work of Wheeler,[3] who obtained such an acetyl derivative from thionol prepared by (1) action of 84% sulfuric acid on phenothiazine and (2) hydrolysis of thionine by 65% sulfuric acid.

As pointed out in the introduction, thionol–leuco thionol possesses the properties of a reversible oxidation–reduction system. Since it is conceivable that a sample of thionol prepared from phenothiazine may be more or less contaminated with products representing lower states of oxidation, it appeared logical that the oxidation–reduction potential of a solution in which the ratio of oxidant to reductant is unity could be used as a criterion of the purity of the thionol produced from phenothiazine. For determination of the potential of pure thionol the diacetyl leuco thionol was used as a source of material. A sample of the pure diacetyl derivative with a melting point of 212° was dissolved in a small volume of ethyl alcohol, diluted with water, strongly acidified with hydrochloric acid, and heated to promote hydrolysis. The liberated leuco thionol was oxidized to thionol in the presence of air by adding sodium hydroxide to the cooled solution until an alkaline reaction was produced. The thionol was extracted with chloroform, and brought into solution in a phosphate buffer of *p*H 4.47 by volatilizing the chloroform from the heated buffer, the mixture being stirred constantly until all traces of chloroform were removed. The oxidation–reduction potential of the thionol solution thus prepared was measured by a standard procedure. The potential of this thionol at a temperature of 21° and *p*H 4.47 when the ratio of the concentration of oxidant to reductant was unity was found to be 301.9 mv. more positive than the standard normal hydrogen electrode. Using this value as a standard of reference, it was found that when the method of converting phenothiazine to thionol was successfully carried out there was produced a red dye having a potential of 300 ± 2 mv. at a *p*H of 4.47. The potential values at other hydrogen ion concentrations are given in Table I.

TABLE I

OXIDATION–REDUCTION POTENTIALS OF THIONOL AT DIFFERENT *p*H VALUES. AUTHORS' PREPARATION 81, TEMPERATURE 21°

*p*H	E_h, v.	*p*H	E_h, v.
1.42	+0.4717	6.57	+0.1882
1.85	+ .4576	6.84	+ .1687
2.65	+ .4105	7.14	+ .1516
3.47	+ .3917	7.44	+ .1333
4.03	+ .3450	7.78	+ .1132
4.47	+ .3022	8.70	+ .0700
4.99	+ .2710	9.90	− .0040
5.53	+ .2479		

Potentials have been determined on samples of thionol prepared by oxidation of phenothiazine orthosulfoxide, and thionol prepared by the method of Bernthsen. A summary of potential values obtained on various preparations is given in Table II.

TABLE II

OXIDATION–REDUCTION POTENTIAL OF THIONOL AT *p*H 4.47 AND TEMPERATURE 21°

Method	E_h, v.
Hydrolysis of diacetyl leuco thionol	0.3019
Oxidation of phenothiazine orthosulfoxide	.3010
Thionol by method of Bernthsen	.3040
Authors' Preparation 75	.3008
Authors' Preparation 81	.3022

Summary and Conclusions

1. A simple and rapid method for the conversion of phenothiazine to thionol (hydroxyphenthiazone) has been described.
2. The oxidation–reduction potential of this thiazine dye has been determined.
3. The oxidation–reduction potential has been used as a criterion for purity of thionol.

SAN FRANCISCO, CALIF. RECEIVED FEBRUARY 28, 1938

---

[3] Donald H. Wheeler, personal communication.

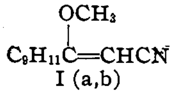
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

The Reaction of Phenylmagnesium Bromide with β-Methoxy-β-mesitylacrylonitriles

BY REYNOLD C. FUSON, G. E. ULLYOT, R. F. STEDMAN AND P. O. TAWNEY

β-Methoxy-β-mesitylacrylonitriles derived from α-cyanoacetomesitylene and α-cyanopropiomesitylene and described elsewhere[1] generally react normally, but their behavior toward the Grignard reagent has led to interesting results. This paper reports a study of their reactions with phenylmagnesium bromide.

