

SYNTHESIS OF SUBSTITUTED ANTHRANILS BY DEOXIDATION OF o-NITROSOACETYL BENZENES

Yu. S. Shabarov, S. S. Mochalov,
A. N. Fedotov, and V. V. Kalashnikov

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Substituted anthranils with both electron-donor and electron-acceptor substituents in the 6 position were obtained by deoxidation of o-nitrosoacylbenzenes with triphenylphosphine.

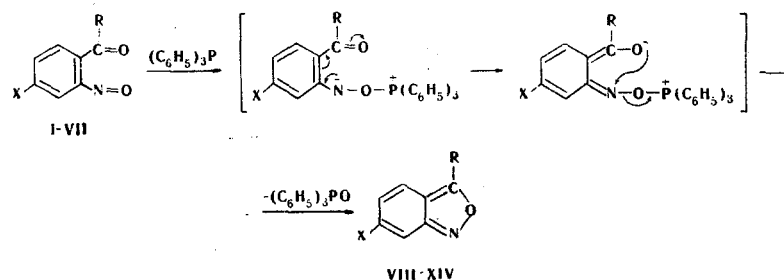
We have previously [1] proposed a general method for the synthesis of halo-substituted anthranils consisting in the action of hydrogen chloride on o-nitrosoacylbenzenes, which are readily obtained by isomerization of o-nitrosophenylcyclopropanes [2] and o-nitrostyryls [3].

The incorporation of a chlorine atom in the 5 or 7 position always occurs in the indicated reaction during the formation of anthranils.

In the present research in order to expand the possibilities of the utilization of o-nitrosoacylbenzene for the synthesis of substituted anthranils we suggest triphenylphosphine, which was previously used for the preparation of an isolog of anthranil - benzofurazan from o-dinitrobenzene [4] - as the cyclizing agent for the synthesis of anthranils.

It was found that the corresponding anthranils (VIII-XIV) are formed when o-nitrosoacylbenzenes (I-VII) are treated with triphenylphosphine in benzene or alcohol at room temperature.

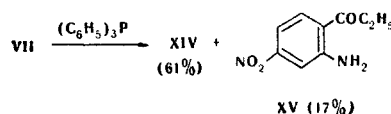
On the basis of data on the structures of complexes of nitrosobenzenes with triphenylphosphine [5], the following mechanism for the transformation can be proposed:



I, VIII R=CH₃; II-VII, IX-XIV R=C₂H₅; I, II, VIII, IX X=H; III, X X=C₂H₅; IV, XI
X=(CH₃)₃C; V, XII X=Br; VI, XIII X=COCH₃; VII, XIV X=NO₂

The structures of the anthranils obtained (see Table 1) were proved by their PMR spectra (see Table 2).

It should be noted that in the deoxidation of 4-nitro-2-nitrosopropiophenone (VII) a considerable amount (17%) of 2-amino-4-nitropropiophenone (V) is formed in addition to the corresponding anthranil (XIV).



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TABLE 1. Substituted Anthranils (VIII-XIV)

| Com- pound | R | X | Reaction time, h | bp, °C (mm) | n_D^{20} | Empirical formula | Found, % | | | Calc., % | | | Yield, % |
|-------------------|-------------------------------|-----------------------------------|---------------------|----------------|------------|---|----------|-----|------|----------|-----|------|-------------|
| | | | | | | | C | H | N | C | H | N | |
| VIII ^a | CH ₃ | H | 2 | 71—72 (2) | 1,5790 | C ₈ H ₇ NO | 72,4 | 5,4 | 10,3 | 72,3 | 5,3 | 10,5 | 67 |
| IX | C ₂ H ₅ | H | 2 | 90—92 (2) | 1,5666 | C ₉ H ₉ NO | 73,4 | 6,1 | 9,7 | 73,5 | 6,1 | 9,5 | 65 |
| X | C ₂ H ₅ | C ₂ H ₅ | 1 | 103—104 (2) | 1,5550 | C ₁₁ H ₁₃ NO | 75,5 | 7,4 | 8,1 | 75,5 | 7,4 | 8,0 | 85 |
| XI | C ₂ H ₅ | (CH ₃) ₃ C | 1 | 122—123 (2) | 1,5440 | C ₁₃ H ₁₇ NO | 77,0 | 8,4 | 7,1 | 76,9 | 8,4 | 6,9 | 90 |
| XII | C ₂ H ₅ | Br | 24 | 120—122 (2) | 1,6134 | C ₉ H ₈ BrNO | 48,0 | 3,7 | 6,5 | 47,8 | 3,5 | 6,2 | 73 |
| XIII | C ₂ H ₅ | CH ₃ CO | 24 | mp 65—66 | — | C ₁₁ H ₁₁ NO ₂ | 69,7 | 5,9 | 7,5 | 69,9 | 5,8 | 7,4 | 75 |
| XIV | C ₂ H ₅ | NO ₂ | 24 | mp 47—49 | — | C ₉ H ₈ N ₂ O ₃ | 55,8 | 4,2 | 14,5 | 56,2 | 4,2 | 14,6 | 61 |

^aThe boiling point of VIII is presented in [6].

