

solution of an excess of ethylmagnesium bromide in ether. After standing at room temperature for some time, the product was hydrolyzed with saturated ammonium chloride solution. The ether layer was separated, dried and evaporated. The residue was heated with 0.2 g. of 10% palladium-charcoal under nitrogen at 270° for one-half hour and at 320° for ten minutes. The product was treated with 0.12 g. of picric acid in ethanol. On concentrating and cooling, the picrate was obtained as orange needles; m. p. 124–125.5°. Recrystallization from ethanol gave a product of m. p. 127–128°. When mixed with the picrate of the phenanthrene derivative from podocarpinol (m. p. 126–126.5°), the substance melted at 126–128°.

The styphnate, was prepared from the compound recovered from the picrate by treatment with sodium bicarbonate. Treatment with 70 mg. of styphnic acid in ethanol gave light orange crystals melting at 141°. When mixed with the styphnate of the natural derivative (m. p. 139–140.5°) the substance melted at 139–140°.

The trinitrobenzene derivative prepared in a similar manner was obtained as fluffy needles from methanol; m. p. 139–140°. Recrystallization from methanol raised the melting point to 140–140.5°. Mixed with the trinitrobenzene derivative of the natural product (m. p. 137–137.5°), the substance melted at 137–140°.

### Summary

The structures of podocarpic acid and ferruginol are proved by the conversion of both podocarpic and dehydroabietic acids into ferruginol.

The 6-hydroxy derivative of dehydroabietic acid differs from the 7-isopropyl derivative of podocarpic acid only in the configuration of the methyl and carboxyl groups at C<sub>1</sub>.

The stereochemistry of these substances is discussed.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF TEXAS]

## Reactions Between *sym*-Diphenyltriazene and Mercury(II) Salts

BY CECIL M. KNOWLES AND GEORGE W. WATT

In a recent publication, Mandal<sup>1</sup> described products obtained by the interaction of solutions of mercury(II) salts and alcoholic solutions of *sym*-diphenyltriazene (diazoaminobenzene). The properties described suggested that these products might be identical with the mercury salt previously prepared by the reaction between mercury and *sym*-diphenyltriazene.<sup>2</sup> Although the compounds prepared by Mandal were formulated as having the composition represented by the formula  $(C_6H_5N=N-NHC_6H_5)_4HgX_2$ , where X = Cl, Br, NO<sub>3</sub>, or C<sub>2</sub>H<sub>3</sub>O<sub>2</sub>, the present study shows that either a salt of the base is formed or molecular compounds which contain one equivalent of the mercury salt combined with two of the base, and not four as claimed by Mandal.

### Experimental

**Reaction with Mercury(II) Chloride.**—To a saturated solution of pure *sym*-diphenyltriazene (10.0 g.), m. p. 98°, in ethanol was added with stirring a saturated ethanolic solution of 6.9 g. of mercury(II) chloride. Dilution with water followed by cooling resulted in the precipitation of a tan-colored solid which was separated by filtration, treated with "Norite," and recrystallized from 50% ethanol. The purified product consisted of a tan-colored crystalline solid, m. p. 161–165° dec. (cor.); yield, 13.7 g. or 81%. *Anal.* Calcd. for C<sub>24</sub>H<sub>22</sub>Cl<sub>2</sub>N<sub>6</sub>Hg: C, 43.40; H, 3.32; N,

12.62. Found: C, 43.15; H, 3.16; N, 12.78. Qualitative tests for mercury and chlorine were positive.

**Reaction with Mercury(II) Bromide.**—By a similar reaction involving 2.19 g. of *sym*-diphenyltriazene and 2.00 g. of mercury(II) bromide there was obtained 3.0 g. (71% yield) of the corresponding tan-colored mercury(II) bromide addition compound, m. p. 132–134° dec. (cor.). The color of this product is slightly more intense than that of the corresponding mercury(II) chloride compound. *Anal.* Calcd. for C<sub>24</sub>H<sub>22</sub>Br<sub>2</sub>N<sub>6</sub>Hg: N, 11.15. Found: N, 11.30. Qualitative tests for mercury and bromine were positive.