The methylation product derived from α-cyanoacetomesitylene, β-methoxy-β-mesitylacrylonitrile (I), exists in two forms which are presumably *cis* and *trans* isomers. These melt at 66° (Ia) and 82.5–83.5 (Ib). When mixed in equal amounts they form a solid solution melting at 67–68°.



$$C_9H_{11}\overset{\overset{\displaystyle OCH_3}{|}}{C}{=}CHCN$$

I (a,b)

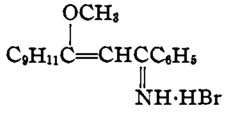
The action of phenylmagnesium bromide was essentially the same on the two forms, and most

---

[1] Fuson, Ullyot and Gehrt, THIS JOURNAL, **60**, 1199 (1938).

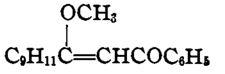
of the studies were carried out with the mixture. In general five moles of the Grignard reagent was used for each mole of the nitrile.[2] In all runs some unchanged nitrile was recovered. This was always the low-melting form of the nitrile (Ia) even when the starting material was the high-melting form (Ib) or the mixture. Evidently the high-melting form underwent isomerization at least in part.

The expected imine hydrobromide (II) and its hydrolysis product, the keto ether (III), were isolated. The diketone (IV) and its imino derivative (V) were also produced.



$$C_9H_{11}\overset{\overset{OCH_3}{|}}{C}=CH\underset{\underset{NH\cdot HBr}{\|}}{C}C_6H_5$$

II

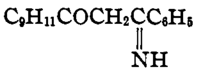


$$C_9H_{11}\overset{\overset{OCH_3}{|}}{C}=CHCOC_6H_5$$

III

$C_9H_{11}COCH_2COC_6H_5$

IV



$$C_9H_{11}COCH_2\underset{\underset{NH}{\|}}{C}C_6H_5$$

V

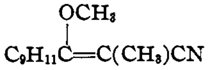
When heated the imine hydrobromide (II) decomposed into the imino ketone (V) and methyl bromide. The latter was identified by conversion to methylquinolinium bromide.

The keto ether (III) was synthesized by methylation of the diketone (IV) with sodium amide and methyl sulfate. This reaction is an interesting example of the tendency of the mesityl radical to promote O-alkylation. Dibenzoylmethane, by contrast, gives only C-methylation.

The imino ketone (V) was made by treatment of the diketone with ammonia under pressure. It is interesting to note that under similar conditions dibenzoylmethane and 1,1-dibenzoylethane undergo chain cleavage.

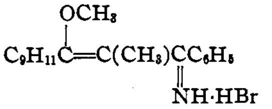
The diketone could be obtained from the imine hydrobromide (II), the keto ether (III) or the imino ketone (V) by hydrolysis with alcoholic hydrochloric acid.

α-Methyl-β-methoxy-β-mesitylacrylonitrile (VI) reacted with phenylmagnesium bromide in much the same fashion as did the methoxyacrylonitrile (I).



$$C_9H_{11}\overset{\overset{OCH_3}{|}}{C}=C(CH_3)CN$$

VI

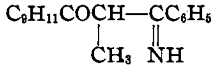


$$C_9H_{11}\overset{\overset{OCH_3}{|}}{C}=C(CH_3)\underset{\underset{NH\cdot HBr}{\|}}{C}C_6H_5$$

VII

$$C_9H_{11}CO\underset{\underset{CH_3}{|}}{C}HCOC_6H_5$$

VIII



$$C_9H_{11}CO\underset{\underset{CH_3}{|}}{C}H-\underset{\underset{NH}{\|}}{C}C_6H_5$$

IX

The products were the imine hydrobromide (VII) and the diketone (VIII). The former resembled the lower homolog (II); it was decomposed by heat to give methyl bromide. The expected imine (IX) could not be induced to crystallize. The oil, however, gave the diketone (VIII) when hydrolyzed, indicating that the imine was present. The diketone (VIII) likewise failed to crystallize and was identified by the fact that it gave a positive ferric chloride test and a copper derivative. Finally, it was synthesized from propiomesitylene by a method to be reported later.

Experimental Part

Action of Phenylmagnesium Bromide on β-Methoxy-β-mesitylacrylonitrile (I).—A number of experiments were conducted on each isomer. The general procedure was as follows.

