# ORGANIC AND BIOLOGICAL CHEMISTRY

[CONTRIBUTION FROM THE CHEMISTRY DIVISION, OAK RIDGE NATIONAL LABORATORY, AND THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF TENNESSEE]

## The Reaction of Cyanogen with Arylmethylmagnesium Halides[1]

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When treated with cyanogen, benzylmagnesium chloride has been found to yield *o*-tolunitrile. This new *o*-substitution reaction has been found to occur also with cyanogen and three other benzyl-type Grignard reagents. Particularly interesting is the case with 2,6-dimethylbenzylmagnesium chloride, whose substitution by cyanogen yields the non-aromatic triene VII.

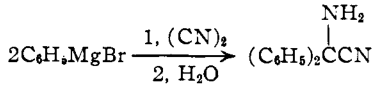
The reactions of cyanogen with Grignard reagents have received little attention. After the initial work of Blaise[2] and of Grignard, Bellet and Courtot,[3] which was concluded in 1919, no new reactions of this type were reported until 1954. In accord with its pseudohalogen character, cyanogen was found by Grignard and co-workers to yield an alkyl or aryl cyanide when treated with an equivalent of the corresponding alkyl or aryl Grignard reagent.[3]

$$C_6H_5MgBr + (CN)_2 \longrightarrow C_6H_5CN + MgBrCN \qquad (1)$$

With excess ethylmagnesium iodide, cyanogen was found by Blaise to yield 3-pentanone,[2] a product

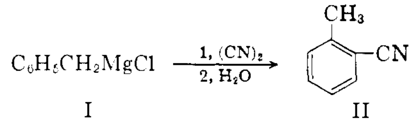
$$C_2H_5MgX \xrightarrow[2,\ H_2O]{1,\ C_2H_5CN} (C_2H_5)_2CO \qquad (2)$$

from the interaction of excess Grignard reagent with the nitrile first formed. By operating at a low temperature, Lynn[4] has succeeded in isolating biacetyl in poor yield (10%) along with a small amount of acetamide as products of the reaction between cyanogen and two moles of methylmagnesium bromide or iodide. Other products of the reaction were not identified. In one of a series of studies made with cyanogen, Woodburn and Lathroum[5] found that the product of the reaction of cyanogen with two moles of Grignard reagent was a modest yield of a disubstituted glycinonitrile if a saturated aqueous solution of ammonium chloride was used as the hydrolyzing agent. Hydrolysis by a mineral acid yielded only the ketone. No examples of the reaction of arylmethylmagnesium halides (benzyl-type Grignard reagents) have been reported previously.



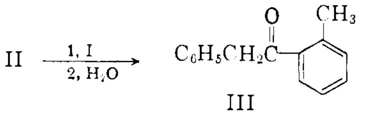
$$2C_6H_5MgBr \xrightarrow[2,\ H_2O]{1,\ (CN)_2} (C_6H_5)_2\overset{NH_2}{\overset{|}{C}}CN \qquad (3)$$

In the present work cyanogen was treated with four benzyl-type Grignard reagents. In each case the reaction proceeded with substitution of a cyano group *ortho* to the original methylmagnesium group, as illustrated for benzylmagnesium chloride.



(4)

No attempt has been made to determine the optimum conditions for this reaction, but in the first experiment with each benzyl-type Grignard reagent studied, a yield in the range of 40–60% of the *o*-cyano derivative was isolated. Each reaction was carried out by the addition of the Grignard reagent in ether to a slight excess of ethereal cyanogen. After the usual work-up and evaporation of the ethereal solutions, products were isolated from the residue by distillation and/or crystallization. The first three Grignard reagents tried were prepared from benzyl chloride, 2-methylbenzyl bromide and α-chloromethylnaphthalene and were found to yield, respectively, *o*-tolunitrile (II), 2,3-dimethylbenzonitrile and 1-methyl-2-naphthonitrile. For characterization, each nitrile was hydrolyzed to the expected carboxylic acid. After removal of II from the reaction of cyanogen and benzylmagnesium chloride (I), *o*-methyl-α-phenylacetophenone (III) also was isolated as its 2,4-dinitrophenylhydrazone.



