

## The Structure of Side Product in the Synthesis of Substituted 1,3-Tropolones

V.V. Tkachev<sup>1</sup>, S.M. Aldoshin<sup>1</sup>, G.V. Shilov<sup>1</sup>, Yu.A. Sayapin<sup>2</sup>,  
 V.N. Komissarov<sup>2</sup>, and V.I. Minkin<sup>2</sup>

<sup>1</sup>Institute of Problems of Chemical Physics, Russian Academy of Sciences, Chernogolovka, Moscow oblast', 142432 Russia  
 e-mail: sma@icp.ac.ru

<sup>2</sup>Institute of Physical and Organic Chemistry at Rostov State University

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**Abstract**—The structure of pyrocatechol *p*-toluenesulfonate resulting from the reaction between 3,5-di(*tert*-butyl)-1,2-benzoquinone and substituted 2-methylquinolines was proved by X-ray diffraction analysis.

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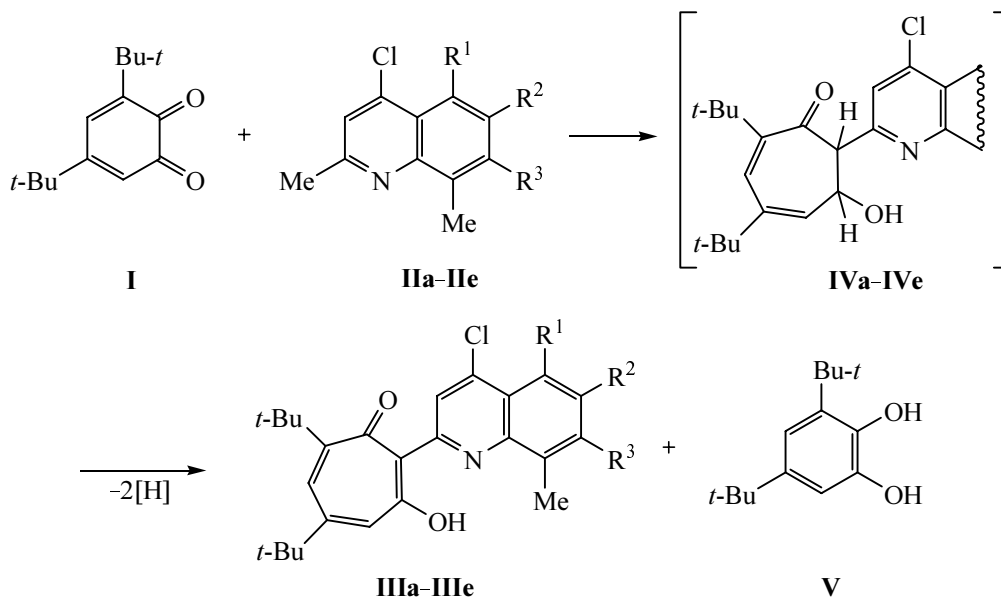
We showed formerly [1, 2] that 3,5-di(*tert*-butyl)-1,2-benzoquinone (**I**) reacted with substituted 2-methylquinolines **IIa–IIIf** to afford 2-(quinolin-2-yl) derivatives of 1,3-tropolone **IIIa–IIIIf**. Dihydrotropolones **IVa–IVf** should form intermediately in this process to be subsequently dehydrated with excess quinone **I** giving tropolones **IIIa–IIIIf** and 3,5-di(*tert*-butyl)pyrocatechol (**V**) (Scheme 1).

The reaction is catalyzed with *p*-toluenesulfonic acid (**VI**). Alongside tropolones **IIIa–IIIIf** we isolated from

the reaction mixture and characterized by elemental analysis, <sup>1</sup>H NMR spectroscopy, and by comparison with an authentic sample prepared by an independent synthesis pyrocatechol *p*-toluenesulfonate (**VII**) (Scheme 2).

