3(β)-Acetoxy-Δ⁵-norcholesten-25-one Diacetylhydrazone.—This compound was prepared from 3(β)-acetoxy-Δ⁵-norcholesten-25-one semicarbazone in the manner described for the preparation of II and was isolated by extraction with ether according to the procedure for the isolation of V. The pure product melted at 121–122°.

Anal. Calcd. for $C_{32}H_{50}O_4N_2$: C, 72.96; H, 9.57. Found: C, 73.51; H, 9.63.

Acetophenone Acetylhydrazone.—Six grams of acetophenone semicarbazone, 6 cc. of acetic acid, and 3.9 cc. of acetic anhydride were boiled under reflux for five hours. All substances which were volatile at 150° were distilled, and the residue was treated with water. The crystallizate which formed was filtered and washed with water. It weighed 2.60 g. and melted at 98–110°. On recrystallization from methanol, 0.85 g. of yellow prisms of m. p. 121–122° was obtained. The melting point of a mixture of this substance and of methyl phenyl ketazine was unchanged.

The filtrate yielded 0.55 g. of substance; m. p. 113–119°. After recrystallization from methanol the almost white crystallizate melted at 126°, undepressed on admixture with acetophenone acetylhydrazone. The latter compound was also prepared from acetophenone and 1.6 equivalents of acetohydrazide in ethanol; yield of pure substance, 75%; m. p. 131–132°.

Anal. Calcd. for $C_{10}H_{12}ON_2$: C, 68.15; H, 6.87; N, 15.90. Found: C, 68.19; H, 6.67; N, 15.78.

Methyl Phenyl Ketazine.—This compound was prepared by heating acetophenone semicarbazone.[2a] After one recrystallization from methanol, yellow prisms of m. p. 121.5–122° were obtained; reported,[2a] 121°.

Acetone Diacetylhydrazone.—Thirty-four grams (0.30 mole) of acetone semicarbazone was boiled under reflux for five hours with 108 cc. (1.90 moles) of acetic anhydride and 200 cc. of pyridine. The mixture was then distilled through a column at 20 mm. pressure. Most of the solution distilled below 60°. That which distilled at 85–92°, 23 g. (50%), was retained and redistilled. The fraction which distilled at 84–85° and 20 mm. was analyzed.

Anal. Calcd. for $C_7H_{12}O_2N_2$: N, 17.94. Found: N, 18.14.

When the distillation of the hydrazone was attempted at atmospheric pressure, it decomposed with evolution of a gas at about 170° When the hydrazone was heated with concentrated hydrochloric acid in ethanol, hydrazine dihydrochloride was formed.

N,N′-Diacetylhydrazine.—A mixture of 1.56 g. of acetone diacetylhydrazone, 0.18 g. of water, and 2 cc. of acetic acid was boiled under reflux for one-half hour and evaporated *in vacuo*. When benzene was added to the residue, a crystallizate formed at once. After having stood one hour in the cold it was filtered; weight, 0.84 g. (72%); m. p. 122–129°, softening at 103°. Although the compound appeared to be dry, it melted at 138–139° after drying *in vacuo* at 78°. On recrystallization from ethanol it melted at 139.0–139.5°, and the melting point of a mixture of the compound with N,N′-diacetylhydrazine was unchanged.

Anal. Calcd. for $C_4H_8O_2N_2$: C, 41.37; H, 6.94. Found: C, 41.21; H, 6.96.

A sample of N,N′-diacetylhydrazine was prepared by boiling 5.00 g. (0.10 mole) of hydrazine hydrate with 30.0 cc. (0.30 mole) of acetic anhydride under reflux for ninety minutes. After distillation of the volatile substances *in vacuo*, the residue was recrystallized from methanol. The colorless crystals weighed 10.4 g. (90%); m. p. 139–139.5°; reported[11] 138°.

Acetone Acetylhydrazone.—Attempts to prepare this compound from acetone semicarbazone and the calculated quantity of acetic anhydride in acetic acid led only to small quantities of the diacetylhydrazone.

