the ethereal solution on concentration and addition of petroleum ether gave 4 g. of pure material (XVII), m. p. 173°, recrystallized from ether–petroleum ether or from methyl alcohol.

Anal. Calcd. for $C_{27}H_{22}O$: C, 89.50; H, 6.08. Found: C, 89.30; H, 6.19.

The product (XVII) examined in the Grignard machine gave one mole of gas and consumed one mole of reagent.

Elimination of Water from (XVII) to Give (XVIII).—Eight drops of concentrated sulfuric acid was added to a solution of 2 g. of carbinol (XVII) in 35 cc. of glacial acetic acid. On allowing to stand for three days 1.5 g. of material (XVIII) was deposited. Recrystallized from chloroform–methyl alcohol it gave colorless, glistening flakes, m. p. 258°.

Anal. Calcd. for $C_{27}H_{20}$: C, 94.13; H, 5.87. Found: C, 94.10; H, 5.79.

Half a gram of the hydrocarbon on oxidation with 0.5 g. of chromic acid in glacial acetic acid solution yielded 0.3 g. of anthraquinone and 0.2 g. of benzophenone.

Action of Phenylmagnesium Bromide on Dihydrophenylanthraphenone (XX).—Three and one-half grams of (XX) dissolved in ether was added to a Grignard solution from 0.72 g. of magnesium and 5.7 g. of bromobenzene. On first addition the solution was deep violet in color, gradually changing to red and on continued stirring to pale yellow. Worked up in the usual manner 2.0 g. of crystalline product was obtained, which was separated by fractional crystallization from ether into 1.2 g. of starting material and 0.7 g. of phenylanthraphenone.

Summary

1. Benzalanthrone gives mainly 1,2-addition with methylmagnesium iodide.

2. Ethylidene anthrone exists in an enolic modification involving a 1,7-shift of hydrogen, the anthranol suffering oxidation to a peroxide, which cleaves spontaneously to anthraquinone and vinyl alcohol.

3. Anthraphenone undergoes 1,6-dimolecular reduction on treatment with phenylmagnesium bromide or iodide, and no reaction with methylmagnesium iodide. Dihydroanthraphenone gives normal 1,2-addition.

4. No clean products could be isolated from the reaction between phenylanthraphenone and phenylmagnesium bromide. Dihydrophenylanthraphenone yielded with phenylmagnesium bromide phenylanthraphenone and unchanged material.

5. Striking analogies have been brought forward between meso-unsaturated anthracene ketones and α,β-unsaturated ketones. The analogies are likewise maintained when the unsaturation is removed in both types of ketones.

GREENCASTLE, INDIANA RECEIVED AUGUST 19, 1935

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF COLUMBIA UNIVERSITY]

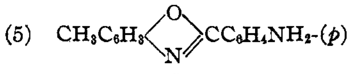
The Preparation and Tinctorial Properties of Certain Benzoxazole Dyes[1]

BY VLADIMIR J. MIKESKA AND MARSTON TAYLOR BOGERT

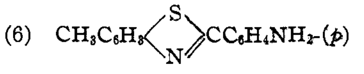
In a previous article,[2] we have pointed out certain of the similarities and dissimilarities which appear on comparing the chemical properties of the structurally related series of oxazoles, thiazoles and imidazoles.

Having been interested for several years in the connection between chemical constitution and tinctorial properties in the thiazole series,[3] we have conducted some experiments also in the oxazole field and the present communication records the results. Our prior paper[2] described the syntheses of the necessary intermediates.

From the standpoint of the dye chemist, the thiazole derivatives of most interest are the intermediates dehydrothio-*p*-toluidine (II) and primuline (III), from which are manufactured dyes of the Thioflavine (IV) (Colour Index No. 815) or Chloramine Yellow (V) (Colour Index No. 814) types; or azo derivatives like the so-called "Ingrain colors" (Colour Index No. 812), prepared by diazotizing (II) or (III), or their sulfonates, and combining with suitable couplers.



(I)



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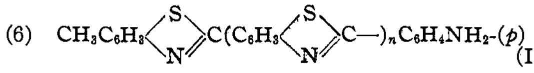

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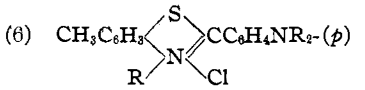

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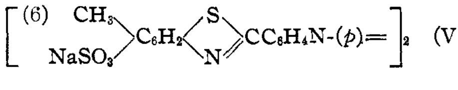

(V)

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[1] Based upon the dissertation submitted by V. J. Mikeska, June, 1934, for the Ph.D. degree under the Faculty of Pure Science, Columbia University, New York, N. Y., to which dissertation the reader is referred for further experimental details and literature citations.—M. T. B.

