THE INFRARED ABSORPTION OF CARBONYL GROUPS IN BRIDGED COMPOUNDS. II. ENDOCARBINOLS

C. F. H. ALLEN, THELMA DAVIS, D. W. STEWART, AND J. A. VanALLAN

In the previous paper (1) it was shown that substances containing the 8-oxo-[2·2·1]-bicycloheptene system (a *para* carbonyl bridge across a six-membered ring) have a characteristic absorption band in the infrared at 5.64 μ. In an earlier paper (2), two polyarylindenes, that arose from the dehydration of certain indenols, were described and their structures carefully proved. One of these hydrocarbons (III, Fig. 1) was obtained by decarbonylating and dehydrating the indenol formed by the action of phenylmagnesium bromide upon the bimolecular product (I) derived from anhydroacetonebenzil (3). Since carbon monoxide was evolved, it was assumed, by analogy with a great many substances known to have a carbonyl bridge (3), that the indenol also had this arrangement of groups; the structure, II, was therefore assigned to the indenol. The use of other Grignard reagents gave analogous indenols and hydrocarbons.

The infrared spectra of several of these indenols were recently routinely recorded; surprisingly, none showed the absorption at 5.64 μ attributed to a carbonyl bridge, whereas all had bands at 6.0 μ corresponding to a carbonyl group conjugated with a double bond (4), *i.e.*, an α,β-unsaturated ketone; the latter was confirmed by the ultraviolet absorption. The Grignard reagent, therefore, must have attacked the bridge; the structure of the products is shown in IV (Fig. 2). The reactions of the carbinols are in accord with this new structure; in every instance there is a C=C—C=O but no carbonyl bridge. The action of the Grignard reagent upon the "unsubstituted" bimolecular products is, therefore, like that with alkylated bimolecular products; it no longer constitutes an exception (5), and a tentatively assigned structure (XVI in Ref. 5) must be discarded.

The carbinols in both methylated (5) and unmethylated (6) series were converted into chlorides and acetates; the structures of the former were written correctly, but those of the latter should now be modified to show the radical on the bridge (Fig. 2, V). A phenylurethan (V; R = C₆H₅NHCO) was prepared by the action of phenyl isocyanate on the carbinol (IV). A methyl ether (VI; R = CH₃) could not be obtained by the action of diazomethane or methyl sulfate, but was readily made using methanolic hydrogen chloride. Like the carbinol, the chlorides, acetates, and methyl ether all gave the same known hydrocarbon (III) on pyrolysis. With alcoholic potassium hydroxide, the carbinol bridge was cleaved in an analogous fashion to the carbonyl bridges (7, 8), resulting in what is presumably a benzoylated indenone (VII); this was previously known, but incorrectly represented as a lactone (XIV in Ref. 7).

The chloride (V) can also be converted to the methyl ether (VI) by simply refluxing in methanol. This behavior is analogous to that of the bicyclic chloride
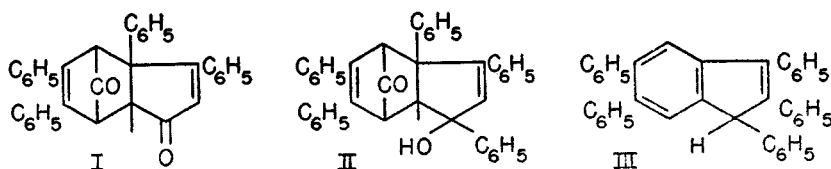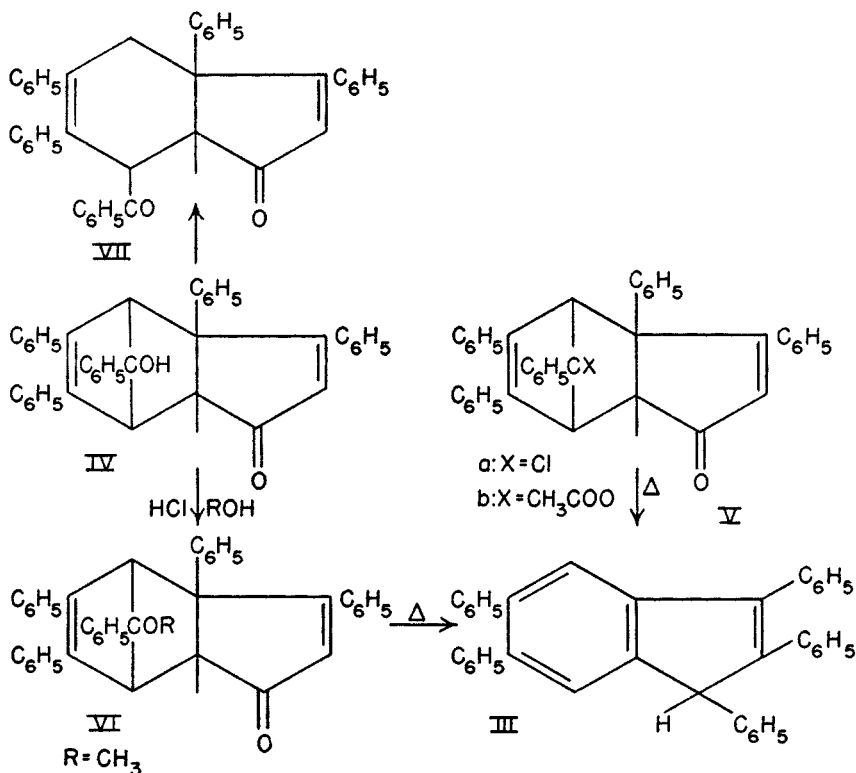
FIG. 1

