ACTA CHEMICA SCANDINAVICA 21 (1967) 1841–1854

Photochemical Studies

VIII. The Formation of Benz[d]-1,3-oxazepines in the Photolysis of Quinoline *N*-Oxides in Solution *

O. BUCHARDT

Chemical Laboratory II (General and Organic Chemistry), University of Copenhagen, The H. C. Ørsted Institute, Copenhagen, Denmark

and

B. JENSEN and I. KJØLLER LARSEN

Chemical Laboratory C, The Royal Danish School of Pharmacy, Copenhagen, Denmark

The photolysis of a series of 2-phenyl- and 2-cyanoquinoline *N*-oxides is described. The main photolytic products are benz[d]-1,3-oxazepines (III). This was shown by X-ray crystallography, and by the examination of some of their chemical and spectroscopic properties. The formation of *N*-acyl-2-hydroxy-2,3-dihydroindoles (V) or the open chain tautomers (V′) in the solvolysis of the presently described benz[d]-1,3-oxazepines indicates the general occurrence of benz[d]-1,3-oxazepines in the photolysis of quinoline *N*-oxides. Minor amounts of some other compounds were also isolated.

Recently the photolysis of a series of 2-phenyl substituted quinoline *N*-oxides (Ia-d) was described in a preliminary communication,[1] and a tentative assignment of benz[d]-1,3-oxazepine structures (IIIa-d) to the main products was put forward. One of the products, IIIa, was previously obtained in the photolysis of Ia by Kaneko *et al.*[2], who assigned an oxaziridine structure (II) to this and some related products.[2–5]

The evidence for our tentative assignment [1] was the chemical and some of the spectroscopic properties of the presumed benz[d]-1,3-oxazepines.**

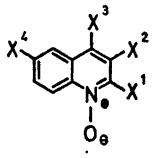
In this paper the photolysis of an extended series of quinoline *N*-oxides (Ia-m) is described. The main products of these photolyses, which according to their elemental analyses are isomers of the starting products, were benz[d]-

* A preliminary report of a part of this work has appeared.[1]

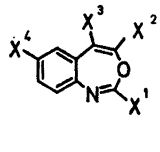
** The experimental details of this work are given in the present paper.

1,3-oxazepines (IIIa-m), and in some of the experiments minor amounts of carbostyrils (IVa, c-d) were also isolated.

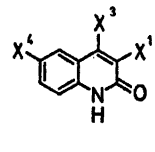
The identification of the benz[d]-1,3-oxazepines is based on an X-ray study of a monobromo compound (IIIe) which unambiguously establishes the seven-membered ring and enables us to infer the relative positions of the hetero atoms. The absolute positions of the two hetero atoms are inferred from some of the chemical data. By comparing the IR, UV, and NMR spectra (Table 1) of the main photolytic products (IIIa-m), it is concluded that they all contain the benzoxazepine structure.



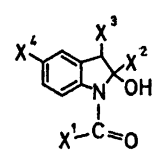
I



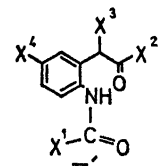
III



IV



V



V'

	X^1	X^2	X^3	X^4
a:	C_6H_5	H	H	H
b:	"	CH_3	"	"
c:	"	H	CH_3	"
d:	"	"	H	CH_3
e:	"	"	"	Br
f:	p-Br-C_6H_4	"	"	H
g:	"	"	"	Br
h:	CN	"	"	H
i:	"	CH_3	"	"
j:	"	H	CH_3	"
k:	"	"	H	CH_3
l:	"	"	"	OCH_3
m:	"	"	CH_3	"

The carbostyrils (IVa, c-d) are identified by elemental analysis, and by IR and UV spectroscopy (Table 2).

The indole derivatives (Va, Vc), and the chain tautomer (V'b), which are formed in the solvolysis of IIIa-c, are identified by IR, UV (Table 2), and NMR spectroscopy (Table 3, Fig. 2).

STRUCTURE ELUCIDATION OF THE BENZ[d]-1,3-OXAZEPINES

A. X-Ray crystallography: The electron density projection $\varrho(xy)$ of IIIe shows the molecule well resolved (Fig. 1). However, the X-ray data used do not permit an unequivocal determination of the absolute positions of the oxygen and nitrogen atoms. The molecule is roughly planar with the plane

approximately parallel to the y-axis and tilted in relation to the x-axis. In the projection (Fig. 1) the O—C-4 distance is very short although it is approximately parallel to the y-axis, and we therefore conclude that the molecule shows some deviation from planarity in this region. The projections of the interatomic distances clearly show that the only bonds which can exist between the atoms in the molecule are those shown between the neighbouring atoms in the figure.