(5)

The side product III was expected from the further reaction of II with the Grignard reagent.[6]

Since Tiffeneau and Delange[7] first showed that formaldehyde substitutes *ortho* to benzylmagnesium chloride to produce *o*-methylbenzyl alcohol, numerous other examples of *o*-substitution on the benzyl-type Grignard reagent have been reported.

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[1] This paper is based upon work performed at Oak Ridge National Laboratory, which is operated for the Atomic Energy Commission by Union Carbide Corporation, and was presented in a preliminary communication, J. F. Eastham and V. F. Raaen, *Proc. Chem. Soc.*, 149 (1958).

[2] E. E. Blaise, *Compt. rend.*, **132**, 38 (1901).

[3] V. Grignard, E. Bellet and C. Courtot, *Ann. chim.*, [9] **12**, 364 (1919), and earlier papers by Grignard.

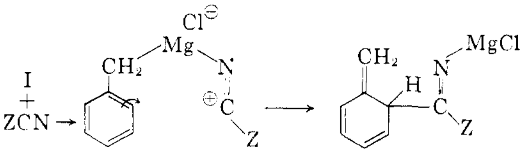
[4] K. R. Lynn, *Australian J. Chem.*, **7**, 303 (1954).

[5] H. M. Woodburn and L. B. Lathroum, *J. Org. Chem.*, **19**, 285 (1954).

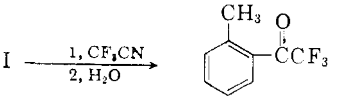
[6] The m.p. (191–192°) of the 2,4-dinitrophenylhydrazone of the side product is very different from the value (146–147°) previously reported [P. Hill and W. F. Short, *J. Chem. Soc.*, 1123 (1935)] for that derivative of III, but is the value (190°) reported for the 2,4-dinitrophenylhydrazone of 2,2'-dimethylbenzophenone, another conceivable product from *o*-tolunitrile and benzylmagnesium chloride. To be certain of its identity the 2,4-dinitrophenylhydrazone of the side product was compared with the same derivative of III prepared by an independent synthesis (see Experimental). The 2,4-dinitrophenylhydrazone (m.p. 191–192°) of the authentic III (m.p. *ca.* 16°) shows no m.p. depression when admixed with that derivative of the side product, and the m.p. of the semicarbazone (196–198°) of the authentic III is the same as that reported by Blaise [E. E. Blaise, *Compt. rend.*, **133**, 1217 (1901)], who first prepared III by equation 5. It therefore seems likely that the previously reported m.p. of 146° for the 2,4-dinitrophenylhydrazone of III is in error.

[7] M. Tiffeneau and R. Delange, *Compt. rend.*, **137**, 573 (1903).

A recent summary[8] of the reported examples shows that all have involved reaction of the Grignard reagent at a carbon–oxygen bond. Our new example involves reaction (rupture) of the carbon–carbon bond. That cyanogen should react in this manner may be rationalized as a consequence of the electron withdrawal of one cyano group (Z in IV) allowing an electrophilic attack on the ring by the other cyano group while the latter is in a sterically favorable position. That electron withdrawal by the Z group in IV is necessary is seen by the fact that when Z is an ordinary alkyl or aryl group, normal reaction with the benzyl-type Grignard reagent occurs. It is now known, however, that when Z is trifluoromethyl, another strongly electronegative group, *o*-substitution occurs (equation 7).[9]



IV V (6)

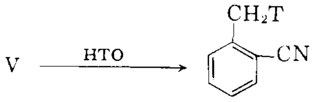


(7)

In one experiment the effect of bromine as the electron-withdrawing Z group was examined by treatment of benzylmagnesium chloride (I) with cyanogen bromide. In this case, however, normal reaction occurred and benzyl bromide was isolated in 70% yield.

$$I \xrightarrow{BrCN} C_6H_5CH_2Br \qquad (8)$$

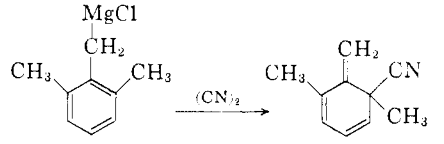
After *o*-substitution by cyanogen on I, an intermediate such as V (equation 6) must tautomerize to yield the final product II.[10] Since it was conceivable that this tautomerism does not occur before hydrolytic work-up of the reaction mixture, in one experiment the hydrolysis was carried out with tritiated water. Tritium-labeled *o*-tolunitrile was produced (equation 9), as would be expected if the water participates in the tautomerization of V. The reaction was accompanied by a large isotope effect (see Experimental). With this information suggesting the stability in ether of an intermediate having the benzene aromaticity interrupted, it seemed of interest to treat cyanogen with a benzyl-type Grignard reagent having no *o*-hydrogen available for substitution (tautomerization).



