearrangement involving a stereospecific, concerted *cis* elimination. In the cycloalkenimine series, it was observed that attempted preparation of N-benzoylcyclooctenimine or N-benzoylcyclodecenimine gave directly the respective isomeric, unsaturated amides.[11] In these instances the benzoylaziridines apparently were formed and rearranged very rapidly below 80°. In contrast, N-benzoylcyclohexenimine was found to be stable at 150°, and required heating at 200–210° to complete the rearrangement.[4b]



(2)

We now have found that an even higher temperature is required for isomerization of the benzoyl derivative of our new aziridine, IX. Upon heating to 235–250°, IX gave a 33% yield of the oxazoline XI, and not the anticipated amide XIII. If the amide had been formed, it would have been isolated readily, since our previous experience has shown that the amides are invariably higher melting, less soluble, and more readily crystallizable than the isomeric oxazolines.

A reasonable interpretation of this evidence is that considerably greater strain is involved in the attainment of the transition state of eq. 2 when the three carbon atoms are part of a six-membered ring than when they are part of an eight- or ten-membered ring. A logical extension of this argument is that, when the three carbon atoms are included in a five-membered ring, the attainment of transition state X, leading to the unsaturated amide XIII, is so severely hindered that an alternative path *via* transition state VIII predominates, leading to the formation of the oxazoline XI.

An alternative explanation, namely that the amide XIII is formed first, and is subsequently rapidly cyclized to XI under the conditions of the reaction, is also possible, but is a less acceptable explanation, since it has been observed that similar unsaturated amides are perfectly stable to heat but are rapidly cyclized to oxazolines in concentrated sulfuric acid at room temperature.[9] Analogously, the unsaturated amide XIII would be expected to cyclize to XI only under conditions sufficiently acidic to cause the generation of the carbonium ion XIV, which would provide an electrophilic site for attack by the amide oxygen, resulting in ring closure to the oxazolinium ion (nitrogen-protonated XI) (see Scheme I).

It was also observed that the same oxazoline XI was obtained from the treatment of the benzoylaziridine

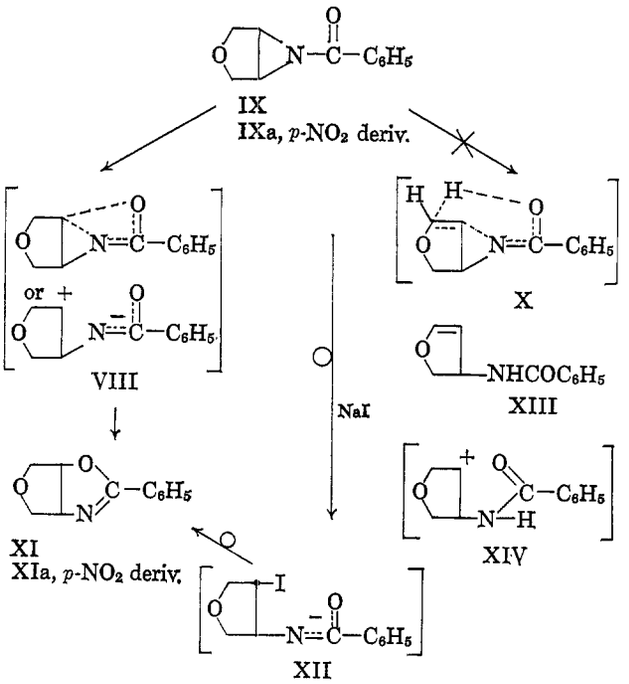
(8) The ion-pair mechanism was suggested by a referee, who observed that, compared to the concerted mechanism, less strain is required if carbon–nitrogen bond breaking precedes carbon–oxygen bond formation. The ion pair would close only to a *cis*-oxazoline because of the steric barrier to the fusion of the oxazoline ring *trans* to the five-membered tetrahydrofuran ring; *cf.* G. E. McCasland and E. C. Horswill, *J. Am. Chem. Soc.*, **73**, 3745 (1951).

