

Synthesis of 6-(2-Benzotriazolyl)-2,2'-alkylenediphenols

^aI. JEŽO, ^bM. KARVAŠ and ^bJ. DURMIS

^a*Institute of Chemistry, Slovak Academy of Sciences,
Bratislava 9*

^b*Chemical Works of G. Dimitroff, Research Institute,
Bratislava 10*

Received October 15, 1969

The preparation of 6-(2-benzotriazolyl)-2,2'-alkylenediphenol derivatives by the reaction of *o*-nitrobenzenediazonium chloride with corresponding 2,2'-alkylenediphenols is described. In an analogous way also 2,2'-methylenedi[6-(2-benzotriazolyl)phenols] were prepared. Finally, these substances were also synthesized by applying the reaction of 2-(2-benzotriazolyl)phenol with formaldehyde in the presence of sulfuric acid.

2-Phenylbenzotriazole derivatives having a hydroxyl group in *o*-position on the phenyl ring are known as good ultraviolet absorbers for plastic materials and therefore they have been thoroughly studied [1–4]. The drawback of these substances consists in their relatively high volatility at higher temperatures used for treating plastic materials [5]. So, attention was paid to the preparation of analogous compounds with relatively higher molecular weights, of possibly higher melting points and lower volatility. The synthesis of some derivatives with the expected properties was performed as follows:

1. The reaction of *o*-nitrobenzenediazonium chloride with 2,2'-alkylenediphenols and the reduction of the appropriate *o*-nitroazo-dyes (*A*, *B*) with zinc powder in alkaline medium gave 6-(2-benzotriazolyl)-2,2'-alkylenediphenols (*I*, *II*) and 2,2'-methylenedi[6-(2-benzotriazolyl)phenol] (*IV*). The product *I* was then alkylated by isobutylene under formation of 6-(2-benzotriazolyl)-4,4'-dimethyl-6'-*t*-butyl-2,2'-methylenediphenol (*III*).

2. The reaction of 2-(2-benzotriazolyl)phenol derivatives with formaldehyde in sulfuric acid medium yielded methylenedibenzotriazolyl phenols (*IV*, *V*, *VI*).

Experimental

All melting points are uncorrected. The analysed samples were chromatographically purified and dried in standing over P₂O₅ at 1 Torr for 24 hours.

The ultraviolet absorption spectra were measured by means of the universal spectrophotometer VSU-1 (Zeiss, Jena).

2,2'-Methylenedi(4-methylphenol) was prepared from formaldehyde and *p*-cresol in a procedure analogous to [14] in 35% yield; b.p._{0.8} 186°C, m.p. 126°C (benzene). According to ref. [15] m.p. is 124–126°C.

2,2'-Isopropylidenedi(4-methylphenol) was prepared by reaction of acetone with *p*-cresol in a procedure analogous to [16] in 55.2% yield; b.p._{0.5} 152.5°C.

For C₁₇H₂₀O₂ (256.34) calculated: 79.6% C, 7.84% H; found: 79.92% C, 7.90% H.

2-(2-Benzotriazolyl)-4-methylphenol was a commercial product of Geigy (Switzerland), trade-name Tinuvin P.

2-(2-Benzotriazolyl)-4-*n*-butylphenol was prepared according to [4] in 26.6% yield; m.p. 80–81°C.

2-[2-(5-Chlorobenzotriazolyl)]-4-methylphenol was synthesized from 2-nitro-5-chloroaniline and *p*-cresol in 45% yield according to [2]; m.p. 111.5–112.5°C.

6-(2-Benzotriazolyl)-4,4'-dimethyl-2,2'-methylenediphenol (I)

A solution of diazonium salt, prepared from 27.6 g (0.2 mole) of *o*-nitroaniline according to the method stated in [17], was dropped into a solution of 22.8 g (0.1 mole) of 2,2'-methylenedi(4-methylphenol) in 10 g of NaOH, 75 g of Na₂CO₃, and 400 ml of water during 30 minutes at 10.–15°C. After two hours' stirring of the reaction mixture at room temperature, the separated product was filtered off, washed thoroughly with water, and dried (90%). The unpurified product was dissolved in 90 ml of ethanol and 500 ml of concentrated ammonia were added. Then 160 g of zinc powder was added into the solution in small portions during one hour under constant stirring. After one hour's heating at 60°C and subsequently per one hour at 80°C, 8 g of NaOH and 2 g of sodium dithionite in 32 ml of water were added into the reaction mixture which was heated for another hour at 80°C. The reaction product was hot-filtered, the filtrate was acidified with diluted HCl (4 : 1), the precipitate was filtered, recrystallized in ethanol, sublimated at 190–200°C and 0.5 Torr pressure and finally recrystallized again in ethanol. The product obtained (32.1%) showed m.p. 195.5–197°C (ethanol).