[2] Mikeska and Bogert, THIS JOURNAL, **57**, 2121 (1935).

[3] Bogert and Allen, *ibid.*, **49**, 1315 (1927).

Our own experiments in the benzoxazole series have been mainly with the azo derivatives and dyes of the Chloramine Yellow class.

In so far as azo dyes of the oxazole, thiazole and imidazole series are concerned, all three yield substantive cotton dyes, which show generally about the same fastness to light, acids or alkalies.[4]

The azo derivatives of benzoxazole described beyond carry the azo grouping either in the *p*-position on the 2-phenyl nucleus, or in position 5 on the benzoxazole portion. One object in preparing these two series was to learn what effect this difference in the location of the azo group would have upon the tinctorial properties of the resulting dyes.

In this part of our research, the investigations of Lellmann and his associates were of especial interest, for Lellmann and Haller[5] prepared an imidazole analog of dehydrothio-*p*-toluidine (II) which, when diazotized and coupled, gave azo dyes as fast to cotton as the corresponding thiazole dyes. This was followed in 1895 by the work of Lellmann and Ebel,[6] who synthesized an oxazole analog (I) from *m*-nitro-*p*-cresol, then diazotized and coupled it. The azo compounds resulting closely resembled the analogous thiazole and imidazole derivatives in the color and fastness of their dyeings.

Our azo dyes, therefore, differed from those of Lellmann and Ebel[6] in carrying a phenyl in place of a methyl group on the benzene portion of the benzoxazole molecule, and from dehydrothio-*p*-toluidine in having this substituent in position 5 instead of 6. It was believed that the phenyl would have certain advantages over the methyl group in increasing the stability of the derivatives and in giving deeper shades on dyeing. The researches of Bogert and Allen,[3,7] in the benzothiazole series, have shown that such a change in the location of the hydrocarbon radical has but little influence upon the color or fastness of the dyeings obtained, and the results reported by Lellmann and his co-workers, in the benzoxazole series, lend support to this view. The replacement of sulfur by oxygen is ordinarily hypsochromic, so far as tinctorial effects are concerned, whereas the substitution of a methyl by a phenyl group, as just mentioned, generally exerts a bathochromic influence. In the case of the dyes synthesized by us, it was interesting to find that the former factor was the more potent one, for all of them gave paler shades than the corresponding dehydrothio-*p*-toluidine derivatives; and a repetition of the work of Lellmann and Ebel[6] showed that neither the depth of shade, nor the fastness of the dyeing, was greatly affected by whether the hydrocarbon radical in position 5 was a methyl or a phenyl.

Of the two amines (or their sulfo acids) used as initial materials for the production of our dyes, *viz.*, 2-*p*-aminophenyl-5-phenylbenzoxazole (A) and 2,7-diphenyl-5-aminobenzoxazole (B), both yielded azo dyes which were substantive for cotton and could be applied either direct or developed in the fabric. Of the two sets of dyes, those prepared from (B) were much the weaker. In other words, the azo grouping in the *p*-position on the 2-phenyl nucleus gives much better dyes than when this same grouping is in position 5 on the benzoxazole nucleus. On silk or wool, however, the (B) dyes also gave good deep shades by either method.

This influence of the position of the azo grouping upon the affinity of these dyes for cotton, coincides with the experience of Kym,[8] who investigated a few azo dyes of these types and found that the dyeings on cotton were much weaker when the azo grouping was moved from the *p*-2-phenyl position to the benzoxazole nucleus.

The same was true in the case of the Chloramine Yellow types obtained from (A) and from (B), those from the former being far superior as direct cotton dyes. Both could be developed in the fabric to deep shades. There was but little difference in depth of color, whether the dyeings were made on cotton, wool or silk, in the case of the (A) dyes; but the dyeings obtained with the (B) dyes on cotton were much paler than those on wool or silk.

In so far as the method of dyeing was concerned, examination of the dyed samples after the lapse of five years, showed in every case that the direct dyed fabric held its color much better than those samples dyed by the "ingrain" process.

