TABLE III

REACTION OF SODIUM PHENOXIDE WITH 2,4-DINITROCHLOROBENZENE IN 60% DIOXANE AT 25.20°

$[ArCl]_0$, mole/l.	NaOH used, mole/l.	Phenol used, mole/l.	Moles phenol / Mole NaOH	Rate Coefficient,[a] l. mole^{-1} sec.$^{-1}$ × 10^3
0.0149	0.0299	0.0299	1.00	11.75
.0151	.0302	.0302	1.00	11.58
.0151	.0302	.0608	2.01	11.95
.0151	.0151	.0670	4.44	12.38
.0151	.0151	.0712	4.71	12.07
.0151	.0151	.1212	8.02	11.12
.0152	.0152	.1206	7.96	11.18
.0154	.0154	.1207	7.81	11.12
.0151	.0151	.0151	1.00	11.58
.0152	.0152	.0304	2.00	12.23
.0151	.0151	.0469	3.11	11.92
.0152	.0152	.0765	5.04	11.67
.0152	.0152	.0605	3.97	12.72
.0152	.0152	.0718	4.74	12.40

[a] Runs are listed in the chronological order in which they were performed.

aqueous dioxane were prepared as previously described.[2] Aniline was redistilled and stored under nitrogen. 2,4-Dinitrodiphenylamine, m.p. 157–157.5° (lit.[8] 156–156.4°), was prepared from aniline and 2,4-dinitrochlorobenzene and was recrystallized twice from absolute ethanol. Commercial 2,4-dinitrophenylhydrazine was recrystallized.

Apparatus.—Thermostats were constant to ±0.02°, and thermometers were checked against National Bureau of Standards-certified thermometers. Pipets were calibrated. Photometric measurements were made with a Beckman model B spectrophotometer.

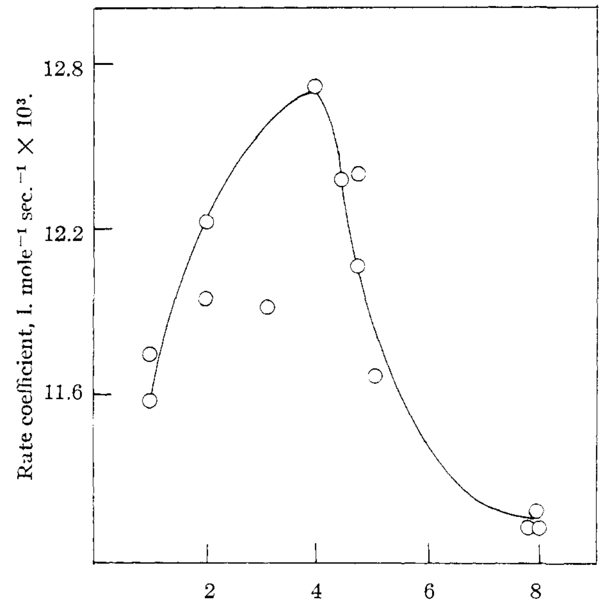

Fig. 1.—Rate of reaction of phenoxide ion with 2,4-dinitrochlorobenzene as affected by phenol concentration.

Rate Measurements.—All runs with phenoxide ion and two runs with aniline were followed by titration of chloride ion according to the procedure previously described.[2] Most of the aniline runs and all the hydrazine runs were followed by photometric measurements,[9] made at 400 or 410 mμ for aniline runs and at 450 mμ for hydrazine runs. Some difficulty was experienced with deterioration of hydrazine standard solutions. Eventually, a procedure was developed whereby a stock solution of hydrazine of approximately the desired concentration was prepared and aliquots were withdrawn as nearly simultaneously as possible (a) for combination with 2,4-dinitrochlorobenzene in 60% dioxane to start a kinetic run and (b) for addition to excess aqueous acid in preparation for titration against standard potassium iodate solution.[10] Rate coefficients and energies and entropies of activation were calculated by appropriate standard expressions.

CHAPEL HILL, N. C.

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[9] J. F. Bunnett and H. D. Crockford, *J. Chem. Education*, **33**, 552 (1956).

