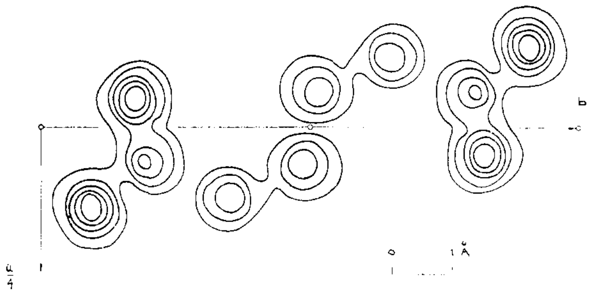

Fig. 1.—Electron-density projection $\rho(x,y)$; contours at intervals of 2 e/Å.^{2}, starting at 2e/Å.^{2}.

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 ($hk0$) data collected photographically. A trial structure was derived for the molecule lying along the shorter of the two long axes, with hydrogen bonded $-CO_2H$ 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.

[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).

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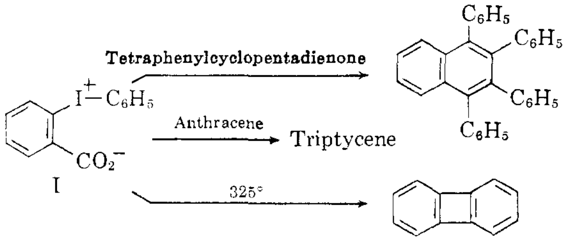
APROTIC GENERATION OF BENZYNE FROM DIPHENYLIODONIUM-2-CARBOXYLATE[1]

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.

[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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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

[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-