The monoacetylhydrazone was prepared when 0.74 g. (0.01 mole) of acetohydrazide and 2.35 g. (0.04 mole) of acetone were boiled under reflux for thirty minutes. The cooled mixture gave 0.96 g. of white needles (84%); m. p. 138–139.5°. On recrystallization from methanol the substance melted at 139.5–140°.

Anal. Calcd. for $C_5H_{10}ON_2$: N, 24.55. Found: N, 24.54.

Summary

Semicarbazones of ketones may be converted into the corresponding acetylhydrazones and diacetylhydrazones by heating with acetic anhydride. A mechanism for this reaction and for similar reactions is advanced.

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[11] Stollé, *Ber.*, **32**, 796 (1899).

SUMMIT, NEW JERSEY RECEIVED SEPTEMBER 18, 1946

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

The Reaction of Aryllithium Compounds with 2-Arylquinolines

BY HENRY GILMAN AND GORDON C. GAINER

Incidental to the preparation of 2-(*p*-aminophenyl)-quinoline from quinoline and the lithium salt of *p*-aminophenyllithium, a secondary product was isolated. This was considered to be a 2,4-disubstituted quinoline which may have formed as a consequence of 1,4-addition to the previously formed 2-substituted quinoline. In order to throw light on the structure of the compound, as well as to examine the generality of the reaction, 2-phenylquinoline was brought into reaction with phenyllithium.

Ziegler and Zeiser[1] obtained from a reaction between quinoline and *n*-butyllithium not only the expected 2-*n*-butylquinoline but an isomeric by-product (isolated as the picrate) which they considered to be 4-*n*-butylquinoline. However, the quantity of this product was insufficient to make identification decisive. Also, from a reaction between quinoline and phenyllithium they isolated in addition to 2-phenylquinoline a small quantity of a lower melting product which they suggested might be 4-phenylquinoline. Then Bergmann and Rosenthal[2] reported that reaction of quinoline and benzylmagnesium chloride gave 2-benzylquinoline and small quantities of 4-benzylquinoline and 2,4-dibenzylquinoline. The picrate of their 4-benzylquinoline had a melting point in agreement with that reported for 4-benzylquinoline prepared by another method.

From our reaction of 2-phenylquinoline with phenyllithium there was obtained a compound melting at 86–87°. This compound was not 2,4-

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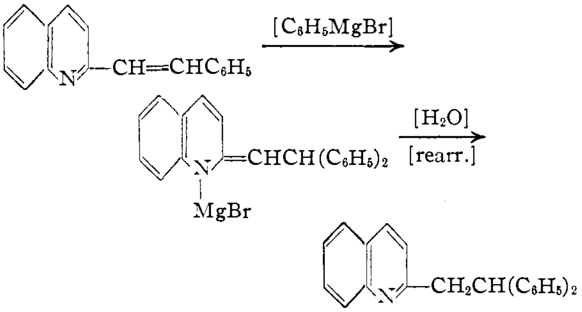
[1] Ziegler and Zeiser, *Ann.*, **485**, 174 (1931).

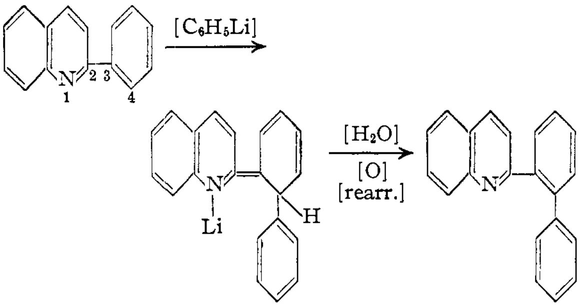
[2] Bergmann and Rosenthal, *J. prakt. Chem.*, [2] **135**, 274 (1932).

diphenylquinoline which has been prepared by another procedure[3] and which melts at 112°. However, on the basis of analysis a phenyl group and hydrogen had added to 2-phenylquinoline to give the product melting at 86–87°.

