

CHEMISTRY OF PHENOXAZINES

II.* SYNTHESIS OF BENZO[c]PHENOXAZIN-3-ONE AND

SPECTROSCOPIC STUDY OF BENZOPHENOXAZINONES

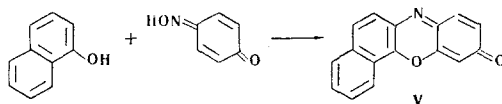
G. B. Afanas'eva, K. I. Pashkevich,
and I. Ya. Postovskii

UDC 547.867.6:543.4

Benzo[c]phenoxazin-3-one was synthesized, and the IR and electronic absorption spectra of phenoxazin-3-one and six of its benzo derivatives were studied.

Benzo[c]phenoxazin-3-one (V) was synthesized in order to make a comparative study of the properties of phenoxazinones. It was obtained by the condensation of α -naphthol with p-nitrosophenol in acetic acid in the presence of zinc chloride (the yield was about 2%). A second product of the reaction is 1,4-naphthoquinone, formed as a result of oxidation of α -naphthol by p-nitrosophenol.

It is interesting to note that β -naphthol undergoes a similar reaction to give 25-27% of benzo[a]phenoxazin-9-one (III) [2]. The sharp reduction of the yield in the case of α -naphthol is probably associated with the reduced reactivity of the β -carbon atom of the naphthalene ring as compared with the α -carbon atom.



The preparation of benzo[c]phenoxazin-3-one by the oxidative condensation of 2-nitroso-1-naphthol with resorcinol and its isolation by chromatography on silica gel are described in [3] by Ruzicka and Simanek. The benzo[c]phenoxazin-3-one (V) that we obtained differs considerably from the compound obtained in [3] with respect to the IR and electronic spectra. It is known that alkyl groups have little effect on the absorption spectra of conjugated systems in the visible region [4,5], but, according to the data in [3], the absorption maximum of 1-methyl-benzo[c]phenoxazin-3-one (495 nm) is shifted by 49 nm to higher wavelengths as compared with the absorption maximum of benzo[c]phenoxazin-3-one (446 nm [3]). The visible spectrum of the benzo[c]phenoxazin-3-one synthesized in our study is close to the spectrum of 1-methylbenzo[c]phenoxazin-3-one [3] and is in good agreement with the previously obtained calculated values [1] for benzo[c]phenoxazin-3-one.

Repetition of the synthesis described in [3] and chromatography of the product on aluminum oxide yielded a red compound (R_f 0.667 in the system in [3]) that, according to elementary analysis and electronic spectrum, was identical to V obtained by the condensation of α -naphthol with p-nitrosophenol. †

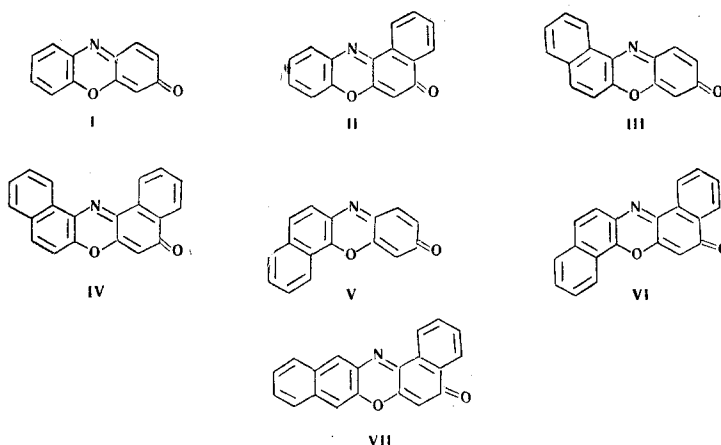
The IR and UV spectra of phenoxazin-3-one (I) and its derivatives have been studied repeatedly for the identification of a number of natural products with phenoxazinone skeletons [6,7]. Annulation of the benzene ring introduces a substantial change [1] in the electron distribution in I, and the IR and electronic spectra of not only benzo[c]phenoxazin-3-one and I but also of five benzoannulated phenoxazinones were therefore studied to confirm the structure of the synthesized benzo[c]phenoxazin-3-one.

* See [1] for communication I.

† According to a private communication that we received from E. Ruzicka, a reinvestigation of the compound synthesized in [3] gave results that were identical to ours.