(9)

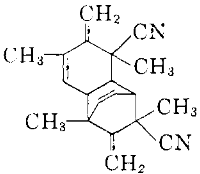
The Grignard reagent (VI) was prepared from 2,6-dimethylbenzyl chloride, which itself was prepared in a conventional manner (see Experimental) labeled with carbon-14 in order to assist in characterizing its reaction products. Treatment of VI with cyanogen gave, in 45% yield, a product whose elemental analysis and radioassay agree with the formula $C_{10}H_{11}N$. The product did not appear to be an aryl or benzyl cyanide since it polymerized when attempts were made to hydrolyze it to an acid, but it was reduced easily to an amine by lithium aluminum hydride. The product, a liquid, was not identical with 2,6-dimethylphenylacetonitrile, a solid prepared by an independent synthesis. The liquid product slowly changed to a crystalline derivative upon standing at room temperature.

On the basis of the above chemical properties, of its method of preparation and of the spectroscopic data, the product is assigned the structure VII, 5-cyano-1,5-dimethyl-6-methylene-1,3-cyclohexadiene. In the ultraviolet region above 210 mμ the product has a single absorption maximum (304 mμ, log ε 3.82) which is characteristic both in position and intensity of the particular triene chromophore in VII.[11,12] In the infrared region, VII has a sharp absorption maximum at 2242 cm.⁻¹, characteristic of the aliphatic nitrile group,[13] and has moderately strong maxima at 1740 and 895 cm.⁻¹ both characteristic of the exomethylene group.[14]



VI VII (10)

The radioactivity and elemental analysis of the solid derived from VII indicated that it was a simple polymer. The result of a Rast molecular weight determination of this derivative lay between the values for a dimer and trimer of VII. Because of its relatively low m.p. (145°) and by analogy to similar dimerizations,[15] the derivative is assigned the dimeric structure VIII. In the infrared region,



VIII

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[8] M. S. Kharasch and O. Reinmuth, "Grignard Reactions of Nonmetallic Substances," Prentice-Hall, Inc., New York, N. Y., 1954, pp. 1134–1140.

[9] The authors wish to thank Dr. Reuben G. Jones for a private communication concerning the reaction in equation (7). Jones [THIS JOURNAL, **70**, 143 (1948)] first carried out the reactions between benzylmagnesium chloride and trifluoroacetonitrile and between benzylzinc chloride and trifluoroacetyl chloride. He assumed that each of these reactions, which resulted in the same compound, produced the expected benzyl trifluoromethyl ketone. When the latter compound later was prepared by W. R. Nes and A. Burger [*ibid.*, **72**, 5409 (1950)] and found to be isomeric with Jones' product, Jones treated his product with aqueous base and obtained *o*-toluic acid.

[10] Obviously an intermediate such as V must also lose the elements of MgClZ in producing II. Although there is no evidence as to when that loss occurs, it should be independent of the tautomerization.

[11] See L. F. Fieser and M. Fieser, "Natural Products Related to Phenanthrene," 3rd Ed., Reinhold Publishing Corp., New York, N. Y., 1949, p. 188; *cf.* also ref. 12.

[12] The novel triene system of VII with different substituents has been obtained recently by C. R. Hauser and D. N. Van Eenam [THIS JOURNAL, **79**, 5512 (1957)] by a molecular rearrangement.

[13] See L. J. Bellamy, "The Infra-Red Spectra of Complex Molecules," 2nd Ed., Methuen and Co., London, England, 1958, p. 264.

[14] *Ibid.*, p. 51.

[15] T. L. Brown, D. Y. Curtin and R. R. Fraser, THIS JOURNAL, **80**, 4339 (1958); H. Conroy and R. A. Firestone, *ibid.*, **78**, 2290 (1956).