We next considered the possibility of another type of 1,4-addition of phenyllithium to 2-phenylquinoline. It is known[4] that a lateral-nuclear 1,4-addition takes place in the reaction of benzophenone-anil and phenylmagnesium bromide to give *o*-phenylbenzohydrylaniline. Furthermore, Fuson and co-workers[5] have shown that phenylmagnesium bromide adds in the 1,4-position to the related lateral-nuclear conjugated system of benzalquinaldine to give α-benzohydrylquinaldine.

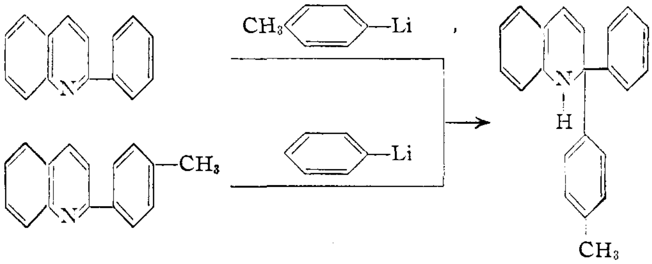


If an analogous reaction occurs with 2-phenylquinoline and phenyllithium then 2-(*o*-biphenylyl)-quinoline should result in accordance with the following sequence of reactions



We observed, however, that the product of the reaction between quinoline and *o*-biphenylyllithium was unlike that obtained from 2-phenylquinoline and phenyllithium.

Despite the attractiveness of the postulated addition to a conjugated system, based on the earlier work mentioned with quinoline as well as on the known 1,4-addition of organomagnesium[2] and organolithium[1] compounds to acridine,[6] it appeared that a simpler mode of addition might be involved. A 1,2-addition of phenyllithium to the azomethine linkage of 2-phenylquinoline should give, subsequent to hydrolysis, 2,2-diphenyl-1,2-dihydroquinoline. Apparently, compounds of this type have not been prepared.



However, this type of addition could be demonstrated by comparing the product of two separate reactions. If the compound melting at 86–87° were 2,2-diphenyl-1,2-dihydroquinoline, then the product from reaction of 2-phenylquinoline and *p*-tolyllithium should be identical with the product from reaction of 2-*p*-tolylquinoline and phenyllithium. This was shown to be the case by the method of mixed melting points.

It should be stated that in a reaction of *p*-biphenylyllithium with quinoline to give 2-(*p*-biphenylyl)-quinoline there was no need to oxidize the intermediate dihydro derivative, for lithium hydride was eliminated smoothly at the boiling point of ether to give an 82% yield of the 2-substituted quinoline. The 2-(*p*-biphenylyl)-quinoline was not prepared to rule out the remote possibility of 1,6-addition of phenyllithium to 2-phenylquinoline. Actually the reaction was forced on us when in a series of experiments it was discovered that the supposedly pure commercial *o*-bromobiphenyl was contaminated with *p*-bromobiphenyl.

Experimental

2,2-Diphenyl-1,2-dihydroquinoline.—To a solution of 40 g. (0.2 mole) of 2-phenylquinoline[1] in 200 cc. of ether was added (with stirring and in a dry nitrogen atmosphere) 0.3 mole of phenyllithium[7] in 350 cc. of ether. The solution immediately turned dark green in color and a small quantity of a yellow precipitate formed. After stirring and refluxing for twelve hours, the mixture was hydrolyzed by pouring into water. The dark color in the ether was replaced by a deep red color, and then the solution assumed a pale yellow color. A small amount of insoluble yellow material was removed by filtration; the ether was removed by distillation; 50 cc. of nitrobenzene[8] was added; and the solution was heated for one-half hour in an oil-bath at 190–200°, during which time no reaction appeared to occur. Subsequent to removal of the nitrobenzene under reduced pressure (0.5 mm.), unreacted 2-phenylquinoline was distilled off at 0.02–0.03 mm., and then 36 g. of material was collected as a thick glassy distillate at 155–165° (0.02–0.03 mm.), the metal-bath temperature being 225–250°.

