

change rate in basic solutions, proceeding solely *via* the attack of water on the neutral molecule, therefore is markedly slower. Further work on these and related compounds is in progress.

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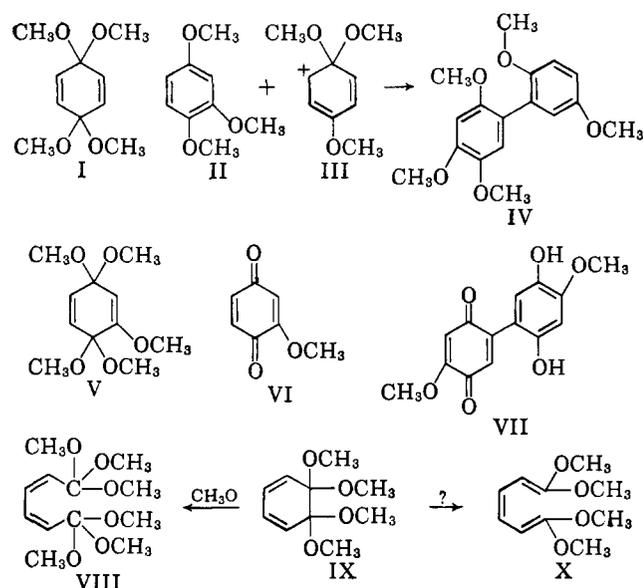
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F. A. LONG

RECEIVED JUNE 8, 1963

Electrochemical Syntheses. The Methoxylation of Dimethoxybenzenes to Quinone Ketals and the Ring Fission of 1,2-Dimethoxybenzene to Hexamethyl *cis,cis*-Orthomuconate¹

Sir:

With the exception of the Kolbe reaction² and various oxidation and reduction reactions which have found wide synthetic utility, very few explorations of the application of electrochemical methods to organic synthesis have been reported. The subject has been reviewed by Allen.³ Recently, Corey, *et al.*,⁴ have described an electrochemical method for the generation of carbonium ion from acids whereas Clauson-Kaas and



Elming⁵ developed a method for the electrochemical methoxylation of furans. It is the purpose of this communication to report on the electrochemical methoxylation of the isomeric dimethoxybenzenes to quinone ketals, a novel class of quinone derivatives which have thus far remained inaccessible by classical routes.⁶ In addition, we wish to report on a novel type of reaction which consists in the methoxylation accompanied by fission of veratrole to hexamethyl *cis,cis*-orthomuconate (VIII), an unusual substance of intriguing synthetic potentialities.

The electrolysis cell consisted of two platinum gauze anodes with a total surface area of 160 cm.² and a

nickel cathode with a surface area of 240 cm.² The two anodes were arranged concentrically about the cathode. The all-glass container was provided with a cold finger for internal cooling. Stirring was maintained magnetically during the course of all reactions. The source of direct current consisted in a conventional 6-2-v. battery charger connected to a variable transformer. The current was kept approximately constant by manually adjusting the transformer; in general, the applied current was in the range of 2 to 4 amp. All reactions were carried out at or below room temperature (−10 to 25°). The anodic current density was approximately 0.025 amp./cm.² In general, a two- or threefold excess of current equivalents was applied. A 1% methanolic potassium hydroxide solution was used as the solvent; the substrate concentrations were kept in the range of 10%. Under these conditions, electrolysis at 0° of 0.1 mole of hydroquinone dimethyl ether (2.0 amp., 3.6–3.8 v., 3 hr.) gave 3,3,6,6-tetramethoxy-1,4-cyclohexadiene (*p*-benzoquinone tetramethyl ketal) (I) in 75% yield,⁷ m.p. 42.5°. *Anal.* Calcd. for C₁₀H₁₆O: C, 59.98; H, 8.05. Found: C, 60.18, H, 7.89. The n.m.r. spectrum⁸ (CCl₄ as solvent) showed peaks at 6.75 and 4.02 τ ; the peak areas were in the ratio of 3:1 in agreement with the structure. An aqueous solution of the ketal deposits *p*-benzoquinone in quantitative yield when treated with a trace of mineral acid. Treatment of a 20% solution of I in dry benzene with one drop of boron trifluoride etherate (exothermic reaction) gives a mixture of 1,2,4-trimethoxybenzene (II) and a pentamethoxybiphenyl⁹ (IV), m.p. 112–113.5° [*Anal.* Calcd. for C₁₇H₂₄O₅: C, 67.09; H, 6.62; mol. wt., 304. Found: C, 66.34; H, 6.35; mol. wt., 347 (Rast)] in 36% and 19% yields, respectively. Similar treatment of a more dilute solution (10%) of I in benzene produces II and IV in 81 and 12% yields, respectively, thus suggesting the cation III as a common intermediate in these reactions. A simple route to certain polymethoxybiphenols therefore is provided.

