

ception to the general mode of addition of reagents of the type HX to quinones.

Although not emphasized in the original literature,^{2,4} the addition of hydrogen cyanide to benzoquinone is very sensitive to the temperature. It is essential to operate between 20 and 30° to secure any 2,3-dicyanohydroquinone. Neither we nor Graves and Adams⁵ have been able to obtain any product by Helferich's procedure.

(4) German Patent 117,005 [*Frdl.*, VI, 113 (1900-1902)]; Helferich, *Ber.*, **54**, 155 (1921).

(5) Graves and Adams, *THIS JOURNAL*, **45**, 2447 (1923).

CONTRIBUTION NO. 804

KODAK RESEARCH LABORATORIES

ROCHESTER, NEW YORK

RECEIVED APRIL 14, 1941

The Activation of Aromatic Halogen

BY RICHARD BALTZLY AND JOHANNES S. BUCK

Some attempts to produce alkyl-*p*-bromoarylamines by direct alkylation of *p*-bromoarylamines failed and the trouble was traced to the action of the hydrobromic or hydriodic acid produced in the reaction, on the *p*-bromoarylamine.

Subsequent work showed that the bromine was unexpectedly mobile. Thus, *p*-bromoaniline, refluxed with hydriodic acid (57%), with red phosphorus to suppress the iodine produced, gave a 92% yield of aniline.

The action of hydrobromic acid was less complete. *p*-Bromoaniline heated with hydrobromic acid (48%), preferably at 150° under pressure, gave considerable amounts of aniline and 2,4-dibromoaniline, the over-all effect being that of a disproportionation.

The writers are not pursuing this line of research, since effectively the same subject is being studied in other laboratories.

BURROUGHS WELLCOME & Co. U. S. A.

EXPERIMENTAL RESEARCH LABORATORIES

TUCKAHOE, N. Y.

RECEIVED MAY 2, 1941

Note on the Theory of Displacements of Mixtures Giving Maximum Flame Velocities*

BY A. R. T. DENUES

It was indicated recently¹ that in the slow propagation of flame for both types of ordinary combustible gases apparently continuous relations exhibiting maxima exist between the displacements toward excess combustible of mixtures giving

* Work done in the Department of Chemical Engineering of the University of Maryland. Original manuscript received August 16, 1940.

(1) Denues with Huff, *THIS JOURNAL*, **62**, 3045 (1940).

ing maximum flame velocity and the content of oxygen in the atmosphere used for premixing. The following development accounts for these effects and seems an interesting illustration of the present utility of the inadequate thermal theory.²

The displacement was early ascribed to dissociation³ and to opposing effects of temperature and thermal conductivity,⁴ but it has been treated more successfully by the elaborated thermal theory.^{5,6} The present development is based on the generalized Nusselt equation as derived by Jahn.⁶ This equation gives the flame velocity as a product of factors representing reaction velocity and thermal effects; its use introduces all lacks of the thermal theory.

According to this theory, the displacement results from competition between these factors representing reaction velocity and thermal effects, and specifically between a reaction velocity factor demanding maximum flame velocity with a great excess of combustible, except for combustion with pure oxygen, and the thermal effects demanding maximum flame velocity near equivalence. This view may be extended to include the weights of the two factors, comprising constituents representing magnitude and position.

If it be assumed that the weight of the thermal factor is substantially constant regardless of the composition of the atmosphere used and that it attains its maximum with a mixture near equivalence, the magnitude of the displacement will depend largely on the weight of the factor for reaction velocity, abbreviated *W*; the displacements will then exhibit a maximum coinciding with any maximum in *W*.

Such a maximum in *W* is seen if its constituents be viewed, from the equation cited, as a mass action product and as a function of *a*, the volume-fraction of oxygen in the atmosphere used, that affects the content of combustible for maximum flame velocity not directly but through its contributions to the absolute magnitude of the factor for reaction velocity: the constituent of position is given by divergences *d* between curves representing contents of combustible for maximum mass action product and for equivalence. As the factor for reaction velocity has for hy-

(2) For discussions see Lewis and von Elbe, *Chem. Rev.*, **21**, 347 (1937) and Coward and Payman, *ibid.*, **21**, 359 (1937).

(3) E. Mallard, *Ann. Mines*, [7] **7**, 355 (1875).

(4) Mallard and Le Chatelier, *ibid.*, **4**, 274 (1883).

(5) William Payman, *J. Chem. Soc.*, **117**, 48 (1920).

(6) Georg Jahn, "Der Zündvorgang in Gasgemischen," R. Oldenbourg, Berlin, 1934.

drogen and carbon monoxide the form $\sqrt{X^2(1-X)a}$, X representing the volume-fraction of hydrogen or of carbon monoxide in mixtures before combustion, these divergences have the form $\frac{2}{3} - \frac{2a}{2a+1}$ or $\frac{2-2a}{6a+3}$, and W has the form $\frac{2a^{1/2} - 2a^{3/2}}{6a+3}$ which has a maximum for $2a^2 + 5a - 1 = 0$ or for $a = 0.19$. Similarly for methane, the form $\sqrt{\text{CH}_4(1-\text{CH}_4)a^2}$ relates d to a through $\frac{2-2a}{3a+6}$ and W becomes $\frac{2a-2a^2}{3a+6}$ which has a maximum for $a^2 + 4a - 2 = 0$ or for $a = 0.45$.