S. M. Kirov Ural Polytechnical Institute, Sverdlovsk. Translated from *Khimiya Geterotsiklicheskikh Soedinenii*, No. 6, pp. 742-745, June, 1971. Original article submitted May 4, 1970.

© 1973 Consultants Bureau, a division of Plenum Publishing Corporation, 227 West 17th Street, New York, N. Y. 10011. All rights reserved. This article cannot be reproduced for any purpose whatsoever without permission of the publisher. A copy of this article is available from the publisher for \$15.00.



The IR spectra of I and its derivatives contain characteristic bands at 1500–1660 cm^{-1} . In [8, 9], the intense band at 1626–1650 cm^{-1} was ascribed to the valence vibrations of the C=O bond, the band at 1585–1620 cm^{-1} to the vibrations of the C=N bond, and the band at 1500–1572 cm^{-1} to the vibrations of the C=C bonds in the quinoid and benzoid rings. In [10], on the basis of the isotopic shifts on introduction of an ^{18}O carbonyl or an ^{15}N bridge into the phenoxazolin-3-one molecule, the intense first band (1642–1657 cm^{-1}) was assigned to the vibrations of the C=C bond, the second (1614–1636 cm^{-1}) was assigned to the vibrations of the C=O group, the bands at 1564–1606 cm^{-1} were relegated to the vibrations of the C=C bonds of the aromatic and quinoid rings, and the band at 1493–1516 cm^{-1} was assigned to the vibrations of the C=N bond.

The data obtained from the IR spectra of I–VII for 1500–1660 cm^{-1} are presented in Table 1. The assignment of bands made in [10] is undoubtedly the most accurate one but, in the intervals indicated in [10], bands are absent for several benzo derivatives of phenoxazin-3-one (for example, the bands of the C=C bonds at 1642–1657 cm^{-1} for II, III, and VI, and others), while the band of the vibrations of the C=N bond at 1493–1516 cm^{-1} is very weak in all of the benzophenoxazinones. The mutual effect of multiple bonds in conjugated systems of this type is extremely complex, and it is therefore difficult to isolate the vibrations of

TABLE 1. IR and Electronic Spectra of Phenoxazinones I–VII

Comp.	Vibrational bands of the double bonds in the IR spectra of the phenoxazinones cm^{-1} *				Electronic spectra of alcohol solutions of phenoxazinones, λ_{max} , nm (log ϵ)					
					A	B	C	D	K	L
I	1641 (9)	1616 (10)	1573 (8)	1513 (7)	217 (4,40)	247 (4,29)	254† (4,26) 265 (4,26)	—	354 (4,15)	450 (3,98)
II	1636 (10)	1596 (8)	1584 (5) 1565 (4)	1523 (2)	220 (4,44)	237 (4,35) 244 (4,34)	260 (4,18)	—	368 (4,09)	432 (4,06)
III	1635 (7)	1611 (9)	1572 (4) 1562 (5)	1513 (3)	219 (4,60)	232 (4,40)	256 (4,39) 261 (4,39)	292 (4,16) 313 (3,99)	—	498 (4,25)
IV	1640 (9)	1595 (7)	1572 (5) 1565 (4)	1504 (4)	217 (4,62)	246 (4,50)	256 (4,40)	296 (4,20) 305** (4,17)	384† (3,81)	486 (4,37)
V	1648 (5)	1619— 1604 (9)	1564 (6)	1500 (7)	222 (4,43)	233† (4,40)	—	2,95 (4,15) 308 (4,19)	368 (3,96)	505 (4,13)
VI	1630†— 1626 (8)	1607 (5) 1585 (5)	1563 (5)	1512 (2)	218 (4,49)	247† (4,38)	254 (4,45)	310 (4,27)	376 (4,00)	484 (4,23)
VII	1643 (9)	1618 (7) 1607 (7)	1575 (4)	1531 (2)	208 (4,25)	230 (4,39)	267 (4,35)	305 (3,83)	345† (3,75)	430 (4,31)

*The intensities on a ten-point scale are given in parentheses.

†Shoulder.

one concrete bond. In this connection, the characteristic bands of the vibrations of the double bonds of I-VII are presented in Table 1 without their individual assignments, which is quite adequate for a confirmation of the phenoxazinone nature of V.