VIII retains the aliphatic cyano and exomethylene absorption found with its precursor VII, whereas in the ultraviolet region VIII has the absorption maximum (239 m$\mu$, log $\epsilon$ 4.18) characteristic both in intensity and position of the particular diene chromophore shown.[11]

It appears that *o*-substitution on the benzyl-type Grignard reagent occurs with greater facility with cyanogen than with any previously studied reagents. Thus with the 1-naphthylmethyl system, carbon dioxide undergoes normal Grignard reaction and formaldehyde substitutes to a very small extent at the *o*-position,[16] whereas cyanogen appears to react exclusively at the *o*-position. No other reagent has been demonstrated to react at an *o*-position of a Grignard reagent which is already substituted there.

## Experimental

Carbon-14 in samples for radioassay was converted by a conventional wet-combustion to carbon dioxide, which was counted in an ionization chamber. Tritium in samples was determined by the method of Wilzbach, Kaplan and Brown.[17] Elemental analyses were performed by Weiler and Straus, Oxford, England. Infrared and ultraviolet spectra were determined with, respectively, Perkin-Elmer model 21 and Beckman model DU spectrophotometers and in, respectively, potassium bromide disks and ethanol solutions. Melting points are uncorrected.

**Cyanogen.**—Cyanogen was prepared by treating a warm aqueous solution of copper sulfate with an aqueous solution of sodium cyanide. Cyanogen gas liberated from the aqueous solution was delivered into ether contained in a weighed, 3-necked flask that was equipped with an efficient mechanical stirrer and Dry Ice–ether reflux condenser. A 43% yield of cyanogen was obtained; the cyanogen could be stored in dry ether at 0° for several hours without appreciable loss.

***o*-Tolunitrile from Benzyl Chloride.**—Benzylmagnesium chloride prepared from 26 g. of benzyl chloride and 10 g. of magnesium turnings in 200 ml. of ether was added slowly with vigorous stirring to 11 g. of cyanogen in 200 ml. of ether at 0°. A white precipitate began to form at the beginning of the addition and became very heavy when all the Grignard reagent had been added, after which the mixture was refluxed for 20 minutes and then treated with 20 ml. of tritium-labeled water, 32.01 mc./mole. The mixture was stirred vigorously and filtered to remove a light yellow precipitate. The ether layer was dried and evaporated. The residue was distilled to yield 12.2 g. (52%) of crude *o*-tolunitrile, b.p. 50–60° (0.5 mm.). Redistillation yielded 6.6 g. of pure *o*-tolunitrile, b.p. 56–58° (0.5 mm.), $n^{24}\text{D}$ 1.5284 (lit.[18] value $n^{23.1}\text{D}$ 1.5272), 2.27 mc./mole. A sample of the nitrile and 65% sulfuric acid was refluxed for two hours and worked up in the usual manner to yield *o*-toluic acid, m.p. 103–104°, undepressed by authentic material.

A solution of the tarry residue that remained after the distillation of the *o*-tolunitrile, 2,4-dinitrophenylhydrazine, sulfuric acid and ethanol was stirred for 16 hours at room temperature. The brown precipitate that formed was crystallized from tetrahydrofuran–ethanol (1:4) to yield a dark yellow crystalline product, which melted at 191–192° and did not depress the m.p. of the 2,4-dinitrophenylhydrazone derivative of *o*-methyl $\alpha$-phenylacetophenone prepared in an independent synthesis by treating phenylacetyl chloride with di-*o*-tolylcadmium. After isolation the ketone was purified by distillation, b.p. 125–127° (1 mm.). When cooled and stirred to cause crystallization, the solid ketone melted at 14–15°.