**Reaction with Mercury(II) Acetate.**—By the reaction between 10.0 g. of *sym*-diphenyltriazene and 4.6 g. of mercury(II) acetate in ethanol there was obtained immediately (*i. e.*, without dilution, etc.) 8.5 g. (99% yield) of the lemon yellow mercury salt of the triazene. The product was purified by recrystallization from benzene and from pyridine. With rapid heating the pure salt melted at 232° dec. (cor.) which corresponds to the melting point recorded by Ciusa and Pestalozza.<sup>3</sup> Upon slow heating, melting occurred at 227° dec. (cor.) which agrees with the melting point reported by Watt and Fernelius.<sup>2</sup> *Anal.* Calcd. for C<sub>24</sub>H<sub>20</sub>N<sub>6</sub>Hg: N, 14.18; Hg, 33.84. Found: N, 14.03; Hg, 33.70.

**Reaction with Mercury(II) Nitrate.**—To an ethanolic solution of 5.0 g. of *sym*-diphenyltriazene was added an ethanolic solution and suspension of 4.25 g. of mercury(II) nitrate.<sup>4</sup> If (1) the resulting yellow precipitate was filtered immediately, or (2) the reaction mixture was immediately made alkaline by addition of aqueous ammonia,

(1) Mandal, *Science and Culture*, **6**, 59–60 (1940).

(2) Watt and Fernelius, *Z. anorg. allgem. Chem.*, **221**, 187 (1935).

(3) Ciusa and Pestalozza, *Gazz. chim. ital.*, **41**, 1, 394 (1911).

(4) Identical results are obtained when finely divided solid mercury(II) nitrate is added to ethanolic solutions of the triazene.

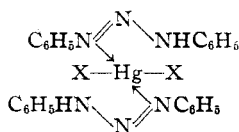
there were obtained high yields of the mercury salt of *sym*-diphenyltriazene, m. p. 232°, identical with the product obtained using mercury(II) acetate. *Anal.* Calcd. for  $C_{24}H_{20}N_6Hg$ : N, 14.18. Found: N, 14.10.

If the precipitate (from 10.0 g. of *sym*-diphenyltriazene and 8.23 g. of mercury(II) nitrate) was allowed to stand in contact with the mother liquor for twenty-four hours, nitrogen gas was evolved slowly. The reaction mixture was filtered and the resulting brown solid was washed with ethanol and the washings added to the dark red filtrate, from which was obtained (by evaporation of the solvent) 4.5 g. of purple colored crystals, m. p. >140° dec. This material was too unstable to permit purification by ordinary methods. The brown ethanol-insoluble solid (13.0 g.) was dried and extracted several times with boiling benzene. Concentration of this extract, followed by cooling, yielded a red crystalline solid which was recrystallized from benzene, m. p. 212° dec. (cor.). *Anal.* Calcd. for  $C_{24}H_{20}N_6Hg$ : N, 14.18. Found: N, 14.20. Recrystallization from pyridine yielded an orange-red crystalline solid, m. p. 216° dec. (cor.). *Anal.* Calcd. for  $C_{24}H_{20}N_6Hg \cdot (C_5H_5N)_2$ : C, 54.35; H, 4.02; N, 14.91; Hg, 26.70. Found: C, 54.75; H, 3.74; N, 14.90; Hg, 27.15. Further extraction of the brown insoluble solid with benzene and with ethanol resulted in slow decomposition accompanied by a progressive decrease in nitrogen content from 7.0 to 4.5%.

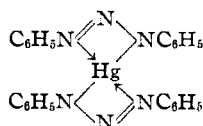
By following the above procedure but by separating the precipitate after six hours, there were obtained relatively small quantities of the purple, red, and brown solid products. Fractional crystallization of the benzene extract yielded, as the main product of this reaction, an orange-colored compound which was recrystallized from benzene, m. p. 187° dec. (cor.). The intensity of color of this product did not change upon repeated recrystallization. *Anal.* Calcd. for  $C_{24}H_{20}N_6Hg$ : N, 14.18. Found: N, 14.30.

