ACTA CHEMICA SCANDINAVICA 23 (1969) 2149–2157

Photochemical Studies

XVI. Photolysis of Phenylquinoline *N*-Oxides in Solution. A Novel Light-Induced Reaction. Solvent Influence on the Product Distribution *

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The photolysis of 3- and 4-phenylquinoline *N*-oxide in various solvents is reported. A reaction mechanism involving intermediate oxaziridine formation is presented and discussed in terms of the observed solvent effect. The light-induced rearrangement of 4-phenylquinoline *N*-oxide to 3-phenyl-2-indolecarboxaldehyde, which is an example of a novel photochemical reaction in the quinoline *N*-oxide series, is explained *via* a nitrene intermediate. Thermal rearrangement of benz[d][1,3]oxazepines to 3-acylindoles is reported.

Irradiation of quinoline *N*-oxides has previously been shown to result in deoxygenation,[2–10] rearrangement to carbostyrils,[2,3,6,7,10–16] formation of benz[d][1,3]oxazepines [8,15,16] *** or their hydrolysis products (*i.e.* *N*-acyl-2-indolinols or their open-chain tautomers) [5–8,14–16] and in two cases 3-acylindoles.[8] Furthermore, 4-nitroquinoline *N*-oxides [19] and 4-azidoquinoline *N*-oxide [20] have been subjected to photolysis and it has been shown [21] that photolysis of 2-cyano-4-methylquinoline *N*-oxide in the presence of amines can lead to the formation of *N*-aminocarbostyrils.

From the previous work [2–18] it can be concluded that polar protic media favour carbostyril formation, while non-polar aprotic media favour benz-

* For the previous paper in this series, see Ref. 1.

** NATO Research fellow 1967–68.

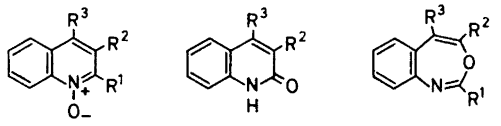
*** The benz[d][1,3]oxazepines were first believed to be oxaziridines.[4,9,13,17,18]

[d][1,3]oxazepine formation. It is noteworthy, that with the exception of the presently described 4-phenylbenz[d][1,3]oxazepine formation from 3-phenylquinoline *N*-oxide, only 2-aryl or 2-cyano substituted quinoline *N*-oxides [16] have yielded benz[d][1,3]oxazepines stable enough to be isolated and characterized.

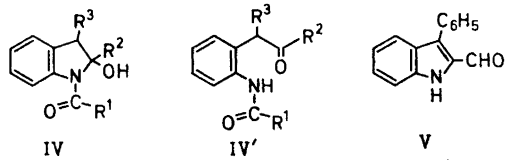
The purpose of the studies described in this paper was to gain further insight into the effect of substituents and solvents in quinoline *N*-oxide photochemistry. The 3- and 4-phenylquinoline *N*-oxides were chosen for this study because of the large amount of data available concerning the photolysis of 2-arylquinoline *N*-oxides.

IRRADIATIONS

Irradiation of 3-phenylquinoline *N*-oxide (Ib) in 96 % ethanolic solution resulted in an almost quantitative rearrangement to 3-phenylcarbostyril (IIb). If the irradiation of Ib was performed in acetone solution, however, the major product was 4-phenylbenz[d][1,3]oxazepine (IIIb) and 3-phenylcarbostyril (IIb) was the only minor product isolated.