[8] T. L. Davis and A. A. Ashdown, THIS JOURNAL, **46**, 1052 (1924).

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[CONTRIBUTION FROM NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

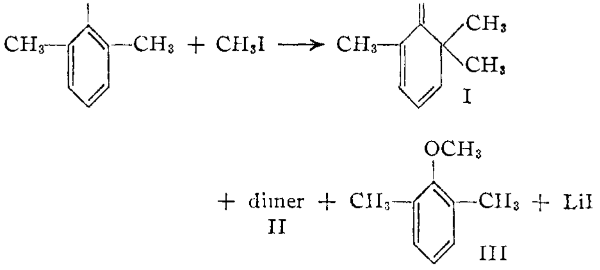
Structure of 2,6,6-Trimethyl-2,4-cyclohexadienone Dimer[1]

BY THEODORE L. BROWN, DAVID Y. CURTIN AND ROBERT R. FRASER

RECEIVED FEBRUARY 26, 1958

The lithium salt of 2,6-dimethylphenol has been found to react with methyl iodide (in the absence of any other solvent) to form, in addition to 38% of the expected methyl ether III, 22% of 2,6,6-trimethyl-2,4-cyclohexadienone (I). The dienone readily forms a dimer (II) which is now shown by an examination of the infrared and ultraviolet spectra and the dipole moment of 1.71 D. measured in cyclohexane to have the structure A. The dienone, after dimerization, readily can be separated by distillation of the ether III under reduced pressure. The dienone can then be recovered from the dimer (which may be purified by recrystallization) by distillation at higher temperatures. The method thus is a practical one for the synthesis of such dienones.

In the course of a study of the formation of cyclohexadienones by the direct *o*-alkylation of phenol salts with organic halides[2] it has been found that 2,6,6-trimethyl-2,4-cyclohexadienone (I) is readily prepared by the reaction of lithium 2,6-



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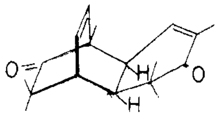
[1] Supported in part by the Office of Ordnance Research, U. S. Army.

[2] (a) D. Y. Curtin and R. J. Crawford, *Chemistry & Industry*, 313 (1956); (b) THIS JOURNAL, **79**, 3156 (1957); (c) D. Y. Curtin and R. R. Fraser, *Chemistry & Industry*, 1358 (1957); (d) D. Y. Curtin, R. Crawford and M. Wilhelm, THIS JOURNAL, **80**, 1391 (1958); (e) D. Y. Curtin and M. Wilhelm, *J. Org. Chem.*, **23**, 9 (1958).

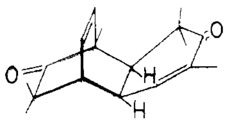
dimethyl-phenoxide with methyl iodide at 150°. The dienone I forms a solid dimer II on standing at room temperature. The yield of dienone I together with dienone present in the form of the dimer II amounted to 22%. It was accompanied by 38% of 2,6-dimethylanisole (III) (formed by O-methylation of the lithium salt). The ratio of oxygen to carbon attack is thus 1.7 and the ratio of attack of oxygen to attack of carbon at a single *o*-position, 3.4. The ether III was readily removed from the dimer by distillation under reduced pressure and, since the dimer can be reconverted to dienone by distillation at higher temperatures, a simple method of separating dienone from the ether III is available.

The structure of the dimer II is the principal subject of the present report. Absorption at 1723 and 1682 cm.$^{-1}$ in the infrared spectrum of a 10% solution of II in carbon tetrachloride leads to the conclusion that there is present one conjugated and one unconjugated carbonyl function and thus to the consideration of structures A-D. The generalization that such Diels-Alder additions lead to the *endo*-product favors structures A or B, but exceptions have been noted previously[3] to the rule of *endo*-addition and so this argument cannot be considered conclusive. Examination of molecular models suggests that methyl-oppositions would be present in structure B which would be absent in A and so might be considered to favor structure A. This argument, however, cannot be considered compelling. Several investigators[4-6] have prepared dienone dimers from dienones related to I but in no case has there been evidence which would justify a final structural assignment to the dimers studied.