(9) D. W. Kashelikar and P. E. Fanta, *ibid.*, **82**, 4930 (1960), and previous papers in this series.

(10) P. E. Fanta and M. K. Kathan, *J. Heterocyclic Chem.*, **1**, 293 (1964).

(11) P. E. Fanta, L. J. Pandya, W. R. Groskopf, and H.-J. Su, *J. Org. Chem.*, **28**, 413 (1963).

SCHEME I[a]



[a] Hypothetical intermediates and transition states are in brackets.

IX with sodium iodide in acetone or acetonitrile. Evidence has already been presented that this type of isomerization occurs *via* an iodoamide or iodoamide ion XII.[5] This mechanism involves two consecutive SN2 inversions at the substituted carbon atom and the two rings of oxazoline XI therefore must be fused *cis*. The n.m.r. spectrum, Figure 2, clearly supports the oxazoline structure XI and definitely excludes the isomeric unsaturated amide XIII. The bridgehead protons of XI are responsible for the pair of multiplets at about 5.0 p.p.m., corresponding to two protons, while the pair of multiplets centered at 4.0 p.p.m. are due to the four methylene ring protons. The spectrum expected for XIII would be more complex because of the presence of five different kinds of protons, exclusive of the phenyl group.

The *p*-nitrobenzoyl analog IXa also rearranged to the isomeric oxazoline XIa on treatment with sodium iodide in acetone or acetonitrile. The structure is also supported by an n.m.r. spectrum similar to Figure 2.

In the course of exploratory work designed to find compounds suitable for X-ray study, the following additional N-substituted derivatives of 3-oxa-6-azabicyclo[3.1.0]hexane were prepared: *p*-chlorobenzoyl, benzenesulfonyl, *p*-bromobenzenesulfonyl, trichloromethylmercapto, *p*-chlorophenylmercapto, *p*-bromophenylmercapto, phenylcarbamyl, and phenylthiocarbamyl.

The n.m.r. spectra of aziridine IIIa and its derivatives are relatively simple and easily interpreted. Each spectrum has a distinctive multiplet centered at about 3.6 p.p.m. due to the ring methylene protons and a band due to the bridgehead protons which appears as a singlet. In this respect, the spectrum is identical with that reported for the analogous oxygen heterocycle 3,4-epoxytetrahydrofuran.[12] As expected, variation of the N-substituent has a large effect on the location of the sharp band due to the nearby bridgehead protons, but almost no effect on the multiplet due to the ring methylene protons. Thus, the spectrum of the N-trichloromethylmercapto derivative demonstrates that no skeletal alteration occurred in the formation of the derivative.

(12) N. S. Bhacca, D. P. Hollis, L. F. Johnson, and E. A. Pier, "High Resolution Nuclear Magnetic Resonance Spectra Catalog," Vol. 2, Varian Associates, Palo Alto, Calif., 1963, Spectrum No. 405.

Experimental Section

Analyses were performed by Micro-Tech Laboratories, Skokie, Ill. The n.m.r. spectra were obtained on a Varian A-60 spectrophotometer with the help of Dr. B. L. Shapiro.

dl-trans-**3-Amino-4-tetrahydrofuryl Hydrogen Sulfate (IIa). A.**—A solution of 53 ml. of concentrated sulfuric acid in 100 ml. of water was added with cooling and stirring to a solution of 101.6 g. of *dl-trans*-3-amino-4-hydroxytetrahydrofuran[13] in 200 ml. of water. The water was removed by distillation at reduced pressure and the residue was heated for 20 min. at 100° and 2 mm. The yield was 176.0 g. (97.8% yield) of brown solid.