FIG. 2

(VIII), which is likewise converted to an ether (IX, Fig. 3) by refluxing of its methanolic solution (9). This appears to be a unimolecular solvolytic reaction. An ethyl ether (IXb) of the bicyclic compound was made but it was not possible to prepare an isopropyl ether by the same procedure. If this mechanism just proposed is indeed true, then the initial stage of the reaction involves a planar carbonium ion, and the approach of a bulky isopropoxy anion would be greatly hindered in the tricyclic series.

The question now arises as to the path followed in the conversion of the endo-carbinol (IV) to the hydrocarbon (III), which, in all probability, arises from the isomeric indenol (II). Since carbon monoxide is given off, there must be an intermediate carbonyl bridge compound; this could easily be the indenol, if a suitable mechanism could be devised to account for the transformation. Such a route is proposed (Fig. 4), involving a thermal cleavage as the initial step, giving
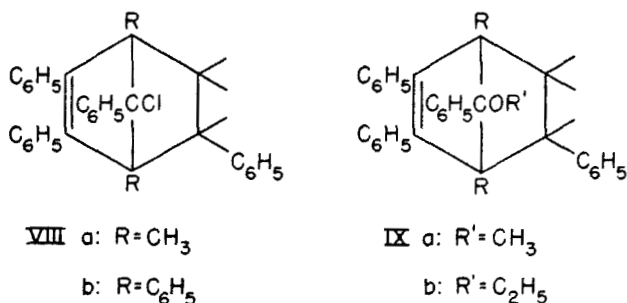
$VIII$ a: $R = CH_3$

b: $R = C_6H_5$

IX a: $R' = CH_3$

b: $R' = C_2H_5$

FIG. 3

FIG. 4

IV' II'
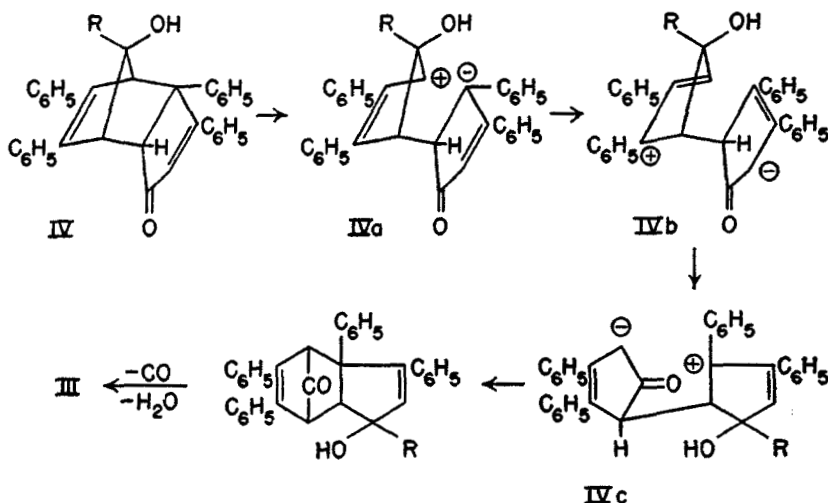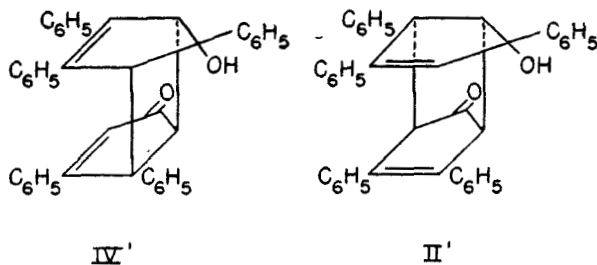
FIG. 5

