chloroform and the calculated amount of bromine in chloroform added separately to each. The resulting dibromides were then distilled under vacuum. From comparisons with the published constants of Boord and Schmidt[5] for the olefins and their dibromides it is probable that the hydrogenation products obtained were as follows: Fraction I, b. p. 53.0°, 4-methyl-1-pentene; Fraction II, b. p. 58.0°, *cis*-4-methyl-2-pentene; Fraction III, b. p. 65.0°, 2-methyl-2-pentene.

The per cent. yields on these fractions were 5.9, 44.4, and 40.7, respectively. It is possible that Fraction I was *trans*-4-methyl-2-pentene, b. p. 54.2–55.2,[5] instead of 4-methyl-1-pentene, b. p. 53.6–53.9.[5] An insufficient quantity was available for conversion to the dibromide and complete identification.

## Summary

The reactions of 4-methyl-1,3-pentadiene with bromine, sulfur dioxide, a diazonium salt, phosphorus pentachloride, and hydrogen have been investigated and the products characterized. Additions to the 1,2-, 3,4- and 1,4-positions were observed.

Reactions of 4-methyl-1,3-pentadiene with several activated mono-enes under various conditions could not be made to yield cyclic products of the Diels–Alder type. This inertness is attributed to steric hindrance.

LAFAYETTE, IND.

RECEIVED FEBRUARY 18, 1944

---

[5] Boord and Schmidt, THIS JOURNAL, **54**, 754, 760 (1932).

---

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, PURDUE UNIVERSITY]

# Utilization of Aliphatic Nitro Compounds. X. The Condensation of Aromatic Diazonium Salts and Hydroxides with Amino-Substituted Secondary Nitroalkanes

BY GERHARD VAN BIEMA[1] WITH ED. F. DEGERING

It has been shown by Feasley and Degering[2] and Gochenour and Degering[3] that arylazo derivatives can be prepared from secondary nitroparaffins, $RCH(NO_2)R'$, as well as from secondary nitroalcohols of the type $RCH(NO_2)(CH_2)_x$-OH. The products obtained by coupling such compounds with various diazonium compounds were brightly colored, crystalline substances, some of which were capable of dyeing fabrics.

TABLE I

| Amine diazotized | Nitro-amine coupled[a] | Appearance of azo-compound | Corrected m. p. of product, °C. | Nitrogen, % Calcd. | Nitrogen, % Found | | Approximate yield, % |
|---|---|---|---|---|---|---|---|
| Aniline | M | Yellow crystals | 127.6 | 20.15 | 20.1 | 20.1 | 22 |
| β-Naphthylamine | M | Red plates | 152.1 | 17.07 | 16.4 | 16.5 | 25 |
| β-Naphthylamine | B | Red powder | 130.8 | 14.58 | 14.0 | 14.6 | 17 |
| Anthranilic acid | M | Gold plates | 172.5 | 17.40 | 11.8 | 12.1[d] | 13 |
| *p*-Aminobenzoic acid | M[b] | Yellow crystals | 198.4 | 17.40 | 17.0 | 17.3 | 26 |
| *p*-Chloroaniline[c] | B | Orange needles | 109.9 | 15.18 | 15.0 | 15.3 | 7 |
| *p*-Chloroaniline[c] | M | Orange crystals | 126.8 | 17.90 | 17.6 | 17.6 | 26 |
| *o*-Nitroaniline | M | Orange needles | 117.8 | 21.65 | 21.6 | 20.9 | 32 |
| *m*-Nitroaniline | M | Yellow crystals | 129.6 | 21.65 | 21.2 | 21.4 | 41 |
| *p*-Nitroaniline | M | Yellow needles | 147.9 | 21.65 | 26.0 | 25.9[d] | 46 |
| 2,4-Dichloroaniline | M | Orange needles | 92.6 | 16.13 | 15.5 | 15.7 | 48 |
| *p*-Aminoazobenzene | M | Lt. brown powder | 166.8 | 22.0 | 22.2 | 22.4 | 80 |

[a] M = 1-N-morpholino-2-nitropropane; B = 1-di-*n*-butylamino-2-nitrobutane. [b] = basic coupling. [c] Decomposes on prolonged standing. [d] Constitution not satisfactorily established.

The present investigation was undertaken with the object of preparing from 1-di-*n*-butylamino-2-nitrobutane and 1-N-morpholino-2-nitropropane, derivatives which might be useful as dyes. The diazotization of the two nitroamines, prepared by the method of Cerf de Mauny,[4] is illustrated by the preparation of 1-N-morpholino-2-nitro-2-(4-chlorophenylazo)-propane, as follows:

*p*-Chloroaniline, 3.18 g. (0.025 mole), was dissolved in 15 ml. of concentrated hydrochloric acid (sp. gr. 1.19) and 20 ml. of water. Sodium nitrite, 1.88 g., in about 30 ml. of water, was then added from a dropping funnel with constant stirring. Stirring was continued for ten more minutes after the addition. A solution of 4.35 g. (0.025 mole) of 1-N-morpholino-2-nitropropane in 10 ml. of concentrated hydrochloric acid (sp. gr. 1.19) and 30 ml. of water was similarly added. The solution turned yellow, then orange, and a bright orange solid was formed which was recovered from the solution by filtration. The product was dried over anhydrous potassium carbonate in a vacuum desiccator and recrystallized from 200 ml. of 30% ethanol, yielding 2 g. of bright orange needles melting at 124.5° (cor. 126.8°).