B.—A solution of 14.5 ml. of chlorosulfonic acid in 50 ml. of carbon tetrachloride was slowly added to a suspension of 22.6 g. of *dl-trans*-3-amino-4-hydroxytetrahydrofuran in 100 ml. of carbon tetrachloride, while stirring and cooling at 10–15°. After 17 hr. of stirring, the reaction mixture was refluxed for 30 min., cooled, and filtered to give 38.3 g. (95.6% yield) of product. Recrystallization of the crude sulfate ester from ethanol gave a white solid, which melted above 300°. *Anal.* Calcd. for $C_4H_9NO_5S$: C, 26.19; H, 4.95; N, 7.65. Found: C, 25.98; H, 5.00; N, 7.64.

N-Methyl-*dl-trans***-3-amino-4-hydroxytetrahydrofuran (Ib).**—To 400 ml. of 40% aqueous methylamine was added 37.0 g. of *dl-trans*-3-chloro-4-hydroxytetrahydrofuran[13] while stirring at 0–5°. After 2 days of stirring at 25°, a solution of 24.2 g. of sodium hydroxide in 25 ml. of water was added, and the mixture was evaporated to dryness on a steam bath. The residue was extracted with 300 ml. of ethanol, and the mixture was filtered to remove sodium chloride. Distillation of the extract gave 25.5 g. (72.4% yield), b.p. 110–111° (2 mm.), $n^{25}D$ 1.4841. *Anal.* Calcd. for $C_5H_{11}NO_2$: C, 51.26; H, 9.47; N, 11.96. Found: C, 51.34; H, 9.60; N, 11.43.

N-Methyl-*dl-trans***-3-amino-4-tetrahydrofuryl Hydrogen Sulfate (IIb).**—A solution of 11.0 ml. of concentrated sulfuric acid in 20 ml. of water was added with cooling and stirring to a solution of 24.8 g. of compound Ib in 50 ml. of water. The water was removed by distillation at reduced pressure and the residue was heated for 1 hr. at 130° and 2 mm., yield 36.8 g. (98.2%), m.p. 240° after recrystallization from ethanol. *Anal.* Calcd. for $C_5H_{11}NO_6S$: C, 30.45; H, 5.65. Found: C, 30.09; H, 5.81.

3-Oxa-6-azabicyclo[3.1.0]hexane (IIIa).—To a solution of 50 g. of sodium hydroxide in 120 ml. of water was added 100 g. of compound IIa. The reaction mixture was stirred, then gradually heated to boiling, and distilled. The distillate was collected in an ice-cooled flask containing 250 ml. of ether and 25 g. of solid sodium hydroxide. The ether extract was separated and the aqueous phase was extracted with two additional 300-ml. portions of ether. The combined ether extracts were dried first over sodium hydroxide, then over sodium metal, and distilled, giving 23.0 g. (49% yield) of colorless liquid, b.p. 82–83 (103 mm.), $n^{25}D$ 1.4695. *Anal.* Calcd. for C_4H_9NO: N, 16.46. Found: N, 16.20.

Addition of an alcoholic solution of the compound to an alcoholic solution of picric acid gave a yellow, crystalline **picrate**, which darkened at 151–154° and melted at 161°. *Anal.* Calcd. for $C_{10}H_{10}N_4O_8$: C, 38.22; H, 3.21; N, 17.83. Found: C, 38.50; H, 3.43; N, 17.90.

6-Methyl-3-oxa-6-azabicyclo[3.1.0]hexane (IIIb) was prepared in a similar manner by the reaction of compound IIb with aqueous sodium hydroxide. The yield of colorless, liquid product was 58%, b.p. 67° (47 mm.), $n^{25}D$,1.4561. The yellow, crystalline **picrate**, prepared in ethanol, melted at 156–158°. *Anal.* Calcd. for $C_{11}H_{12}N_4O_8$: C, 40.25; H, 3.68; N, 17.07. Found: C, 40.42; H, 4.01; N, 17.33.

N,N-Dimethyl-*dl-trans***-3-iodotetrahydro-4-furylammonium Iodide (IVa).**—A precipitate was slowly formed when a solution of 2.0 ml. of methyl iodide and 0.292 g. of compound IIIa in 25 ml.

