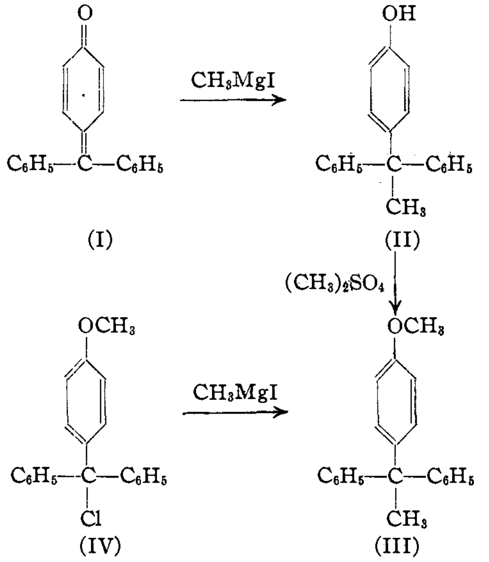
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF DEPAUW UNIVERSITY]

The Action of the Grignard Reagent on Certain Fuchsones[1]

BY PERCY L. JULIAN AND WILLIAM J. GIST

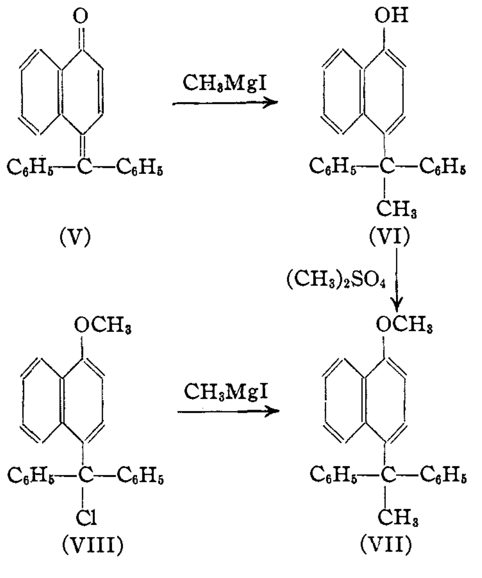
The only conclusively proven case of 1,6-addition of the Grignard reagent to a conjugated system of multiple linkages is the recently reported reaction between this reagent and methylene anthrone.[2] Of the three other cases found in the literature[3] only that one reported by Baeyer and Villiger deserves further attention, since the two cases recorded by Nakanishi have been reinvestigated and shown not to represent 1,6-addition.[2,4]

Baeyer and Villiger suggest without proof that the reaction product which they secure on treating fuchsone (I) with methylmagnesium iodide has the constitution (II). It is, if their assumption is correct, a product formed by 1,6-addition to a conjugated system similar to that found in methylene anthrone.



In connection with an investigation of the hindrance to 1,6-addition offered by various groupings, we have reëxamined the reaction studied by Baeyer and Villiger. To prove the constitution of the phenol (II) we methylated it in the usual manner with methyl sulfate. The product should have the constitution (III). The only other attractive possibility of synthesizing a compound like (III) arises out of Gomberg's observation[4a] that triphenylchloromethane reacts with methylmagnesium iodide, giving 1,1,1-triphenylethane in 70% yield. Accordingly, we treated the triaryl halide (IV) with methylmagnesium iodide, and secured a product identical with (III) obtained by methylating the addition product of Baeyer and Villiger. Their assumption was therefore a good one and the reaction is another case of 1,6-addition.

We have extended this study to include naphthofuchsone (V) and anthrafuchsone (IX). To the former methylmagnesium iodide adds 1,6 as in the case of fuchsone, but in much poorer yield. The constitution of the addition product has been proved in similar fashion, the triaryl halide (VIII) reacting smoothly with methylmagnesium iodide, yielding (VII).



With anthrafuchsone (IX) no trace of 1,6-addition could be detected, and the substance secured is the 1,2-addition product (X), the constitution of which has been proved by oxidation with chromic acid to anthraquinone and benzophenone.

Inasmuch as the completely arylated analogs of (II)—methyl group replaced by aryl residue—are among the easiest substances to prepare[5] it

---

[1] Abstracted from the senior research of William J. Gist at DePauw University, 1934–1935.