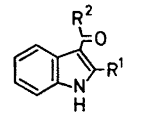


I II III



IV IV′ V

	R^1	R^2	R^3
a.	C_6H_5	H	H
b.	H	C_6H_5	H
c.	H	H	C_6H_5
d.	C_6H_5	H	CH_3



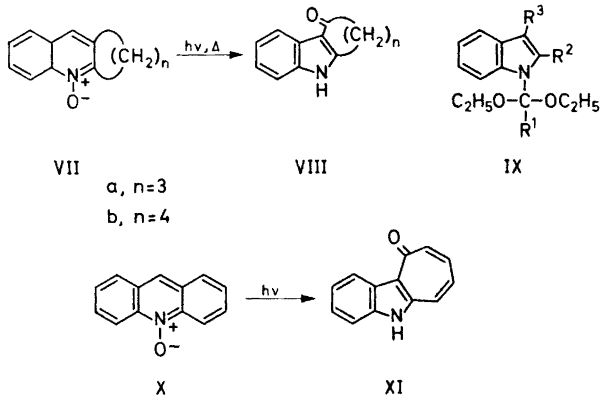
VI

Irradiation of 4-phenylquinoline *N*-oxide (Ic) in ethanol also resulted in an almost quantitative rearrangement to the corresponding carbostyril (IIc). If the irradiation of Ic was performed in ethyl acetate a high yield of IIc again was realized. In addition to IIc, minor amounts of 4-phenylquinoline were isolated and four unidentified components were observed by TLC. Irradiation of Ic in cyclohexane resulted in the formation of a complicated mixture which upon preparative layer chromatography was separated into three main fractions. Fraction 1 consisted of 4-phenylcarbostyril (IIc), fraction 2 of *N*-formyl-3-phenyl-2-indolinol (IVc), and fraction 3 was identified as 3-phenyl-2-indolecarboxaldehyde (V).

SOLVOLYSIS OF BENZ[d][1,3]OXAZEPINES (III)

In order to obtain more information on the structure of the products from these photolyses we solvolyzed 4-phenylbenz[d][1,3]oxazepine (IIIb), obtained from 3-phenylquinoline *N*-oxide (Ib), in cold aqueous ethanol. This resulted in the formation of two compounds, the expected [16] 2-formamidophenylacetophenone (IV'b) and the unexpected 3-benzoylindole (VIb). Compound VIb was formed in an almost quantitative yield by boiling an ethanolic solution of IIIb until no more starting material could be detected by thin layer chromatography.

This led us to reexamine some of our results, as well as those of other workers, and we found that the formation of an unidentified isomer of 2-phenylbenz[d][1,3]oxazepine (IIIa) previously reported [18] had also been observed in this laboratory.[22] We solvolyzed ethanolic solutions of 2-phenylbenz[d][1,3]oxazepine (IIIa) and 2-phenyl-4-methylbenz[d][1,3]oxazepine (IIId). Preparative layer chromatography of the reaction mixtures resulted in the isolation of compounds identified as 2-phenyl-3-indolecarboxaldehyde (VIa) and 3-acetyl-2-phenylindole (VId), respectively. It should furthermore be noted that the previously described [8] formation of compounds VIII in the photolysis of VII a and VIIb, respectively, consists of analogous processes, which presumably [8] also proceed *via* the corresponding benz[d][1,3]oxazepines.



VII a, n=3 b, n=4 VIII IX

X XI

In addition to compounds of type VI we have also isolated compounds which we believe to have structure IX from both of the above solvolyses (*cf.* Refs. 18 and 23). Very recently [24] it was reported that acridine *N*-oxide (X) upon photolysis in aprotic solvents rearranged to compound XI.

IDENTIFICATION OF PRODUCTS

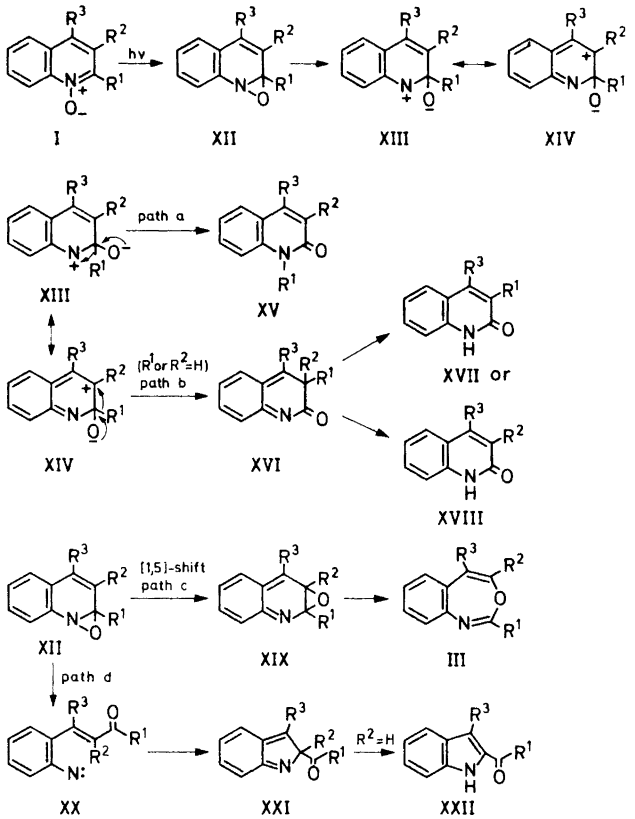
The IR spectra of the carbostyrils IIb and IIc were identical with the spectra of samples prepared by other methods and the substances had the expected melting points and elemental analyses. 4-Phenylquinoline was

