# PHOTO-INDUCED REACTIONS—XVIII

# THE PHOTOCHEMICAL TRANSFORMATION OF 4-HYDROXY-AND 4-ACETOXY-2,5-CYCLOHEXADIENONES<sup>1</sup>

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Abstract—The UV irradiation of 2,4,6-tri-t-butyl-4-hydroxy-2,5-cyclohexadienone (I) in petroleum ether yielded the diketone V (11%) and the enedione VII (54%) in addition to the cyclopentenone VIII (3%) and the bicyclopentanone X (8%). The formation of V and VII can be rationalized by considering a common intermediate, the lumi-type ketone III. This result indicates that 4-hydroxy-2,5-cyclohexadienones undergo photorearrangement similar to that of usual 2,5-cyclohexadienones. Irradiation of I in methanol gave the bicyclopentanone XI (60%) predominantly. However, on photolysis of I in dimethylformamide the isomeric bicyclopentanone X was formed as a major product (49%) together with the bicyclopentanone XI (22%). Photolysis of 2,4,6-tri-t-butyl-4-acetoxy-2,5-cyclohexadienone (II) afforded 2,4,6-tri-t-butyl-phenol (3%), the lumiketone XV (11%) and the photophenol XVI (47%). The mechanisms of these reactions are discussed.

2,5-CYCLOHEXADIENONES have been found to provide one of the most interesting and extensively studied photochemical reactions and to undergo two basic types of transformations on their irradiation in neutral media; i.e. (a) skeletal rearrangement which furnish bicyclo[3.1.0]hex-3-en-2-ones capable of further photoisomerization and (b) expulsion of one of the 4-substituents followed by phenol formation.<sup>2</sup> On the other hand, photolysis of certain 4-hydroxy-2,5-cyclohexadienones was reported to afford 4-acyl-2-cyclopentenones in poor yields and two reaction pathways were proposed (paths 1 and 2 in Scheme 1). For example, Jeger et al.,<sup>3</sup> found that the photorearrangement of 3-oxo-10 $\beta$ -hydroxy-17 $\beta$ -acetoxy- $\Delta^{1,4}$ -estradiene affords a 4-acyl-2-cyclopentenone derivative along with 17-O-acetyl-estradiol, and they proposed a zwitterion intermediate leading to the acylcyclopentenone via path 1 (Eq. 1). Altwicker and Cook<sup>4</sup> showed that irradiation of 2,6-di-t-butyl-4-hydroxy-4-phenyl-2,5cyclohexadienone gives 2,5-di-t-butyl-4-benzoyl-2-cyclopentenone, and they considered the possibility of path 2 for its formation (Eq. 2). Recently, Burkinshaw et al.<sup>5</sup> reported the photolysis of several 4-hydroxy-2,5-cyclohexadienones giving 4-acyl-2cyclopentenone derivatives, some of which undergo further photochemical rearrangement to form  $\Delta^1$ -butenolidest (e.g., Eq. 3). Up to the present there has been no unquestionable report on the photochemical formations of bicyclo[3.1.0]hex-3-en-2ones and of its secondary products from 4-hydroxy-2,5-cyclohexadienones. We initiated the photochemical reaction of 2,4,6-tri-t-butyl-4-hydroxy-2,5-cyclohexadienone (I), in order to investigate whether the competition between the formation of

<sup>&</sup>lt;sup>†</sup> We have already proposed the mechanism for the formation of the  $\Delta^1$ -butenolides from the 4-acyl-2cyclopentenones via bicyclo[2.1.0]pentanone intermediates. See Ref. 6.

2,5-di-t-butyl-4-pivaloyl-2-cyclopentenones and the rearrangement into 1,3,6-tri-tbutyl-6-hydroxybicyclo[3.1.0]hex-3-en-2-ones occurs or not. Since 2,4,6-tri-t-butyl-4-methoxy-2,5-cyclohexadienone gives photochemically a mixture of 2,4,6-tri-tbutyl-3-methoxy-2,5-cyclohexadienone and 3,6-di-t-butylguaiacol in neutral media (Eq. 4),<sup>7</sup> it is also interesting to see whether 2,4,6-tri-t-butyl-3-hydroxy-2,5-cyclohexadienone (IV), the ketone tautomer of 2,4,6-tri-t-butylresorcinol, is formed from I.



