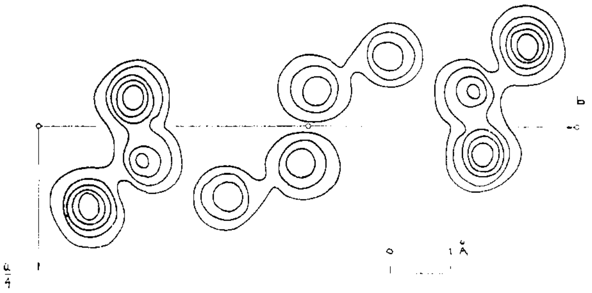
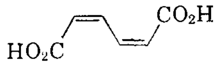


Fig. 1.—Electron-density projection $\rho(x,y)$; contours at intervals of $2\,e/\text{Å}.^2$, starting at $2e/\text{Å}.^2$.

The centric symmetry of the *cis*-isomer is surprising in view of its preparation from benzene derivatives (peracetic acid oxidation of phenol[2] and enzymatic oxidation of catechol[3]). To confirm the crystallographically required conformation (I) we have carried out a partial structure analysis based on the (*hk*0) data collected photographically. A trial structure was derived for the molecule lying along the shorter of the two long axes, with hydrogen bonded –CO$_2$H contacts across the centers at (0,0) and (0,1) and with the center of the >CH–CH< bond at (0,$^1/_2$). This model was smoothly refined, by means of an anisotropic least-squares program, to $R = 0.112$ ($F_0 = 0$ excluded). The electron-density projection $\rho(x,y)$ based on 90 out of 98 observed reflections is shown in Fig. 1.



I

Three-dimensional structure analyses of the two isomers are being undertaken.

Acknowledgment.—We thank Dr. T. Sadeh for the preparation of *cis,cis*-muconic acid.

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[2] J. A. Elvidge, R. P. Linstead, B. A. Orkin, P. Sims, H. Baer and D. B. Pattison, *J. Chem. Soc.*, 2232 (1950).

[3] O. Hayaishi, M. Katagiri and S. Rothberg, *J. Biol. Chem.*, **229**, 905 (1957).

DEPARTMENT OF X-RAY CRYSTALLOGRAPHY
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RECEIVED AUGUST 16, 1962

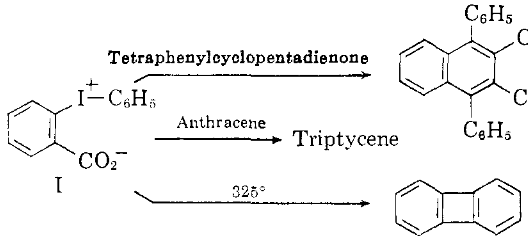
APROTIC GENERATION OF BENZYNE FROM DIPHENYLIODONIUM-2-CARBOXYLATE[1]

Sir:

While it has been demonstrated that benzyne[2] can be generated under aprotic conditions by fragmentation of appropriate *ortho*-disubstituted benzenes,[3] most of the reported methods are of limited synthetic utility.

It has been found that diphenyliodonium-2-carboxylate, I, a readily prepared and stable inner salt, undergoes smooth thermal cleavage of carbon dioxide and iodobenzene under aprotic conditions to afford products which are consistent with the intermediacy of benzyne. Refluxing a mixture of I and tetraphenylcyclopentadienone in diglyme (*ca.* 160°) for two hours afforded a 68% yield of 1,2,3,4-tetraphenylnaphthalene.

Under the same condition I and anthracene gave triptycene (23%).



Flash pyrolysis of solid I at 325° affords, among other products, biphenylene (gas chromatographic retention time and ultraviolet spectrum identical with that of an authentic sample) and iodobenzene.

Diphenyliodonium-2-carboxylate, I, is prepared readily in high yields.[4] To a concentrated sulfuric acid (170 ml.) solution of *o*-iodobenzoic acid (20 g.) at 0° was added potassium persulfate (42 g.). After one-half hour 75 ml. of benzene was added and the mixture stirred at 25–35° for 18 hours. This mixture was poured over ice, made alkaline with strong aqueous sodium hydroxide keeping the temperature below 40°, and finally extracted with chloroform. Evaporation of most of the chloroform gave a crystalline slurry to which ether was added. There was collected 21.7 g. (84%) of white crystalline I, m.p. 220.5–221° (dec.); reported[5] m.p. 229–230°. It exhibited a broad peak at 6.15 μ (chloroform) consistent with the inner salt formulation.

The author wishes to express his appreciation to Dr. J. Gordon for his valuable suggestions, to R. B. LaCount and C. J. Lindemann for their skillful assistance, and to Dr. H. Günther for the authentic biphenylene.