Electrochemical methoxylation (at 0°, 4.5 amp., 7.5–7.9 v., 10 hr.) of resorcinol dimethyl ether (0.1 mole) also proceeded smoothly to give 2,3,3,6,6-pentamethoxy-1,4-cyclohexadiene (V) in 61% yield, b.p. 105–110° (3 mm.), *n*_D²⁷ 1.4750. *Anal.* Calcd. for C₁₁H₁₈O₅: C, 57.58; H, 7.88. Found: C, 56.84; H, 7.89. The n.m.r. spectrum (in CCl₄) showed peaks at 6.80 and 6.38 τ and a group of 8 peaks (identified as an ABX system) extending from 5.12 to 3.93 τ ; the relative areas of the two characteristic regions were in the ratio of 4:1 in agreement with the structure. In dilute aqueous acid, it was converted in high yield to the intensely blue biphenyl quinhydrone (VII) by way of methoxy-*p*-benzoquinone (VI) which has been shown^{10,11} to couple to VII under acid conditions. Direct comparison (mixture m.p., infrared spectra) with an authentic specimen of VII prepared by the published procedure^{10,11} served to establish the identity of the acid hydrolysis product of the ketal V. The structure of the latter was confirmed by an alternative electrochemical synthesis (at 10°, 4.0 amp., 6–6.6 v., 2.5 hr.) from 1,2,4-trimethoxybenzene (0.05 mole) (II) which afforded in 89% yield a ketal (V) identical in every respect with the one derived from resorcinol dimethyl ether.

(7) The current efficiency was calculated to be 66%. An 88% yield resulted when a fivefold increase in current was applied.

(8) Determined at 60 Mc./sec. with a Varian-V-4302 spectrometer.

(9) Structure IV is inferred. When the ketal is similarly treated but in 1,2,4-trimethoxybenzene as the solvent, the diphenyl (IV) is the major product as would be expected.

(10) H. G. H. Erdtman, *Proc. Roy. Soc. (London)*, **A143**, 191 (1934).

(11) I. S. Ioffe and A. F. Sukhina, *J. Gen. Chem. U.S.S.R.*, **23**, 1370 (1953); *Chem. Abstr.*, **48**, 632i.

(1) This investigation was supported by a grant from the National Cancer Institute of Canada.

(2) B. C. L. Weedon, *Advan. Org. Chem.*, **1**, 1 (1960).

(3) M. J. Allen, "Organic Electrode Processes," Reinhold Publishing Corp., New York, N. Y., 1958.

(4) E. J. Corey, N. L. Bauld, R. T. Lalonde, J. Casanova, and E. T. Kaiser, *J. Am. Chem. Soc.*, **82**, 2645 (1960).

(5) N. Elming, *Advan. Org. Chem.*, **2**, 67 (1960).

(6) An anthraquinone ketal has been suggested as an intermediate in the free radical reaction of anthrahydroquinone dimethyl ether with tetrachloro-*p*-cresol: R. Pummerer, G. Schmidutz, and H. Leifert, *Chem. Ber.*, **85**, 541 (1952).