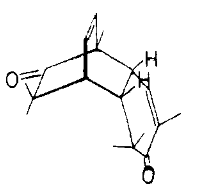
The dipole moment of the dimer II determined in cyclohexane makes possible a choice among the structures A-D. The measured moment was 1.71 D. This value is almost certainly too large, however, because in the structures under consideration the atom polarization must be appreciable. The moments calculated for structures A-D are recorded under their respective formulas. The calculations were made from "ball and stick" models and because of their crudeness liberal allowances have been made for angular distortion from what appeared to be the most likely conformation. It will be seen that even with such allowances only the range of values for structure A are in agreement with the measured dipole moment.



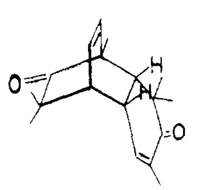
A 1.06-2.95 D.



B 2.95-3.91 D.



C 4.58-6.10 D.



D 4.98-6.65 D.

It appears likely that those factors responsible for the preferential formation of structure A in the dimerization of I operate similarly in the dimerization of the related dienones 6-allyl-2,6-dimethyl-2,4-cyclohexadienone,[2b] 6-propyl-2,6-dimethyl-2,4-cyclohexadienone[4] and 6-benzyl-2,6-dimethyl-2,4-cyclohexadienone[2b] and that the structures of their dimers are those to be derived from A by replacing one of each of the pairs of *gem*-dimethyl groups by the appropriate allyl, propyl or benzyl group. It will be noted that this leads to agreement with the structure suggested by Conroy and Firestone for the 6-propyl-2,6-dimethyl-2,4-cyclohexadienone dimer.

Experimental[7]

2,6,6-Trimethyl-2,4-cyclohexadienone Dimer (II).—The lithium salt (0.080 mole) of 2,6-dimethylphenol was prepared by heating under nitrogen 10 g. (0.084 mole) of 2,6-dimethylphenol with 0.56 g. (0.080 mole) of finely cut lithium metal in refluxing toluene for 18 hr. At the end of this time the toluene was removed by distillation and the residual white solid lithium salt was transferred to a heavy-walled Pyrex tube containing 100 g. (0.70 mole) of methyl iodide. The tube was sealed and heated for 24 hr. at 150°. Thereafter the tube was cooled, opened, its contents transferred to a flask and the methyl iodide distilled. The residue was taken up in 100 ml. of ether and extracted with a 50/50 mixture of water and Claisen alkali.[8] The aqueous extracts were re-extracted with ether and the combined ether extracts washed with water and dried over sodium sulfate for 16 hr. After removal of the solvent, distillation of the residue gave 7.35 g. of yellow liquid, b.p. 85-110° (15 mm.), which contained 4.1 g. (38%) of 2,6-dimethylanisole (estimated from the intensity of the absorption in the infrared at 1095 cm.$^{-1}$) and 0.62 g. (6%) of dimer II (estimated from the intensity of the infrared band at 1723 cm.$^{-1}$) and 1.73 g. (16%) of monomeric dienone I estimated from the absorption at 299 mμ in the ultraviolet. The dienone was not separated at this stage, but the crude mixture of dienone, dimer and methyl ether was allowed to stand for 24 hr. in order to allow the dienone to dimerize. The 2,6-dimethylanisole was then evaporated slowly at room temperature and 0.3 mm. pressure. After 36 hr. the white crystalline dimer II amounted to 1.75 g. (16% of theoretical). Recrystallization from hexane gave 1.35 g. of white crystals, m.p. 109.5–110.5°. Two further recrystallizations from water–methanol gave dimer II, m.p. 110–110.5° (λ_{max}^{EtOH} 240, ϵ 9000; infrared in 10% carbon tetrachloride showed bands at 1723 and 1682 cm.$^{-1}$).

Anal. Calcd. for $C_{18}H_{24}O_2$: C, 79.4; H, 8.9. Found: C, 79.3; H, 9.1.