## **RESULTS AND DISCUSSION**

Synthesis of dienones I and II. An acetoxydienone (II), which was produced as a by-product on oxidation of 2,4,6-tri-t-butylphenol with lead tetraacetate,<sup>1</sup> was also obtained in a high yield by the treatment of 2,4,6-tri-t-butyl-4-bromo-2,5-cyclo-hexadienone<sup>8</sup> with potassium acetate in acetic acid. Furthermore, hydrolysis of the acetoxydienone II afforded 2,4,6-tri-t-butyl-4-hydroxy-2,5-cyclohexadienone (I) in higher yield than in the previous report.<sup>9</sup>

*Photolysis of* I. On irradiation of the hydroxydienone I in petroleum ether with a high-pressure mercury lamp (Pyrex filter), 11% of a diketone V, 54% of an enedione VII, 3% of a *trans*-cyclopentenone VIII,<sup>10</sup> and 8% of a bicyclopentanone  $X^{10}$  were isolated. Irradiation of I in benzene under the similar conditions gave the diketone V (14%), the *trans*-cyclopentenone VIII (6%) and the bicyclopentanone X (4%).

The diketone V was shown by its IR bands at 1736 and 1690 cm<sup>-1</sup> to have two CO groups and by its UV absorption at 236 mµ with a shoulder at 257 mµ to possess a conjugated system. The NMR spectrum of the diketone V show two doublets at  $\tau$  3.33 and 6.98 (J = 2.5 c/s) and four singlets at  $\tau$  8.82 (9H), 8.86 (9H), 8.93 (9H) and 6.67 (1H), which suggested the presence of a moiety —CH—CH—, three t-butyl groups and an uncoupled aliphatic proton. Structure V was given for the diketone from the spectral data mentioned above and from the fact that acid treatment of the diketone V gave 4,6-di-t-butylresorcinol.<sup>11</sup> The enedione VII showed IR bands at 1674 (sh), 1663 and 1605 cm<sup>-1</sup> and an UV maximum at 225 mµ. The NMR spectrum of the enedione VII exhibits two doublets at  $\tau$  3.65 (1H, J = ca. 1 c/s) and 7.50 (1H, J = ca. 1 c/s), three singlets at  $\tau$  7.38 (1H), 8.75 (9H, C—C—t-Bu<sup>10</sup>) and 9.08 (18H, two t-butyl groups†). These spectral properties are similar to those of the compounds i and ii<sup>12</sup> except for the differences in the UV absorption maximum and in the chemical shift of the olefinic proton. The differences may be due to replacement of a t-butyl group for a methoxyl group or an acetoxyl group. Therefore, structure VII was assigned to the enedione.

$$RO \qquad i: R = Me$$
  
ii: R = Ac

Irradiation of I in methanol afforded a bicyclopentanone XI<sup>10</sup> in a good yield (60%) in addition to a small amount of a  $\Delta^1$ -butenolide<sup>10</sup> XII (2%). On photolysis of I in dimethylformamide the bicyclopentanone X was formed as a main product (49%) along with the bicyclopentanone XI (22%). Irradiation of I in acetic acid-ethanol-water (2:2:1) gave the bicyclopentanones X and XI in yields of 77% and 22%, respectively. The photochemical reaction of I leading to V, VII, the cyclopentenones VIII and IX, and the bicyclopentanones X and XI, was carried out in various solvents and the results were summarized in Table 1. The solvent effect in the photolysis of I will be discussed later.

Photolysis of II. Irradiation of II in benzene or petroleum ether with a high-pressure

<sup>&</sup>lt;sup>†</sup> It may be summarized that t-butyl protons appearing in a higher field than  $\tau$  90 belong to one of the t-butyl group on a  $sp^3$ -carbon. See Ref. 10 and the refs cited therein.