For C₂₁H₁₉N₃O₂ (345.38) calculated: 73.02% C, 5.54% H, 12.16% N; found: 73.31% C, 5.58% H, 12.12% N.

6-(2-Benzotriazolyl)-4,4'-dimethyl-2,2'-isopropylidenediphenol (II)

The solution obtained by diazotation of 5.52 g (0.04 mole) of *o*-nitroaniline in 80 ml of acetic acid according to [18] was added by drops into a solution of 5.12 g (0.02 mole) of 2,2'-isopropylidenedi(4-methylphenol), 30 g of crystalline sodium acetate, and 1 ml of pyridine in 110 ml of glacial acetic acid at 10–15°C.

After 2 hours' stirring at room temperature, the reaction mixture was diluted with water, the separated product was filtered, washed with water and dried (99%). The unpurified azo-dye was reduced with zinc powder in a mixture of ethanol and concentrated ammonia by the method previously described and applied to the purification of product I. By several crystallization in ethanol and by column chromatography on Al₂O₃ (II activity, elution with benzene), the pure product was obtained in 54% yield; m.p. 164–165.5°C.

For C₂₃H₂₃N₃O₂ (373.43) calculated: 73.97% C, 6.21% H, 11.25% N; found: 74.12% C, 6.18% H, 11.16% N.

6-(2-Benzotriazolyl)-6'-*t*-butyl-4,4'-dimethyl-2,2'-methylenediphenol (III)

3.6 g of concentrated sulfuric acid was added into a solution of 14.9 g (0.04 mole) of I in 200 ml of chloroform and the solution was saturated with isobutylene under constant stirring at room temperature. After 3 hours' saturation, the reaction mixture was washed with 2.5% solution of Na₂CO₃ and afterwards, with water to neutral reaction. After evaporation of the solvent, the distillation residue was extracted two times with 30 ml of petroleum ether, the insoluble portion (1.4 g) was filtered off, and the filtrate was eva-

porated to dryness; the residue was three times recrystallized in heptane and subsequently purified by column chromatography on Al_2O_3 (II activity, elution with benzene). The product thus obtained (11%) has its m.p. 117–118°C.

For $\text{C}_{25}\text{H}_{27}\text{N}_3\text{O}_2$ (401.49) calculated: 74.79% C, 6.78% H, 10.47% N; found: 74.89% C, 6.79% H, 10.68% N.

2,2'-Methylenedi[6-(2-benzotriazolyl)-4-methylphenol] (IV)

a) By using *o*-nitroaniline and 2,2'-methylenedi(4-methylphenol) (molar ratio 4 : 1), the procedure employed for the preparation of *I* gave a mixture of azo-dyes which was subjected to reduction as described above. Part of the crude product was dissolved in boiling ethanol and product *I* (30%) was obtained from the filtrate. Sublimation of the insoluble portion at 260°C and 0.5 Torr and subsequent crystallization in chloroform gave the required product *IV* (10%); m.p. 287.5–289.5°C.

For $\text{C}_{27}\text{H}_{22}\text{N}_6\text{O}_2$ (462.49) calculated: 70.11% C, 4.79% H, 18.17% N; found: 69.91% C, 4.63% H, 18.44% N.

b) 3.75 g of 40% aqueous solution of formaldehyde were added by drops into a solution of 22.5 g (0.1 mole) of 2-(2-benzotriazolyl)-4-methylphenol in 100 ml of concentrated sulfuric acid. After 48 hours, the reaction mixture was poured on crushed ice and the precipitate formed was washed with water, 5% solution of Na_2CO_3 and again with water to neutral reaction. After drying, the crude product was sublimated at 260°C and 0.5 Torr and crystallized in chloroform (99% yield). The mixed melting point of this product with that obtained by procedure a) was 287.5–289.5°C.

*2,2'-Methylenedi[6-(2-benzotriazolyl)-4-*n*-butylphenol] (V)*

By the procedure b) as used for the preparation of *IV*, the required product was prepared from 2-(2-benzotriazolyl)-4-*n*-butylphenol in 92.1% yield; m.p. 163–164.5°C (ethanol).

For $\text{C}_{33}\text{H}_{34}\text{N}_6\text{O}_2$ (546.65) calculated: 72.50% C, 6.27% H, 15.37% N; found: 72.44% C, 6.33% H, 15.67% N.

2,2'-Methylenedi[6-[2-(5-chlorobenzotriazolyl)]-4-methylphenol] (VI)

The reaction between formaldehyde and 2-[2-(5-chlorobenzotriazolyl)]-4-methylphenol according to procedure b) yielded the required product (54.8%); m.p. 304.5–306.5°C (chloroform).