2,6,6-Trimethyl-2,4-cyclohexadienone (I).—The dimer II (0.69 g., m.p. 110-110.5°) was decomposed by distillation under reduced pressure into a weighed flask immersed in a Dry Ice–acetone mixture. The b.p. of dienone was approximately 90° at 25 mm. pressure. Cyclohexane (10 ml.) was then pipetted into the flask and 0.30-ml. samples were withdrawn for ultraviolet and infrared analysis. Solutions were kept at −80° until they were used in order to prevent dimerization. The ultraviolet spectrum showed $\lambda_{max}^{cyclohexane}$ 299 mμ, ϵ 5250. The infrared showed maxima

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[3] *Cf.* R. B. Woodward and H. Baer, THIS JOURNAL, **66**, 645 (1944).

[4] H. Conroy and R. A. Firestone, *ibid.*, **78**, 2290 (1956).

[5] F. Kalberer and H. Schmid, *Helv. Chim. Acta*, **40**, 779 (1957).

[6] K. Alder, F. H. Flock and H. Lessenich, *Chem. Ber.*, **90**, 1709 (1957).

[7] Melting points are corrected. The microanalysis was carried out by Mrs. M. Stingl. The infrared spectrum was determined with a Perkin–Elmer model 21 spectrophotometer by Mr. Brian Cloonan. The ultraviolet spectrum was determined by Mr. M. Chao with a Cary model 14 M spectrophotometer.

[8] Potassium hydroxide, 350 g./l. of solution; water, 250 ml./l. of solution; in methanol.

at 1665 and 1645 cm.$^{-1}$. Removal of the cyclohexane under vacuum gave a partially dimerized residue.

Anal. Calcd. for $C_9H_{12}O$: C, 79.4; H, 8.9. Found: C, 79.4; H, 8.9.

Dipole Moment Determination. Apparatus.—The apparatus used in determining the electric moment consisted of a BC-221 Frequency meter adapted in the manner described by Thompson and Rogers.[9] The cell was constructed of three stainless steel cylinders held concentrically by Teflon spacers, the assembly being mounted in a glass envelope. The cell of aboutt 30-ml. capacity was filled and drained through a tube entering at the bottom. All such operations were carried out with the cell fixed in position in the constant temperature bath. The apparatus was calibrated by obtaining frequency readings as a function of dielectric constant of the medium in the cell; the purified liquids used for this purpose were benzene, cyclohexane and toluene. The cell was immersed in a constant temperature bath of 23.97 ± 0.02°. Density and refractive index determinations were also made at this temperature. In determining densities a 5-ml. pycnometer was used; the refractive indices were determined by use of a Bausch and Lomb precision refractometer fitted with a sodium lamp as source.

Materials.—Thiophene-free reagent-grade benzene was purified by recrystallization followed by distillation from phosphorus pentoxide in an efficient column packed with glass helices. The product of this distillation was stored over sodium wire; d_{24} 0.87435. Reagent grade toluene was purified by passing it through a 60 × 1.2 cm. column of alumina, 100 mesh, and carefully fractionating the middle portion. Storage was over sodium wire; d_{24} 0.86310. Cyclohexane was purified by passage through a 60 × 1.2 cm. column of 100 mesh alumina, followed by careful fractionation. The product, d_{24} 0.77410, was stored over sodium wire.

Procedure.—The cyclohexane solutions of II were made up by weight, and were of weight fractions 0.03829, 0.02060 and 0.00929. The dielectric constant, refractive index and density of each solution was determined, from which values of $\partial\epsilon/\partial w_2$, $\partial n^2/\partial w_2$, and $\partial\nu/\partial w_2$ of 1.048, 0.157 and −0.345 were calculated, where w_2 is mole fraction of solute, ϵ is dielectric constant, n is refractive index and ν is volume per g. The method of Halverstadt and Kumler[10] was employed in calculating the polarization per gram of solute, p_2, and the refractivity per gram, r_2. The values so obtained were 0.4915 and 0.2794, respectively, leading to values of 133.7 and 76.0 cm.^{3}, respectively, for the total molar polarization P_2 and the molar refractivity, R_2. The latter value is to be compared with the value 78.1 cm.^{3} determined from the sum of bond refractivities.[11] The difference between P_2 and R_2, 57.7 cm.^{3}, represents the sum of the orientation and atom polarizations.