Experimental

To economize space in what follows, the two dye intermediates used, *i. e.*, 2-*p*-aminophenyl-5-

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[4] (a) Bayer & Co., German Patent 165,102; *Friedländer*, **8**, 693 (1905); (b) Meister, Lucius and Brüning, German Patent 284,181; *Friedländer*, **12**, 458 (1915); (c) Fischer, *J. prakt. Chem.*, [2] **73**, 436 (1906); (d) Kym, *Ber.*, **44**, 2919 (1911).

[5] Lellmann and Haller, *ibid.*, **26**, 2759 (1893).

[6] Lellmann and Ebel, *ibid.*, **28**, 1128 (1895).

[7] Bogert and Allen, *Ind. Eng. Chem.*, **18**, 532 (1926).

[8] Kym, *Ber.*, **33**, 2847 (1900).

phenylbenzoxazole and 2,7-diphenyl-5-aminobenzoxazole, will be referred to respectively as (A) and (B), and their sulfo acids similarly as (A^1) and (B^1).

I. Azo Dyes from (A) or (A^1)

These dyes are akin to the so-called "Ingrain Colors" of Green,[9] and were prepared in the customary way, by diazotizing the intermediate and combining the diazo product with suitable couplers, the basic dyes being coupled in acid and the acid ones in alkaline solution. All of these products gave good deep shades on cotton, either as direct or as developed dyes.

The direct dyeing was carried out with 1 g. of unbleached cotton, 20 cc. of 0.1% dye solution, 4 drops of 10% sodium carbonate solution, 15 cc. of 1% sodium chloride solution and 25 cc. of water, the bath being heated for thirty minutes. Silk was dyed in a weakly acid bath.

For the developed dyeings, with the sulfo acids for example, the cotton was boiled for thirty minutes in a 5% solution of (A^1) or (B^1), after neutralization with sodium carbonate, and to the boiling solution there was added 5% (by weight) of sodium chloride. After this impregnation, the cloth was washed thoroughly in cold water, to avoid surface colors and subsequent bleeding, and was passed through a bath containing 1 g. of sodium nitrite in 400 cc. of water and faintly acid with sulfuric acid. Diazotization was completed in about twenty minutes and, after washing in cold water, the cotton was immersed in a bath of the coupler selected. If a red color (Oxazole Red) was desired, a 1% solution of beta-naphthol was used dissolved in the calculated amount of caustic alkali and containing an excess of sodium carbonate. The color developed rapidly and after five minutes the cloth was removed and freed from surface dye by thorough washing with cold water and soap. Amines were coupled in acid solution.

The results with the developed dyes can be tabulated as follows.

TABLE I

DEVELOPED AZO DYEINGS FROM (A) OR (A^1)

	Base	Coupler	Shade on cotton	Type
(1)	(A)	α-Naphthol	Bluish-red	Mono-azo
(2)	(A^1)	Phenol	Yellow	Mono-azo
(3)	(A^1)	β-Naphthol	Orange-red	Mono-azo
(4)	(A^1)	Resorcinol	Orange	Mono-azo
(5)	(A^1)	α-Naphthylamine	Purple	Mono-azo
(6)	(5)	α-Naphthylamine	Black	Bis-azo

Through the courtesy of Professor Hal T. Beans and Dr. A. Dingwall, of the Columbia University Department of Chemistry, the two beta-naphthol azo dyes were examined spectrographically and their absorption curves plotted, as shown on Fig. 1. Of these two dyes, the one designated "Ingrain Red" was prepared by diazotizing dehydrothio-*p*-toluidine and coupling with beta-naphthol. The analogous "Oxazole Red" was prepared similarly from (A^1). An examination of the graph will show the similarity of the two curves. Both show maximum absorption at about 4980 Å. Practically all of the blue and none of the red is absorbed in each case. Both transmit a portion of the yellow, so that the dyes have an orange shade, but the oxazole transmits more and is therefore a lighter orange-red than the thiazole dye. Further, the thiazole dye has a wider absorption range and this accounts for its greater intensity. These results are in harmony with previous observations made on the tinctorial properties and the colors of solutions of such dyes. It is quite clear, therefore, that the bathochromic effect of the benzothiazole is slightly but definitely greater than that of the benzoxazole nucleus in dyes of analogous structure.