### Discussion

The compounds formed between *sym*-diphenyltriazene and mercury(II) chloride and bromide are probably of the type



in which the central mercury atom is 4-covalent.<sup>5</sup> In the mercury salt obtained using mercury(II) acetate (or mercury(II) nitrate, under suitable conditions) the 4-covalence of mercury might conceivably be maintained in a structure which involves a four-membered ring in which the triazene group acts as a chelating group,



(5) Cf. Dwyer, *This Journal*, **63**, 78 (1941).

although preliminary studies of the ultraviolet absorption spectra of *sym*-diphenyltriazene and its metal salts in benzene and pyridine solutions<sup>6</sup> suggest that such a structure is improbable.

From the triazene and mercury(II) nitrate, there is obtained the yellow mercury salt only if the nitric acid formed in the reaction is neutralized at once or if the precipitated salt is removed from the acidic medium<sup>7</sup> before further reactions can occur. Upon standing in contact with the mother liquor for twenty-four hours, however, the yellow salt reacts to form nitrogen, an unstable brown solid of low nitrogen content, and a red crystalline solid which is isomeric with the yellow salt and which is capable of coordinating two molecules of pyridine. This latter fact was apparently overlooked by Mangini and Dejudicibus<sup>8</sup> who claim that the yellow salt is converted to an orange-colored isomer simply by recrystallization from pyridine. In the course of the experiments described above, it was found that the yellow salt may be recrystallized repeatedly from pyridine without change. The orange-colored compound isolated from the six-hour reaction with mercury(II) nitrate may be identical with the isomer described by Mangini and Dejudicibus or it may consist of a mixture of the red and yellow isomers. Further studies on the absorption spectra of these isomers and related compounds will be described in a later communication.

### Summary

1. *sym*-Diphenyltriazene and mercury(II) chloride or bromide in ethanol react to form compounds corresponding to the formula  $(C_6H_5N=NNHC_6H_5)_2 \cdot HgX_2$ , where X = Cl or Br.

2. *sym*-Diphenyltriazene and mercury(II) acetate in ethanol react to form a yellow salt having the composition represented by the formula  $(C_6H_5N=N-N-C_6H_5)_2Hg$ .

3. Depending upon the procedure employed,

(6) Brode, Fernelius and Watt, unpublished work.  
(7) In connection with the work described here, the authors have had occasion to study the action of acids on *sym*-diphenyltriazene and its salts in both alcoholic and aqueous media. Kidd [*J. Org. Chem.*, **2**, 199 (1937)] states that "No mention has been found of a previous attempt to isolate aniline from an acidified solution of diazoaminobenzene." We wish, here, to call attention to the fact that the formation of aniline (and phenol) by the acidic decomposition of diazoaminobenzene and its salts has been reported by Fischer [*Ber.*, **17**, 642 (1884)], by Watt and Fernelius,<sup>2</sup> by Cain ["The Chemistry and Technology of the Diazo-compounds," Edward Arnold, London, 1908, p. 77; 2nd edition, 1920, p. 90], and by Earl, *Proc. Roy. Soc. N. S. Wales*, **63**, 89-94 (1929).

(8) Mangini and Dejudicibus, *Gazz. chim. ital.*, **63**, 801-812 (1933).

*sym*-diphenyltriazene and mercury(II) nitrate in ethanol react to form (a) a yellow salt identical with that obtained using mercury(II) acetate, (b) a red isomer which may be isolated as such or

in the form of a di-solvate from pyridine, (c) an orange-colored compound which may be isomeric with the yellow and red salts.

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[JOINT CONTRIBUTION FROM THE JONES CHEMICAL LABORATORY, UNIVERSITY OF CHICAGO, AND THE FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY]

## The Reduction of Dipole Moment by Steric Hindrance in Di-*t*-butylhydroquinone and its Dimethyl Ether

BY P. F. OESPER, C. P. SMYTH AND M. S. KHARASCH

The dipole moments of di-*t*-butylhydroquinone and di-*t*-butylhydroquinone dimethyl ether have been measured, with the object of studying the steric effects of the bulky *t*-butyl groups upon the adjacent hydroxy or methoxy groups. The moments were obtained by means of the apparatus and methods previously described,<sup>1,2</sup> the dielectric constants at a frequency of 520 kilocycles and the densities of solutions of the substances in benzene being determined. The benzene was purified by standard methods.