It was found that the glassy material when heated with warm dilute hydrochloric acid (1:1) in the presence of a little ethanol gave a highly insoluble tan-colored powder, which on drying weighed 22 g. (35%) and melted with decomposition over the range 150–168°. The treatment

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[3] Beyer, *Ber.*, **20**, 1772 (1887).

[4] Gilman, Kirby and Kinney, THIS JOURNAL, **51**, 2252 (1929).

[5] Hoffman, Farlow and Fuson, *ibid.*, **55**, 2000 (1933).

[6] 2-Phenylquinoline may be viewed formally as an open-model of acridine: see Gilman and Spatz, THIS JOURNAL, **66**, 623 (1944), and Gilman, Towle and Spatz, *ibid.*, **68**, 2017 (1946).

[7] Gilman, Zoellner and Selby, THIS JOURNAL, **54**, 1957 (1932).

[8] The nitrobenzene was added as a routine procedure to effect any possible dehydrogenation.

with dilute hydrochloric acid was particularly effective because it dissolved out residual 2-phenylquinoline.

On treatment of the hydrochloride with an excess of warm (60°) sodium hydroxide solution, a viscous brown-colored oil resulted. After decantation, and washing several times with cold water, the oil solidified. The solid was dissolved in 95% ethanol, charcoaled, filtered, and on slow cooling there was obtained 13 g. (23%) of colorless needles melting at 82–84°. The product for analysis melted at 86–87° after crystallization from petroleum ether (b. p., 60–68°) to which a few drops of benzene had been added.

Anal. Calcd. for $C_{21}H_{17}N$: N, 4.98. Found: N, 5.13.

2-Phenyl-2-(*p*-tolyl)-1,2-dihydroquinoline. [A] **Reaction of 2-Phenylquinoline with *p*-Tolyllithium.**—In essential accordance with the procedure described for the preparation of 2,2-diphenyl-1,2-dihydroquinoline, a reaction was carried out between 40 g. (0.2 mole) of 2-phenylquinoline in 500 cc. of ether and 0.3 mole of *p*-tolyllithium in 375 cc. of ether. The solution, which immediately turned dark brown in color, was refluxed for twelve hours. The yield of glassy distillate, which distilled over the range 172–182° (0.004 mm.), was 27 g. (45.5%). The insoluble hydrochloride formed satisfactorily when the temperature was held below 20°, and in this manner separation was effected from unreacted 2-phenylquinoline. Liberation of the base by means of 10% sodium hydroxide solution, followed by crystallization from petroleum ether (b. p., 60–68°) gave colorless crystals melting at 83–84°. It was found helpful to add about .5% of absolute ethanol to the petroleum ether to inhibit oil formation. The melting point after recrystallization from absolute ethanol was 85.5–87°.

[B] **Reaction of 2-(*p*-Tolyl)-quinoline with Phenyllithium.**—From 22 g. (0.1 mole) of 2-(*p*-tolyl)-quinoline in 300 cc. of ether and 0.15 mole of phenyllithium in 190 cc. of ether there was obtained 15 g. (51%) of a thick, viscous glass which distilled over the range 175–185° (0.01 mm.). Crystallization by the procedure mentioned in [A] gave a product which melted at 85–86°, and this compound was shown to be identical with the product from [A].

Anal. Calcd. for $C_{22}H_{19}N$: N, 4.72. Found: N, 4.84 and 4.91.

2-(*o*-Biphenylyl)-quinoline.—To 25 g. (0.2 mole) of freshly distilled quinoline in 50 cc. of dry ether was added 0.076 mole of *o*-biphenylyllithium (prepared in 80% yield from 0.095 mole of *o*-bromobiphenyl and 0.21 g. atom of lithium). A yellow precipitate separated, and the mixture was refluxed with stirring for twelve hours. Subsequent to hydrolysis by pouring into water, the ether layer was separated and dried. To the oil remaining after removal of the ether was added 15 cc. of nitrobenzene and the solution was heated for one-half hour at 180–190°. Following removal of the excess of nitrobenzene and quinoline at about 0.5 mm. there was obtained 14 g. (50%) of a thick viscous glass which distilled at 162–166° (0.007 mm.). The compound, purified by crystallization from 95% ethanol, melted at 102–103°.