Solvent	Yields of the products (%)					
			"trans-route"		"cis-route"	
	v	VII	VIII	х	IX	XI
Petroleum ether	11	54	3	8	_	
Benzene	14	-	6	4		
Methanol		_		a		60
Dimethylformamide	_	_	_	49		22
AcOH-EtOH- $H_2O(2:2:1)$	-	—	—	27	_	22

TABLE 1. SOLVENT EFFECT IN THE PHOTOLYSIS OF I

<sup>a</sup> the  $\Delta^1$ -butenolide XII, which might be derived thermally from X,<sup>10</sup> was isolated in a low yield (2%).

mercury lamp (Pyrex filter) gave 3% of 2,4,6-tri-t-butylphenol (XVII), 11% of a lumiketone XV and 47% of a photophenol XVI. The photophenol XVI exhibits IR bands at 1750 cm<sup>-1</sup> (aryl acetate) and 810 cm<sup>-1</sup> (two adjacent H atoms on a benzene ring) and an UV maximum at 271 mµ. The NMR spectrum of the photophenol XVI shows the presence of two adjacent protons on a benzene ring (two d's at  $\tau$  2.92 and 3.13; J = 8 c/s), an acetoxy group (s at  $\tau$  7.63), a hydroxyl group (s at  $\tau$  5.03) and two t-butyl groups (two s's at  $\tau$  8.61 and 8.69). The structure XVI for the photophenol was given from its physical properties mentioned above and from the fact that methylation of the photophenol gave 3,6-di-t-butylveratrole.<sup>7</sup>

An IR band at  $1703 \text{ cm}^{-1}$  and UV maxima at 225 mµ ( $\varepsilon$  8800) and 271 mµ ( $\varepsilon$  1520) of the lumiketone XV are characteristic of a bicyclo[3.1.0]hex-3-en-2-one skeleton.† The NMR spectrum shows five singlets at  $\tau$  3.20 (an olefinic proton), 7.86 (an aliphatic proton), 7.95 (an acetoxyl group), 8.90 (two t-butyl groups) and 9.05 (a t-butyl group). Alkaline hydrolysis of the lumiketone XV gave the enedione VII which might be formed *via* the ketone VI. These data indicate that the lumiketone is represented by formula XV.

Mechanictic consideration. It is noteworthy that the diketone V and the endione VII were formed only when I was photolysed in inert solvents such as benzene and petroleum ether. The diketone V seems to be formed via the lumi-type ketone III and the ketone IV (Scheme 2), because the diketone V is a tautomer of the ketone IV which is the analogous product to 2,4,6-tri-t-butyl-4-methoxy-2,5-cyclohexadienone (Eq. 4). The formation of the endione VII can be rationalized by the lumi-type rearrangement of the ketone IV into 1,3,6-tri-t-butyl-5-hydroxybicyclo[3.1.0]hex-3en-2-one (VI) followed by its isomerization as pictured in Scheme 2. The hydroxyketone VI should be so unstable that it could not be isolated from the reaction mixture. The instability of VI may be supported by the fact that mild hydrolysis of the lumiketone XV did not afford the corresponding hydroxyketone VI, but the enedione VII.<sup>‡</sup>

It should be noted that the diketone V, the ketone tautomer of 2,4,6-tri-t-butylresorcinol, is stable either in the crystalline state§ or in solution (neutral solvents and

- † For more details on the spectral data of lumi-products, see Ref. 2.
- ‡ For the facile isomerization of hydroxycyclopropanes, see Ref. 4 and the refs cited therein.
- § However, on standing for several months, V became yellow and decomposed completely.



acetic acid) and does not tend to aromatize. The stability of the ketone tautomer V may be attributed to the steric hindrance between t-Bu groups and OH groups in its phenol form, similar to that of the ketone tautomers of other phenols.<sup>1, 7</sup> Since it has been shown in our previous papers<sup>6, 10</sup> that the bicyclopentanones, X and XI, are formed *via* the cyclopentenones, VIII and IX, respectively, hereafter we designate the pathway to the *trans*-cyclopentenone VIII and the bicyclopentanone X as "*trans*-route" and the pathway to the *cis*-cyclopentenone IX and the bicyclopentanone XI as "*cis*-route" (Table 1). In acidic media, the formation of the cyclopentenones VIII and IX seems to be rationalized by a nucleophilic attack of a water molecule to an intermediate XVIII, analogous to that proposed for the photolysis of 2,4,6-tri-t-butyl-4-methoxy-2,5-cyclohexadienone in the same media.<sup>10</sup>