identified by IR spectroscopy. *N*-Formyl-3-phenyl-2-indolinol (IVc) and 2-formamidophenylacetophenone (IV'b) were identified by elemental analysis and by their IR, UV, and NMR spectra which showed excellent agreement with those of the previously described analogs [6,10,16,25] (see also experimental section). The 3-acylindoles (VI) and 3-phenyl-2-indolecarboxaldehyde (V) were identified by IR and NMR spectroscopy and they had the expected melting points and elemental analyses; 3-benzoylindole (VIb) was identical (m.p., mixed m.p., IR) with an authentic sample, (see experimental section). Compounds IX were identified by NMR only.

DISCUSSION

The present results are in good agreement with the previously [2-18] reported solvent effects, and the results from 3-phenylquinoline *N*-oxide offer a particularly striking example of this.

To explain this effect we partly adopt our previously (*e.g.* Ref. 10) suggested mechanism.



The first step is presumed to involve intermediate oxaziridine (XII) formation.* Heterolysis of XII results in the formation of the zwitterion XIII—XIV, which can then react by either of the pathways *a* or *b*. This description of carbostyril (XV, XVII, XVIII) formation can be regarded as competitive nucleophilic attack. Previously, several explanations have been put forward (see, *e.g.*, Refs. 16, 25) to explain the light-induced ring expansions of aromatic amine *N*-oxides. We wish to modify our previous point of view.[16] Although it cannot be excluded with certainty that formation of the benz[d][1,3]oxazepines takes place *via* zwitterionic intermediates [16] or *via* free radical species [25] we wish to point out that the rearrangement of the presumed precursors, *i.e.* the oxaziridines (XII) to intermediates XIX, can be formulated as a thermally allowed suprafacial [1,5]- or [1,9]-sigmatropic shift.[27] Analogies to the XII→XIX rearrangement have recently been discussed in similar terms in bicyclic systems [28] and are known in tricyclic systems as well.[29] The thermally induced rearrangement of XIX to III has many precedents.[30] This mechanistic scheme is in very good agreement with the observed solvent effect. In polar protic media the zwitterionic species (XIII—XIV), and the transition state leading to these, are expected to be energetically more favoured than in non-polar aprotic media. It is indeed observed that carbostyril formation is dominant in the former media whereas carbostyrils are only minor products in the latter media and *vice versa* for the benz[d][1,3]-oxazepine formation. It should be noted that similar arguments can be invoked to explain the results from other aromatic amine *N*-oxide photolyses (see previous papers in this series and references cited therein).

Formation of 3-phenyl-2-indolecarboxaldehyde (V) in the photolysis of 4-phenylquinoline *N*-oxide (Ic) represents a new type of rearrangement in quinoline *N*-oxide photochemistry, whereas it has ample precedent in pyridine *N*-oxide photochemistry (Ref. 1 and papers cited therein).

The latter reaction is supposed to take place as outlined in the chart (path *d*).

The very recent results obtained in the pyridazine *N*-oxide series,[31] in which a transient diazo compound was formed and detected, lead us to suggest a similar mechanism in the present case. We believe that the nitrene XX is formed directly from the oxaziridine XII in either a thermal or photochemical process. The nitrene could be converted to the 2-acylindole XXII *via* the indicated pathway or by direct insertion into the vinyl C—H bond of the α,β-unsaturated ketone system present in XX. At present no attempt to