B. Spectroscopy of the benz[d]-1,3-oxazepines: The IR spectra of the benz[d]-1,3-oxazepines (Table 1) all show two characteristic absorptions in the 1600 cm^{-1} region, which we tentatively assign to the vibrations of the seven-membered ring.

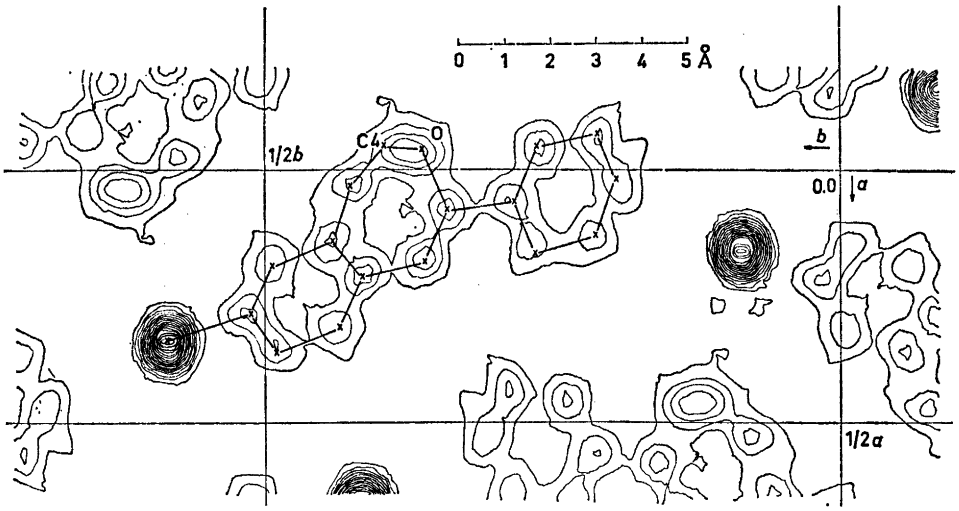
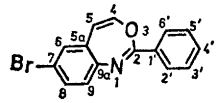


Fig. 1. Electron density projection $\varrho(xy)$ of IIIc.



III e

The UV spectra (Table 1) show absorption at slightly longer wavelength than found in the spectrum of *cis*-stilbene. Apparently, the delocalization of the electrons in the seven-membered ring is of the same magnitude as that found in other heterocyclic seven-membered ring systems with a number of π-electrons that does not agree with the Hückel $(4n + 2)$-rule.[6]

In the NMR spectra of the benz[d]-1,3-oxazepines (Table 1), the signals due to the protons in the seven-membered ring are very characteristic, and appear to be of considerable diagnostic value.

Table 1. Characteristic infrared absorptions in the 1600 cm^{-1} region,[a] long wavelength ultraviolet absorption, and nuclear magnetic resonance spectra[b] of benz[d]-1,3-oxazepines.

Compound	IR (in KBr)		UV (in 96 % EtOH)		NMR		
	cm^{-1}	cm^{-1}	λ_{max} mμ	log ε	H-4	H-5	CH_3
IIIa[c]	1670	1635	317	3.75	3.71, d, $J = 5.8$	4.08, d, $J = 5.8$	
IIIb	1675	1645	312	3.76		4.08, q, $J \sim 1$	7.95, d, $J \sim 1$
IIIc	1660	1640	309	3.81	3.70, q, $J = 1.5$		8.05, d, $J = 1.5$
IIId	1670	1635	327	3.76	3.75, d, $J = 6$	4.10, d, $J = 6$	7.72, s
IIIe	1675	1635	321	3.90	3.62, d, $J = 6$	4.00, d, $J = 6$	
IIIf	1665	1635	324	3.89	3.80, d, $J = 5.5$	4.08, d, $J = 5.5$	
IIIg	1665	1635	337	3.92	3.78, d, $J = 5.5$	4.16, d, $J = 5.5$	
IIIh[c]	1660	1640	320	3.50	4.07, d, $J = 6$	4.27, d, $J = 6$	
IIIi	1685	1645	318	3.52		4.27, q, $J \sim 1$	7.98, d, $J \sim 1$
IIIj[c]	1670	1645	314	3.53	3.85, q, $J = 1.5$		8.01, d, $J = 1.5$
IIIk	1670	1640	327	3.58	4.11, d, $J = 6$	4.38, d, $J = 6$	7.73, s
IIIl[d]	1685	1655	344	3.62	3.83, d, $J = 6$	4.11, d, $J = 6$	6.21, s
IIIm	1665	1645	341	3.79	3.83, q, $J = 1.5$		6.17, s; 8.01, d, $J = 1.5$

[a] Medium intensity, the band near 1670 cm^{-1} being the most intense.