For $\text{C}_{27}\text{H}_{20}\text{Cl}_2\text{N}_6\text{O}_2$ (531.39) calculated: 61.02% C, 3.79% H, 15.82% N; found: 60.75% C, 3.88% H, 15.56% N.

3-(2-Benzotriazolyl)-2-hydroxy-5-methylbenzenesulfonic acid (dihydrate)

The solution of 4.5 g of 2-(2-benzotriazolyl)-4-methylphenol in 10.6 ml of sulfuric acid was kept for 48 hours at room temperature. The reaction mixture was then poured into a mixture of water and ice. The separated product was washed and dried and thereafter, it was crystallized first in pyridine and subsequently in ethanol (86.8%); m.p. 310°C.

For $\text{C}_{13}\text{H}_{11}\text{N}_3\text{O}_4\text{S} \cdot 2\text{H}_2\text{O}$ (341.33) calculated: 45.80% C, 3.82% H, 12.30% N, 9.39% S, 10.51% H_2O ; found: 45.75% C, 3.65% H, 12.34% N, 9.19% S, 10.30% H_2O .

Results and Discussion

The synthesized derivatives and their ultraviolet absorption spectra within the range of 280–300 nm are presented in Table 1.

Table 1

No.	Compound	Ultraviolet absorption spectra				Solvent
		λ_{\max_1} [nm]	ϵ_{\max_1}	λ_{\max_2} [nm]	ϵ_{\max_2}	
I	6-(2-benzotriazolyl)-4,4'-dimethyl-2,2'-methylene-diphenol	305	15.870	341	15.550	ethanol
II	6-(2-benzotriazolyl)-4,4'-dimethyl-2,2'-isopropylidenediphenol	302	13.700	341	14.820	ethanol
III	6-(2-benzotriazolyl)-4,4'-dimethyl-6'- <i>t</i> -butyl-2,2'-methylene-diphenol	304	16.520	342	16.700	ethanol
IV	2,2'-methylene-di[6-(2-benzotriazolyl)-4-methylphenol]	286	18.100	345	12.200	dimethyl-formamide
V	2,2'-methylene-di[6-(2-benzotriazolyl)-4- <i>n</i> -butylphenol]	287	19.800	345	12.900	dimethyl-formamide
VI	2,2'-methylene-di{6-[2-(5-chlorobenzotriazolyl)]-4-methylphenol}	296	21.000	356	9.100	dimethyl-formamide

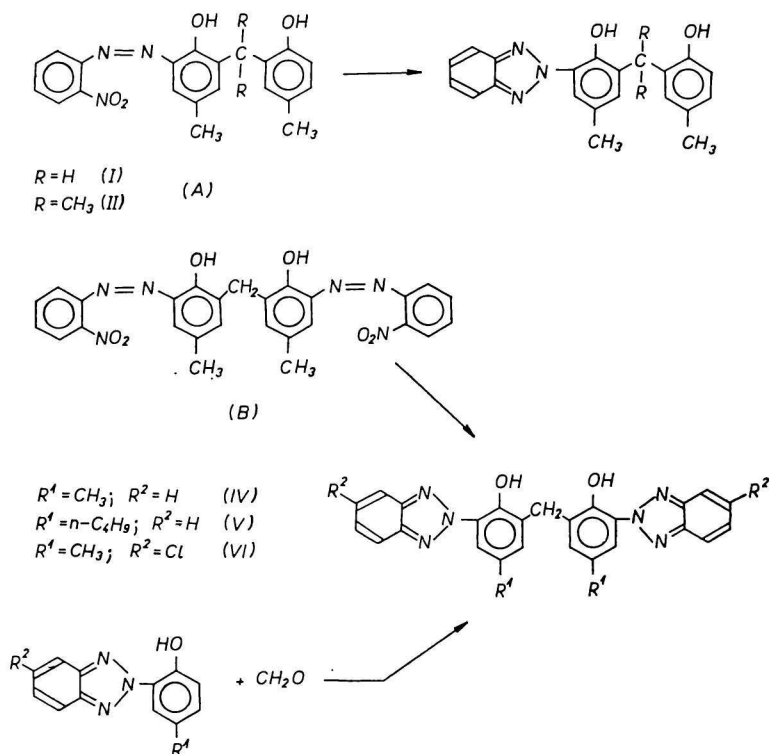
It has been found that the formation of the azo-dye (*A*) and bisazo-dye (*B*) due to the copulation of *o*-nitrobenzenediazonium chloride with 2,2'-methylene-di(4-methylphenol) in aqueous alkaline medium depends on the molar ratio of the reacting components. If the molar ratio is 2 : 1, only the azo-derivative (*A*) is formed while at the molar ratio of 4 : 1 also the bisazo-derivative (*B*) appears. The reason why the azo-dye (*A*) does not react with another molecule of diazonium salt may consist in the fact that the azo-dye (*A*) is precipitated during reaction from the homogeneous medium decreasing the reactivity of the heterogeneous system thus created.