In aprotic solvents, dimethylformamide and petroleum ether, "trans-route" is predominant over "cis-route". The isomerization of I in an aprotic solvent into



the *trans*-cyclopentenone VIII may be caused by a intramolecular hydrogen shift, because these results are quite different from that ("*cis*-route" predominant) of photolysis of I in a protic solvent, methanol. Although the michanism for the formation of the *trans*-cyclopentenone VIII from I in aprotic solvents has not yet been established, we wish to mention three possible pathways; (a) hydrogen migration from the hydroxyl to the cationic carbon of the zwitterion XVIII, (b) proton shift from the hydroxyl to the carbonyl oxygen of the lumi-type ketone III, and (c) proton shift from the hydroxyl to the 1-carbon of III, as depicted in Scheme 4. On the other hand, the photolysis of I in methanol gave "*cis*-route" products predominantly. The attack of a methanol molecule to the lumi-type ketone III as shown in Scheme 4 (pathway d) seems to be a possible mechanism for the formation of the *cis*-cyclopentenone IX, but we cannot exclude different pathways, e.g., the attack of a methanol molecule to the zwitterion XVIII.

In the photolysis of the acetoxydienone II, a possible mechanism for the formation of the lumiketone XV and the photophenol XVI can be shown as in Scheme 3, by considering the analogous transformation of 2,5-cyclohexadienones reported previously.<sup>2</sup> It seems reasonable to suggest that 2,4,6-tri-t-butylphenol is formed via 2,4,6-tri-t-butylphenoxy radical<sup>†</sup> which might be produced by  $n-\pi^*$  excitation of I.

<sup>&</sup>lt;sup>†</sup> Although this phenoxyl radical is known to be very stable in benzene, ether, etc, we found that the rate of hydrogen abstraction of the radical from hydrogen donor molecules increases remarkably when irradiated by UV light. Details will be published elsewhere.



analogous to the mechanism proposed by Schuster and Patel<sup>12</sup> in the photochemical reaction of 4-methy-4-trichloromethyl-2,5-cyclohexadienone.<sup>†</sup>

### EXPERIMENTAL

### 2,4,6-Tri-t-butyl-4-acetoxy-2,5-cycloxadienone (II)

A mixture containing 6 g of 2,4,6-tri-t-butyl-4-bromo-2,5-cyclohexadienone<sup>8</sup> and 12 g AcOK in 50 ml AcOH was warmed at 60–65° for 8 hr. After addition of water (50 ml), the reaction mixture was extracted with ether (100 ml  $\times$  3). The ethereal layer was washed with water and dried on Na<sub>2</sub>SO<sub>4</sub>. Removal of the solvent gave 5.49 g of brown oil which crystallized. Recrystallization from MeOH containing a small amount of water yielded 2.63 g pale yellow prisms, m.p. 76–77.5°, which were identified as II<sup>1</sup> by IR and mixture m.p. Furthermore, the mother liquor afforded 1.20 g of II. The total yield amounted to 68%.

#### 2,4,6-Tri-t-butyl-4-hydroxy-2,5-cyclohexadienone (I)

A soln containing 50 mg of II in 0.5 N KOH-EtOH was allowed to stand at room temp overnight. Addition of water (5 ml) deposited 37 mg pale yellow needles, m.p. 113-125° (lit<sup>9</sup> m.p. 133-134°), which were identified as I by IR and mixture m.p.

#### Photolysis of 2,4,6-tri-t-butyl-4-hydroxy-2,5-cyclohexadienone (I)

(a) In benzene. A soln containing 1.00 g of I in 150 ml benzene was irradiated under bubbling  $N_2$  using a 100 W high-pressure mercury arc lamp (Ushio UM 102) with a water-cooled Pyrex jacket for 1.5 hr.

<sup>†</sup>After completion of our work, Rieker and Zeller<sup>14</sup> reported that irradiation of I in wet ether with 254 mµ light yielded two isomeric bicyclopentanones, A (m.p. 145–147°) and B (m.p. 101–102·5°), which appear to be identical with XI and X, respectively. Although they proposed structure XI for A, the structure for B is different from X.

Removal of the solvent under reduced press, followed by crystallization of the residue from pet. ether (b.p. 40–70°) gave 130 mg colorless crystals of an unknown compound. Evaporation of the mother liquor followed by crystallization of the residue from MeOH gave 140 mg (14%) of V as pale yellow crystals, m.p. 103–110°, which, on recrystallization from MeOH, afforded colorless prisms, m.p. 114–115.5°;  $\lambda_{m,v}^{KBT}$  1736 and 1690 cm<sup>-1</sup>:  $\lambda^{EtOH}$  236 ( $\epsilon$  4400) and 257 mµ (sh. 2800):  $\lambda^{cyclohexme}$  231 ( $\epsilon$  4800), 236 (sh, 4500) and 254 mµ (sh, 2000): NMR spectrum:  $\tau$  (CDCl<sub>3</sub>) 3.33 (1H. d. J = 2.5 c/s), 6.67 (1H. s), 6.98 (1H. d. J = 2.5 c/s), 8.82 (9H, s), 8.86 (9H, s) and 8.93 (9H, s). (Found: C, 77.47; H, 10.89. Calc. for C<sub>18</sub>H<sub>30</sub>O<sub>2</sub>: C, 77.65; H, 10.86%).