TABLE 2. PMR Spectra of Substituted Anthranils (VIII-XIV)

| Com- pound | Chemical shifts, δ , ppm ^a | | | | | | J, Hz | |
|------------------|--|-----------------|--------------------------|-------------------|-----|---------|--------------------|-------------------|
| | CH ₃ | CH ₂ | 4-H | 5-H | 6-H | 7-H | J _{ortho} | J _{meta} |
| VIII | s, 2,53 | — | — | m (4H), 6,57—7,43 | — | — | — | — |
| IX _b | t, 1,28 | q, 2,98 | — | m (4H), 6,52—7,43 | — | — | — | — |
| X _b | t, 1,30 | q, 3,01 | d, 7,23 | dd, 6,60 | — | d, 7,09 | 9 | 1,6 |
| XI _b | t, 1,32 | q, 3,04 | d, 7,29 | dd, 6,86 | — | d, 7,22 | 9 | 1,4 |
| XII _b | t, 1,36 | q, 3,08 | d, 7,24 | dd, 6,81 | — | d, 7,61 | 9,4 | 1,8 |
| XIII | t, 1,41 | q, 3,12 | s ₂ (2H) 7,36 | — | — | s, 7,95 | — | — |
| XIV | t, 1,46 | q, 3,25 | d, 7,63 | dd, 7,50 | — | d, 8,18 | 10 | 2 |

^aAbbreviations: s is singlet, d is doublet, t is triplet, q is quartet, dd is doublet of doublets, and m is multiplet. Signal of the ethyl group in the 6 position of anthranil X: 1.15 t (3H) and 2.56 q (2H); signal of the tert-butyl group in XI: 1.21 s (9H); signal of the acetyl group in XIII: 2.51 s (3H).

The molecular weight (determined by mass spectrometry) of amino ketone XV was 194 (calculated value 194). The PMR spectrum recalled the spectrum of the corresponding anthranil, but the signals of the ethyl group (triplet centered at 1.01 ppm and quartet centered at 2.42 ppm) were shifted to stronger field: this was apparently due to weakening of the deshielding effect caused by disruption of the heterocyclic ring of anthranil XIV. In addition, the spectrum contained a signal at δ 6.42 ppm (broad singlet, 2H), which should have been assigned to the protons of the amino group formed in the reaction. The IR spectrum of amino ketone XV contained bands of NH stretching vibrations (3360 and 3490 cm^{-1}) and a characteristic set of bands of medium intensity due to intramolecular interaction of the spatially adjacent amino and carbonyl groups at 1530–1670 cm^{-1} .

EXPERIMENTAL

The UV spectra of ethanol solutions of the compounds were obtained with a Cary-15 spectrophotometer. The IR spectra of mineral oil suspensions were recorded with a UR-20 spectrometer. The PMR spectra of CCl₄ and benzene solutions of the compound were recorded with a JNM H-20 spectrometer with hexamethyldisiloxane as the internal standard. The molecular weight was determined with a Varian-MAT-111 mass spectrometer with an ionizing voltage of 80 eV.

Nitroso ketones I-III and V-VII were obtained as described in [2, 3], whereas IV was obtained in analogy with the two-step synthesis: 2-nitro-4-tert-butylphenylcyclopropane [67% yield, bp 130–132° (2 mm), n_D^{20} 1.5429] was synthesized by the method in [7] by nitration of 4-tert-butylphenylcyclopropane [by 240° (758 mm) and n_D^{20} 1.5214 [8]]. PMR spectrum, δ , ppm: 0.41–1.07 m (4H), 1.21 s (9H), 2.03–2.52 m (1H), 6.95 d (J_0 = 8.4 Hz), 7.41 dd (J_0 = 8.4, J_m = 2 Hz), 7.74 d (J_m = 2 Hz) ArH. Found: C 71.5; H 7.8; N 6.6%. C₁₃H₁₇NO₂. Calculated: C 71.3; H 7.8; N 6.4%. 4-tert-Butyl-2-nitrosopropiophenone (IV) [4 g (90%), mp 116–117° (from alcohol)] was obtained as described in [2] but at –30° from 4.39 g of 2-nitro-4-tert-butylphenylcyclopropane. PMR spectrum, δ , ppm: 0.84 s (9 H), 1.09 t (3H), and 2.57 q (2H). IR spectrum: 1695 cm^{-1} (C=O). UV spectrum: 755 nm (ϵ 36, C–N=O). Found: C 71.2; H 7.9; N 6.6%. C₁₃H₁₇NO₂. Calculated: C 71.3; H 7.8; N 6.4%.

Synthesis of Anthranils (VIII-XIV). A mixture of 0.01 mole of the appropriate nitrosoacylbenzene (I-VII) and an equimolecular amount of diphenylphosphine in 250 ml of absolute benzene (or dry alcohol)

was stirred at room temperature for a definite time (see Table 1), after which the solvent was removed by distillation, and the residue was dissolved in ~15 ml of ether and chromatographed with a column filled with activity II aluminum oxide in an ether-petroleum ether (40-70°) system (1:3). The yields, physical constants, and the results of elementary analyses are presented in Table 1.

2-Amino-4-nitropropiophenone (XV). This compound was obtained as a side product in the synthesis of anthranil XIV via the method described above. A product with mp 124-125° was obtained in 17% yield. PMR spectrum (chloroform, acetone), δ , ppm: 1.01 t (3H), 2.42 q (2H), 6.42 broad s (2H), 7.23 dd ($J_0=9.2$ Hz, $J_m=2.4$ Hz), 7.58 d ($J_m=2.4$ Hz), and 7.96 d ($J_0=9.2$ Hz) ArH.

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