2,2'-Isopropylidenedi(4-methylphenol) is in aqueous alkaline medium insoluble. Therefore, its copulation with the diazonium salt of *o*-nitroaniline was performed in a solution of acetic acid in which diazo-acetates are very reactive and rapidly copulate [6].

2,2'-Methylene-di[6-(2-benzotriazolyl)-4-methylphenol] was also prepared by the condensation of 2-(2-benzotriazolyl)-4-methylphenol with formaldehyde. Condensation between these compounds does not occur under conditions convenient for the condensation of phenols with aldehydes or ketones [7–9, 11].

The effect of the 2-benzotriazolyl substituent on the reactivity of the benzene ring is only poorly elucidated till now. Čepčiansky *et al.* [10] have determined $\sigma_p^- = +0.566$ for this substituent that means that it belongs to a group of electron acceptor substituents. The deactivation effect of this ring substituent may be interpreted by this fact.

Since the 2-benzotriazolyl substituent reduces considerably the reactivity of phenol, more drastic reaction conditions (medium of sulfuric acid) [12] must be chosen for the condensation process at least in the case of formaldehyde. On the other hand, acetaldehyde, benzaldehyde, crotonaldehyde, and acetone do not



react with the starting compound under the given conditions and on the contrary, sulfonation of 2-(2-benzotriazolyl)-4-methylphenol takes place. This reaction occurs even in the absence of these aldehydes or acetone in the medium of sulfuric acid. It follows from these facts that the rate of the electrophilic substitution reaction

in the above syntheses is greater in the presence of the CH₂OH cation than in that of [HSO₃]⁽⁺⁾, similarly as in the reaction of γ -methoxyquinoline, with formaldehyde in H₂SO₄ medium [13]. On the contrary, [HSO₃]⁽⁺⁾ is much more reactive in the case of CH₃-CHOH, CH₃-C⁽⁺⁾-CH₃, and C₆H₅CH-OH.



We are thankful to Ing. V. Kosljar, Ing. K. Špirková, and Ing. Š. Takáč for the elementary analyses and the records of the ultraviolet spectra.

References

1. Karvaš M., Holčík J., *Chem. Prům.* **17**, 543 (1967).
2. Karvaš M., Hrdlovič P., Durmis J., Holčík J., *Chem. Prům.* **19**, 109 (1969).
3. Heller H., Keller E., Gysling H., Mindermann F., *U.S. Patent* 3 004 896 (1961).
4. Michajlov V. V., Kochanov J. V., *Sintez stabilizatorov*, p. 21. Tambovskoje knižnoje izdatelstvo, Tambov, 1963.

5. Karvaš M., Holčík J., Jexová E., Balogh A., *Chem. Prům.* **18**, 428 (1968).
6. Zollinger H., *Chimija azokrasitelej*, p. 169. Gosudarstvennoje naučno-techničeskoje izdatelstvo chimičeskoj literatury, Leningrad, 1960.
7. Jansen J. E. (B. F. Goodrich Co.), *U.S. Patent* 2 468 982 (1948).
8. Union Carbide Co., *Brit. Patent* 794 476 (1958).
9. Dow Chemicals Co., *U.S. Patent* 2 535 014 (1950).
10. Čepčiansky I., Majer J., *Collect. Czech. Chem. Commun.* **34**, 72 (1969).
11. Scott G., *Atmospheric Oxidation and Antioxidants*, p. 184. Elsevier, Amsterdam, 1965.
12. Karvaš M., Durmis J., Bömches H., *PV-738/68* (ČSSR).
13. Kaslow C. E., Raymond S., *J. Amer. Chem. Soc.* **70**, 3912 (1948).
14. Rubcov V. M., et al., *Ž. Obšč. Chim.* **23**, 1209 (1953).
15. Badische Anilin und Soda Fabrik, *German Patent* 301 451 (1917).
16. Standard Oil Co., *U.S. Patent* 2 628 212 (1953).
17. Fierz-David H. E., Blangey L., *Grundliegende Operationen der Farbenchemie*, p. 189. Springer-Verlag, Wien, 1938.
18. Witt O. N., Mayer F., *Ber.* **26**, 1072 (1893).

Translated by R. Domanský