[b] 60Mc/s NMR spectra with $CDCl_3$ as solvent and TMS as internal reference; chemical shifts are in τ units, coupling constants in cps; s = singlet, d = doublet, q = quartet; (note that another nomenclature than in Ref. 1 is employed).

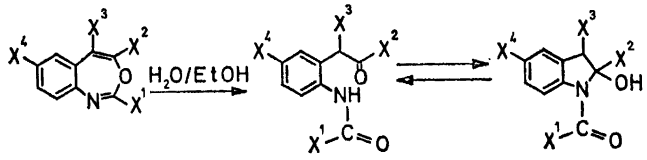
[c] *cf.* Ref. 2.

[d] Like *b*, with $DMSOd_6$ as solvent.

Table 2. The characteristic infrared absorptions, and long wavelength ultraviolet absorptions of carbostyrils (IV), 2-hydroxy-2,3-dihydro-indoles (V), and the chain-tautomer (V′).

Compound	IR (in KBr)		UV (in 96 % EtOH)					
	NH/OH cm^{-1}	C=O cm^{-1}	λ_{max} mμ	log ε	λ_{max} mμ	log ε	λ_{max} mμ	log ε
IVa	*ca.* 3000	1670	338	4.05	289	4.07		
IVc	*ca.* 3000	1660	329	3.98	277	3.97		
IVd	*ca.* 3000	1665	344	4.05	290	4.13		
Va	3300	1635	260	4.03	272sh	3.93	279sh	3.82
V′b	3300	1720 1655	249sh	3.99				
Vc	3250	1630	257	4.08	276sh	3.97	284sh	3.91

C. Chemical reactions: As a result of the X-ray crystallographic study, the relative positions of the two hetero atoms could be inferred. The absolute positions were elucidated by solvolysis of the benz[d]-1,3-oxazepines (III) under very mild conditions in aqueous ethanol. This yields either the indole derivatives (V), or the chain tautomers (V'). The ring forms (V) and the open forms (V') are believed to form equilibrium mixtures in solution.[7-8] As expected,[7] the ring tautomer (V) is the most stable if $X^2 = H$, while the chain tautomer (V') is preferred when $X^2 = CH_3$.



III V' V

Compounds Va, Vc, and V'b were identified by elemental analysis (Table 6), and by the similarity of their IR, UV (Table 2), and NMR spectra (Table 3, Fig. 2) with those of the previously described *N*-formyl and *N*-acetyl analogues.[7-10]

N-Benzoyl-2-hydroxy-3-methyl-2,3-dihydroindole (Vc) exists as a *ca.* 1:2 mixture of the *cis* and *trans* forms in solution, as seen from the NMR spectrum * (Fig. 2, Table 3).

Table 3. Nuclear magnetic resonance spectra[a] of 2-hydroxy-2,3-dihydroindoles (V), and the chain-tautomer (V').

Compound	Aliphatic methylene and methine protons		Methyl protons
Va[b]	H-2	4.43, d, $J = 6.5$	
	$H\text{-}3_A$	6.60, dd[c], $J_1 = 6.5$, $J_2 = 17$	
	$H\text{-}3_B$	7.20, d, $J = 17$	
V'b		6.18, s	7.95, s
cis Vc[d]	H-2	4.41, dd, $J_1 = 8.0$, $J_2 = 6.6$	8.62, d, $J = 7.3$
	H-3	6.5, m[c]	
trans Vc[d]	H-2	4.72, d, $J = 6.7$	8.75, d, $J = 7.3$
	H-3	6.81, q, $J = 7.3$	

[a] Chemical shifts are in τ units, coupling constants in cps; s = singlet, d = doublet, dd = doublet of doublets, q = quartet, m = multiplet.
[b] 60Mc/s with TMS as internal reference and $DMSOd_6$ as solvent.
[c] Partly obscured by the signal from H_2O present in the solvent.
[d] 100 Mc/s with TMS as external reference and $DMSOd_6$ as solvent.

* For a detailed discussion of the NMR spectra of type V compounds, see Refs. 7—8.