The mother liquor from V was evaporated and the residue was chromatographed on 40 g silica gel. Elution with 30 ml benzene-pet. ether (1:1) gave 163 mg crystals which were shown by IR spectrum and TLC analysis to consist of V and an unknown compound. Elution with 250 ml benzene-pet. ether (1:1) and then with 50 ml benzene afforded 129 mg oil which was not further investigated. Elution with 100 ml benzene yielded 60 mg crystals which on recrystallization from MeOH gave 12 mg colorless crystals, m.p. 74-78°, which were identified as the *trans*- VIII<sup>10</sup> by IR and mixture m.p. Elution with 40 ml benzene afforded 44 mg yellow oil which was not further investigated. Elution with 200 ml benzene yielded 36 mg crystals which on recrystallization from pet. ether gave 13 mg colorless crystals, identified as  $X^{10}$  by IR.

(b) In petroleum ether. A soln containing 2.70 g of I in 500 ml pet. ether  $(40-70^{\circ})$  was irradiated under bubbling N<sub>2</sub> for 70 min. using 450 W high-pressure mercury arc lamp (Ushio UM 450) with a water-cooled Pyrex jacket. After removal of the solvent under reduced press, the residue was chromatographed on 100 g silica gel. Elution with 140 ml pet. ether-benzene (1:1) gave 46 mg yellow oil which was shown by IR and TLC analysis to consist of V and an unknown product. Elution with 50 ml pet. ether-benzene (1:1) afforded 309 mg (11%) pale yellow crystals which were identified as V by IR. Elution with 150 ml pet. ether-benzene (1:1) and then with 50 ml benzene gave 1 406 g yellow crystals which, on recrystallization from MeOH, afforded VII as pale yellow needles, m.p. 85-87°;  $v_{max}^{Emat}$  1663, 1674 and 1605 cm<sup>-1</sup>;  $\lambda_{max}^{Emoth}$ 225 mµ ( $\varepsilon$  8400); NMR spectrum:  $\tau$  (CCl<sub>4</sub>) 3.65 (1H, d, J = 1 c/s), 7.38 (1H, s), 7.50 (1H, d, J = 1 c/s), 8.75 (9H, s) and 9.08 (18H, s). (Found: C, 77.61; H, 11-03. Calc. for C<sub>18</sub>H<sub>30</sub>O<sub>2</sub>: C, 77.65; H, 10.86%).

Elution with 50 ml benzene gave 17 mg oil which was not further investigated. Further elution with 150 ml benzene afforded 74 mg pale yellow crystals which were identified as *trans*-VIII<sup>10</sup> by IR. Elution with 100 ml benzene yielded 12 mg oil which was not further investigated. Final elution with 700 ml benzene yielded 224 mg (8%) colorless crystals, which were identified as  $X^{10}$  by IR.

(c) In methanol. A soln containing 100 g of I in 110 ml MeOH was irradiated for 100 min under the conditions as described in (a). Removal of the solvent gave yellow crystals containing a small amount of oil. Recrystallization from pet. ether afforded 523 mg colorless crystals, m.p. 139–141°, which were identified as  $XI^{10}$  by IR and mixture m.p. The mother liquor was evaporated and the residue was chromatographed on 25 g silica gel. Elution with 420 ml pet. ether-benzene (1:1) gave 161 mg yellow oil which was not further investigated. Further elution with 50 ml benzene afforded 21 mg crystals which were identified as  $XII^{10}$  by IR. Elution with 100 ml benzene yielded 80 mg pale yellow crystals which were identified as XI by IR. The bicyclopentanone X could not be isolated.