Anal. Calcd. for $C_{21}H_{15}N$: N, 4.97. Found: N, 5.05.

2-(*p*-Biphenylyl)-quinoline.—By a procedure similar to that described for the *ortho*-isomer, 0.1 mole of quinoline and 0.087 mole of *p*-biphenylyllithium (prepared in 87% yield from *p*-bromobiphenyl) gave 20 g. (82%) of product. Nitrobenzene was not used in this preparation when it was found that of the 20 g. of product 11 g. melting at 175–178° was obtained readily by filtration. Subsequent hydrolysis of the ethereal filtrate yielded 9 g. of compound melting at 165–170°. The melting point reported for 2-(*p*-biphenylyl)-quinoline, prepared by a different procedure, is 175–177°.[9] Recrystallization of our compound from methyl cellosolve gave yellow platelets melting at 178–179°.

Anal. Calcd. for $C_{21}H_{15}N$: N, 4.97. Found: N, 5.10.

Initially, the preparation of *o*-biphenylyllithium was made from a supposedly pure commercial sample of *o*-bromobiphenyl. When the product with lithium was treated with quinoline there were obtained two compounds. These were subsequently identified as 2-(*o*-biphenylyl)-quinoline and 2-(*p*-biphenylyl)-quinoline, the *para*-isomer being formed to a minor extent. These results were confirmed in a duplicate experiment. Then to make certain that no rearrangements were involved in the reaction between quinoline and the supposed *o*-biphenylyllithium two separate sets of experiments were carried out. First, the commercial *o*-bromobiphenyl was shown to be a mixture by treating with lithium and then carbonating to obtain *o*-phenylbenzoic acid and *p*-phenylbenzoic acid (mixed melting points). Second, authentic specimens of *o*-bromobiphenyl and *p*-bromobiphenyl were obtained (the *ortho* by means of the diazo reaction on pure *o*-aminobiphenyl); these RBr compounds were converted to the corresponding RLi compounds; and the RLi compounds were reacted separately with quinoline to give the isomeric compounds whose properties and analyses are reported earlier in this paper.

2-(*m*-Biphenylyl)-quinoline.—Addition of 0.045 mole of *m*-biphenylyllithium (prepared in 72% yield from 0.056 mole of *m*-bromobiphenyl[10] and 0.12 g. atom of lithium) to 0.04 mole of quinoline by a procedure similar to that described for the *ortho*-isomer gave (subsequent to hydrolysis, followed by nitrobenzene oxidation) a thick oil after removal of volatile materials by heating the flask in an oil-bath at 180° and at 0.15 mm. The oil was treated with picric acid in ethanol to give 15 g. (71%) of picrate melting at 174–178°. Recrystallization from methyl cellosolve raised the melting point to 182–184°. The picrate was decomposed by hot 10% sodium hydroxide, and the resulting thick, colorless glass was first washed with water and then converted to the insoluble hydrochloride by treatment with dilute hydrochloric acid. In this manner residual quantities of the more soluble quinoline hydrochloride were removed.

The insoluble hydrochloride was treated with 10% sodium hydroxide solution to give an oil which was dissolved in petroleum ether (b. p., 60–68°). The colorless crystals which came out of this solvent melted at 77–78°, and the m. p. was not raised after recrystallization from 95% ethanol.

Anal. Calcd. for $C_{21}H_{15}N$: N, 4.97. Found: N, 5.05.

The **picrate of 2-(*m*-biphenylyl)-quinoline** was obtained as glistening yellow crystals melting at 184–185°.