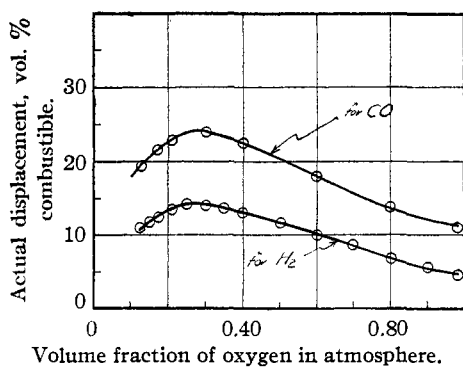


Fig. 1.—Relations, derived from data of Jahn, between displacements of mixtures giving maximum flame velocities for hydrogen and for carbon monoxide and the composition of the atmosphere used for combustion.

These indications of maxima in the displacements with changing oxygen content of the atmosphere used for combustion agree with the observed effects for the combustion of methane as reported recently¹ and for the combustion of hydrogen and of carbon monoxide as shown by the similar relations in Fig. 1 derived from data of Jahn.⁶ These maxima occur nearly coincidentally for hydrogen and for carbon monoxide at a lower value of a than for methane: values from the curves are, in the order named, about 0.28 and 0.5 as compared with 0.19 and 0.45 from these calculations.

BRUCETON, PENNSYLVANIA

RECEIVED MAY 5, 1941

Mono-metalation of 9-Phenylcarbazole

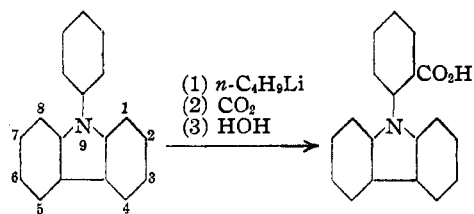
BY HENRY GILMAN, C. G. STUCKWISCH AND A. R. KENDALL

Metalation generally takes place ortho to a hetero element or ortho to a group containing a hetero element. The exceptional cases are metalation of dibenzothiophene by phenylcalcium io-

dide,^{1a} and metalation by *n*-butyllithium of methyl phenyl sulfide,^{1b} triphenylamine,^{1c} and possibly 9-hydroxy- and 9-methoxyphenanthrene.^{1d} The anomalous metalation of triphenylamine is particularly noteworthy, for aniline, *n*-butylaniline, diphenylamine and *N*-methyldiphenylamine are metalated by *n*-butyllithium in the ortho position.^{1e}

Houben and co-workers^{2a} have shown that under conditions of high temperature and pressure para-amino acids are obtained predominantly by carbonation of intermediates derived from various primary and secondary amines with the Grignard reagent. These reactions, not shown by tertiary amines, probably involve the rearrangement of precursory $-\text{NMgX}$ linkages.^{2b}

In connection with studies of substituted 9-arylcarbazoles, we have examined the metalation of 9-phenylcarbazole. On the basis of earlier work one might have predicted that mono-metalation by *n*-butyllithium would take place either in the meta position of the 9-phenyl group or in the 1-position. The former orientation would have been expected because of the known metalation of the related triphenylamine in the meta position. The latter orientation would conform with the metalation of carbazole and *N*-ethylcarbazole in the 1-position.³ Actually, neither position was involved to any detectable extent, and metalation took place in the ortho position of the 9-phenyl group.



Experimental

Metalation of 9-Phenylcarbazole.—A mixture of 20 g. (0.082 mole) of 9-phenylcarbazole⁴ and 0.25 mole of *n*-

(1) (a) Gilman, Jacoby and Pacevitz, *J. Org. Chem.*, **3**, 120 (1938); (b) Gilman and Webb, *THIS JOURNAL*, **62**, 987 (1940); (c) Gilman and Brown, *ibid.*, **62**, 3208 (1940). Mr. G. E. Brown has also shown that triphenylphosphine is metalated by *n*-butyllithium in the meta position; (d) Gilman and Cook, *ibid.*, **62**, 2813 (1940); (e) Gilman, Brown, Webb and Spatz, *ibid.*, **62**, 977 (1940). Mr. S. M. Spatz (unpublished studies) has established the position of metalation of *N*-methyldiphenylamine.

(2) (a) Houben and co-workers, *Ber.*, **46**, 3833 (1913) and preceding papers; (b) Gilman and Yablunsky, *THIS JOURNAL*, **63**, 839 (1941).

(3) Gilman and Kirby, *J. Org. Chem.*, **1**, 146 (1936). See also, Gilman and Spatz, *THIS JOURNAL*, **63**, 1553 (1941).

(4) Hager, "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1932, p. 532.