**2,3-Dimethylbenzonitrile from *o*-Methylbenzyl Bromide.**—The Grignard reagent prepared from 28.0 g. of *o*-methylbenzyl bromide and 10 g. (0.410 mole) of magnesium turnings in 200 ml. of dry ether was added slowly and with vigorous stirring to a solution of 12 g. of cyanogen in 150 ml. of dry ether at 0°. An initial white precipitate changed to a viscous orange oil. The reaction mixture was refluxed for 20 minutes, cooled and treated with a saturated solution of ammonium chloride and, after the hydrolysis reaction subsided, with dilute hydrochloric acid. The ether layer was evaporated and a residual oil fractionated. An 8.3-g. fraction (42%), b.p. 55–65° (1 mm.), of 2,3-dimethylbenzonitrile was collected; its characterization is described in the next paragraph. The continued distillation of the remaining reaction product yielded 6 g. of a crystalline fraction, b.p. 116–122° (1 mm.), which after recrystallization from ethanol yielded 1.6 g. of a white crystalline substance, m.p. 67–68°, presumed to be 1,2-di-*o*-tolylethane.[19] The distillation residue was chromatographed on alumina; elution with benzene yielded a viscous yellow oil that could not be caused to crystallize and that was unreactive toward 2,4-dinitrophenylhydrazine.

Redistillation of the 2,3-dimethylbenzonitrile gave material with b.p. 60–62° (1 mm.), $n^{24}\text{D}$ 1.5325; the b.p. given in the literature[20] is 98–100° (11 mm.). A sample of the nitrile was hydrolyzed by heating with 70% sulfuric acid for two hours at reflux temperature to yield crystalline 2,3-dimethylbenzoic acid, m.p. 144°.[21]

**1-Methyl-2-naphthonitrile from Chloromethylnaphthalene.**—The Grignard reagent prepared from 35.3 g. of freshly distilled 1-chloromethylnaphthalene and 12 g. of magnesium turnings in 300 ml. of dry ether was added to 17 g. of cyanogen in 300 ml. of dry ether. A yellow, flocculent precipitate began to form immediately. After the usual work-up, the ether was evaporated and the residue was fractionated. About 1 g. of methylnaphthalene distilled first, b.p. 43–45° (1 mm.), $n^{13}\text{D}$ 1.6202, reported[22] value $n^{13}\text{D}$ 1.6212. A fraction which distilled in the range 120–140° (1 mm.) turned to a solid on cooling and was recrystallized from ethanol to yield 5.2 g. of 1-methyl-2-naphthonitrile as white needles, m.p. 64–66°.

*Anal.* Calcd. for $C_{12}H_9N$: C, 86.19; H, 5.43. Found: C, 86.42; H, 5.57.

The undistilled residue was dissolved in 50 ml. of ethanol, and the solution was treated with 1 g. of Norit, filtered, and cooled to yield 12 g. of a brown semi-crystalline material. Two additional recrystallizations of the semi-crystalline material from ethanol yielded an additional 9.0 g. of crystalline 1-methyl-2-naphthonitrile, m.p. 60–63°. One gram of this nitrile was refluxed in 25 ml. of 75% sulfuric acid for one hour. The mixture was poured onto 100 g. of ice. Filtration yielded 0.8 g. of crude material, which was twice recrystallized from 90% ethanol and sublimed to yield 1-methyl-2-naphthamide, m.p. 202–203°.

*Anal.* Calcd. for $C_{12}H_{11}NO$: C, 77.80; H, 6.00. Found: C, 78.12; H, 5.93.

For hydrolysis, 0.4 g. of the 1-methyl-2-naphthamide, 3 g. of phosphorus pentoxide and 7 g. of 85% phosphoric acid were mixed and heated at 135–140° for 40 min. with stirring and poured in 50 ml. of water. Filtration yielded a crude acid, which was recrystallized from ethanol-water (1:1) to yield 0.15 g. of 1-methyl-2-naphthoic acid, m.p. 176–176.5°, reported[23] value 176°.

**The Reaction of Cyanogen Bromide with Benzylmagnesium Chloride.**—A Grignard reagent, prepared from 25.3 g. (0.200 mole) of benzyl chloride and 10 g. (0.41 mole) of magnesium turnings in 300 ml. of ether, was added over a 10-minute period to 42.4 g. (0.40 mole) of cyanogen bromide in 300 ml. of ether. A white precipitate formed immediately and more heat was evolved than in the addition of benzylmagnesium chloride to cyanogen. After the addition was complete, the mixture was refluxed for 30 minutes and then was cooled to 20° before it was decomposed with a cold, saturated solution of ammonium chloride. The ether layer was washed with water, dried and evaporated. The residue was fractionated to yield 23.6 g. (69%) of benzyl bromide, b.p. 40–42° (1 mm.), characterized by its b.p. at

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(16) H. Gilman and J. E. Kirby, THIS JOURNAL, **51**, 3475 (1929); D. Sonntag, *Ann. chim.*, [11] **1**, 359 (1934); M. Mousseron and N. P. Du, *Bull. soc. chim. France*, [5] **15**, 91 (1948).