* Oxaziridines have neither been isolated nor detected as transient intermediates in aromatic amine N-oxide photochemistry. This failure to isolate the oxaziridines can be explained in several ways. *A*. The oxaziridines are too thermally unstable to be isolated but are photochemically stable when Pyrex-filtered light (or the least energetic light able to affect the aromatic amine *N*-oxides) is employed. If this is the case, low temperature photolysis, combined with spectroscopy, should be of great help in demonstrating oxaziridine formation. *B*. Atomic arrangements corresponding to oxaziridines exist, but only as transition states or species with a similar short lifetime. *C*. Oxaziridines are formed but break down photochemically with a quantum yield equal to or greater than the quantum yield for oxaziridine formation. *D*. The mechanisms suggested so far, assuming oxaziridines as intermediates or oxaziridine-like transition states, are wrong, and an entirely different mechanism is in operation.

discuss the substituent or the solvent effect on this type of light-induced reaction will be undertaken owing to the limited amount of data available.

The thermal rearrangement of benz[d][1,3]oxazepines (III) to 3-acylindoles (VI) is apparently a general process. A mechanism for this transformation has previously been suggested by Kaneko *et al.*[18,24] in the case of formation of compounds VIII and XI. Although the valence tautomerization of the benz[d][1,3]oxazepines (III) to XIX could not be detected by NMR spectroscopy, the above reaction and particularly the formation of 3-hydroxyquinolines [9] from compounds III is regarded as evidence that the isomerization III→XIX takes place to some extent.

It is obvious from the present and previous results [2-18] that the reaction pathways followed in the photolyses of quinoline *N*-oxides are governed not only by solvent, but also by the substituents, particularly by those in the nitrogen containing ring. A further discussion of the latter phenomenon, however, must be postponed until further results have been obtained.

EXPERIMENTAL

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

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

Infrared spectra were recorded on a Perkin Elmer "Infracord" or 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 spectrometer model A 60 A.

Methods of irradiation. A. The light source was two medium pressure mercury lamps (Philips KL 7070). The sample to be irradiated was placed in a water cooled Pyrex container. *B.* External light source (Rayonet reactor, type RPR-208, RUL 3500 lamps). The sample to be irradiated was placed in a magnetic stirred Pyrex flask. All irradiations were performed at 20—40°C.

Quinolines. 3-Phenylquinoline was prepared by the previously reported method [32] and 4-phenylquinoline by the previously reported method.[33] 4-Phenylquinoline picrate: (Found: C 57.80; H 3.43; N 12.84. Calc. for $C_{21}H_{14}N_4O_7$: C 58.07; H 3.25; N 12.90). M.p. 224—225°.

Quinoline N-*Oxides.* Both 3-phenylquinoline *N*-oxide [34] and 4-phenylquinoline *N*-oxide were prepared by the previously described [16] oxidation of the parent amines with 3-chloroperbenzoic acid.

4-Phenylquinoline N-*oxide.* Yield 80 %. M.p. 124—125°. (Found: C 81.30; H 5.12; N 6.35, Calc. for $C_{15}H_{11}NO$: C 81.42; H 5.01; N 6.33). λ_{max}(EtOH) 343 sh, $\log\varepsilon = 3.89$; 334, $\log\varepsilon = 3.90$; 233, $\log\varepsilon = 4.40$.

Irradiation of 3-phenylquinoline N-*oxide in 96 % ethanol.* 3-Phenylquinoline *N*-oxide (Ib) (270 mg) in 96 % ethanol (325 ml) was irradiated by method *B* until no more starting material could be detected by TLC. Evaporation of the solvent afforded a crystalline compound, which was identical (IR, m.p.) with an authentic sample of 3-phenylcarbostyril,[16] in 98 % yield.

Irradiation of 3-phenylquinoline N-*oxide in acetone.* 3-Phenylquinoline *N*-oxide (Ib) (523 mg) in analytical grade acetone (250 ml) was irradiated by method *B* until no more starting material could be detected by TLC. Evaporation of the solvent *in vacuo* afforded a semicrystalline residue. By extraction with petroleum ether a crystalline substance remained, which was shown to be 3-phenylcarbostyril (20 %). Evaporation of the petroleum ether gave a crystalline yellow substance, m.p. 48—53°. Several recrystallizations from pentane raised its m.p. to 56—57°. The compound was identified as 4-phenylbenz[d][1,3]oxazepine (IIIb). (Found: C 81.00; H 5.20; N 6.49. Calc. for $C_{15}H_{11}NO$: C 81.42; H 5.01; N 6.33). IR: 1670 cm^{-1}, 1635 cm^{-1}. UV: λ_{max}(cyclohexane) 311, $\log\varepsilon = 3.88$;

258, logε=4.32. NMR: 2.1—2.9τ, 9 H, m, phenyl protons; 3.08τ, 1 H, s, H-2; 3.43τ, 1 H, s, H-5.