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[1] *Chemical Abstracts* nomenclature: (*o*-carboxyphenyl)-phenyliodonium hydroxide, inner salt.

[2] A number of recent reviews on benzyne are available: (a) H. Heaney, *Chem. Rev.*, **62**, 81 (1962); (b) J. F. Bunnett, *J. Chem. Ed.*, **38**, 278 (1961); (c) R. Huisgen in "Organometallic Chemistry," edited by H. Zeiss, Reinhold Publishing Corp., New York, N. Y., 1960, pp. 36–87.

[3] (a) L. Horner and H. Bruggemann, *Ann.*, **635**, 22 (1960); (b) M. Stiles and R. G. Miller, *J. Am. Chem. Soc.*, **82**, 3802 (1960); (c) R. S. Berry, G. N. Spokes and R. M. Stiles, *ibid.*, **82**, 5240 (1962); (d) G. Wittig and H. F. Ebel, *Angew. Chem.*, **72**, 564 (1960); (e) G. Wittig and H. F. Ebel, *Ann.*, **650**, 20 (1961); (f) G. Wittig and R. W. Hoffmann, *Angew. Chem.*, **73**, 435 (1961).

[4] This procedure is a modification of a previously described preparation in which the yields of I were unstated.[5]

[5] F. M. Beringer and I. Lillien, *J. Am. Chem. Soc.*, **82**, 725 (1960).

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RECEIVED AUGUST 1, 1962

CYCLOBUTANE-1,3-DIONE

Sir:

Despite considerable interest[1,2,3,4], in the properties of four-membered cyclic β-diketones, the parent compound in this series, cyclobutane-1,3-dione,[5,6] has hitherto proved inaccessible. We now

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[1] R. B. Woodward and G. Small, Jr., *J. Am. Chem. Soc.*, **72**, 1297 (1950).

[2] E. A. LaLancette and R. E. Benson, *ibid.*, **83**, 4867 (1961).

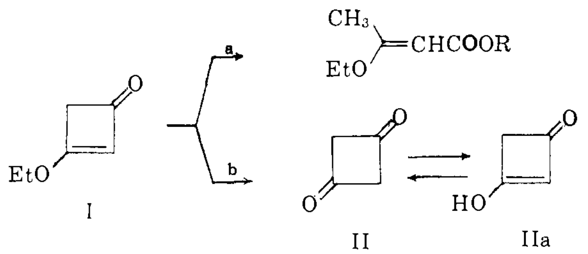
[3] E. F. Silversmith and J. D. Roberts, *ibid.*, **80**, 4083 (1960).

[4] E. J. Smutny, M. C. Caserio and J. D. Roberts, *ibid.*, **82**, 1793 (1960).

[5] In the earlier literature the cyclobutane-1,3-dione structure was assigned to ketene dimer. For a review of this subject, see R. N. Lacey, "Ketene in Organic Synthesis," "Advances in Organic Chemis-

wish to report a simple two-step synthesis of this reactive molecule from readily available intermediates.

As described in an earlier communication,[7] I, the enol ethyl ether of cyclobutane-1,3-dione can be prepared from the reaction of ethoxyacetylene with ketene and separation of the product from the crude reaction mixture. Although the reaction of I with water, dilute acids or alcohol leads mainly to ring opening with the formation of β-ethoxycrotonic acid derivatives (path a), treatment with cold concentrated sulfuric acid readily brings about the desired hydrolysis to the β-diketone (path b). Thus, when I is dissolved in 90% H_2SO_4, refrigerated overnight, and then poured on ice, cleavage of the enol ether takes place with formation of II (30% yield).



Cyclobutane-1,3-dione is readily soluble in water but can be extracted from aqueous solution with methylene chloride. The product is an almost white solid which crystallizes from ether in thin plates m.p. 119–120° (vigorous decomposition to a red liquid). *Anal.* Calcd. for $C_4H_4O_2$: C, 57.14; H, 4.80; neut. equiv., 84. Found: C, 57.01; H, 5.10; neut. equiv., 92. With diazoethane, II is reconverted to the enol ether, I.

The infrared spectrum of II in $CHCl_3$ shows a strong band at 1755 cm.$^{-1}$ and a weak band at 1570 cm.$^{-1}$. The latter peak appears as the most intense peak in the spectrum of I, and can be correlated with the double bond.[7,8] The diminished intensity of this particular band in the spectrum of II suggests a relatively small contribution of the enol form IIa in chloroform.[9] The n.m.r. spectrum in $DCCl_3$, showing a single sharp peak at 6.14 τ, is consistent with the presence of II in that solvent, but the possibility of a very rapid equilibration between keto and enol forms is not excluded.

