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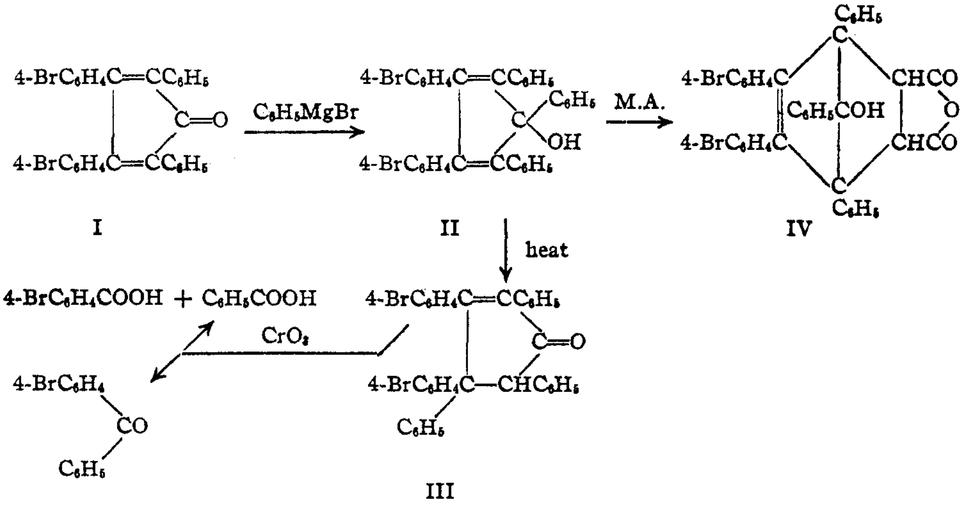
On the 1,3-Rearrangement of a Phenyl Group

BY C. F. H. ALLEN AND J. VANALLAN

The action of phenylmagnesium bromide upon tetraphenylcyclopentadienone gives either a carbinol, formed by 1,2-addition to the carbonyl group, or a ketone, resulting from 1,4-addition to the α,β-unsaturated carbonyl system.[1] Furthermore, the carbinol is converted into the ketone by being heated. This isomerization was accounted for by assuming that there had been a 1,3-rearrangement of the phenyl radical from the carbon atom of the original carbonyl group to one in the β-position of the unsaturated system. The evidence for such a change was the production of benzophenone upon oxidation of the isomerized substance.

All attempts to synthesize this rearranged product were unsuccessful. The use of *p*-methoxyphenylmagnesium bromide, with a view to obtaining *p*-methoxybenzophenone by degradation of the substance resulting from a rearrangement was likewise unsuccessful.[1]

What appears to amount to a positive proof has finally been secured, making use of the known 4,4′-dibromotetraphenylcyclopentadienone, I.[2] The phenyl carbinol, II, which was formed by the action of phenylmagnesium bromide in benzene, was rearranged by heating at 260–265° to the cyclopentenone, III.



The evidence that the carbinol II and ketone III have the structure indicated is important, since rearrangements are assumed to have occurred. The bromine-free pentaphenylcyclopentadienol, to which type II belongs, was first described and its structure proved by Ziegler.[3] In our previous paper,[1] were added the significant data (1) that it adds maleic anhydride, and (2) that it shows one active hydrogen in the Grignard machine. These two observations, plus the formation of a characteristic deep red color, on treatment with concentrated sulfuric acid, afford convenient experimental means for confirming this type of structure. When considering the interaction of a Grignard reagent and tetraphenylcyclopentadienones, it is only necessary to distinguish between 1,2 and 1,4 or 1,6-additions. Since the dibromo carbinol II was obtained by this standard reaction, shows one active hydrogen and no addition, adds maleic anhydride IV, and gives a deep red halochromism with sulfuric acid, there is no reasonable doubt as to its structure. The fact that it is rearranged by heating to form a ketone is also analogous to the behavior of Ziegler's carbinol.[1]

By similar analogies to the corresponding halogen-free ketone,[1] the structure III is assigned to the ketone resulting from the rearrangement. It was formed from the same type of compound by the same sort of reaction. A highly-hindered carbonyl group, such as the one present in the ketone III, is best detected by the Grignard machine, in which it shows one addition. The new ketone III has no active hydrogen, but shows one addition; it also exhibits a yellow halochromism with concentrated sulfuric acid. Upon oxidation by chromium trioxide in acetic acid, it gives 4-bromobenzophenone, 4-bromobenzoic and benzoic acids; this means that in the ketone a phenyl and a 4-bromophenyl are attached to the same carbon atom.

Since the carbinol has been isomerized to a ketone, the phenyl group originally attached to this particular carbon atom must have moved else-

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(1) Allen and VanAllan, THIS JOURNAL, 65, 1384 (1942).

(2) Dilthey, Trösken, Plum and Schömmer, *J. prakt. Chem.*, 141, 1346 (1934).