(17) K. E. Wilzbach, L. Kaplan and W. G. Brown, *Science*, **118**, 522 (1953).

(18) J. W. Brühl, *Physik. Chem.*, **16**, 218 (1895).

(19) M. P. Carre, *Bull. soc. chim. France*, [3] **5**, 489 (1909).

(20) L. F. Fieser and J. Cason, THIS JOURNAL, **61**, 1740 (1939).

(21) O. Jacobsen, *Ber.*, **19**, 2518 (1886).

(22) K. von Auwers and A. Fruhling, *Ann.*, **422**, 200 (1921).

(23) M. Mousseron and Nguyen-Phuoc-Du, *Compt. rend.*, **218**, 281 (1944).

atmospheric pressure, 193–196°, and by its conversion to phenylacetic acid through a Grignard reagent in the usual manner.

**2,6-Dimethylbenzyl Alcohol.**—A solution of 78 g. of 2,6-dimethyliodobenzene in 100 ml. of dry ether was added to 12 g. of magnesium turnings in 200 ml. of dry ether. The solution was refluxed for two hours and then cooled to −40°. The solution of Grignard reagent was stirred vigorously while an excess of gaseous carbon dioxide was passed through the reaction vessel during a one-hour period. The reaction mixture was then warmed to room temperature and treated with an excess of dilute hydrochloric acid. The ether layer was washed with water and extracted with 200 ml. of aqueous sodium hydroxide, which was in turn acidified and extracted with ether. This ether solution was dried and evaporated, and the residue was heated with 50 g. of thionyl chloride for one hour. Fifty milliliters of absolute ethanol was added to the reaction mixture, which then was refluxed for 30 minutes. Finally, 100 ml. of benzene was added, and the mixture was fractionally distilled to remove ethanol, benzene and hydrogen chloride. The crude ester (residue) was added to a solution of 15 g. of lithium aluminum hydride in 500 ml. of dry ether, which then was refluxed for three hours and treated with 30 ml. of methanol, followed by 10 ml. of water. The precipitate was removed by filtration, and the ethereal solution was washed with dilute hydrochloric acid and with water, dried and evaporated. The residue was recrystallized from methanol–water (3:1) to yield 24.5 g. of 2,6-dimethylbenzyl alcohol, m.p. 81–82°.

*Anal.* Calcd. for $C_9H_{12}O$: C, 79.34; H, 8.90. Found: C, 79.66; H, 9.11.

**2,6-Dimethylphenylacetonitrile.**—An excess (30 g.) of thionyl chloride was added to 24.5 g. of 2,6-dimethylbenzyl alcohol. The reaction mixture was heated on the steam-bath for 20 minutes and then fractionated to yield 23 g. of crude 2,6-dimethylbenzyl chloride, b.p. 75–80° (1 mm.). The chloride was added to a solution of 10 g. of sodium cyanide in 10 ml. of water and 20 ml. of ethanol. The reaction mixture was refluxed for one hour, although from the heat evolved and salt precipitated the reaction appeared to be complete in 5 min. The mixture was cooled to room temperature and filtered. The sodium chloride residue was washed with ethanol, and the combined filtrates were distilled; a 17.2-g. fraction, b.p. 44–58° (0.5 mm.), was collected. This fraction crystallized on cooling and was recrystallized once from ethanol–water (4:1) and twice from petroleum ether (30–60°) to give 2,6-dimethylphenylacetonitrile, m.p. 39.5–40.5°.

*Anal.* Calcd. for $C_{10}H_{11}N$; C, 82.71; H, 7.64. Found: C, 82.43; H, 7.62.