An ether solution of phenylmagnesium bromide was prepared from bromobenzene and magnesium in a three-necked flask equipped with a mercury-sealed stirrer, a reflux condenser and a dropping funnel. An ether solution of the nitrile was added dropwise to the Grignard reagent. The reaction mixture was then refluxed, with stirring, cooled, and decomposed by pouring it into a beaker of ice to which sulfuric acid had been added. In early experiments hydrochloric acid was used but was found unsatisfactory because the product apparently consisted of a mixture of the hydrobromide and hydrochloride.

On decomposition of the reaction mixture a yellow solid (X) formed. This was collected on a filter and aqueous and ether layers were separated. The ether layer was washed with water, dried over sodium sulfate and evaporated. In the case of each isomer some unchanged Ia was recovered.

The aqueous layer was allowed to stand for several days in an open beaker. During this time two crystalline substances were deposited, one in the form of fine needles (III) and the other as short stubby crystals (II). These could be separated by hand or III could be dissolved in hot high-boiling ligroin leaving II unaffected. A further quantity of these substances could be obtained by moderately warming the aqueous solution on a steam-bath and blowing a stream of air across the solution until the volume was reduced to a point where magnesium sulfate began to crystallize.

In some of the experiments the aqueous filtrate was concentrated by vigorous heating on a steam-bath and with a current of air. An oily sticky substance was deposited. The aqueous layer was decanted and the oily material was extracted with ether. The residue was crystallized from methyl alcohol. The diketone (IV) was obtained. Dilution of the filtrate produced a small amount of V. From the ether solution a further quantity of IV was isolated.

The following summarizes the results of nine experiments.

---

[2] See Shriner and Turner, This Journal, **52**, 1267 (1930).

	Moles of nitrile		Moles of Grignard reagent	Time, hours	Products isolated, g.					
					Ia	II	III	IV	V	X
1	Ia	0.050	0.080	3 (refluxing)	1.0	[a]	[a]	...	...	[a]
2	Ia	.027	.049	1 (room temp.)	1.8	1.0	0.1	...	...	[a]
3	Ic	.100	.472	2 (room temp.)	...	[a]	[a]	4.2	[a]	7.0
4	Ic	.100	.472	7 (refluxing)	...	[a]	[a]	[a]	[a]	[a]
5	Ic	.050	.148	9 (room temp.)	3.0	...	2.5	...	...	[a]
6	Ic	.100	.362	5 (refluxing)	2.5	8.3	...	...	1.8	2
7	Ic	.025	.023	1.5 (room temp.)	2.3	1.0	[a]	...	...	...
8	Ic	.025	.092	4 (refluxing)	1.0	2.5	1.1	...	...	0.1
9	Ib	.027	.069	2.5 (refluxing)	0.5	1.0	...	...	...	4.0

[a] Product isolated but not weighed.

In most of the experiments, during the interaction of the Grignard with the nitrile, an insoluble layer precipitated. In experiment seven the upper ethereal solution was decanted. The remaining viscous material was decomposed with ice and acid. This mixture was extracted with ether. The aqueous layer was added to the main part of the reaction mixture. By drying and evaporating the ether solution 1.6 g. of Ia was isolated.

In order to find conditions which would favor the formation of the yellow solid (X) the following experiments were carried out.

Forty-five grams of Ic was caused to react with phenylmagnesium bromide prepared from 16.2 g. of magnesium and 105 g. of bromobenzene. Ether was distilled from the reaction mixture until the contents of the reaction flask became sirupy. Heating at the temperature of the steam-bath was continued one hour longer. Ether was added to the reaction mixture and the subsequent procedures were as previously described. A greatly increased yield of X was obtained.

In another experiment the same quantities of reactants were used but the ether was not removed. Two grams of X was obtained.

A description of the various products follows.

(a) **1-Mesityl-1-methoxy-3-phenyl-1-propene-3-imine Hydrobromide** (II).—It is insoluble in benzene, petroleum ether, and carbon tetrachloride but soluble in alcohol, and hot chloroform. It is somewhat soluble in water but less so in aqueous salt solutions. Purification was best accomplished by dissolving it in a minimum amount of warm methyl alcohol, adding ether and cooling. Colorless needles were obtained. The melting point varied between 110 and 130°.