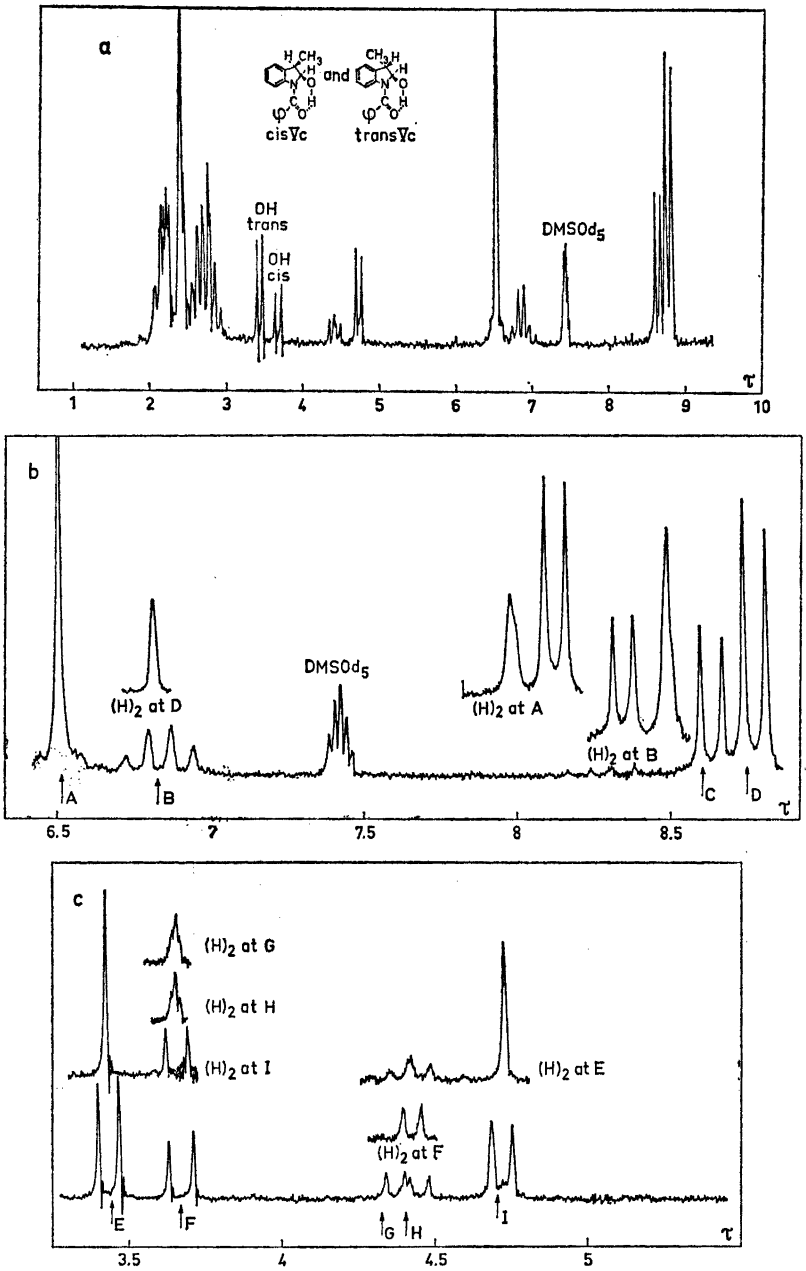


Fig. 2a. 100 Mc/sec NMR spectrum of Vc in $DMSOd_6$ with TMS as external reference. The peak at 6.5 τ is mainly due to water present in the solvent. *b, c.* Part of the spectrum of Vc, with various spin decouplings shown. With spin decoupling at C, the signal at 6.5 τ was slightly changed.

The benz[d]-1,3-oxazepines consume iodine in neutral aqueous solution, and it was shown that IIIa consumes 1 mole of iodine per mole, and that the benz[d]-1,3-oxazepines reduce copper(II) chloride under quite mild conditions.

Finally it was found that IIIa gives *N*-benzylindole by reduction with lithium aluminium hydride.

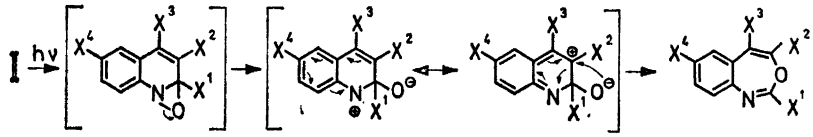
RESULTS AND DISCUSSION

The formation of benz[d]-1,3-oxazepines (III) is considered to be of general occurrence in the photolysis of quinoline *N*-oxides. Type III compounds have so far only been isolated from quinoline *N*-oxides with a phenyl group or a cyano group in the 2-position, but the formation of *N*-formyl-2-hydroxy-2,3-dihydroindoles in the photolysis of quinoline *N*-oxides with H in the 2-position [8,10] and of *N*-acetyl-2-hydroxy-2,3-dihydroindoles or their chain tautomers in the photolysis of 2-methylquinoline *N*-oxides [7,9] strongly point towards benz[d]-1,3-oxazepines (III) as precursors for the *N*-acylindoles. (Note that this is a change in the mechanistic pathway suggested previously [7,10]).

Furthermore, the unstable intermediates detected in the photolysis of 2-methylquinoline *N*-oxide [4] and 2,4-dimethylquinoline *N*-oxide [7] probably were the corresponding benz[d]-1,3-oxazepines.