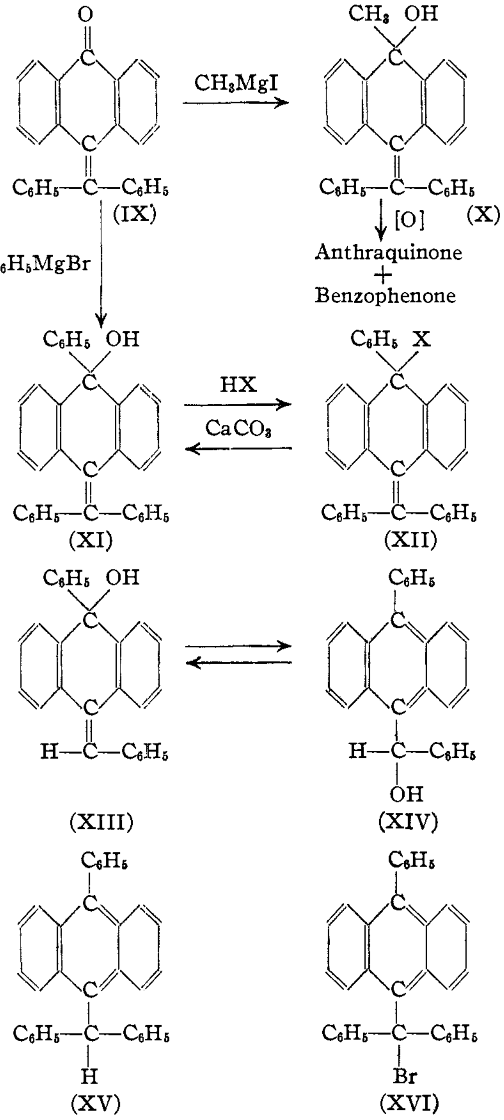
[2] (a) Julian and Magnani, THIS JOURNAL, **56**, 2174 (1934); (b) Julian and Cole, *ibid.*, **57**, 1607 (1935).

[3] Baeyer and Villiger, *Ber.*, **36**, 2793 (1903); Nakanishi, *Proc. Imp. Acad. Tokyo*, **9**, 394–397 (1933).

[4] Allen and Overbaugh, THIS JOURNAL, **57**, 740 (1935).

[4a] Gomberg and Cone, *Ber.*, **39**, 2964 (1906).

[5] Gomberg and Kamm, THIS JOURNAL, **39**, 2014 (1917).



seemed probable that phenylmagnesium bromide would likewise add 1,6 to fuchsone and to naphofuchsone. Despite numerous attempts, however, none of the readily crystallizing oxytetraarylmethanes could be isolated, only intractable gums resulting. Even on methylating these gums we could distil none of the pure methyl ethers from the products. The action of phenylmagnesium bromide on fuchsone and naphthofuchsone, therefore, is in marked contrast to that of methylmagnesium iodide on these substances, and if any amount of the 1,6-addition product is formed, it is present in such small quantities that the isolation of it is extremely difficult. One is reminded of the observation of Kohler[6] that "in most cases in which both 1,2- and 1,4-addition occur, the relative quantity of 1,4-addition product is always larger with alkyl than with arylmagnesium compounds." Our results indicate a similar conclusion with respect to 1,6-addition of aryl and alkyl magnesium derivatives.

Phenylmagnesium bromide reacts readily with anthrafuchsone (IX), the product being the 1,2-addition compound (XI).[7] This compound interested us because of the similarity in structure to another substance (XIII) on which we recently reported,[2a] and which we found to rearrange readily into the isomer (XIV). The new dihydroanthranol (XI), subjected to the same treatment, underwent no rearrangement and was recovered unchanged. In the earlier paper dealing with compound (XIII) we expressed the belief that certain steric influences might conceivably render the dihydroanthracene modification the more stable of the two, although generally the tendency to pass over into the modification containing the anthracene structure is so marked that least provocation effects this rearrangement. The additional phenyl group attached to the ω-carbon atom of (XI) seems to offer the necessary hindrance to rearrangement and it is the stable modification, while in the case of (XIII) and (XIV), the latter is certainly the more stable isomer, and no treatment could reconvert it into (XIII), although evidence for equilibrium between the two forms in solution could be adduced.

All attempts at replacement of the hydroxyl group in compound (XIII) led to derivatives having the structure corresponding to (XIV) and gave back (XIV) on hydrolysis. When the hydroxyl group in (XI) was replaced by halogen, and the resulting halide warmed for half an hour with moist calcium carbonate in acetone, the original carbinol was recovered. This is not satisfactory evidence that the halides have the structure (XII) since rearrangement might have occurred in the course of reconversion into carbinol. Moreover, solutions of both chloride and bromide (XII) are distinctly fluorescent, indicating that these might have the anthracene structure (XVI). To gain more light on this we prepared, according to Bergmann,[7] a substance to which he ascribes the formula (XV). From our experience with brominating phenylbenzylanthracene,[2a] we should secure (XVI) on brominating (XV). We did get a bromo compound, but one entirely different from our bromo derivative (XII). Hydrolysis of it

(6) Kohler and Nygaard, THIS JOURNAL, **52**, 4132 (1930).

(7) Bergmann, *Ber.*, **63**, 1041 (1930).

with calcium carbonate yielded none of our carbinol (XI). Whether Bergmann's compound (XV) has actually the structure assigned we have not investigated, for when we found that it and its bromo derivative had no relationship to our substances, further work with it was discontinued.

The authors acknowledge gratefully a generous grant from the Rosenwald Fund and likewise the assistance and unstinted support of their first teacher of chemistry, Dean W. M. Blanchard, Head of the Department.