**The Reaction of Cyanogen with 2,6-Dimethylbenzylmagnesium Chloride.**—2,6-Dimethylbenzyl chloride, labeled with carbon-14 in the benzyl carbon, was prepared by the series of reactions described above except for the use of radioactive carbon dioxide in the carbonation of 2,6-dimethylphenylmagnesium iodide. The crystalline 2,6-dimethylbenzyl alcohol intermediate had an activity of 2.542 ± 0.004 mc./mole. 2,6-Dimethylbenzylmagnesium chloride prepared from 41.5 g. of 2,6-dimethylbenzyl chloride and excess magnesium in 300 ml. of ether was added to 19 g. of cyanogen in 400 ml. of ether at −20°. A white precipitate product formed immediately. The mixture was stirred at reflux temperature for one hour and treated with 100 ml. of a cold, saturated solution of ammonium sulfate. The mixture then was poured onto a mixture of 400 g. of ice and 50 ml. of concentrated hydrochloric acid. After all the solid had dissolved, the ether layer was separated. The aqueous phase was washed with water and with aqueous sodium bicarbonate, dried and evaporated. The residue was fractionated. The first fraction was 17.6 g. (45%) of 1,5-dimethyl-5-cyano-6-methylene-1,3-cyclohexadiene (VII), b.p. 58–66° (1 mm.); its characterization is described in the next paragraph. The second fraction, 7 g., b.p. 120–140° (1 mm.), solidified during the distillation. After the solid was recrystallized from acetone the yield of it was 4.8 g., m.p. 124–125°. This compound is believed to be 1,2-bis-(2,6-dimethylphenyl)-ethane produced by the Würtz reaction in the synthesis of a benzyl-type Grignard reagent.

*Anal.* Calcd. for $C_{18}H_{22}$: C, 90.65; H, 9.35; mol. wt., 238.2; radioequiv. wt.,[24] 119.1. Found: C, 90.52, 90.57; H, 9.22, 9.26; mol. wt., 236; radioequiv. wt., 122.

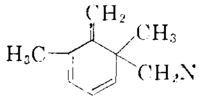
Just before analysis, the 1,5-dimethyl-5-cyano-6-methylene-1,3-cyclohexadiene (VII) was redistilled, b.p. 40–43° (0.5 mm.), 2.49 ± 0.01 mc./mole, $\lambda_{max}$ 304 mμ (log ε 3.82), $\lambda_{min}$ 235 mμ (log ε 2.37).

*Anal.* Calcd. for $C_{10}H_{11}N$: C, 82.70; H, 7.64; N, 9.66. Found: C, 82.75; H, 7.79; N, 9.61.

After standing for two weeks, VII crystallized to a compound found to be identical with a product isolated by the chromatography of the residue from the original distillation of VII. This compound is assigned the dimeric structure VIII, m.p. 145–146°, $\lambda_{max}$ 239 mμ (log ε 4.18).

*Anal.* Calcd. for $C_{20}H_{22}N_2$: C, 82.70; H, 7.64; mol. wt., 290.2; radioequiv. wt., 145.1. Found: C, 82.78, 82.65; H, 7.71, 7.69; radioequiv. wt., 145; mol. wt., 358.

**Reduction of Nitrile VII.**—To 1.50 g. of VII of b.p. 40–43° (0.5 mm.), dissolved in 25 ml. of ether, there was added a solution of 1.00 g. of lithium aluminum hydride in 75 ml. of ether. The mixture was stirred for one hour and then was decomposed by the cautious addition first of 25 ml. of methanol and then of 10 ml. of water. The mixture was filtered, and the filtrate was evaporated to leave 1.2 g. of an oil, most of which dissolved upon treatment with 6 *N* hydrochloric acid. The amine was reisolated from the acid solution and then was treated with 8 ml. of 10% aqueous potassium hydroxide and 0.6 g. of benzenesulfonyl chloride. After the mixture had been stirred for one hour, the alkaline layer was removed by decantation, and the residual oil, 0.5 g., was crystallized and recrystallized from ethanol to give a compound assigned the structure of the disulfonamide IX, m.p. 173–174°. The disulfonamide was insoluble in both acid and base.



IX

*Anal.* Calcd. for $C_{22}H_{23}NO_4S_2$: C, 61.52; H, 5.40; radioequiv. wt., 429.5. Found: C, 61.63; H, 5.38; radioequiv. wt., 430.

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[24] *The radioequivalent weight* of a product is defined as its weight in grams that possesses the radioactivity of one gram molecular weight of that product's precursor.