If all of the net polarization, 57.7 cm.^{3}, is considered to be due to orientation polarization, a calculated moment of 1.71 D. results.

The carbonyl groups in II are pointing in nearly opposite directions, the angle between them being probably 160–170°. In *p*-benzoquinone the arrangement of oppositely directed carbonyl groups leads to an atom polarization[12] of 8–10 cm.^{3}. This presumably arises as a result of each carbonyl having one degree of bending freedom. If oppositely directed polar groups have additional degrees of freedom as a result of deformation modes peculiar to the atoms which separate them, the atom polarization is further increased. For example, 4,4′-dicyanobiphenyl has an atom polarization of 35 cm.^{3}, whereas for *p*-dicyanobenzene it is only 12 cm.^{3}.[13]

In the compound under consideration here there are a number of possibilities for low-frequency bending modes which would cause a change in the angle between the carbonyl groups, and thus contribute to atom polarization. If it is assumed that the atom polarization is 25 cm.^{3} a moment of 1.27 D. is calculated. This amount of atom polarization is not unlikely for the molecule under consideration. Thus, although a precise value of the moment cannot be calculated because of the uncertainty in the atom polarization, a reasonable estimate of the latter quantity leads to a value for the moment which is of the same magnitude as that estimated from models of one of the isomers. Any improved value must be smaller and therefore still consistent only with structure A.

Calculation of Theoretical Moments for Structures A-D.—The carbonyl–carbonyl angles assumed are angles shown under the structures presented in the text. They were estimated visually from "Student Molecular Models" of the O. H. Johns Glass Co., Toronto, Canada, a liberal allowance being made for distortion from what is believed to be the most stable conformation. The moments were calculated from the equation

$$u = [(2.9)^2 + (3.8)^2 + (2)(2.9)(3.8)\cos\theta]^{1/2}$$

the values of 3.8 and 2.9 D being those reported for 3,5-dimethyl-2-cyclohexenone and fenchone, respectively,[14] chosen as the closest models for which data are available.

URBANA, ILLINOIS

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[9] H. B. Thompson and M. T. Rogers, *J. Chem. Educ.*, **32**, 20 (1955).

[10] I. F. Halverstadt and W. D. Kumler, THIS JOURNAL, **64**, 2988 (1942).

[11] A. I. Vogel, W. T. Cresswell, G. H. Jeffrey and J. Leicester *J. Chem. Soc.*, 514 (1952).

[12] J. W. Smith, "Electric Dipole Moments," Butterworths, London, 1955, p. 271.

[13] Reference 12, p. 272.

[14] H. L. Donle and G. Volkert, *Z. physik. Chem.*, **B8**, 60 (1930).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF SOUTHERN CALIFORNIA]

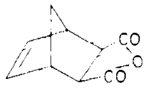
The Hydration of *exo-cis*-3,6-Endomethylene-Δ^4-tetrahydrophthalic Anhydride[1]

BY JEROME A. BERSON AND SHIGETO SUZUKI

RECEIVED JANUARY 19, 1957

The hydration reaction of the title gives *exo*-4-hydroxy-*exo-cis*-3,6-endomethylenehexahydrophthalic acid. The structure of the product is proved by alternate synthesis from *exo*-4,5-epoxy-*exo-cis*-3,6-endomethylenehexahydrophthalic anhydride.

In connection with another study, it was necessary for us to prepare *exo*-4-hydroxy-*exo-cis*-3,6-endomethylenehexahydrophthalic acid (II).



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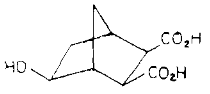
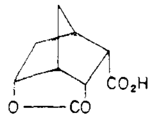


II



III

A substance (IIα) to which this structure had been assigned had been reported by Alder and co-work-

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