Experimental Part

1,1-Diphenyl-1-*p*-anisylethane (III)

(a) **From Fuchsone.**—Five grams of fuchsone, which we find is most conveniently prepared in large quantity according to the method of Bistrzycki,[8] was treated in the usual manner with 3 moles of methylmagnesium iodide. The crude product obtained on working up the Grignard was methylated in 10% sodium hydroxide solution with methyl sulfate. After destroying excess alkylating agent with alkali, the product was poured into water, extracted with ether, the ethereal solution washed and distilled. At 0.1 mm. and with air-bath temperature of 196°, 3.5 g. of a greenish-blue liquid distilled. Recrystallized from ether–petroleum ether it melted at 77°.

Anal. Calcd. for $C_{21}H_{20}O$: C, 87.50; H, 6.94. Found: C, 87.41; H, 7.23.

(b) **From Diphenyl-*p*-anisylchloromethane (IV).**—Five grams of the chloromethane (IV) was treated with 3 moles of methylmagnesium iodide, worked up on the usual way and distilled. The product, which came over at the same temperature as recorded above, melted at 77° and was identical in all respects with (III) secured from fuchsone.

Preparation of Naphthofuchsone (V).—The preparation described in the literature[9] we found to be troublesome and result in poor yields. The same type of procedure employed in the preparation of fuchsone, however, gave excellent results. The methyl ether of benzoyl α-naphthol was prepared according to the method employed by Scholl and Seer[10] for the ethyl ether, all heating avoided during the Friedel–Crafts reaction. We had little success with the method suggested by Fierz-David and Jaccard.[11] Our product, however, melted at 83° and was identical with that described by these authors.

Diphenyl-4-methoxynaphthylcarbinol, which resulted from the action of phenylmagnesium bromide on the methyl ether of benzoyl-α-naphthol, seems not to have been described heretofore. It melts at 162°, recrystallized from ether–petroleum ether.

Anal. Calcd. for $C_{24}H_{20}O_2$: C, 84.66; H, 5.93. Found: C, 84.59; H, 5.83.

The chloride (VIII), m. p. 151°, could not be isolated readily by passing hydrogen chloride into the ether solution of the carbinol. It was obtained on treating the carbinol with thionyl chloride. Conversion into the fuchsone (V) was effected by heating at 180–200° until evolution of methyl chloride was complete. Our fuchsone was identical with that described in the literature.[9]

1,1 - Diphenyl - 1,4 - methoxynaphthylethane (VII), secured from naphthofuchsone (V) as well as from the chloride (VIII) described above, distilled at 220–230° (temperature of air-bath) and 0.1 mm., and melted at 144°, recrystallized from ether–petroleum ether.

Anal. Calcd. for $C_{25}H_{22}O$: C, 88.70; H, 6.56. Found: C, 88.68; H, 6.78.

9 - Methyl - 10 - benzhydrylidene - 9,10 - dihydroanthranol-9 (X).—Obtained by the action of methylmagnesium iodide on anthrafuchsone, this substance melted at 223°, recrystallized from ether–petroleum ether.

Anal. Calcd. for $C_{28}H_{22}O$: C, 89.79; H, 5.93. Found: C, 89.68; H, 6.04.

On oxidation with chromic acid in glacial acetic acid solution it yielded anthraquinone and benzophenone. In the Grignard machine it gave one mole of gas and consumed one mole of reagent.

9 - Phenyl - 10 - benzhydrylidene - 9,10 - dihydroanthranol-9 (XI) has already been described by Bergmann. On passing dry hydrogen chloride into an ethereal solution, the tertiary halide (XII) slowly crystallized out. Recrystallized from chloroform and ether, it melted at 220° with decomposition, beginning to turn dark at 185°.

Anal. Calcd. for $C_{33}H_{23}Cl$: C, 87.09; H, 5.10. Found: C, 86.78; H, 5.39.

When a benzene solution of the chloride is shaken with molecular silver it gives a deep reddish-brown solution, the color of which is almost completely discharged by passing in atmospheric oxygen. The peroxide, however, could not be induced to crystallize. Petroleum ether threw out an amorphous powder.

The bromide prepared as was the chloride melted at 165° with decomposition, while a bromo derivative of Bergmann's hydrocarbon (XV) melted at 143° and mixed melting point showed strong depression. When the 143° bromo derivative was hydrolyzed with moist calcium carbonate in acetone, only low melting material having no resemblance to the carbinol (XI) was secured.

Summary

1. The reaction between fuchsone and methylmagnesium iodide is another case of 1,6-addition. α-Naphthofuchsone behaves like fuchsone toward this reagent. None of the 1,6-addition products could be isolated from the reaction of these fuchsones with phenylmagnesium bromide.

2. 10-Benzhydrylidene - 9 - phenyl - 9,10 - dihydroanthranol-9 is stable and does not rearrange into its isomer with the anthracene structure. Its halogen derivatives likewise have apparently the dihydroanthracene structure.

GREENCASTLE, INDIANA RECEIVED JULY 29, 1935

---

[8] Bistrzycki and Herbst, *Ber.*, **36**, 2335 (1903).

[9] Mazurkiewicz and Bistrzycki, *ibid.*, **45**, 1436 (1912).

[10] Seer and Scholl, *Ann.*, **398**, 85 (1913).

[11] Fierz-David and Jaccard, *Helv. Chim. Acta*, **11**, 1042–1046 (1928).