

separated on dilution of the filtrate with water was found to contain no selenium.

The reaction was also tried with unsubstituted selenosemicarbazide prepared according to Huls and Renson¹¹ with the same result.

I want to thank Prof. K. A. Jensen for the suggestion to carry out this work.

1. Jensen, K. A. *et al. Acta Chem. Scand.* To be published.
2. Jensen, K. A. and Frederiksen, E. *Z. anorg. allgem. Chem.* **230** (1936) 31.
3. Huls, R. and Renson, M. *Bull. Soc. Chim. Belges* **65** (1956) 684.
4. Collard-Charon, C. and Renson, M. *Ibid* **71** (1962) 531.
5. Collard-Charon, C., Huls, R. and Renson, M. *Ibid* **71** (1962) 541.
6. Rheinboldt, H. and De Campo, H. V. *J. Am. Chem. Soc.* **72** (1950) 2784.
7. Tarantelli, T. and Pecile, C. *Ann. Chim. (Rome)* **52** (1962) 79.
8. Lieber, E., Rao, C. N. R. and Ramachandran, J. *Spectrochim. Acta* **13** (1959) 296.
9. Ham, N. S. and Willis, I. B. *Ibid* **16** (1960) 279.
10. Ugi, I. and Meyer, R. *Chem. Ber.* **93** (1960) 239.
11. Huls, R. and Renson, M. *Bull. Soc. Chim. Belges* **65** (1956) 511.

Received April 29, 1963.

Photochemical Studies

I. The Photorearrangement of Quinoline-N-oxide

O. BUCHARDT

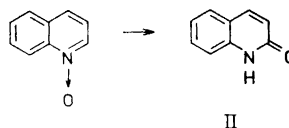
Chemical Laboratory II (General and Organic Chemistry), University of Copenhagen, Copenhagen, Denmark

Photochemical isomerizations of tertiary amine-N-oxides and a few related compounds have been known for some time¹⁻⁵, but the scope and variety of these reactions have not been investigated further.

On irradiation of a solution of quinoline-N-oxide in absolute ethanol a white crystalline precipitate was formed, which was almost insoluble in most organic and in-

organic solvents. After isolation of the precipitated compound (I), the filtrate on evaporation of the solvent yielded a crystalline residue (II) which, after recrystallization, melted at 197–198°C. Elementary analysis and molecular weight established the empirical formula of (II) as C₉H₇N₂O, an isomer of the starting material (m.p. 57–58.5°C).

If quinoline-N-oxide rearranges in the same manner as quinoxaline-N-oxide and quinoxaline-N,N'-dioxide^{1,2}, it would give carbostyryl (II):



The melting point of the rearranged product corresponds to that of carbostyryl, and the ultraviolet, infrared and nuclear magnetic resonance spectra showed no difference from spectra of an authentic sample of carbostyryl. The 60 Mc/sec nuclear magnetic resonance spectrum (20% in trifluoroacetic acid with tetramethylsilane as internal reference) consisted of three peaks: a broad peak at 770 cps (amide proton), two doublets at 527 cps and 448 cps (olefinic protons), and a strong multiplet at 480 cps (aromatic protons).

The other product (I) which was insoluble in ethanol melted at ca. 300°C under sublimation. Elementary analysis and molecular weight corresponded to the formula C₁₈H₁₄N₂O₂. The presence of a nonconjugated-CO-NH-group was strongly indicated by the infrared spectrum which showed carbonyl absorption at 1715 cm⁻¹, whereas carbostyryl and other conjugated lactams show carbonyl absorption at 1680–1630 cm⁻¹⁶. On sublimation the compound was almost quantitatively reconverted to carbostyryl, and these results together with spectroscopical and analytical data suggested that it was a dimer of carbostyryl, initially formed by the rearrangement of quinoline-N-oxide. To prove this, a solution of carbostyryl in absolute ethanol was irradiated. This gave almost quantitatively a crystalline precipitate which was shown to be identical with (I), by infrared and nuclear magnetic resonance spectra.

It is known⁷⁻⁹ that 2-pyridones and N-methylcarbostyryl dimerize, and the 2-pyridone dimers have been assigned

structures presumably resulting from 3,6-addition⁸⁻⁹. It would be reasonable to assign a similar structure to the dimer of carbostyryl; however, the pattern of the nuclear magnetic resonance spectrum seems in disagreement with this assignment. The 60 Mc/sec spectrum (20% in trifluoroacetic acid with tetramethylsilane as internal reference) showed a sharp peak at 604 cps (amide protons), a multiplet at 435 cps (aromatic protons), and a single, very sharp peak at 250 cps (aliphatic protons). The structure of the dimer is now under further examination.