In polar media, substantial amounts of IIa appear to be present. Thus, the n.m.r. spectrum in dimethylsulfoxide shows a more complex series of peaks, and the ultraviolet spectrum in absolute alcohol shows a maximum at 237 mμ (ϵ, 11,800). Enol ethers of β-diketones in this series exhibit similar absorption.[7,10] The enol character of II is further shown by the instantaneous decolorization of bromine in $CHCl_3$, by vigorous reaction with diazomethane in ether, and coloration with ferric chloride in water. As has been observed with other cyclobutanediones in this series,[1,4,7,11] II behaves like a strong acid ($\mathrm{p}K\mathrm{a} \simeq 3$) and can be recovered substantially unchanged after titration, by acidification and extraction with methylene chloride.

Further aspects of the chemical and physical properties of this substance are under study.

This work was supported in part by U.S. Public Health Service Grant RG-7874 (Cl).

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try," Vol. II, Interscience Publishers, Inc., N. Y., 1960, p. 240.

(6) Although reference has been made to the formation of this product under other reaction conditions (J. D. Roberts and C. M. Sharts, "Cyclobutane Derivatives from Thermal Cycloaddition Reactions," "Organic Reactions," Vol. 12, John Wiley and Sons, Inc., New York, N. Y., 1962, p. 8), it has not actually been isolated or characterized (private communication from Prof. J. D. Roberts).

(7) H. H. Wasserman and E. V. Dehmlow, *Tetrahedron Letters*, in press (1962).

(8) J. Druey, E. F. Jenny, K. Schenker and R. B. Woodward, *Helv. Chim. Acta*, **45**, 600 (1962).

(9) In KBr, the double bond peak is virtually absent.

(10) B. Rosebeck and J. F. Arens, *Rec. Trav. Chim. Pays-Bas*, **81**, 549 (1962).

(11) S. Cohen, J. R. Lacher and J. D. Park, *J. Am. Chem. Soc.*, **81**, 3480 (1959).

CONTRIBUTION NO. 1714 FROM
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RECEIVED AUGUST 27, 1962

THE PHOTOLYSIS OF 1,2-DIIODOBENZENE: A PHOTOCHEMICAL SOURCE OF BENZYNE

Sir:

Wolf and Kharasch recently have reported[1] that photolytic cleavage of the carbon–iodine bond of aryl iodides can serve as a synthetically useful source of aryl radicals. In a typical experiment, irradiation of a dilute solution of 2-iodophenol in benzene at room temperature gave 2-hydroxybiphenyl in 60% yield. We were prompted to examine the behavior of 1,2-diiodobenzene (I) under similar conditions because of the possibility that light-induced loss of both iodine atoms might give benzyne. Evidence for the formation of benzyne in the thermal and photolytic decompositions of 2-iodophenylmercuric iodide,[2] phthaloyl peroxide,[2,3] benzenediazonium-2-carboxylate[4,5] and benzothiadiazole-1,1-dioxide[6] has been reported previously.

We have studied the photolysis of 1,2-diiodobenzene in dilute solution (*ca.* 10^{-2} *M*) in cyclohexane, furan, benzene and benzene containing tetraphenylcyclopentadienone[7] (tetracyclone). Experiments were conducted near room temperature in cylindrical quartz cells utilizing the light from an external Hanovia[8] SC 2537 low pressure mercury vapor lamp. Free iodine was formed readily in all photolyses involving aryl iodides and hindered further reaction, presumably by returning reactive intermediates to starting material. It was therefore necessary, in some experiments, to maintain the free iodine concentration at a low level by periodic extraction of the reaction mixture with aqueous bisulfite.

Qualitative gas chromatographic, infrared and ultraviolet analyses of the products of the photolysis of I in cyclohexane demonstrated that iodobenzene was a major product of the reaction. Photolysis in benzene for 43 hours gave 2-iodobiphenyl as the major product, isolated and char-

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[1] W. Wolf and N. Kharasch, *J. Org. Chem.*, **26**, 283 (1961).

[2] G. Wittig and H. F. Ebel, *Ann.*, **650**, 20 (1961).

[3] L. Horner and H. Brüggemann, *ibid.*, **635**, 22 (1960).

[4] M. Stiles and R. G. Miller, *J. Am. Chem. Soc.*, **82**, 3802 (1960).

[5] R. S. Berry, G. N. Spokes and R. M. Stiles, *ibid.*, **82**, 5240 (1960).

[6] G. Wittig and R. W. Hoffmann, *Angew. Chem.*, **73**, 435 (1961).

[7] G. Wittig and E. Knauss, *Ber.*, **91**, 895 (1958).

[8] Hanovia Chemical and Manufacturing Co., Newark, N. J.