Irradiation of 4-phenylquinoline N*-oxide in ethyl acetate.* 4-Phenylquinoline *N*-oxide (Ic) (600 mg) in ethyl acetate (300 ml) was irradiated by method *A* until no more starting material could be detected by TLC. Evaporation of the solvent yielded a crystalline substance, which, after recrystallization, was shown to be identical with an authentic sample (IR, m.p.) of 4-phenylcarbostyril.[35] (483 mg). Preparative layer chromatography of the mother liquor yielded a further amount (32 mg) of 4-phenylcarbostyril, and 28 mg 4-phenylquinoline, identical with an authentic sample (IR, m.p.).

Irradiation of 4-phenylquinoline N*-oxide in cyclohexane.* 4-Phenylquinoline *N*-oxide (Ic) (900 mg) in cyclohexane (900 ml) was irradiated by method *A* until no more starting material could be detected by TLC. After evaporation of the solvent *in vacuo* the remaining oil was separated into three main crystalline fractions by preparative layer chromatography. Fraction 1 (most polar) consisted of 135 mg 4-phenylcarbostyril[35] (see above). Fraction 2 (133 mg) after several recrystallizations from benzene-pentane melted at 157—158°. This compound was identified as *N*-formyl-3-phenyl-2-indolinol (IVc). (Found: C 75.43; H 5.62; N 5.48. Calc. for $C_{15}H_{13}NO_2$: C 75.29; H 5.48; N 5.86). UV: λ_{max}(EtOH) 286, logε=3.45; 279, logε=3.50; 248, logε=4.09. IR (KBr): 3400 cm^{-1} (OH), 1665 cm^{-1} (CO). NMR (DMSO-d_6, TMS as internal reference): 0.83τ, s, 0.2 H and 1.32τ, s, 0.8 H (*N*-formyl protons of **s-*cis*-** and **s-*trans*-**conformers,[25] respectively); 2.12τ, d, J=8 cps, 0.8 H and 2.3—3.1τ, m, 8.2 H (aromatic protons); 4.28τ, broad singlet, 1 H, H-3; 5.7τ, two overlapping broad singlets, 1 H, H-2; 6.67τ, s, signal from OH and H_2O present in the solvent. Addition of a drop of D_2O caused the signal at 4.28τ to change to a narrow doublet with J=2 cps. Fraction 3 (401 mg) after several recrystallizations from benzene melted at 197—198°. (Found: C 81.20; H 5.14; N 6.23. Calc. for $C_{15}H_{11}NO$: C 81.42; H 5.01; N 6.33). UV: λ_{max}(EtOH) 350sh, logε=3.86; 318, logε=4.24; 248, logε=4.29; 227, logε=4.14. IR: 3320 cm^{-1} (NH); 2870 cm^{-1} (aldehyde CH); 1650 cm^{-1}, (CHO). NMR: 0.02τ, s, 1 H (aldehydic proton); 0.2—1.0τ, broad signal, 1 H (NH); 2.0—2.8τ, m, 9 H (aromatic protons). On this evidence the compound was identified as 3-phenyl-2-indolecarboxaldehyde (VI). Recorded m.p. 195—197°.[36]