It still seems attractive to consider that the primarily formed species leading either to carbostyrils (*cf.* Ref. 7) or benz[d]-1,3-oxazepines (III) are the oxaziridines (II).

The zwitterionic intermediate (II′—II″), suggested in the previous papers,[7,10] still seems reasonable, since the formation of benz[d]-1,3-oxazepines (III) can be explained by way of the latter ion. The benz[d]-1,3-oxazepines (III) can then react with water to form type V—V′ compounds, *cf.* p. 1846. However, it is emphasized that the mechanism suggested is purely speculative.



II II′ II″ III

Besides the pathway from II′—II″ leading to benzoxazepines, another pathway leading to carbostyrils is believed to exist.[7] It is found that the formation of type III compounds or their hydrolysis products V—V′ can be more or less inhibited, depending on the substituents, when the photolyses are run in protic solvents.[7,11] A control experiment to verify that the carbostyrils are not formed from III by irradiation has been performed.[1] Finally it should be noted that deoxygenation of the quinoline *N*-oxides during irradiation can also take place.[7]

EXPERIMENTAL

Microanalyses were carried out in the microanalysis department of this laboratory by Mr. Preben Hansen and his staff.

Melting points (uncorrected) were determined on a Reichert melting point microscope.

Infrared spectra for identification were recorded on a Perkin Elmer "Infracord", infrared spectra for analytical purposes on a Perkin Elmer Model 337 grating infrared spectrophotometer.

Ultraviolet spectra were recorded on a Perkin Elmer Model 137 UV spectrophotometer.

Nuclear magnetic resonance spectra were recorded on a Varian A-60 or a Varian HA-100 spectrometer.

X-Ray crystallography. 2-Phenyl-7-bromobenz[d]-1,3-oxazepine crystallizes from pentane as yellow, needle-shaped orthorhombic crystals. The cell dimensions, determined from rotation and Weissenberg photographs, are: $a = 11.0$ Å, $b = 25.2$ Å, $c = 4.55$ Å, $Z = 4$. From the absence of reflections $h00$ when h is odd and $0k0$ when k is odd the symmetry of the (001) projection was found to be *pgg*.

A crystal of dimensions $0.16 \times 0.1 \times 0.8$ mm³ was rotated around the needle axis, and Weissenberg photographs of the $hk0$ reflections were made, using Cu$K\alpha$ radiation and multiple film technique. The intensities were estimated visually. Corrections for absorption were not undertaken.

Table 4. Final positional and thermal parameters and their estimated standard deviations.

Atom	x	σx	y	σy	B	σB
Br	0.1596	0.0007	0.0852	0.0003	5.20	0.26
C-7	0.218	0.005	0.013	0.002	2.5	1.4
C-6	0.681	0.005	0.003	0.002	2.5	1.6
C-5a	0.638	0.006	0.059	0.002	4.3	1.9
C-9a	0.707	0.005	0.086	0.002	3.2	1.5
C-9	0.811	0.006	0.065	0.003	4.2	2.3
C-8	0.862	0.006	0.010	0.002	4.4	1.7
C-5	0.531	0.006	0.072	0.003	5.7	2.1
C-4	0.452	0.004	0.104	0.002	2.6	1.2
O	0.460	0.005	0.136	0.002	6.5	1.7
C-2	0.577	0.005	0.156	0.002	2.4	1.4
N	0.678	0.004	0.137	0.002	4.1	1.3
C-1′	0.555	0.006	0.216	0.003	4.2	1.7
C-2′	0.454	0.006	0.236	0.002	3.7	1.9
C-3′	0.429	0.006	0.289	0.003	4.1	1.8
C-4′	0.518	0.007	0.304	0.002	4.4	1.9
C-5′	0.627	0.007	0.287	0.003	5.1	2.1
C-6′	0.656	0.007	0.234	0.003	7.1	2.3

The Patterson function $P(xy)$ was calculated from 185 independent $hk0$ reflections, and the structure was determined from this by use of the heavy atom technique. Refinements of the coordinates were performed using the step method of Bhuiga and Stanley,[13] and by least squares refinements [14] of the co-ordinates and the individual isotropic temperature factors, the R-index was lowered to 14.6 %. The final parameters are given in Table 4, together with their estimated standard deviations.

Table 5. Quinolines and quinoline *N*-oxides (I).