When 1,2-dimethoxybenzene (veratrole) (0.5 mole) in turn electrochemically methoxylated (4.0 amp., 7.3–8.6 v., 22 hr.) a mixture of four products resulted. Fractional distillation afforded the already known ketal V (15% yield) as established by direct comparison with a sample secured as described above. The second component consisted of 1,2,4-trimethoxybenzene and appeared to result from the decomposition of a labile precursor during the process of distillation. A third component (15% yield; homogeneous by v.p.c. analysis), b.p. 108–111° (25 mm.), n_D^{27} 1.4766, was shown to consist of 5,5,6,6-tetramethoxy-1,3-cyclohexadiene (*o*-benzoquinone tetramethyl ketal) (IX). *Anal.* Calcd. for $C_{10}H_{16}O_4$: C, 59.95; H, 8.05. Found: C, 59.77; H, 7.85. The n.m.r. spectrum (in CCl_4) showed peaks at 6.72 and 4.27 τ (unresolved multiplet), the areas under which were in the ratio of 3:1 in agreement with the structure. The diene chromophore of IX was revealed as a peak in the ultraviolet at 265 $m\mu$ (ϵ 2500).¹² Acid hydrolysis in the presence of zinc produced catechol (25% yield) as ascertained by v.p.c. analysis.

Of special interest was the fourth component (10% yield), a crystalline substance m.p. 100°, the structure of which was established as hexamethyl *cis,cis*-orthoquinone (VIII). *Anal.* Calcd. for $C_{12}H_{22}O_6$: C, 54.95; H, 8.45. Found: C, 55.59; H, 8.43. The n.m.r. spectrum showed a single peak at 6.92 τ and two symmetrical octets (A_2B_2 system) between 4.8 and 3.0 τ . The area ratio of the two characteristic regions was 4.5:1 in agreement with the structure. It exhibited a peak in the ultraviolet at 234 $m\mu$ (ϵ 10,200) as expected and was quantitatively converted in cold dilute mineral acid to dimethyl *cis,cis*-muconate, m.p. 74°, which proved identical in every respect with an authentic specimen. That the ketal IX is a precursor of the bis-ortho ester VIII was confirmed by electrochemical methoxylation (4.0 amp.; 6 v.; 6 hr.) of IX (0.026 mole), which was transformed into VIII in 77% yield.

The formation of the bis-ortho ester VIII deserves special comment because the mechanisms involved appear to be unique. The presence of four vicinal oxygen atoms in the intermediate ketal IX ought to be energetically unfavorable¹² and thus may facilitate fission to the triene X which would then accept two methoxyl radicals from the electrode to give the final product VIII. The fact that the *cis,cis* isomer is actually formed rules out the participation of long-lived free radicals as intermediates since delocalization of the unpaired electrons would allow isomerization to the thermodynamically more stable *trans,trans* isomers of VIII. It is clear that IX must undergo fission on the electrode surface so that the process leading to VIII may involve species that are stabilized by adsorption on it. The mechanisms and scope of these novel electrochemical syntheses are under investigation.

Acknowledgments.—The authors are grateful to Miss E. Busk and Dr. L. Hall for the determination of the n.m.r. spectra and to Dr. R. R. Fraser, Bristol Laboratories, for valuable comments.

(12) Unexpectedly, a second peak at 235 $m\mu$ (ϵ 2500) was also observed. Another similar structure to be described in our full paper also shows this anomalous band. It seems probable that the appearance of this peak marks a $\pi \rightarrow \pi^*$ transition of lower energy than normal for a single double bond; oxygen-oxygen interactions in IX can be more effectively relieved if one C-C bond is free to twist. This effect should tend to stabilize the $\pi \rightarrow \pi^*$ transition.

(13) Predoctoral fellow of the National Cancer Institute of Canada.

