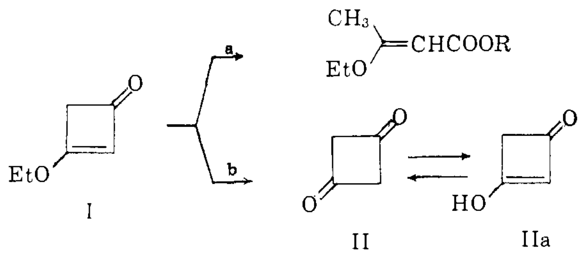
wish to report a simple two-step synthesis of this reactive molecule from readily available intermediates.

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 (p$Ka \simeq 3$) 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.

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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).

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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).

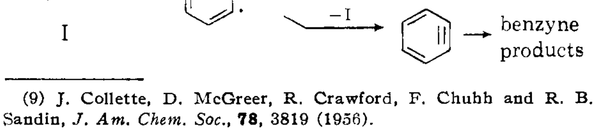
(7) G. Wittig and E. Knauss, *Ber.*, **91**, 895 (1958).

(8) Hanovia Chemical and Manufacturing Co., Newark, N. J.

acterized in 42% yield as biphenyleneiodonium sulfate, identified by a comparison of m.p. and infrared spectrum with those of an authentic sample.[9] A similar photolysis in benzene for 175 hours gave a small amount of biphenyl, identified by m.p. and ultraviolet spectrum; 2-iodobiphenyl as the major product, identified by infrared and ultraviolet spectra; and 4% triphenylene[10] (two aromatic rings assumed to come from solvent), identified by m.p., infrared and ultraviolet spectra and m.p. of trinitrobenzene derivative. Triphenylene could not be detected by careful adsorption chromatography and ultraviolet analysis of the reaction mixture from the 43 hour photolysis. In a control experiment the photolysis of 2-iodobiphenyl in benzene for 60 hours gave 7% triphenylene (one aromatic ring from solvent) and 67% recovered 2-iodobiphenyl. These data clearly imply that triphenylene is formed by further reaction of 2-iodobiphenyl rather than directly from I.

The photolysis of I for 41 hours in benzene containing an equimolar amount of tetracyclone gave 2-iodobiphenyl as the major product and approximately a 10% yield of the expected Diels–Alder adduct of benzyne and tetracyclone, 1,2,3,4-tetraphenylnaphthalene,[7] identified by a comparison of m.p. and infrared and ultraviolet spectra with those of an authentic sample, which must arise from I since the photolysis of tetracyclone in benzene gave no tetraphenylnaphthalene. Photolysis of I for 65 hours in distilled furan gave a complex mixture from which well-defined products could not be isolated. It was possible to demonstrate the presence of small amounts of the anticipated adduct, 1,4-dihydronaphthalene-1,4-endoxide,[11] by converting it to α-naphthol.[11] The latter was identified by a comparison of its ultraviolet spectrum and the ultraviolet and visible spectra of the azo dye resulting from coupling with diazotized sulfanilic acid with those derived from authentic α-naphthol. A control experiment showed that α-naphthol was not formed from the photolysis of furan in the absence of I. In all of these experiments biphenylene was carefully sought by adsorption chromatography and spectrophotometric analysis. The characteristic ultraviolet absorption[12] of biphenylene was never observed.

The observed products clearly suggest the formation of both the 2-iodophenyl radical and benzyne[13] in the course of the reaction. It seems possible that the 2-iodophenyl radical is an intermediate common to both the "radical path" and the "benzyne path." Thus, it can either react directly with solvent or lose an iodine atom and give benzyne. In the absence of tetracyclone or furan, free iodine presumably functions as an efficient benzyne scavenger and leads to the regeneration of starting material. Another possible interpretation of the observed results is that the 2-iodophenyl radical is not an intermediate in the formation of benzyne, but that both the radical and benzyne arise directly from I. The two modes of photolytic decomposition in question would presumably proceed from different excited states. The present data do not permit a clear decision concerning the relative merits of these two schemes. Further experiments are in progress.[14]



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[9] J. Collette, D. McGreer, R. Crawford, F. Chubb and R. B. Sandin, *J. Am. Chem. Soc.*, **78**, 3819 (1956).

[10] C. M. Buess and D. D. Lawson, *Chem. Revs.*, **60**, 313 (1960).

[11] G. Wittig and L. Pohmer, *Ber.*, **89**, 1334 (1956).

[12] W. Baker, M. P. V. Boarland and J. F. W. McOmie, *J. Chem. Soc.*, 1476 (1954).

[13] It is conceivable, but not particularly likely for steric reasons,[2] that the observed Diels–Alder adducts are the result of a two-step radical addition mechanism.

[14] We have been informed by N. Kharasch and W. Wolf that they have independently investigated the photolysis of 1,2-diiodobenzene. Their results, which they have kindly made available to us, will be published shortly.

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AN INTERPRETATION OF THE FORMATION OF *trans*-CYCLOALKENES IN THE PARTIAL HYDROGENATION OF CERTAIN CYCLIC DIENES

Sir:

We wish to report certain observations made in the course of studies of the chemistry of cyclic allenes and acetylenes which are relevant to the mechanism(s) of catalytic hydrogenation.

When conventional preparative procedures are employed, partial hydrogenation of 1,2-cyclononadiene (I)[1] and 1,2-cyclodecadiene (II)[1] under one atmosphere of hydrogen in methanol at *ca.* 25° over 10% palladium on charcoal poisoned with pyridine gives exclusively *cis*-cyclononene from I[1,2] and predominantly *cis*-cyclodecene accompanied by some *trans*-cyclodecene from II.[1] However, under the conditions of hydrogenation, we find that the *trans* olefins are isomerized to the thermodynamically more stable *cis* isomers.[3] When aliquots removed during the rapid hydrogenation of I (*ca.* 0.98 equiv. in 4 min.) were analyzed by gas chromatography,[3] a substantial quantity of *trans*-cyclononene was detected. Extrapolation to the beginning of the hydrogenation established that a minimum of 17% of the olefin produced initially was the *trans* isomer. Similarly, we find that at least 32% of *trans*-cyclodecene is produced initially during the hydrogenation of II.[4]

The adsorption of an allene must occur such that the plane of the adsorbed double bond (only one can be involved) is essentially parallel to the surface of the catalyst. Thus, as shown in III, there are four ways an allene can be adsorbed. If adsorption is followed by the *cis* addition of two hydrogen atoms from the surface of the catalyst, two modes of adsorption, *a* and *b*, would give a *cis* olefin and two, *c* and *d*, would give a *trans* olefin. Many

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[1] Some aspects of the chemistry of I and II are discussed in a paper by W. R. Moore and R. C. Bertelson, *J. Org. Chem.*, in press.

[2] P. D. Gardner and M. Narayana, *ibid.*, **26**, 3518 (1961).

[3] In acetic acid at 25°, *cis/trans* ratios at equilibrium are C_9 *ca.* 650 and C_{10} *ca.* 41; A. C. Cope, P. T. Moore and W. R. Moore, *J. Am. Chem. Soc.*, **82**, 1744 (1960).

[4] A small amount (*ca.* 5%) of II also isomerized to VI which was reduced more slowly than II.