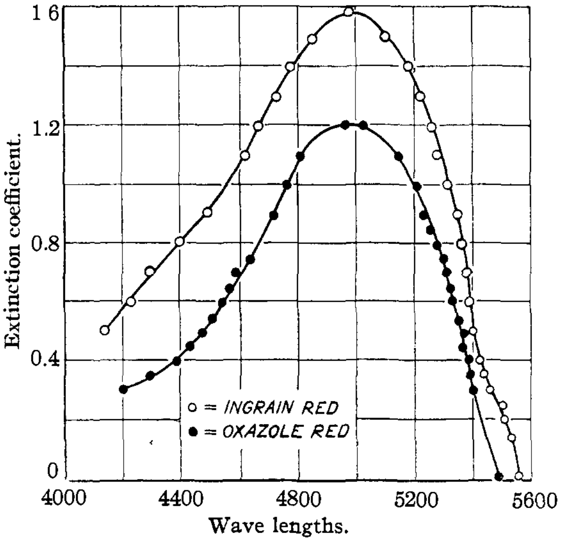

Fig. 1.—Absorption spectra curves.

The solvent for both dyes was 95% ethanol. The concentration of the oxazole was 1:37,500; of the thiazole, 1:50,000.

The fastness of these developed dyes on cotton was tested with the results exhibited in Table II. The dyes are represented by the Arabic numerals used in Table I.

For purposes of comparison, a similar set of developed azo dyes was prepared from 2-*p*-aminophenyl-5-methylbenzoxazole (I), as described by Lellmann and Ebel,[6] and subjected to similar tests for fastness. The results are given in Table III, the Arabic numerals used for the column headings representing the same type of dye as in Table II.

In general, these azo dyes were much the same as the original "Ingrain Colors" of Green,[9] in the thiazole series, prepared from Primuline. Although Green's results showed that there was but little difference between the corresponding dyes prepared from Primuline and from dehydrothio-*p*-toluidine sulfo acid, nevertheless we prepared the same series of dyes as listed above from the latter and our results were in entire accord with his.

Identical dyeings were carried out with the corresponding azo dyes from dehydrothio-*p*-toluidine sulfo acid and from the oxazole analog (A^1). In general, the shade of the thiazole was deeper than that of the corresponding oxazole dye; the red dyes were fastest in both series; in both, the purples were turned brown by alkali, but the original color was restored by acid; the orange dyeings were less fast, and the yellow ones lost most of their color when boiled with 10% sodium hydroxide.

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(9) (a) Green, *J. Soc. Chem. Ind.*, **7**, 179 (1888); (b) *J. Chem. Soc.*, **55**, 229 (1889).

TABLE II

FASTNESS OF DEVELOPED AZO DYEINGS FROM (A) OR (A^1)

Reagent	(1)	(2)	(3)	(4)	(5)	(6)
Boil + 5% HCl	Fair	Fair	Fast	Fast	Fast	Fast
Boil + 10% NaOH	Bleeds	Bleeds	Fair	Bleeds	Browns	Brownish-black
Boil + soap soln.	Bleeds	Bleeds	Fair	Bleeds	Browns	Fair
Bleaching	Bleached	Bleached	Fair	Fair	Browns	Fast
Light	Fugitive	Fugitive	Fair	Fugitive	Fair	Fair

TABLE III

FASTNESS OF DEVELOPED AZO DYEINGS FROM 2-*p*-AMINOPHENYL-5-METHYLBENZOXAZOLE (I)

Reagent	(1)	(2)	(3)	(4)	(5)	(6)
Boil + 5% HCl	Fair	Fair	Fast	Fast	Fast	Fast
Boil + 10% NaOH	Bleeds	Bleeds	Fair	Bleeds	Browns	Browns
Boil + soap soln.	Bleeds	Bleeds	Fair	Bleeds	Browns	Fair
Bleaching	Bleached	Bleached	Fair	Fair	Browns	Fast
Light	Fugitive	Fugitive	Fair	Fugitive	Fair	Fair

II. Azo Dyes from (B) or (B^1)

These were prepared and used in essentially the same manner as already recorded for the azo dyes from (A) or (A^1), *i. e.*, either as direct or as developed dyes ("ingrain colors"), and gave good deep shades on wool or silk by either process. As substantive cotton dyes, however, they were far inferior to those obtained from (A) or (A^1), the shades produced being weak and poor.

The results secured with these as developed dyes, are given in Table IV.