Compound	Yield %	M.p. °C	Analysis							
			% C		% H		% N		% Br	
			Found	Calc.	Found	Calc.	Found	Calc.	Found	Calc.
2-Phenyl-6-bromo-quinoline	60	123–125	63.55	63.43	3.24	3.54	5.14	4.93	27.55	28.14
2-(4-Bromophenyl)-quinoline	60	119–120	63.40	63.43	3.36	3.54	4.90	4.93	27.88	28.14
2-Cyano-3-methyl-quinoline	50	130–131	78.60	78.55	5.20	4.79	16.66	16.66		
2-Cyano-4-methyl-6-methoxyquinoline	70	206–207	72.65	72.71	5.18	5.09	14.09	14.13		
Ia	90	144–145	81.08	81.43	4.85	5.01	6.42	6.33		
Ib	95	165–166	81.60	81.68	5.36	5.57	5.86	5.95		
Ic	75	119–120	80.92	81.68	5.78	5.57	5.76	5.95		
Id	65	143–144	81.70	81.68	5.71	5.57	5.94	5.95		
Ie	90	182–183	60.20	60.05	3.45	3.36	4.64	4.67	26.40	26.64
If	90	181–182	59.80	60.05	3.26	3.36	4.51	4.67	26.78	26.64
Ig	95	221–122	47.39	47.53	1.91	2.38	3.95	3.70	42.14	42.17
Ii	90	215–216	71.60	71.71	4.48	4.38	15.07	15.21		
Ik	90	184–186	71.22	71.71	4.28	4.38	15.30	15.21		
Il	90	222–223	66.20	65.99	4.12	4.03	13.95	13.99		
Im	90	262–263	67.40	67.28	4.87	4.71	12.98	13.08		

Methods of irradiation. The procedures previously described,[7] methods A or B, were employed in the present investigation. When specified, deoxygenated nitrogen was flushed through the solutions during the irradiations.

Chromatography. Thin layer chromatography (TLC) was performed on 8 × 10 cm plates (Kieselgel PF_{254} or $PF_{254+366}$, Merck, 0.25 mm). Preparative layer chromatography (PLC) was performed as described by Halpaap.[15] The plates were 40 × 100 cm. The thickness of the layer (Kieselgel PF_{254} or $PF_{254+366}$, Merck) varied between 0.5 mm and 2.5 mm. Various solvent mixtures were employed for development. The fractions were isolated by extraction with ethyl acetate, using a Soxhlet apparatus. The chromatograms were visualized with UV light.

Quinolines. (Table 5). 2-Phenyl-, 2-phenyl-3-methyl-, 2-phenyl-4-methyl, and 2-phenyl-6-methylquinoline were prepared according to the method described in Ref. 16. 2-Phenyl-6-bromo-, 2-(4-bromophenyl)-, and 2-(4-bromophenyl)-6-bromoquinoline were prepared by the Pfitzinger reaction.[17] 2-Cyano-, 2-cyano-3-methyl-, 2-cyano-4-methyl-, 2-cyano-6-methyl-, 2-cyano-6-methoxy-, and 2-cyano-4-methyl-6-methoxyquinoline were prepared by cyanation of the parent *O*-methylated quinoline *N*-oxide methyl sulfates.[18]

Quinoline-N-oxides. (Table 5). These were all prepared as described for 2-phenylquinoline *N*-oxide. The reaction times varied between two and ten days.

2-Phenylquinoline N-oxide (Ia). 2-Phenylquinoline (41.0 g) and *ca.* 80 % 3-chloroperbenzoic acid (50 g) were dissolved in chloroform (0.7 l). The solution was left in the dark for 48 h at room temp. After this, the solution was shaken with an excess of 1 N sodium hydroxide, washed once with *ca.* 0.1 N sodium hydroxide, twice with saturated sodium chloride and dried over anhydrous magnesium sulfate. After filtration and evaporation of the chloroform, 42 g of crude 2-phenylquinoline *N*-oxide was isolated.

Photolysis of quinoline N-oxides in aprotic solvents. The irradiations were all performed analogously to the irradiation described for 2-phenylquinoline *N*-oxide (Ia) in acetone (Table 6).

Photolysis of 2-phenylquinoline N-oxide (Ia) in acetone. 2-Phenylquinoline *N*-oxide (10.0 g) was dissolved in acetone (1.25 l) and irradiated after method B[7] for 12 h, after which time no more starting material could be detected by TLC. On evaporation of the solvent, an oily yellow residue was obtained. The residue was extracted several times with boiling hexane. Evaporation of the hexane yielded crude 2-phenylbenz[d]-1,3-oxazepine. After several recrystallizations from pentane, the melting point was raised to 65—66° (Table 6).