(13) W. Reppe, *Ann.*, **598**, 80 (1955).

TABLE I

PROPERTIES OF THE 6-SUBSTITUTED 3-OXA-6-AZABICYCLO[3.1.0]HEXANE DERIVATIVES

6-Substituent	Formula	Yield, %	M.p., °C.	Calcd, %			Found, %		
				C	H	N	C	H	N
Benzoyl	$C_{11}H_{11}NO_2$	83	73–75	69.82	5.86	7.40	69.98	5.77	7.58
p-Chlorobenzoyl	$C_{11}H_{10}NO_2Cl$	92	106	59.07	4.51	6.26	59.12	4.63	6.09
p-Nitrobenzoyl	$C_{11}H_{10}N_2O_4$	95	158–159	56.41	4.31	11.96	56.53	4.29	11.76
Benzenesulfonyl	$C_{10}H_{11}NO_3S$	87	78–80	53.31	4.92	6.22	53.60	5.03	6.49
p-Bromobenzenesulfonyl	$C_{10}H_{10}NO_3SBr$	96	140–141	39.48	3.31	4.60	39.70	3.60	4.62
p-Iodobenzenesulfonyl	$C_{10}H_{10}NO_3SI$	81	137–139	34.20	2.87	3.99	33.98	2.88	4.26
Trichloromethylmercapto	$C_5H_6NOSCl_3$	32	71–74	25.60	2.58	5.97	26.01	2.69	5.92
p-Chlorophenylmercapto	$C_{10}H_{10}NOSCl$	96	77–79	52.74	4.43	6.15	53.02	4.30	6.00
p-Bromophenylmercapto	$C_{10}H_{13}NOSBr$	92	81–83	44.13	3.70	5.15	44.45	3.69	4.80
Phenylcarbamyl	$C_{11}H_{12}N_2O_2$	47	128–130	64.69	5.93	13.72	64.95	6.02	13.94
Phenylthiocarbamyl	$C_{11}H_{12}N_2OS$	88	115–119	59.97	5.49	12.72	60.19	5.69	21.69

of benzene was stirred at room temperature under a nitrogen atmosphere. After 2 days, the product was collected by filtration and recrystallized from benzene–alcohol, yield 1.0 g. (78%), m.p. 199–202°. *Anal.* Calcd. for $C_6H_{13}I_2NO$: C, 19.53; H, 3.55; N, 3.79. Found: C, 19.77; H, 3.76; N, 3.68.

N,N,N-Trimethyl-*dl-trans*-3-iodotetrahydro-4-furylammonium Iodide (IVb).—Formation of a white precipitate commenced within 10 min. when a solution of 3.0 ml. of methyl iodide and 1.0 ml. of compound IIIb in 25 ml. of benzene was stirred at room temperature under a nitrogen atmosphere. After 2 days the product was collected by filtration, yield 4.4 g., m.p. 207° with violent decomposition. The melting point was not altered upon recrystallization from ethanol. *Anal.* Calcd. for $C_7H_{15}I_2NO$: C, 21.95; H, 3.95; N, 3.61. Found: C, 21.92; H, 4.29; N, 3.37.

Other Derivatives of 3-Oxa-6-azabicyclo[3.1.0]hexane.—The aroyl, arenesulfonyl, and organomercapto derivatives were prepared by treatment of the parent aziridine IIa with the corresponding acid chloride in benzene solution in the presence of triethylamine. The carbamyl derivatives were prepared by treatment of the aziridine with phenyl isocyanate and isothiocyanate in benzene solution. All of the derivatives were solids, which were recrystallized from ethanol or benzene–petroleum ether. Yields, melting points, and elemental analyses are summarized in Table I.