If quinoline-N-oxide is irradiated in aqueous solution, it rearranges to carbostyryl in good yield with negligible formation of the dimer.

Experimental. The light source was a 600 W sun lamp, and the irradiations were all carried out in 25 ml 16 × 160 mm pyrex test tubes closed with a cork stopper. These tubes were wrapped with aluminium foil above the surface of the reaction mixture to avoid formation of strongly coloured oxidation products. The distance to the lamp was 15 cm, and no precautions were taken to avoid the presence of small amounts of air.

Infrared spectra were recorded on a Perkin-Elmer model Infracord or 21 double beam spectrophotometer. Ultraviolet spectra were recorded on a Perkin-Elmer model 137 UV spectrophotometer. Nuclear magnetic resonance spectra were recorded on a Varian A 60.

1. *Irradiation of quinoline-N-oxide in absolute ethanol.* Quinoline-N-oxide (1.00 g) dissolved in 95 ml absolute ethanol was irradiated for 21 h at ca. 35°C. The precipitated crystals (128 mg) were separated by filtration. A small sample was recrystallized from dimethylformamide to give colourless plates. M.p. ca. 300°C (subl.). (Found: C 73.45; H 4.97; N 9.42; Mol. wt. 266. Calc. for C₁₈H₁₄N₂O₂: C 74.47; H 4.86; N 9.65; Mol. wt. 290).

Infrared spectrum. Bands in cm⁻¹. 3210 m, 3070 m, 2995 m, 2940 m, 1715 vs, 1675 vs, 1610 m sh, 1593 m, 1493 s, 1425 m sh, 1376 s, 1307 m, 1250 m sh, 1238 m, 1205 w, 1184 m, 1170 w, 1154 vw, 1113 vw, 1034 w, 938 vw, 864 w, 837 vw, 806 vw, 787 w, 745 s, 720 m, 698 w, 680 vw, 660 vw.

The solvent was evaporated from the filtrate and the residue recrystallized from ethanol to give colourless needles (491 mg). M.p. 197–198°C. (Found: C 74.85; H 4.91; N 9.67; Mol. wt. 137. Calc. for C₉H₇NO: C 74.47; H 4.68; N 9.65; Mol. wt. 145).

The infrared, ultraviolet and nuclear magnetic resonance spectra were identical with spectra of an authentic sample of carbostyryl.

A further amount (250 mg) of less pure carbostyryl was obtained from the mother liquor.

2. *Irradiation of quinoline-N-oxide in water.* Quinoline-N-oxide (501 mg) dissolved in 45 ml water was irradiated for 15 h at ca. 35°C, the reaction mixture cooled in ice water, and the precipitated colourless crystals separated by filtration (276 mg). The mother liquor on further treatment yielded 50 mg less pure material. After recrystallization from ethanol the product was shown by infrared spectroscopy to be identical with carbostyryl.

3. *Irradiation of carbostyryl in ethanol.* Carbostyryl (105 mg) dissolved in 20 ml absolute ethanol was irradiated for 20 h at ca. 35°C. The precipitated crystals (95 mg) were separated by filtration. A small sample was recrystallized from dimethylformamide to give colourless plates. M.p. ca. 300°C (subl.). (Found: C 73.25; H 5.03; N 9.42.). The product was shown by infrared and nuclear magnetic resonance spectroscopy to be identical with the insoluble compound from experiment 1.

A number of substituted quinoline-N-oxides are under further examination, and results will be reported presently.

Acknowledgement. The author wishes to thank Professor K. A. Jensen for most helpful discussions.

1. Schönberg, A. *Präparative Organische Photochemie*, Springer, Berlin 1958, pp. 19–21.
2. De Mayo, P. and Reid, S. T. *Quart. Rev.* **15** (1961) 393.
3. Hata, N. *Bull. Chem. Soc. Japan* **34** (1961) 1440.
4. Hata, N. *Ibid.* **34** (1961) 1444.
5. Hata, N. *J. Chem. Phys.* **36** (1961) 2072.
6. Bellamy, L. J. *The Infrared Spectra of Complex Molecules*, 2nd Ed., John Wiley & Sons, New York 1951.
7. Taylor, E. C. and Paudler, W. W. *Tetrahedron Letters* **1960** 1.
8. Ayer, W. A., Hayatsu, R., de Mayo, P., Reid, S. T. and Stothers, J. B. *Tetrahedron Letters* **1961** 648.
9. Slomp, G., MacKellar, F. A. and Paquette, L. A. *J. Am. Chem. Soc.* **83** (1961) 4472.

Received April 29, 1963.