In order to determine whether the yields could be improved by varying the *p*H of the coupling solution a series of couplings was carried out quantitatively, the *p*H of the solutions after coupling being measured by means of a *p*H-meter equipped with a glass electrode. Best results

---

[1] An abstract of a thesis submitted to the Faculty of Purdue University by Gerhard Van Biema in partial fulfillment of the requirements for the degree of Master of Science, December, 1943.

[2] C. F. Feasley and Ed. F. Degering, *J. Org. Chem.*, **8**, 12ff. (1943).

[3] C. Gochenour, M.S. Thesis, Purdue University, 1943.

[4] H. Cerf de Mauny, *Bull. soc. chim.*, [5] **4**, 1451-1460 (1937).

were obtained at a *p*H of about 1. A note of caution should be added here concerning attempts to couple in solutions of a *p*H between 7 and 10: such solutions have been observed to explode with great violence during the coupling process, even though kept at temperatures below 5°.

In a few cases it was possible to couple 1-N-morpholino-2-nitropropane in basic solution. The other nitroamine was insoluble even in hot sodium hydroxide solution. For coupling in alkaline solution the diazotized solution was neutralized in the cold with an excess of 2 *N* sodium hydroxide, the nitroamine dissolved in dilute, hot sodium hydroxide solution, cooled and coupled in the cold. The product was precipitated by acidification with hydrochloric acid.

The melting points of all the compounds prepared were sharp, decomposition taking place in some cases. The azo-compounds were insoluble in water and in dilute mineral acids, as well as in most organic solvents. They were slightly soluble in dilute bases and quite soluble in hot ethanol. They ranged from bright yellow to deep red in color. A few of them, particularly those derived from *p*-chloroaniline, decomposed on prolonged standing. A list of the physical constants is given in Table I.

## Summary

Twelve new azo-compounds were prepared by the coupling, usually in acid solution, of amino-substituted secondary nitroparaffins with aryldiazonium salts or hydroxides, and certain of their physical properties determined.

LAFAYETTE, INDIANA RECEIVED MARCH 29, 1944

---

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

# The Quantitative Analysis of Alkyllithium Compounds[1]

BY HENRY GILMAN AND A. H. HAUBEIN

The simple acid titration procedure[2] for the quantitative analysis of organometallic compounds which give bases on decomposition by water yields values that may be high, particularly with RM compounds that cleave ether. For example, the lithium hydroxide formed by hydrolysis of an aliquot of an organolithium compound is derived not only from the RLi compound but from ROLi compound, as well as from lithium hydroxide and lithium oxide due, respectively, to traces of water and oxygen.

Ziegler and co-workers[3] obtained true titration values by a differential based on titration of two aliquots. One titration was for the total lithium hydroxide present. The other titration was for the lithium hydroxide present after destroying the RLi compound, and the difference between the two titrations gave the quantity of RLi compound. Prior to the second titration, the RLi compound was destroyed by adding *n*-butyl bromide and then dibenzylmercury; the benzyllithium, formed by reaction of the RLi compound and dibenzylmercury, was promptly decomposed by the butyl bromide.

We have found that benzyl chloride is a more convenient reagent than the butyl bromide–dibenzylmercury combination for removing the RLi compound. The reaction which occurs appears to be like that observed earlier by Späth[4] and by Fuson[5] with Grignard reagents, three coupling products being formed

$$n\text{-}C_4H_9Li + C_6H_5CH_2Cl \longrightarrow n\text{-}C_8H_{18} + C_6H_5CH_2C_4H_9\text{-}n + C_6H_5CH_2CH_2C_6H_5$$

The above over-all reaction is not a complete picture of the transformations involved. Benzyllithium is an intermediate compound, formed as a consequence of a halogen-metal interconversion[6] reaction

$$C_2H_5Li + C_6H_5CH_2Cl \longrightarrow C_6H_5CH_2Li + C_2H_5Cl$$

The benzyllithium formed in this manner undoubtedly accounts for part of the bibenzyl by a coupling reaction with some of the benzyl chloride. The transitory yellow color observed when benzyl chloride is added to *n*-butyllithium is due to benzyllithium. More particularly, the benzyllithium was captured as phenylacetic acid when a mixture of ethyllithium and benzyl chloride (cooled to −50° to reduce the rate of coupling) was very rapidly carbonated by solid carbon dioxide.

The quantitative analysis procedure is applicable to alkyllithium, but not to aryllithium compounds. It cannot be used with methyllithium and with phenylethynyllithium, very probably because of their lesser reactivity.

## Experimental

**Analytical Procedure.**—The solution of an alkyllithium compound[7] is filtered under nitrogen, preferably through a sintered glass funnel, to remove insoluble material. An

---

[1] Paper LVI in the series: "The relative reactivities of organometallic compounds"; the preceding paper with Van Ess and Shirley is in THIS JOURNAL, **66**, 1214 (1944).

[2] Gilman, Wilkinson, Fishel and Meyers, THIS JOURNAL, **45**, 150 (1923).

[3] Ziegler, Crössmann, Kleiner and Schäfer, *Ann.*, **473**, 31 (1929).

[4] Späth, *Monatsh.*, **34**, 1965 (1913).

[5] Fuson, THIS JOURNAL, **48**, 2681 (1926); Ellingboe and Fuson, *ibid.*, **55**, 2960 (1933).

[6] Gilman and Jones, *ibid.*, **63**, 1441 (1941).

[7] Gilman, Langham and Moore, *ibid.*, **62**, 2327 (1940).