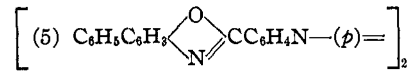
TABLE IV

DEVELOPED AZO DYEINGS FROM (B) OR (B^1)

	Base	Coupler	Shade on cotton	Type
(7)	(B)	α-Naphthol	Saffron	Mono-azo
(8)	(B^1)	Phenol	Yellow	Mono-azo
(9)	(B^1)	β-Naphthol	Orange-red	Mono-azo
(10)	(B^1)	Resorcinol	Orange	Mono-azo
(11)	(B^1)	α-Naphthylamine	Purple	Mono-azo
(12)	(11)	α-Naphthylamine	Black	Bis-azo

Subjected to the same fastness tests as shown in Tables II and III, the results given in Table V were obtained, in which table the Arabic numerals stand for the same dyes as in Table IV.

III. Chloramine Yellow Dyes



$\left[(5)\ C_6H_5C_6H_3\left\langle \overset{O}{\underset{N}{}} \right\rangle CC_6H_4N\text{—}(p)\text{=}\right]_2$

_p,p'_-(5-Phenylbenzoxazole-2)-azobenzene.—A solution of 2 g. of 2-*p*-aminophenyl-5-benzoxazole in 500 cc. of alcohol was treated, at 0–10°, for twenty-four hours with a freshly prepared solution of sodium hypochlorite, the precipitated azo compound collected, washed thoroughly with water, dried and extracted with small portions of hot glacial acetic acid and of toluene, to remove impurities. The insoluble material crystallized from nitrobenzene gave an amorphous brownish-red powder, which did not melt but decomposed above 300°; yield, 1.2 g., or 65.5%.

Anal. Calcd. for $C_{38}H_{24}O_2N_4$: C, 80.21; H, 4.23. Found: C, 79.26; H, 4.22. This low figure for carbon was due to difficulties in eliminating final traces of impurities and in completely burning the compound, because of its azo character and high molecular weight.

The compound was difficultly soluble or insoluble in most of the usual neutral organic solvents. In concentrated sulfuric acid it dissolved to a deep blood-red solution, which color reaction appeared to be a very sensitive one.

A Chloramine Yellow from _p,p'_-(5-Phenyl-benzoxazole-2)-azobenzene.—To a solution of 2 g. of the above azo compound in 4 cc. of concentrated sulfuric acid at 20°, there was added 10 cc. of fuming (50% free sulfur trioxide) sulfuric acid. After standing for twenty-four hours, the mixture was poured upon ice, the orange-red precipitate collected, washed with a cold 15% salt solution, dissolved in dilute sodium hydroxide and the sodium salt precipitated by the addition of alcohol. The dry product was nearly black, but was a deep orange when pulverized. In water, it dissolved freely to an orange-red solution. Its analysis showed it to be a disulfonate.

Anal. Calcd. for $C_{38}H_{22}O_8N_4S_2Na_2$: N, 6.62; S, 8.16. Found: N, 7.25; S, 8.94.

The impossibility of obtaining accurate analytical figures for such dyes is recognized by all dye chemists. The purpose of the analysis was to determine whether our product was a di- or a tetra-sulfo acid, and this it does.

A minute amount was sufficient to impart to concentrated sulfuric acid a deep blood-red color. It dyed cotton, wool or silk, a direct yellow, corresponding closely to com-

TABLE V

FASTNESS OF DEVELOPED AZO DYEINGS FROM (B) OR (B^1)

Reagent	(7)	(8)	(9)	(10)	(11)	(12)
Boil + 5% HCl	Fair	Fair	Fast	Fast	Fast	Fast
Boil + 10% NaOH	Bleeds	Bleeds	Fair	Bleeds	Browns	Browns
Boil + soap soln.	Bleeds	Bleeds	Fair	Bleeds	Browns	Fair
Bleaching	Bleached	Bleached	Fair	Fair	Browns	Fast
Light	Fugitive	Fugitive	Fair	Fugitive	Fair	Fair

mercial Chloramine Yellow in fastness, although somewhat lighter in shade.

The direct dyeing on cotton was carried out as already described for the direct azo dyes.

