

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 $a = 0.45$.

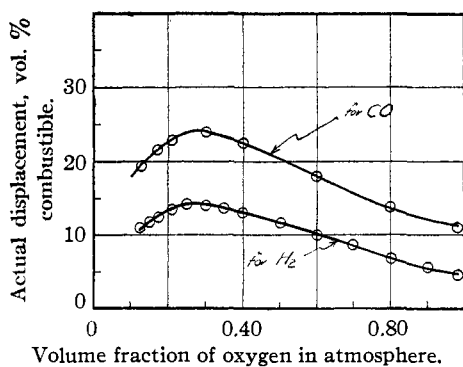


Fig. 1.—Relations, derived from data of Jahn, between displacements of mixtures giving maximum flame velocities for hydrogen and for carbon monoxide and the composition of the atmosphere used for combustion.

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

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Mono-metalation of 9-Phenylcarbazole

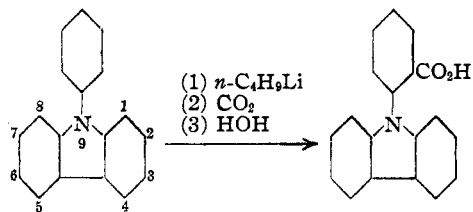
By HENRY GILMAN, C. G. STUCKWISCH AND A. R. KENDALL

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 —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.

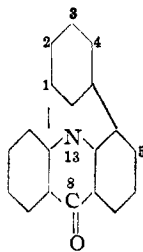
butyllithium in 250 cc. of ether was stirred and refluxed for forty-eight hours, and then carbonated by pouring on crushed, solid carbon dioxide. After working up the reaction products by conventional procedures there was isolated 1.5 g. (6.3%) of 9-(*o*-carboxyphenyl)-carbazole, melting at 182–184°.

Anal. Calcd. for $C_{19}H_{13}O_2N$: N, 4.88; neut. equiv., 287. Found: N, 4.73; neut. equiv., 288.

A mixed melting point determination with an authentic specimen prepared earlier from carbazole, *o*-iodobenzoic acid, potassium carbonate and copper bronze⁵ showed no depression.

Decarboxylation, by heating the acid between 350–360°, gave a 90% yield of 9-phenylcarbazole. 9-(*o*-Carbomethoxyphenyl)-carbazole,⁵ prepared from the acid and diazomethane, melted at 139–140° after crystallization from methanol.

8-Indolo[3,2,1-de]acridin-8-one.—A mixture of 7.5 g. (0.026 mole) of 9-(*o*-carboxyphenyl)-carbazole and 8.5 g. of phosphorus pentachloride was allowed to react in 50 cc. of xylene, at room temperature, for forty-five minutes. The solution was then cooled to 0°; 6 cc. of stannic chloride⁶ was added; and after fifteen minutes, the brick-red complex was hydrolyzed by iced concd. hydrochloric acid. The ketone⁶ obtained in this manner in 70% yield, melted at 180–181° after crystallization



from xylene.

Anal. Calcd. for $C_{19}H_{11}ON$: N, 5.2. Found: N, 5.23.

The oxime of 8-indolo[3,2,1-de]acridin-8-one, prepared from the ketone and hydroxylamine, melted at 175–176° after crystallization from dilute ethanol.

Anal. Calcd. for $C_{19}H_{12}ON_2$: N, 9.85. Found: N, 9.76.

(5) Eckert, Seidel and Endler, *J. prakt. Chem.*, **104**, 85 (1922).

(6) Fieser and Fieser, *THIS JOURNAL*, **57**, 782 (1935).

DEPARTMENT OF CHEMISTRY
IOWA STATE COLLEGE
AMES, IOWA

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On the Reaction of Hydrogenation and Dehydrogenation through Disproportionation of Hydrogen in Abietic Acid

BY TORSTEN HASSELSTROM, E. A. BRENNAN AND
SAM HOPKINS, JR.

When Steele's abietic acid is heated at an elevated temperature in the presence of a catalyst belonging to the platinum or nickel series, a mixture is obtained consisting of dehydro-, dihydro- and tetrahydroabietic acids.¹ The same acid mixture is encountered in the acid fraction of ordinary rosin oil² and in small quantities in the

(1) (a) Fleck and Palkin, *THIS JOURNAL*, **60**, 921 (1938); (b) Littmann, *ibid.*, **60**, 1419 (1938).

(2) Brennan, Cairncross, Hasselstrom and Hull, U. S. Patent 2,272,628 (1937).

resin acid fraction of vacuum distilled sulfate pulp talloel.³

From these acid mixtures the dehydroabietic acid may be isolated as the trihydrate of sulfodehydroabietic acid and dihydroabietic acid as the lactone of hydroxytetrahydroabietic acid.⁴ The sulfodehydroabietic acid, recently designated by Campbell and Morgana⁵ as the 6-sulfo acid yields dehydroabietic acid on hydrolysis with sulfuric acid.⁶

This work was undertaken to investigate further the reactions of dehydrogenation through disproportionation of hydrogen in abietic acid. It was observed that when Steele's abietic acid is heated for a short period of time at about 160–170°, together with 1–2% of iodine, this conversion takes place, inasmuch as such treated abietic acid on sulfonation yielded about 40% of trihydrate of 6-sulfodehydroabietic acid and 20% of lactone of hydroxytetrahydroabietic acid. Furthermore, it was made evident that ordinary gum or wood rosin may be subjected to the same treatment and that the resulting rosin on sulfonation yields the pure trihydrate of 6-sulfodehydroabietic acid and the lactone of hydroxyabietic acid in amounts directly proportional to the amount of iodine used.

Experimental

The Preparation of the Dehydro- and Dihydroabietic Acids from Steele's Abietic Acid.—The starting material used for this purpose was prepared according to Steele⁷ and Palkin and Harries.⁸ The sodium tetrahydroabietate had the following characteristics: m. p. 197–205° (cor.), (α)_D –92.6 (1% ethanol); the regenerated Steele's abietic acid melted at 164–168° (cor.), (α)_D –89 (1% ethanol).—Thirty-five grams of Steele's abietic acid was heated to 160° and while kept at that temperature for about five minutes 0.525 g. of iodine was added in five portions. The heating was then continued for two hours and the temperature kept at 160–170°. After cooling 25 g. of the treated acid was pulverized and added in portions during constant stirring to 125 cc. of concentrated sulfuric acid sp. gr. 1.84. The sulfonation was carried out at a temperature below 20°. After about one and one-half hours the sulfonation mixture was poured into one liter of ice and water and the precipitate then removed by filtration and washed until washings clouded the acid filtrate. The soluble material

(3) Hasselstrom, McPherson and Hopkins, *American Paper Trade Journal*, **68**, 41 (1940).

(4) (a) Hasselstrom, U. S. Patent 2,121,032 (1938). (b) U. S. Patent 2,121,033 (1938). (c) Hasselstrom and McPherson, *THIS JOURNAL*, **60**, 2340 (1938).

(5) Campbell and Morgana, *ibid.*, **63**, July (1941).

(6) Fieser and Campbell, *ibid.*, **60**, 2631 (1938).

(7) Steele, *ibid.*, **44**, 1333 (1922).

(8) Palkin and Harries, *ibid.*, **56**, 1935 (1934).

(9) With equal results the mixture may be heated for 15–20 minutes at 185–195°.