Photolysis of 2-phenylquinoline N-oxide (Ia) in 96 % ethanol. 2-Phenylquinoline *N*-oxide (Ia) (2.00 g) dissolved in 96 % ethanol (210 ml) was irradiated according to method A[7] for 22 h, after which time no more starting material could be detected by TLC. For 0.5 h before, and during the period of irradiation, the solution was flushed with deoxygenated nitrogen. By evaporation of the solvent, a yellow oil was obtained which was treated with ether-petroleum ether (1:1). This yielded a crystalline fraction, identified as 3-phenylcarbostyril (IVa) (8 %), m.p. 232—233° (Lit.[19] 235°). (Found: C 81.75; H 5.17; N 6.45. Calc. for $C_{15}H_{11}NO$: C 81.43; H 5.01; N 6.33). The solvent was evaporated, and the remaining oil extracted with petroleum ether. The petroleum ether was evaporated to yield 1.57 g of crude 2-phenylbenz[d]-1,3-oxazepine (IIIa). The residue from the latter extraction consisted of impure *N*-benzoyl-2-hydroxy-2,3-dihydroindole (Va).

Photolysis of 2-phenyl-4-methylquinoline N-oxide (Ic) in 96 % ethanol. 2-Phenyl-4-methylquinoline *N*-oxide (Ic) (1.00 g) dissolved in 96 % ethanol (410 ml) was irradiated as described for Ia. After evaporation of the solvent, the resulting oil was treated with ether. This yielded a crystalline fraction which was identified as 3-phenyl-4-methylcarbostyril (IVc) (12 %), m.p. 262—263°. (Found: C 81.95; H 5.67; N 6.12. Calc.for $C_{16}H_{13}NO$: C 81.68; H 5.57; N 5.95). The ethereal fraction was separated by PLC (petroleum ether-benzene-acetone, 10:10:1) into nine fractions. One of the fractions consisted of *N*-benzoyl-2-hydroxy-3-methyl-2,3-dihydroindole (Vc) (14 %). One of the other fractions consisted of crystalline material (258 mg), not yet identified, while the remainder fractions were oils.

Photolysis of 2-phenyl-6-methylquinoline N-oxide (Id) in 96 % ethanol. This experiment was performed analogously to the one described for Ia in 96 % ethanol. This yielded 3-phenyl-6-methylcarbostyril (IVd) (9 %), m.p. 225—226°. (Found: C 81.40; H 5.70; N 6.64. Calc. for $C_{16}H_{13}NO$: C 81.68; H 5.57; N 5.95), and 2-phenyl-7-methylbenz[d]-1,3-oxazepine (IIId) (56 %).

Table 6. Benz[d]-1,3-oxazepines (III).

Compound	Yield %	M.p. °C	Analysis							
			C		H		N		Br	
			Found	Calc.	Found	Calc.	Found	Calc.	Found	Calc.
IIIa	90	65– 66	81.30	81.43	5.18	5.01	6.32	6.33		
IIIb	90	72– 73	81.97	81.68	5.94	5.57	5.94	5.95		
IIIc	90	57– 58	81.50	81.68	5.55	5.57	6.06	5.95		
IIId	90	40– 41	81.50	81.68	5.59	5.57	5.99	5.95		
IIIe	65	81– 82	60.25	60.05	3.57	3.36	4.76	4.67	26.93	26.64
IIIf	85	86– 88	59.85	60.05	3.46	3.36	4.70	4.67	26.75	26.64
IIIg	80	138–140	47.70	47.53	2.48	2.38	3.92	3.70	41.99	42.17
IIIh	90	65– 66	70.80	70.58	3.57	3.55	16.40	16.46		
IIIi	70	75– 76	71.40	71.72	4.48	4.38	14.95	15.21		
IIIj	90	64– 66	71.60	71.72	4.54	4.38	15.07	15.21		
IIIk	95	74– 75	71.65	71.72	4.30	4.38	15.16	15.21		
IIIl	90	131–132	65.30	65.99	4.29	4.03	14.01	13.99		
IIIm	65	108–110	67.40	67.28	4.78	4.71	13.23	13.08		

Table 7. 2-Hydroxy-2,3-dihydroindoles (V) and chain-tautomer (V').

Compound	Yield %	M.p. °C	Analysis					
			C		H		N	
			Found	Calc.	Found	Calc.	Found	Calc.
Va	65	107–109	75.00	75.30	5.56	5.48	5.88	5.85
V'b	50	115–117	75.75	75.87	5.98	5.97	5.42	5.53
Vc	60	139–143	75.75	75.87	6.05	5.97	5.53	5.53

Photolysis of Ia, IIIa, and IIIc in 50 % aqueous ethanol. These experiments were performed analogously to the photolyses previously described, *cf.* Ref. 1.

Solvolysis of benz[d]-1,3-oxazepines. (Table 7). The procedure described for 2-phenylbenz[d]-1,3-oxazepine was employed in each experiment.