Anal. Calcd. for $C_{19}H_{22}ONBr$: C, 63.32; H, 6.15; N, 3.89. Found: C, 63.38, 63.25; H, 6.44, 6.32; N, 3.86.

Melting was accompanied by decomposition, methyl bromide being eliminated with the resulting formation of V. The evolved methyl bromide was converted into methylquinolinium bromide which was identified by a mixed melting point determination with an authentic sample.

Hydrolysis of II with alcoholic hydrochloric acid converted it into 2,4,6-trimethyldibenzoylmethane.

(b) **1-Mesityl-1-methoxy-3-phenyl-1-propene-3-one** (III).—This substance was obtained as colorless needles by crystallization from high-boiling ligroin; m. p. 111.5–112.5°.

Anal. Calcd. for $C_{19}H_{20}O_2$: C, 81.46; H, 7.19; OCH_3, 11.77. Found: C, 81.45, 81.51; H, 7.49, 7.05; OCH_3, 11.58, 11.58.

(c) **1-(2,4,6-Trimethylbenzoyl)-2-phenyl-2-iminoethane** (V).—The product crystallized from methyl alcohol as colorless needles; m. p. 145.5–146.5°. It is insoluble in acid and alkali. Hydrolysis with alcoholic hydrochloric acid transformed it into 2,4,6-trimethyldibenzoylmethane.

Anal. Calcd. for $C_{18}H_{19}ON$: C, 81.48; H, 7.20; N, 5.26. Found: C, 81.6; H, 7.16; N, 5.07.

Methylquinolinium Bromide.—Methyl bromide was passed into quinoline. The solution was allowed to stand a short time and then benzene was added. The solid so obtained was crystallized by dissolving it in methyl alcohol and adding several volumes of ether; m. p. 96–97°. Trowbridge[3] gives the melting point as 70°.

Anal. Calcd. for $C_{18}H_{10}NBr$: Br, 35.7. Found: **Br**, 36.0, 36.0.

1-Mesityl-1-methoxy-3-phenyl-1-propene-3-one (III).—A mixture of 1.46 g. of powdered sodamide, 10 g. of 2,4,6-trimethyldibenzoylmethane and 250 cc. of benzene was heated until ammonia was no longer evolved. A colorless solid formed. The reaction flask was then cooled in an ice-bath and 5 g. of methyl sulfate was added dropwise. The mixture was refluxed until the precipitate disappeared and an orange-yellow solution resulted. This was washed with water and the solvent was removed by distillation. The residue was crystallized from high-boiling ligroin: yield 6.3 g.; m. p. 111.5–112.5°. In another preparation 21 g. of product was obtained from 30 g. of starting material.

Synthesis of 1-(2,4,6-Trimethylbenzoyl)-2-phenyl-2-iminoethane (V).—Twenty grams of 2,4,6-trimethyldibenzoylmethane was dissolved in 500 cc. of methyl alcohol which had been saturated with ammonia at room temperature. The solution was placed in a glass-lined steel bomb and the bomb was heated in an oil-bath at 130–140° for twelve hours. The resulting slightly yellow solution was evaporated and the residue was crystallized from methyl alcohol: yield 12.5 g.; m. p. 145.5–146.5°.

In one experiment in which a glass liner was not used in the bomb the chief product was a red iron complex. This could be broken down to the starting material with hydrochloric acid.

Action of Methyl Alcoholic Ammonia on Dibenzoylmethane and · 1,1-Dibenzoylethane.—Treatment of dibenzoylmethane and 1,1-dibenzoylethane according to the above procedure converted them into benzamide and acetophenone and propiophenone, respectively.