### Experimental Results

The dielectric constants,  $\epsilon$ , and the densities,  $d$ , at 25° of the benzene solutions containing the mole fraction,  $c_2$ , of solute are given in Table I; the polarizations,  $P_2$ , are listed in the last column. The polarization of the pure solvent is given as  $P_1$ , and the values of  $P_2$  are extrapolated to  $c_2 = 0$  in order to obtain  $P_\infty$ . From  $P_\infty$  the moments  $\mu$  are calculated by subtracting  $MR_D$ , the molar refraction for the D sodium line calculated from molar and atomic refractions given in Landolt-Börnstein. Any small error resulting from the use of these calculated molar refractions is negligible in comparison to the unusually large experimental errors in the moment values arising from the low solubilities and low dielectric constants of the solutes.

**The Preparation of 2,5-Di-*t*-butylhydroquinone.**—To a solution of hydroquinone (100 g.) in glacial acetic acid (1 liter) was added 200 cc. (160 g.) of *t*-butyl alcohol. The whole was cooled in an ice-bath and 200 cc. of oleum added slowly with good agitation and at a rate to maintain the temperature of the mixture below 20°. In about five to ten minutes after the last addition of the acid, crystallization began and was usually complete in about four hours. If no crystallization occurred at once, it usually could be brought about by keeping the reaction mixture overnight

in an ice box. The solid is collected on a fiber glass filter cloth, washed well with small quantities of cold acetic acid and dried *in vacuo* over sodium hydroxide. The yield is quantitative (98%). The substance melts without decomposition at 210–212° (uncor.)

**The Preparation of 2,5-Di-*t*-butylhydroquinone Dimethyl Ether.**—This substance could not be prepared conveniently by methylation of 2,5-di-*t*-butylhydroquinone with either dimethyl sulfate or diazomethane. It was therefore prepared by treating hydroquinone dimethyl ether with *t*-butyl alcohol in the presence of oleum.

A 70% yield of hydroquinone dimethyl ether was obtained by methylation of hydroquinone (110 g.) with dimethyl sulfate (200 cc.) in the presence of 80 g. (2 moles) of sodium hydroxide in 400 cc. of water.

To introduce the *t*-butyl groups into the dimethyl ether of hydroquinone much higher concentrations of sulfuric acid were necessary. After a few preliminary experiments the following procedure, which gave uniformly between 60 and 70% yields, was adopted.

To 30 g. of hydroquinone dimethyl ether dissolved in 100 cc. of glacial acetic acid, 50 cc. of *t*-butyl alcohol was added. The mixture was cooled and treated in small portions with 100 cc. of oleum. During this addition the reaction mixture was agitated and kept below 20°. The mixture turned very viscous and a solid separated. It was collected on a fiber glass filter cloth and washed well with small amounts of cold acetic acid, dried in a vacuum desiccator over sodium hydroxide, and finally crystallized from dilute alcohol. The material separated in long coarse

TABLE I  
DIELECTRIC CONSTANTS, DENSITIES, POLARIZATIONS AT 25°, AND DIPOLE MOMENTS

$c_2$	$\epsilon$	$d$	$P_2$
Benzene-Di- <i>t</i> -butylhydroquinone			
0.000000	2.2801	0.87200	(26.790 = $P_1$ )
.001345	2.2848	.87253	116
.002070	2.2848	.87276	98
$MR_D = 67, P_\infty = 125 \pm 15, \mu = 1.68 \pm 0.20 \times 10^{-18}$			
Benzene-Di- <i>t</i> -butylhydroquinone Dimethyl Ether			
0.001909	2.2858	0.87235	124
.004330	2.2901	.87286	113
.01044	2.3011	.87406	110
$MR_D = 76, P_\infty = 120 \pm 7, \mu = 1.47 \pm 0.13 \times 10^{-18}$			

(1) Lewis and Smyth, *J. Chem. Phys.*, **7**, 1085 (1939).

(2) Lewis and Smyth, *THIS JOURNAL*, **61**, 3063 (1939).