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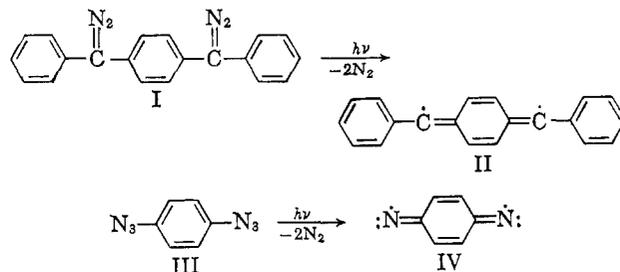
RECEIVED JUNE 7, 1963

The E.p.r. of Dicarbene and Dinitrene Derivatives

Sir:

Recently we reported the electron paramagnetic resonance (e.p.r.) of several methylenes^{1,2} and nitrenes³ which demonstrated the triplet ground state of these species. Each of the previously reported ground-state triplet molecules^{1–4} contained only one electron-deficient atom. We now report the e.p.r. of *p*-phenylenebis-(phenylmethylene) (II) and *p*-phenylenedinitrene (IV), ground-state triplet species containing two electron-deficient atoms. This constitutes the first physical evidence for species of this type.

The intermediates II and IV were formed by the photolytic expulsion of two molecules of nitrogen from 1,4-bis-(α -diazobenzyl)-benzene (I)⁵ and 1,4-diazidobenzene (III), respectively.⁶



Preliminary e.p.r. experiments⁵ as well as chemical evidence had indicated that a radical species was produced in the thermal decomposition of I, but these data gave no information regarding the existence of II. In addition, evidence for the simultaneous or near-simultaneous loss of both molecules of nitrogen in the photolytic decomposition of crystals of I had been obtained from microscopic studies.⁷ The e.p.r. experiments were undertaken to provide further evidence as to the existence of II.

A modification of the experimental technique previously described¹ was employed. A finely ground 5% solid solution of I in 1,4-dibenzoylbenzene was irradiated at 77°K.^{8,9} in the quartz dewar insert of a Varian V-4500 e.p.r. spectrometer with 100-kc. field modulation. The r.f. energy employed was 0.3030 cm^{-1} ($\nu = 9080$ Mc.

(1) R. W. Murray, A. M. Trozzolo, E. Wasserman, and W. A. Yager, *J. Am. Chem. Soc.*, **84**, 3213 (1962).

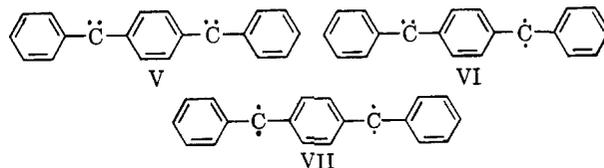
(2) A. M. Trozzolo, R. W. Murray, and E. Wasserman, *ibid.*, **84**, 4990 (1962).

(3) G. Smolinsky, E. Wasserman, and W. A. Yager, *ibid.*, **84**, 3220 (1962).

(4) R. W. Brandon, G. L. Closs, and C. A. Hutchison, Jr., *J. Chem. Phys.*, **37**, 1878 (1962).

(5) R. W. Murray and A. M. Trozzolo, *J. Org. Chem.*, **26**, 3109 (1961).

(6) A number of other possible electronic states can be envisaged for II: (a) a singlet electronic state containing no unpaired electrons (V); (b) a triplet configuration in which only one of the electron-deficient atoms has



its two unshared electrons unpaired and in separate orbitals (VI); and (c) a quintet state containing four unpaired electrons (VII). Analogous alternatives are possible for IV. However, the e.p.r. data are most satisfactorily explained by II and IV, triplet states containing a quinoid structure.⁵ Also, geometrical isomers are possible for II, but these would not be expected to differ greatly in the e.p.r. absorption spectrum.

(7) R. W. Murray and A. M. Trozzolo, "Proceedings, 1961 International Symposium on Microchemical Techniques," N. D. Cheronis, Ed., Interscience, New York, N. Y., 1962, pp. 233–242.

(8) A Hanovia 140-w. mercury arc with Pyrex filter was used. Irradiation times were 5–10 min.

(9) A detailed description of the advantages of the *random crystal* method will be published shortly. In experiments where a glass matrix was used, additional e.p.r. absorptions were detected which probably were due to a species in which only one molecule of nitrogen had been lost from I.