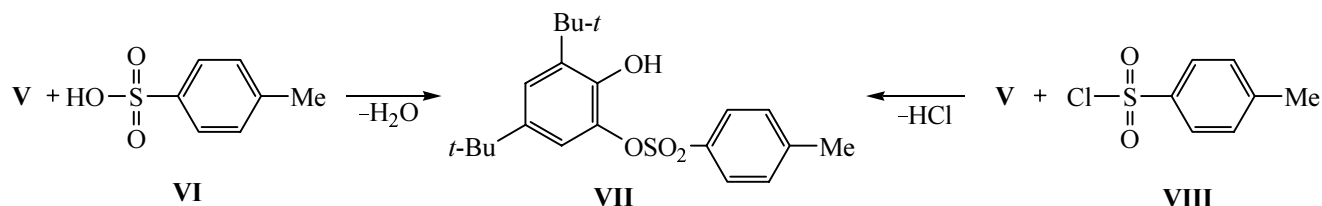
Increasing the amount of *p*-toluenesulfonic acid (**VI**) in the synthesis of tropolones **IIIa–IIIIf** resulted in larger yield of ester **VII**. The formation of ester **VII** confirms the mechanism we assumed in Scheme 1. The structure of ester **VII** established by X-ray diffraction analysis is shown on the figure.

Scheme 1.



**II, III**, R<sup>1</sup> = R<sup>2</sup> = R<sup>3</sup> = H (**a**); R<sup>1</sup> = R<sup>3</sup> = H, R<sup>2</sup> = Me (**b**); R<sup>1</sup> = R<sup>2</sup> = H, R<sup>3</sup> = Me (**c**); R<sup>1</sup> = NO<sub>2</sub>, R<sup>2</sup> = R<sup>3</sup> = H (**d**); R<sup>1</sup> = NO<sub>2</sub>, R<sup>2</sup> = Me, R<sup>3</sup> = H (**e**); R<sup>1</sup> = NO<sub>2</sub>, R<sup>2</sup> = H, R<sup>3</sup> = Me (**f**).

## Scheme 2.



Note that the *p*-toluenesulfonate part of the molecule has a traditional structure similar, e.g., to that in the 2-chlorophenyl 4-methylbenzenesulfonate analog [3] where the plane of the benzene ring  $C^{15}\cdots C^{20}$  projected along the bond has the *syn*-orientation with an orthogonal position of the S–O<sup>3</sup> bond. The torsion angle  $C^{15}\text{SO}^3C^1$  equals  $54.5^\circ$ , and the angle  $\text{O}^3\text{SC}^{15}C^{16}$  is  $92.6^\circ$ .

The atoms O<sup>2</sup>, S, O<sup>3</sup>, and C<sup>1</sup> are located in the same plane within accuracy of  $0.055 \text{ \AA}$  forming a torsion angle of  $170^\circ$ . The distances S–O<sup>1</sup> and S–O<sup>2</sup> are equal to  $1.413(1)$  and  $1.416(1)$ , S–O<sup>3</sup> and S–C<sup>15</sup> are  $1.601(1)$  and  $1.742(1) \text{ \AA}$  respectively. The angle  $\text{O}^3\text{SC}^{15}$  equals  $103.1(1)$ , the angle  $\text{O}^1\text{SO}^2$  is  $119.5(1)^\circ$ , the other angles around the sulfur atom are close to tetrahedral. The atoms C<sup>1</sup>, C<sup>2</sup>, C<sup>3</sup>, C<sup>4</sup>, C<sup>5</sup>, C<sup>6</sup>, C<sup>7</sup>, C<sup>11</sup>, O<sup>3</sup> within  $0.015 \text{ \AA}$  are located in the same plane that is turned around the C<sup>1</sup>–O<sup>3</sup> bond forming torsion angles  $\text{SO}^3\text{C}^1\text{C}^2$  and  $\text{SO}^3\text{C}^1\text{C}^6$  of  $77$  and  $106^\circ$  respectively.