There are also characteristic absorption bands in the electronic spectra of phenoxazin-3-one and its derivatives [11]. It is apparent from an examination of the data presented in Table 1 that short-wave bands A and B are characteristic for all of the indicated compounds and are practically independent of the position of the annelated ring, in contrast to the group of C, D, and K bands at 250-370 nm, the presence of which in the spectrum is associated with annelation. For example, the D band (280-310 nm) is absent in the spectra of I and II, which do not have a benzene ring annelated to the benzoid portion of the phenoxazin-3-one molecule, and does appear in the spectra of the remaining compounds, which do have a benzene ring. The L band in the visible portion of the spectrum, just like the A and B bands, is characteristic for all of the phenoxazinones, but annelation of the benzene ring ($\Delta\lambda_{\max}$ up to 100 nm) has a considerable effect on its position. We previously [1] discussed this dependence on the basis of the calculated λ_{\max} values of nine phenoxazinones obtained by the solution of the inverse spectral problem for five of them. Satisfactory agreement between the experimental λ_{\max} values obtained in this study for the L band with those calculated in [1] was found for the newly synthesized V and for VII, which was not investigated in [1]. The experimental λ_{\max} values for benzene solutions of V and VII are 494 and 428, while the calculated λ_{\max} values are 497 and 427, respectively.

Thus, only A, B, and L bands can be used to confirm the phenoxazinone structure of the compounds. An analysis of the IR and UV spectra of I-VII confirms the phenoxazinone structure of condensation product V.

EXPERIMENTAL

Benzo[c]phenoxazin-3-one (V). A total of 29 g (0.2 mole) of α -naphthol and 37 g (0.3 mole) of p-nitrosophenol were dissolved in 300 ml of glacial acetic acid, 70-80 g of finely ground, freshly fused zinc chloride was added, and the mixture was shaken vigorously for 1 h. (The reaction mixture warmed up strongly in the process.) It was then heated for 1 h on a water bath and allowed to stand for 24 h at room temperature. One liter of hot water was added, and the whole was filtered. The precipitate was washed on the filter with saturated sodium carbonate solution until the filtrate was colorless and was then washed with hot water, dried, and extracted with chloroform in a Soxhlet apparatus. The chloroform solution was chromatographed with a 650 by 30 column filled with neutral aluminum oxide with anhydrous chloroform as the eluant. The first fraction (yellow) contained 1.8-2 g of 1,4-naphthoquinone, as proved by elementary analysis and comparison with a genuine sample. The second fraction (cherry-red) yielded 1.6-2 g (2-3%) of V with mp 236-237° (from butanol) and R_f 0.25 (on neutral activity II aluminum oxide) in an anhydrous chloroform system and R_f 0.66 in a benzene-acetone system (3:1). Found %: C 77.7; H 3.8; N 5.5. $C_{16}H_9NO_2$. Calculated %: C 77.6; H 3.6; N 5.7.

Compounds I-IV and VI were synthesized by the method in [1], while VII was synthesized by the method in [12].

The UV spectra of 10^{-5} M ethanol solutions of phenoxazinones I-VII were recorded with a Perkin-Elmer 402 spectrophotometer. The spectra of 10^{-4} M benzene solutions of V and VII in the visible region were obtained with an SF-10 spectrophotometer. The IR spectra of mineral oil pastes were recorded with a UR-20 spectrophotometer.

LITERATURE CITED

1. K. I. Pashkevich, G. B. Afanas'eva, E. G. Kovalev, and I. Ya. Postovskii, *Khim. Geterotsikl. Soedin.*, **1316** (1970).
2. O. Fischer and E. Hepp, *Ber.*, **36**, 1803 (1903).
3. E. Ruzicka and V. Simanek, *Monatsh.*, **99**, 1718 (1968).
4. E. Ruzicka, J. Adamek, and Z. Stransky, *Monatsh.*, **98**, 2185 (1967).
5. E. Ruzicka and A. Havinger, *Monatsh.*, **99**, 834 (1968).
6. A. Butenandt, U. Schiedt, E. Biekert, and R. Cromartie, *Ann.*, **590**, 75 (1954).
7. G. Cavill and J. Tetas, *Chem. and Ind.*, **37**, 986 (1956).
8. H. Musso and H. Matties, *Ber.*, **90**, 1814 (1957).
9. J. Corbett, *Spectrochim. Acta*, **21**, 1411 (1965).

10. H. Musso, K. Spauke, and K. Walter, Ber., 100, 1436 (1967).
11. W. Schafer, Progress Org. Chem., 6, 135 (1964).
12. H. Goldstein and A. Warnery, Helv. Chim. Acta, 11, 250 (1928).