Solvolysis of 2-phenylbenz[d]-1,3-oxazepine (IIIa) in aqueous ethanol. 2-Phenylbenz[d]-1,3-oxazepine (IIIa) (1.00 g) was dissolved in 96 % ethanol (50 ml), and water (50 ml) was added. The reaction mixture was left at room temperature and the disappearance of IIIa followed by TLC. After 20 h, no more IIIa could be detected, and the solvents were removed *in vacuo*. The oily residue was treated with ether. This yielded 100 mg of crystalline material, m.p. 248–250°, not yet identified (*cf.* Ref. 5). The ether-soluble portion was separated by PLC (petroleum ether-benzene-acetone, 10:10:1). This treatment yielded *N*-benzoyl-2-hydroxy-2,3-dihydroindole (Va) (648 mg). After several recrystallizations from benzene-ether, the melting point was raised to 107–109° (Table 7).

Reduction of 2-phenylbenz[d]-1,3-oxazepine (IIIa) with lithium aluminium hydride. 2-Phenylbenz[d]-1,3-oxazepine (IIIa) (500 mg) dissolved in anhydrous ether (100 ml) was added to a solution of lithium aluminium hydride (1.0 g) in anhydrous ether (100 ml) over a period of 10 min, with stirring. The reaction mixture was stirred for 20 h, after which time it was treated with an excess of water, the precipitated inorganic material filtered off, and the ether evaporated. By PLC, the resulting brown oil yielded *N*-benzylindole (318 mg), m.p. 40–41° (Lit.[20] m.p. 57°). (Found: C 86.75; H 6.50; N 6.81. Calc. for $C_{15}H_{13}N$: C 86.92; H 6.32; N 6.76), (NMR: 2.3τ, multiplet, 1H; 2.85τ, multiplet, 9H; 3.47τ, doublet, J = 3 cps, 1H; 4.83τ, singlet, 2H).

Oxidation of benz[d]-1,3-oxazepines. A. The benzoxazepines, in ethanolic solution, were treated with an excess of potassium triiodide in water for *ca.* 15 min, and the excess of iodine was titrated with sodium thiocyanate. *B.* The benzoxazepines were dissolved in aqueous ethanolic copper(II) chloride solution and heated gently. This caused the precipitation of copper(I) chloride.

Acknowledgements. The authors wish to thank prof. B. Jerslev and prof. K. A. Jensen for their interest in and encouragement of this work, and Dr. J. Feeney, Varian Associates, for the recording of some 100 Mc/sec NMR spectra.

REFERENCES

1. Buchardt, O. *Tetrahedron Letters* **1966** 6221.
2. Kaneko, C. and Yamada, S. *Chem. Pharm. Bull. (Tokyo)* **14** (1966) 555.
3. Kaneko, C., Yamada, S. and Ishikawa, M. *Tetrahedron Letters* **1966** 2145.
4. Kaneko, C. and Yamada, S. *Rept. Res. Inst. Dental Materials, Tokyo Medico-Dental University* **2** (1966) 804.

5. Kaneko, C., Yamada, S. and Yokoe, I. *Tetrahedron Letters* **1966** 4701.
6. Katritzky, A. R. *Physical Methods in Heterocyclic Chemistry*, Academic, London 1963, II p. 66.
7. Buchardt, O., Becher, J. and Lohse, C. *Acta Chem. Scand.* **20** (1966) 2467.
8. Streith, J., Darrah, H. K. and Weil, M. *Tetrahedron Letters* **1966** 5555.
9. Buchardt, O., Becher, J., Lohse, C. and Møller, J. *Acta Chem. Scand.* **20** (1966) 262.
10. Buchardt, O. and Lohse, C. *Tetrahedron Letters* **1966** 4355.
11. Buchardt, O., Becher, J. and Lohse, C. *Acta Chem. Scand.* **19** (1965) 1120.
12. Ishikawa, M., Yamada, S., Hotta, H. and Kaneko, C. *Chem. Pharm. Bull. (Tokyo)* **14** (1966) 1102.
13. Bhuiga, A. K. and Stanley, E. *Acta Cryst.* **16** (1963) 981.
14. Busing, W. R., Martin, K. O. and Levy, H. A. *ORFLS, A FORTRAN crystallographic least square program*, Oak Ridge National Lab. (1962).
15. Halpaap, H. *Chem. Ing. Tech.* **35** (1963) 488.
16. Goldberg, N. N. and Levine, R. *J. Am. Chem. Soc.* **77** (1955) 3647.
17. Buu-Hoï, N. P., Royer, R., Xuong, N. D. and Jacquignon, P. *J. Org. Chem.* **18** (1953) 1209.
18. Feeley, W. E. and Beavers, E. M. *J. Am. Chem. Soc.* **81** (1959) 4004.
19. Pschorr, R. *Ber.* **31** (1898) 1289.
20. Plieninger, H. *Chem. Ber.* **87** (1954) 127.

Received March 22, 1967.