A Chloramine Yellow from 2-*p*-Aminophenyl-5-phenylbenzoxazole Disulfonic Acid.—A solution of 5 g. of the disulfonic acid in 500 cc. of an aqueous solution of excess of sodium carbonate was boiled for thirty minutes, cooled and filtered. The filtrate was subjected to the action of a freshly prepared sodium hypochlorite solution, at 0–10°, for twelve hours, maintaining a slight excess of hypochlorite (as indicated by potassium iodide paper), or until the solution became yellowish-orange, after passing through an intermediate red stage. The dye was then salted out, washed with a 15% salt solution, dissolved in dilute sodium hydroxide and the sodium salt precipitated by the addition of alcohol. The final product resembled closely the dye described in the immediately preceding paragraph, except that the shade produced on cotton was a very pale greenish-yellow. Chemically it differed from the latter in being a tetra- instead of a di-sulfonic acid.

A Chloramine Yellow from 2-*p*-aminophenyl-5-methylbenzoxazole was also prepared by the customary procedure of sulfonation and hypochlorite oxidation and was found to resemble closely the above dye, in its direct dyeings on cotton, both as to shade and fastness.

A Chloramine Yellow from 2,7-diphenyl-5-aminobenzoxazole sulfonic acid, prepared similarly, dyed both wool and silk good deep shades. Its direct dyeings on cotton, however, were much paler and weaker than those obtained with the Chloramine Yellows from the 2-*p*-aminophenyl-5-phenyl- or 5-methylbenzoxazole sulfo acids.

Summary

1. From 2-*p*-aminophenyl-5-phenylbenzoxazole, 2,7-diphenyl-5-aminobenzoxazole, and their sulfo acids, azo dyes have been prepared, of mono- or bis-azo type, as well as some of Chloramine Yellow structure.
2. The tinctorial properties of these new dyes have been studied and it has been shown that those in which the azo grouping is in the *p*-position on the 2-phenyl nucleus are far better substantive cotton dyes than those having this grouping in position 5 on the benzoxazole portion of the molecule.
3. Azo dyes of Ingrain Red type, in the thiazole and oxazole series, were examined spectroanalytically. The curves plotted from these observations paralleled each other closely.
4. In general, these benzoxazole dyes resemble the analogously constituted benzothiazoles but, as expected, give lighter shades.

NEW YORK, N. Y.

RECEIVED AUGUST 21, 1935

[CONTRIBUTION FROM THE CONVERSE MEMORIAL LABORATORY OF HARVARD UNIVERSITY]

The Structure of the Metallic Derivatives Which Are Formed by Adding Grignard Reagents to Unsaturated Ketones

BY E. P. KOHLER, M. TISHLER AND H. POTTER

It is known that when a Grignard reagent is added to an α,β-unsaturated ketone which has a hydrocarbon residue in the α position, the product is an enolate in which a magnesium halide group is joined to oxygen. In all other addition products obtained in this manner the location of the halide residue is uncertain. Magnesium compounds of the type of these addition products can now be obtained in other ways. Thus the magnesium bromide derivative of β,β-diphenylpropionylmesitylene may be prepared by any of the three reactions which are represented by the equations

(1) $C_6H_5CH{=}CHCOC_6H_2(CH_3)_3 + C_6H_5MgBr \longrightarrow [(C_6H_5)_2CHCHCOC_6H_2(CH_3)_3]MgBr$

(2) $(C_6H_5)_2CHCH_2COC_6H_2(CH_3)_3 + C_2H_5MgBr \longrightarrow [(C_6H_5)_2CHCHCOC_6H_2(CH_3)_3]MgBr + C_2H_6$

3) $(C_6H_5)_2CHCHBrCOC_6H_2(CH_3)_3 + C_2H_5MgBr \longrightarrow [(C_6H_5)_2CHCHCOC_6H_2(CH_3)_3]MgBr + C_2H_5Br$

In appearance, in solubility and in many of their chemical properties the magnesium derivatives which are obtained in these various ways seem to be identical but their reactions with benzoyl chloride show that they are not. When the derivative that is formed in the first reaction is treated with benzoyl chloride at least 96% of the product is a benzoyl derivative which melts at 161°, while similar treatment of the magnesium derivative obtained by either of the other two methods leads to an equally high yield of an isomeric benzoyl derivative melting at 148°. These results are not affected by the solvents used or the temperature at which the successive operations are conducted. And in the case of the second and third reactions the nature of the Grignard reagent is likewise of no moment. These reactions—the one addition and the other substitution—therefore give rise to two isomeric magnesium compounds.