Solvolysis of 2-phenylbenz[d][1,3]oxazepine in boiling 99.5 % ethanol. 2-Phenylbenz-[d][1,3]oxazepine (IIIa) (400 mg) in 99.5 % ethanol (30 ml) was refluxed for 50 h. After partial evaporation of the solvent and cooling the precipitated crystals were filtered off (85 mg), fraction *a*. The remainder was separated in six fractions by preparative layer chromatography. Fractions 2, 3, and 5 were oils, and fraction 4 crystalline. Those fractions which were very minor were not characterized. Fraction 1 (150 mg) consisted of crystals identical with fraction *a*. Fractions 1+*a* were identified as 2-phenyl-3-indolecarboxaldehyde. M.p. 252—253°. Lit.[37] 253—254°. UV: λ_{max}(EtOH) 314, logε=4.16; 257, logε=4.46; *cf.*[17] IR: 3000 cm^{-1} (NH). 1630 cm^{-1} (CHO). NMR: —1.18τ, broad signal, 1 H (NH); —0.09τ, s, (aldehydic proton); 1.6τ, m, 1 H and 2.1—3.0τ, m, 8 H (aromatic protons). Fraction 6 (63 mg oil) was presumed to have the structure IXa (see higher) on the basis of its NMR spectrum: 2.25τ, d, J=3.5 cps, 1 H; 3.50τ, doublet of doublets, J_1=3.5 cps, J_2=1 cps, 1 H (five-membered ring protons); 2.3—3.2τ, m, 9 H (remaining aromatic protons); 6.63τ, quartet where the two peaks at lowest field appeared as narrow doublets indicating magnetic non-equivalence of the protons, 4 H (methylene protons); 8.81τ, t, 6 H (methyl protons).

Solvolysis of 4-phenylbenz[d][1,3]oxazepine in cold aqueous ethanol. 4-Phenylbenz[d]-[1,3]oxazepine (IIIb) (500 mg) in 70 % aqueous ethanol (100 ml) was kept at room temperature for 20 h. The resulting colourless solution was concentrated and the resulting oil purified by preparative layer chromatography. This gave two crystalline fractions. Fraction 1 (156 mg) after several recrystallizations from ethanol had m.p. 242—244°. This compound was identified as 3-benzoylindole by the identity of its IR spectrum with that of an authentic sample.[38] Mixed m.p. test showed no depression. NMR: —1.67τ, broad signal, 1 H (NH); 1.8—3.1τ, m, 10 H (aromatic protons). M.S.: *m/e* 221 (68 %), 144 (100 %); remainder ions less than 12 % of *m/e* 144. Fraction 2 (135 mg) after recrystallization from ethanol had m.p. 154—156°. This compound was identified as 2-formamidophenylacetophenone. (Found: C 74.91; H 5.55; N 5.74. Calc. for $C_{15}H_{13}NO_2$: C 75.29; H 5.48; N 5.86). UV: λ_{max}(EtOH) 282sh, logε=3.05; 244, log=4.04. IR: 3330 cm^{-1} (NH); 1690 cm^{-1}, 1670 cm^{-1} (ketone CO and amide CO). NMR, see Ref. 25).

Solvolysis of 4-phenylbenz[d][1,3]oxazepine in 96 % ethanol. By solvolyzing 4-phenylbenz[d][1,3]oxazepine in 96 % ethanol an almost quantitative rearrangement to 3-benzoylindole was observed.

Solvolysis of 2-phenyl-4-methylbenz[d][1,3]oxazepine in 99.5 % ethanol. 2-Phenyl-4-methylbenz[d][1,3]oxazepine (IIId) (160 mg) in 99.5 % ethanol (25 ml) was refluxed for 50 h. The solvent was evaporated and the oily residue separated by PLC into two main fractions. Fraction one (107 mg crystals) upon recrystallization from ethanol had m.p. 222–223°. This compound was identified as 2-phenyl-3-acetylindole,[39] m.p. 220–321. UV: λ_{max}(EtOH) 305, logε=4.10; 252, logε=4.32. IR: 3200 cm^{-1} (NH); 1620 cm^{-1} (CO). NMR: −2.08τ, broad signal, 1 H (NH); 1.6–3.0τ, m, 9 H (aromatic protons) 7.89τ, s, 3 H (CH_3). The second fraction (50 mg oil) was tentatively identified as IXd on the basis of its NMR spectrum which showed the expected features. From the spectrum it could be seen that IXd was impure.

Acknowledgements. This work was supported by the *Carlsberg Foundation* (purchase of the Rayonet reactor). One of the authors (P.L.K.) wishes to acknowledge the support of the *North Atlantic Treaty Organization* in the form of a N.A.T.O. Postdoctoral Fellowship.

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Received November 22, 1968.