(d) In acidic media. A soln containing 400 mg of I in 120 ml AcOH-water-EtOH (2:1:2) was irradiated for 1 hr under the same conditions mentioned. Addition of water (400 ml) deposited 271 mg of a colorless solid, which was shown by a TLC analysis to consist of the isomeric X and XI and other minor components. Treatment of the solid with a small volume of pet. ether gave 195 mg of a colorless solid, which was shown by a NMR analysis to be a mixture of X and XI (11:9).

#### Acid treatment of the diketone V

A soln of V (15 mg) in 2 ml AcOH-HBr (1:1) was allowed to stand at room temp for one day. Addition of water (3 ml) deposited 7 mg colorless crystals, m.p. 115-118° (lit<sup>11</sup> m.p. 123°); which were identified as 4,6-di-t-butylresorcinol by IR and mixture m.p.

### Photolysis of 2,4,6-tri-t-butyl-4-acetoxy-2,5-cyclohexadienone (II)

A soln containing 1-00 g of II in 430 ml benzene was irradiated for 2:25 hr under bubbling  $N_2$  using a 450 W high-pressure mercury arc lamp (Pyrex filter). After removal of the solvent, the residue was chromatographed on 40 g silica gel. Elution with 20 ml pet. ether-benzene (2:3) gave 83 mg pale yellow oil containing some crystals. The oil was absorbed on a clay plate and 30 mg colorless plates, m.p. 118-121°, were isolated. These crystals were identified as 2,4,6-tri-t-butylphenol by IR and mixture m.p. Further elution with 20 ml pet. ether-benzene (2:3) gave 68 mg yellow oil which was not further investigated. Elution with 60 ml pet. ether-benzene (2:3) afforded 105 mg (11%) yellow oil which crystallized by standing in a refrigerator for several weeks. Recrystallization from MeOH yielded 27 mg of XV as colorless crystals, m.p. 77-78°;  $v_{max}^{EDH}$  1755 and 1703 cm<sup>-1</sup>;  $\lambda_{max}^{EOH}$  225 ( $\varepsilon$  3800) and 271 mµ ( $\varepsilon$  1520); NMR spectrum:  $\tau^{CDC1}$  3·20 (1H, s), 7·86 (1H, s), 7·95 (3H, s), 8·90 (19H, s) and 9·05 (9H, s). (Found: C, 75·25; H, 10·33. Calc. for C<sub>20</sub>H<sub>32</sub>O<sub>3</sub>: C, 74·96; H, 10·06%).

Elution with 120 ml pet. ether-benzene (2:3) gave 150 mg yellow oil which was not further investigated. Further elution with 650 ml ether-benzene (2:3) afforded 390 mg pale yellow crystals, m.p. 173-175°, which, on recrystallization from pet. ether, yielded the XVI as colorless needles, m.p. 175-175.5°;  $v_{max}^{KBr}$  3430 and 1750 cm<sup>-1</sup>;  $\lambda_{max}^{EOH}$  271 mµ ( $\epsilon$  2600); NMR spectrum:  $\tau^{CDCI}$  2.92 (1H, d, J = 8 c/s), 3·13 (1H, d, J = 8 c/s), 7·63 (3H, s), 8·61 (9H, s) and 8·69 (9H, s). (Found: C, 72·65; H, 9·21. Calc. for C<sub>16</sub>H<sub>24</sub>O<sub>3</sub>: C, 72·69; H, 9·15%).

### Conversion of the lumiketone XV into the enedione VII

The lumiketone XV (16 ml) was dissolved in 2 ml 0.5N KOH-EtOH and the soln was allowed to stand at room temp under  $N_2$  overnight. Addition of water (2 ml) deposited 12 mg pale yellow crystals, m.p. 79-84°, which were identified as VII by IR and mixture m.p.

#### Methylation of the photophenol XVI

The photophenol XVI was methylated according to the procedure described previously.<sup>7</sup> A soln containing 60 mg of XXXII in 25 ml dried DMSO was stirred with 75 mg NaH at room temp under bubbling N<sub>2</sub> for 30 min. Then, 3 ml MeI was added and the mixture stirred for 40 min. After addition of 30 ml water, the mixture was extracted with pet. ether (50 ml  $\times$  3). The organic layer was washed with water and dried on Na<sub>2</sub>SO<sub>4</sub>. Removal of the solvent under reduced press gave 55 mg crystals. Recrystallization from MeOH afforded 19 mg crystals, m.p. 66–69°, which were identified as 3,6-di-t-butylcatechol dimethyl ether<sup>7</sup> by IR and mixture m.p.

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