Anal. Calcd. for $C_{27}H_{18}O_7N_4$: N, 10.98. Found: N, 11.13.

As in the experiment with the isomeric *ortho* and *para* compounds, the *m*-biphenylyllithium was carbonated to give 90% of crude *m*-phenylbenzoic acid melting at 158–166°, which melted at 165–166° after crystallization from a benzene–petroleum ether (b. p., 60–68°) mixture. The melting point reported for the acid prepared by another procedure is 164°.[11]

2-(*p*-Aminophenyl)-quinoline.—First, the lithium salt of *p*-aminophenyllithium[12] was prepared by a halogen–metal interconversion reaction between 27.5 g. (0.16 mole) of *p*-bromoaniline and 0.47 mole of *n*-butyllithium.[13,14] The mixture was refluxed and stirred for one and one-fourth hours, and after about fifteen minutes a yellow gummy precipitate formed. Then 42 g. (0.32 mole) of freshly distilled quinoline dissolved in an equal volume of ether was added dropwise. The solution assumed a deep red color, the precipitate dissolved slowly, and after stirring and refluxing for twelve hours complete solution

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[9] Steinkopf and Petersdorff, *Ann.*, **543**, 119 (1940).

[10] Marvel, Ginsberg and Mueller, THIS JOURNAL, **61**, 77 (1939).

[11] Shoppee, *J. Chem. Soc.*, 37 (1933).

[12] Gilman and Stuckwisch, THIS JOURNAL, **64**, 1007 (1942), and **63**, 2844 (1941).

[13] Gilman and Stuckwisch, *ibid.*, **65**, 1461 (1943).

[14] The double-titration procedure was used for the quantitative analysis of *n*-butyllithium; see, Gilman and Haubein, *ibid.*, **66**, 1515 (1944).

had been effected. Subsequent to hydrolysis by pouring into water, the ether layer was separated and then dried, and the ether removed by distillation. The residual orange colored oil was heated at 190° for one-half hour with 40 cc. of nitrobenzene to oxidize the intermediate 2-(*p*-aminophenyl)-1,2-dihydroquinoline. Then by distillation under reduced pressure (0.5 mm.) the excess nitrobenzene, unreacted quinoline and 2-*n*-butylquinoline were removed. Further distillation gave 17.5 g. [70% (based on 70% halogen–metal interconversion)][12] of a heavy, viscous orange-colored glassy product which came over in the range 180–190° (0.003 mm.).

This glass was dissolved in hot 95% ethanol, and to the solution was added 55 g. of picric acid in boiling ethanol. After refluxing for 15 minutes, there was obtained 30 g. of mixed picrates which melted over the range 170–190°; and recrystallization from an acetone–95% ethanol mixture gave a m. p. of 188–190°. After extracting 22 g. of the picrates in a Soxhelt extractor with benzene, there remained 20 g. of an orange picrate melting at 194–195°; and from the benzene extract there was obtained 1.8 g. of a yellow picrate melting at 200–210°.

The base, liberated from the orange picrate by dil. ammonium hydroxide, gave 6 g. (33%) of 2-(*p*-aminophenyl)-quinoline which showed no depression in a mixed melting point determination with an authentic specimen prepared by another procedure.[15] The picrate of the authentic specimen was shown to melt at 197–198°, and there was no depression in melting point on admixture with the picrate obtained from the RLi product.

The yellow picrate was decomposed by boiling ammonium hydroxide solution to give a colorless crystalline compound which melted at 148–148.5° after charcoaling and crystallizing from benzene. This compound may be 2-(*n*-butyl)-2-(*p*-aminophenyl)-1,2-dihydroquinoline formed by addition of the lithium salt of *p*-aminophenyllithium to 2-*n*-butylquinoline.[16]

Anal. Calcd. for $C_{19}H_{22}N_2$: N, 10.08. Found: N, 9.60 and 9.75.

The yellow picrate was re-formed by treating a 95% ethanolic solution of the supposed 2-(*n*-butyl)-2-(*p*-aminophenyl)-1,2-dihydroquinoline with a hot ethanolic solution of picric acid. It melted at 220–221° after recrystallization from methyl cellosolve.