(3) Ziegler and Schnell, *Ann.*, 445, 277 (1925).

where. But a phenyl group has turned up on the carbon atom originally containing only a 4-bromophenyl group, three carbons away. Hence, it is reasonable to assume that there has been a 1,3-rearrangement of a phenyl.

It may be suggested that the phenyl has undergone two 1,2-shifts, but this means twice as many assumptions. There does not appear to be any certain way of determining whether any 1,3-shift is actually such, or proceeds by two 1,2-rearrangements, but since 1,3-shifts have been generally accepted in other instances, there is no reason why a phenyl group should be an exception.

This is the first instance which appears to be a direct proof for a 1,3-rearrangement of a phenyl group. We have previously pointed out several reactions that appeared to admit of no other interpretation. In addition to the cyclopentadienol mentioned above,[1] there are the bimolecular products formed by the action of acidic dehydrating agents upon anhydracetonebenzil and many of its substitution products,[4,5] and the formation of 2-phenylquinoline from cinnamalaniline.[6]

The *para*-alkylation of benzoyldurene[7] which the authors suggested might be a case of the rarely-observed 1,6-addition of a Grignard reagent to a conjugated system, could equally well be an analogous case—an instance of the common 1,4-addition to the α,β-unsaturated system, followed by a 1,3-shift of the alkyl group.

Experimental

The necessary 4,4′-dibromobenzil was secured by the bromination[8] of diphenylglyoxalone[9] and converted into the dibromotetraphenylcyclopentadienone following Dilthey's procedure.[2]

Phenylmagnesium bromide (prepared under nitrogen) was added dropwise to 5.4 g. of the ketone suspended in 27 cc. of benzene, until the intense red color faded to a pale pink; the ketone dissolved completely, but, on standing, a magnesium complex separated. After decomposing this with iced acetic acid, and steam distillation, the residue was crystallized from *n*-butyl alcohol: the yield was 4.1 g. The carbinol, II, formed white needles, m. p., 195°.

Anal. Calcd. for $C_{35}H_{24}OBr_2$: Br, 25.8. Found: Br, 25.8.

In the Grignard machine it showed one active hydrogen, but no addition. It gives a deep red color with concentrated sulfuric acid.

The maleic anhydride addition product IV was readily formed on heating a mixture of 1 g. of each component at 200° for five minutes, cooling and triturating with methanol. After recrystallization from xylene it melted at 222°.

Anal. Calcd. for $C_{39}H_{26}O_4Br_2$: Br, 22.3. Found: Br, 21.9.

The rearrangement product, the ketone III, was obtained by heating 11 g. of the carbinol at 260–265° (14 mm.) for two hours, cooling, taking up in ether, adding alcohol, and allowing it to stand overnight. A little floating solid matter was removed, and ether added. A new crystalline material soon separated; after filtration, the filtrate was diluted by ligroin—it soon became full of the solid ketone. The analytical sample was recrystallized from *n*-propyl alcohol and, finally, from acetic acid. The yield was 6.1 g., m. p. 178°; it gives a yellow color with concentrated sulfuric acid. (The change in color from red to yellow affords a convenient qualitative method for following the rearrangement.)

Anal. Calcd. for $C_{25}H_{24}OBr_2$: C, 67.8; H, 3.9; Br, 25.8. Found: C, 67.7; H, 3.9; Br, 25.9.

In the Grignard machine it showed no active hydrogen and one addition.

The oxidation was carried out by adding chromium trioxide in small portions to an acetic acid solution of the ketone; the reaction was vigorous. Since some unoxidized material was left after thirty minutes, the whole was refluxed for eight hours. It was then diluted and the ketone steam-distilled. After appropriate manipulation a 53.5% yield of *p*-bromobenzophenone was obtained. It had a melting point of 77–78° after recrystallization from methanol; the mixed melting point with an authentic specimen was 78–79°. The 2,4-dinitrophenylhydrazone separated in orange-red leaflets from dioxane–ethyl alcohol, m. p. 207–209°.

Anal. Calcd. for $C_{19}H_{13}O_4N_4Br$: Br, 12.7. Found: Br, 13.1.

There were also isolated 63% of benzoic acid and 32% of *p*-bromobenzoic acid.

Summary

An instance of the shift of a phenyl group in an unsaturated five-carbon ring system has been described. This has been interpreted as a 1,3-rearrangement. This conclusion is consistent with the facts.

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[4] Allen and Spanagel, This Journal, **55**, 3773 (1933).

[5] Allen and Gates, *ibid.*, **64**, 2123 (1942).

[6] Peine, *Ber.*, **17**, 2117 (1884).

[7] Fuson and McKusick, This Journal, **65**, 60 (1943).

[8] Biltz, *Ber.*, **41**, 1761 (1908).

[9] "Organic Syntheses," Coll. Vol. 2, 1943, p. 231.