The Action of Phenylmagnesium Bromide on α-Methyl-β-methoxy-β-mesitylacrylonitrile (VI).—One and one-

---

[3] Trowbridge, THIS JOURNAL, **21**, 66 (1899).

tenth grams of magnesium in 25 cc. of ether in a three-necked flask equipped with a mercury-sealed stirrer, a reflux condenser, and a dropping funnel, was converted into phenylmagnesium bromide by 7.3 g. of bromobenzene dissolved in 25 cc. of ether. Two grams of VI dissolved in 40 cc. of dry, thiophene-free benzene, was added dropwise to the Grignard reagent. The water was drained from the reflux condenser, and the reaction mixture was heated for six hours. Stirring was maintained constantly. The ether was removed from the reaction mixture in this way. Stirring was discontinued, and the reaction mixture was refluxed for fourteen hours and decomposed by pouring into a beaker of ice containing a little sulfuric acid. A small precipitate of the imine hydrobromide formed and was collected on a filter. The benzene layer was separated from the water layer, and the aqueous layer was extracted with ether. The combined ether–benzene solution was dried quickly over calcium chloride, and the solvents were removed by distillation. The residue crystallized on cooling, more of the imine hydrobromide being obtained. This was crystallized from benzene. Crystallization was also carried out by dissolving it in a minimum amount of methyl alcohol and adding several volumes of ether. The latter method produced colorless needles: yield 1.3 g.; m. p. 110–130°, with decomposition.

Anal. Calcd. for $C_{20}H_{24}ONBr$: C, 64.18; H, 6.42; N, 3.74. Found: C, 64.18; H, 6.68; N, 3.98.

Methyl bromide was shown to be evolved by melting a sample and passing the evolved gas into quinoline. Methylquinolinium bromide was obtained and identified by a mixed melting point determination.

The aqueous solution was allowed to stand in an open beaker; as evaporation proceeded an oil formed. This was taken up in ether; the ether solution was shaken with a solution of cupric acetate and became deep green in color. Evaporation of the ether solution left a dark green copper derivative. This was dissolved in ether and decomposed by shaking with hydrochloric acid. The ether solution was dried over calcium chloride and evaporated. The remaining oil gave a strong enol test but did not crystallize. The oil was again converted into the copper derivative, and the derivative was recrystallized by dissolving it in hot benzene, adding ligroin and cooling. The composition was that calculated for the copper derivative of VIII.

Anal. Calcd. for $(C_{19}H_{19}O_2)_2Cu$: C, 73.34; H, 6.16; Cu, 10.2. Found: C, 73.41; H, 6.58; Cu, 10.1.

The copper was determined by weighing the copper oxide remaining after the combustion determination. In another experiment, 3 g. of the hydrobromide was obtained from 3 g. of nitrile (VI).

The product obtained from melting the hydrobromide, which is probably the imine, could not be induced to crystallize. However, hydrolysis of this substance with alcoholic hydrochloric acid converted it into an oil (VIII) which formed a copper derivative and gave a strong ferric chloride test.

The imine hydrobromide was likewise converted, by boiling with alcoholic hydrochloric acid, into an oil (VIII) which gave a ferric chloride test and formed a copper derivative.

Summary

The isomeric β-methoxy-β-mesitylacrylonitriles (I) react with phenylmagnesium bromide to give the corresponding imino hydrobromide (II) and its hydrolysis product, the keto ether (III), as well as the diketone (IV) and its imino derivative (V). The three last-named products have been synthesized by other methods.

Similar results were obtained with α-methyl-β-methoxy-β-mesitylacrylonitrile (VI) and phenylmagnesium bromide.

URBANA, ILLINOIS RECEIVED MARCH 17, 1938

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

The Reaction between Sulfur Dioxide and Olefins. VII.[1] Copolymers from Mixtures of Olefins, Acetylenes, and Olefin Derivatives with Sulfur Dioxide

BY C. S. MARVEL, S. JACK DAVIS AND F. J. GLAVIS

Many copolymers of mixed vinyl derivatives have been described in the literature. The physical and chemical properties of these copolymers are sometimes quite different from those which might be expected from an examination of the polymers made from the individual vinyl derivatives. It has therefore seemed desirable to investigate some of the copolymers from mixtures of olefins or olefinic derivatives and sulfur dioxide in order to learn more about this unusual polymerization reaction.

Treatment of mixtures of olefins with sulfur dioxide in the presence of suitable peroxide catalysts gave polymeric products. These products had approximately the composition which would be expected for copolymers if the olefins had combined in the ratio in which they were introduced into the reaction mixtures. When an equimolecular mixture of olefins was used the product was shown definitely to be a copolymer of the type

[1] For the sixth communication in this series see THIS JOURNAL, 59, 1014 (1937).