Anal. Calcd. for $C_{25}H_{25}O_7N_5$: N, 13.78. Found: N, 13.02 and 13.20.

2-(*p*-Salicylideneaminophenyl)-quinoline.—A mixture of 1 g. (0.0045 mole) of 2-(*p*-aminophenyl)-quinoline and 0.6 g. (0.149 mole) of salicylaldehyde was heated for four hours in a bath held at 150° to give a quantitative yield of product melting at 185–186° after removing the excess salicylaldehyde by washing with 95% ethanol. The sample for analysis melted at 188–188.5° after crystallization from methyl cellosolve.

Anal. Calcd. for $C_{22}H_{16}ON_2$: N, 8.65. Found: N, 8.74.

Summary

2-Phenylquinoline adds phenyllithium to the azomethine linkage to give 2,2-diphenyl-1,2-dihydroquinoline. The general course of this reaction was established by showing that 2-phenyl-2-(*p*-tolyl)-1,2-dihydroquinoline is formed from 2-phenylquinoline and *p*-tolyllithium as well as from 2-(*p*-tolyl)-quinoline and phenyllithium.

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(15) John, *J. prakt. Chem.*, [2] **133**, 13 (1932), and [2] **139**, 97 (1934).

(16) 2-(*n*-Butyl)-quinoline might be expected as a consequence of the prompt addition of any excess of *n*-butyllithium to quinoline.

AMES, IOWA RECEIVED DECEMBER 9, 1946

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, UNIVERSITY OF CALIFORNIA AT LOS ANGELES]

The Absorption Spectra of Some Benzene Derivatives with Unsaturated Side Chains

BY TOD W. CAMPBELL,[1] SEYMOUR LINDEN, SYLVIA GODSHALK AND WILLIAM G. YOUNG

Jones[2] has pointed out that there has been but little work done on the absorption spectra of benzene derivatives with unsaturated side chains, particularly compounds of the type $C_6H_5C{=}C$—C—, where the double bond is in conjugation with the benzene ring. Since work is being done in these Laboratories on the reactions of cinnamylmagnesium chloride, and of the sodium derivative of allylbenzene,[3] which may result in the production of allylic isomers, in which the double bond is either in conjugation or out of conjugation with the benzene ring, it was deemed of interest to study the absorption spectra of a number of compounds of these types.

Sufficient differences appear in the spectra of the compounds studied to make possible a rapid estimation of the composition of a mixture of allylic isomers, provided the spectra of one or both of the pure compounds can be obtained. Furthermore, the nature of a single reaction product, when only one product is obtained,[4] can be determined.

At present, an attempt is being made to elucidate the structure of allylic Grignard reagents[4] by means of their absorption spectra.

Experimental

The spectra reported here were determined by means of the Beckmann quartz photoelectric spectrophotometer. The solvent used was in all cases 95% ethyl alcohol. The compounds examined were either Eastman Kodak Co. white label preparations, which had been redistilled or recrystallized once, or laboratory preparations which had been thoroughly purified by standard methods. Some of the latter group of compounds required special synthetic procedures, which will be discussed in forthcoming publications. It should be noted that the spectra of a number of these compounds appear in the literature[5]; however they were repeated, in order that uniform data could be presented.

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[1] Abbott Laboratories Research Fellow, 1944–1945.

[2] R. Norman Jones, *Chem. Rev.*, **32**, 1–45 (1943).

[3] (a) Young, Ballou and Nozaki, THIS JOURNAL, **61**, 12 (1938); (b) Campbell and Young, *ibid.*, **69**, 688 (1947); (c) Young and Campbell, unpublished results.

[4] For a discussion of the reactions of allylic Grignard reagents, see Young and Roberts, THIS JOURNAL, **68**, 1472 (1946), and preceding papers in this series.

[5] See reference (2), and the "International Critical Tables."