Pyrolysis of 6-Benzoyl-3-oxa-6-azabicyclo[3.1.0]hexane (IX).—A solution of 0.531 g. of compound IX in 5 ml. of benzene was heated in an autoclave at 235–250° for 16 hr. Evaporation of the benzene gave a black tar, which was extracted with hot heptane to give a 33% yield of **2-phenyl-*cis*-tetrahydrofuro[3,4-*d*]oxazoline (XI)** white needles, m.p. 112–114°. After recrystallization from benzene–heptane, an analytical sample melted at 114–115°. When the pyrolysis was conducted for 16 hr. at 185–195°, the yield of oxazoline was 6%, and 41% of unreacted starting material was recovered. *Anal.* Calcd. for $C_{11}H_{11}NO_2$: C, 69.82; H, 5.86; N, 7.40. Found: C, 70.05; H, 6.08; N, 7.30.

Reaction of 6-Benzoyl-3-oxa-6-azabicyclo[3.1.0]hexane (IX) with Sodium Iodide.—A solution of 0.378 g. of compound IX and 2.0 g. of sodium iodide in 50 ml. of acetonitrile was stirred under nitrogen at room temperature for 16 hr. The solvent was evaporated and the solid residue was extracted with three 20-ml. portions of benzene. Distillation of the benzene extracts gave 0.30 g. (79% yield) of oxazoline XI, m.p. 111–113°. After recrystallization from benzene–heptane, the sample melted at 115–116°, and was found by mixture melting point and infrared absorption spectrum to be identical with the product obtained by pyrolysis. The same oxazoline was also obtained in 59% yield when the reaction was run in acetone and the distillation step was omitted. Oxazoline XI gave a negative potassium permanganate test for unsaturation, and absence of an NH bond was demonstrated in the infrared absorption spectrum.

Reaction of 6-(*p*-Nitrobenzoyl)-3-oxa-6-azabicyclo[3.1.0]hexane (IXa) with Sodium Iodide.—A solution of 0.300 g. of compound IXa and 2.0 g. of sodium iodide in 50 ml. of acetone was stirred at room temperature for 4 days, then refluxed for 1 hr. Hexane (200 ml.) was added and the reaction mixture was filtered to remove sodium iodide. Evaporation of the filtrate left 0.256 g. (85% yield) of **2-(*p*-nitrophenyl)-*cis*-tetrahydrofuro[3,4-*d*]oxazoline (XIa)**, yellow-white solid, m.p. 204–206°. Recrystallization from alcohol gave an analytical sample, m.p. 209–210°. *Anal.* Calcd. for $C_{11}H_{10}N_2O_4$: C, 56.41; H, 4.31; N, 11.96. Found: C, 56.31; H, 4.36; N, 11.40.

The Reaction of 2,3-Dichloronaphthoquinone with Nucleophiles. III. Reaction with 1,3-Indandione

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The rearrangement of 2-chloro-3-(1,3-dioxoindan-2-yl)-1,4-naphthoquinone into bindone has been investigated. A mechanism for this rearrangement is proposed.

In the previous paper of this series,[1] the reaction of 2,3-dichloro-1,4-naphthoquinone (**1**) with ethyl acetoacetate was investigated and structures were assigned to the reaction products. As part of the general problem of the study of the reaction of **1** with various nucleophilic reagents, we have extended the investigation to the reaction of 1,3-indandione (**2**) with **1**. This reaction proceeded at 25–30° in alcohol, N,N-diisopropylethylamine being used as the base to give **3** in 92% yield. The structure assigned to **3** was demonstrated by allowing *o*-aminobenzenethiol to react with **3** to give the phenothiazine derivative **4** which had an ultraviolet absorption spectrum similar to spectra of related compounds.[2] Treatment of **3** with piperidine and with sodium sulfide, followed by methyl sulfate, resulted in the replacement of the chlorine atom of compound **3** to give compounds **5** and **6**, respectively.

(1) G. A. Reynolds, J. A. VanAllan, and R. E. Adel, *J. Org. Chem.*, **30**, 3819 (1965).

(2) J. A. VanAllan, G. A. Reynolds, and R. E. Adel, *ibid.*, **27**, 1659 (1962).