The carbons of the *tert*-butyl group on the C<sup>11</sup> atom are oriented in such manner with respect to the pyrocatechol ring that the torsion angle  $\text{C}^4\text{C}^5\text{C}^{11}\text{C}^{14}$  is equal to  $4.2^\circ$  resulting in shortened intramolecular contacts between the hydrogen attached to C<sup>4</sup> atom and the nearest hydrogen atoms on C<sup>14</sup> amounting to  $2.23$  and

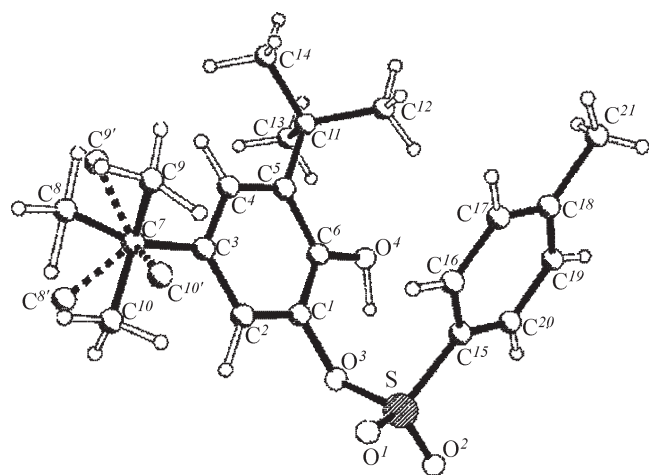
$2.28 \text{ \AA}$ . At the same time the intramolecular contacts between the O<sup>4</sup> and the nearest thereto hydrogens on the atoms C<sup>12</sup> and C<sup>13</sup> are equal to  $2.31$  and  $2.33 \text{ \AA}$ . The second *tert*-butyl group (on C<sup>7</sup>) is disordered by two positions distinguished by the angle of the turn around the C<sup>3</sup>–C<sup>7</sup> bond of  $60^\circ$ , populated to  $85\%$  (the bonds shown by full lines) and to  $15\%$  (bonds shown by dashed lines). For the more populated configuration the torsion angle  $\text{C}^2\text{C}^3\text{C}^7\text{C}^{10}$  amounts to  $0.08^\circ$ , and in the less populated one exists the torsion angle  $\text{C}^4\text{C}^3\text{C}^7\text{C}^{92}$  of  $1.4^\circ$ . In the first configuration the shortest distances between hydrogens on atoms C<sup>2</sup> and C<sup>4</sup> and the corresponding hydrogen atoms attached to C<sup>8</sup>, C<sup>9</sup>, and C<sup>10</sup> fall into the range  $2.19\text{--}2.34 \text{ \AA}$ . Taking into consideration the similarity of the torsion angles for both configurations the analogous distances between hydrogen atoms in the less populated configuration presumably also fall into a like range, and the difference in occupancy cannot be ascribed to the intramolecular sterical reasons.

In the single crystal exist pairs of intermolecular hydrogen bonds between hydrogen of the OH group from one molecule and O<sup>22</sup> of the second (the distance  $\text{O}^{22}\cdots\text{HO}^4$  equals  $1.852 \text{ \AA}$ , angle  $\text{SO}^{22}\text{HO}^4$  is  $171.8^\circ$ , and angle  $\text{O}^{22}\text{HO}^4$  is  $146.7^\circ$ ) resulting in formation of dimer associates.

## EXPERIMENTAL

<sup>1</sup>H NMR spectra were registered on a spectrometer Varian Unity-300.

**X-ray diffraction analysis of compound VII.** Unit cell parameters of the crystal of ester VII ( $\text{C}_{21}\text{H}_{28}\text{O}_4\text{S}$ ) and the three-dimensional set of reflections intensities were obtained on a diffractometer KUMA-DIFFRACTION KM-4 ( $\text{MoK}_\alpha$ -radiation, graphite monochromator) for an isometric single crystal of an arbitrary form with a radius  $\sim 0.025 \text{ mm}$ . Monoclinic crystal with parameters  $a$   $9.259(3)$ ,  $b$   $10.658(3)$ ,  $c$   $21.222(12) \text{ \AA}$ ,  $\beta$   $91.22(5)^\circ$ ,  $V$   $2093.8(15) \text{ \AA}^3$ ,  $M$   $376.49$ , space group  $P2_1/C$ ,  $Z$   $4$ ,  $\rho_{\text{calc}}$   $1.194 \text{ g/cm}^3$ . The intensity of 4375 reflections were measured in the independent part of the reciprocal space ( $2\theta \leq 52.12^\circ$ ) by means of  $\omega/2\theta$ -scanning. On excluding the systematically quenched reflections the operative



Structure of ester VII with numbering of atoms. The bonds with the carbons of the CH<sub>3</sub> groups in the less occupied positions are shown by dashed lines.

array of the measured reflections amounted to 2993 with  $I > 2\sigma(I)$ .

The structure of ester **VII** was solved by the direct method and refined by full-matrix least-squares procedure with respect to  $F^2$  with the use of SHELXL-97 software [4] in the anisotropic approximation for thermal oscillations of the nonhydrogen atoms excluding three carbon atoms in disordered positions with 15% occupancy; here the isotropic approximation was applied. All hydrogen atoms in the structure were found from the difference synthesis and were refined in the isotropic approximation (for the hydrogens in the disordered  $\text{CH}_3$  groups with occupancy of 85% the thermal parameter was set at 0.08). The final value of the  $R$ -factor is 4.2% (7.6% for 4151 reflections), GOF 1.074.

#### 2-(*p*-Tolylsulfoxy)-4,6-di(*tert*-butyl)-phenol (**VII**).

*a.* A solution of 1 g (5 mmol) of compound **IIc**, 2.2 g (10 mmol) of quinone **I**, and 0.9 g (5 mmol) of sulfonic acid **VI** in 10 ml of *o*-xylene was boiled for 2 h. On cooling the solution was applied to a column packed with aluminum oxide, and the products were separated by elution with a mixture chloroform–hexane, 1:2. The bright-yellow fraction containing tropolone **IIIc** was isolated as described in [1]. The next reddish fraction was eluted with chloroform. The solvent was distilled off, the residue was recrystallized from 2-propanol. Yield of the colorless crystalline compound **VII** 0.1 g (5% calculated on sulfonic acid **VI**), mp 154–156°C.  $^1\text{H}$  NMR spectrum ( $\text{CDCl}_3$ ),  $\delta$ , ppm: 1.13 s [9H,  $\text{C}^4(\text{CH}_3)_3$ ], 1.33 s [9H,  $\text{C}^6(\text{CH}_3)_3$ ], 2.43 s (3H,  $4'$ - $\text{CH}_3$ ), 5.80 s (1H, 1-OH), 6.56 d (1H, 5-H,  $J$  2.37 Hz), 7.11 d (1H, 3-H,  $J$  2.37 Hz), 7.3–7.7 m (4H,  $2', 3', 5', 6'$ -H,  $J$  8.08 Hz). Found, %: C 66.73; H 7.39; S 8.55.  $\text{C}_{21}\text{H}_{28}\text{O}_4\text{S}$ . Calculated, %: C 66.99; H 7.50;

S 8.52. Reactions with quinolines **IIa**, **IIb**, **IId–IIf** were carried out in the same way.

*b.* A solution of 1.1 g (5 mmol) of pyrocatechol **V**, 1.1 g (5 mmol) of sulfonyl chloride **VIII** in 5 ml of pyridine was heated at 40–45°C for 2 h. The reaction mixture was diluted with water. The oily precipitate was ground till crystallization, filtered off, and washed with water, dissolved in a mixture chloroform–hexane, 1:1, and subjected to chromatography on a column (30×1.5 cm) packed with aluminum oxide, eluent chloroform–hexane, 1:1. The first fraction was collected. On removing the solvent we obtained 0.52 g (28%) of phenol **VII**. After recrystallization from 2-propanol the melting point was 154–156°C. The elemental analysis and  $^1\text{H}$  NMR spectrum were identical to the data for compound obtained by procedure *a*. No depression of the melting point was observed in the mixed sample.

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#### REFERENCES

1. Komissarov, V.N., Bang, D.N., Minkin, V.I., Aldoshin, S.M., Tkachev, V.V., and Shilov, G.V., *Mendeleev Commun.*, 2003, vol. 13, p. 219.
2. Sayapin, Yu.A., Komissarov, V.N., Minkin, V.I., Tkachev, V.V., Aldoshin, S.M., and Shilov, G.V., *Zh. Org. Khim.*, 2005, vol. 41, p. 1571.
3. Vembu, N., Nallu, M., Garrison, J., and Young, W.J., *Acta Crystallogr.*, 2003, vol. 59, p. 503.
4. Sheldrick, G.M., *The SHELX-97, Manual*, Gottingen: Univ. of Gottingen, 1997.