rise to a carbonium ion (IV to IVa); since the latter is an allylic system, rearrangement to a more stable form (IVb) can take place (rewritten as IVc), followed by a recombination, which results in the indenol (II). For such a rearrangement to take place, the configuration of IV must be in the endo form. Examination of a model of the endo isomer shows that the atoms at the 2 and 6 positions are advantageously situated in space for bond formation to take place. Moreover, this rearrangement proceeds with retention of the endo configuration in the new isomer (see projection formulas IV', II'; Fig. 5). An alternative series of steps
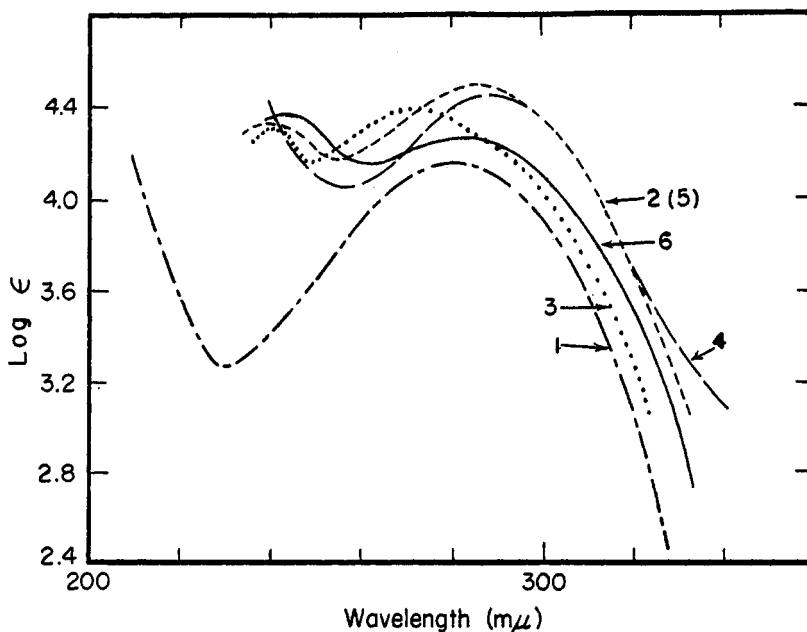
FIG. 6. ULTRAVIOLET ABSORPTIONS OF INDENONES.

from IV to III can be visualized in which the first step is dehydration; at the moment there is no evidence to make a choice between the two. As already mentioned, the rearrangement is not confined to the carbinol; the acetates, chlorides, and methyl ether also form the hydrocarbons with accompanying decarbonylation.

DISCUSSION OF ABSORPTION SPECTRA

Ultraviolet. It is well known that α,β-unsaturated carbonyl compounds have characteristic absorption curves in the ultraviolet (10). 2-Methyl-4-hydroxy-3,4-diphenyl-2-cyclopentenone (1 in Fig. 6) has been selected as a typical example for comparisons. On inspection of the curves in Fig. 6, it is apparent that the absorption of 1, 2 (I in text), and 3 (4,7-dimethyl homolog of I) are alike, *i.e.*, the effect of the groups attached to the 4- and 5-positions of the cyclopentenone ring do not greatly affect the absorption. If the conjugated system is disturbed, as in carbinol formation, this characteristic absorption should disappear. However, there is essentially no change in substances 2–6 (4 = α-naphthyl homolog of IV in text; 5, which overlaps 2, = VI in text; 6 = VII in text), from which it is concluded that the conjugated linkage is still present; this is confirmatory evidence that the Grignard reagent has attacked the carbonyl bridge in the carbinols 2–5. The last substance, 6, is the ketone, formerly incorrectly written as a lactone; if it were the latter, the observed absorption would not be like that of the α,β-unsaturated ketones.

Infrared. The indenone, I, was selected as the model compound. In this, the C=C—C=O absorption comes at 5.98 μ; in seven indenolones (IV, V, VI;

some have the C_6H_5 on the bridge replaced by CH_3 or α-$C_{10}H_7$), the carbonyl band is at 6.0± μ, indicating the indenone structure. In no single instance is there a band at 5.6± μ characteristic of a carbonyl bridge!

The ultraviolet curves were obtained with a Cary double-beam recording spectrophotometer, Model 11. The solutions were run against the same thickness of pure solvent. The solvent was dioxane in each case except with the cyclopentenone, 1, where methanol was employed. The infrared spectra were obtained on a Baird double-beam recording spectrophotometer using rock-salt optics. Samples were prepared either as Nujol mulls or as pressed plates in potassium bromide.

EXPERIMENTAL

Most of the substances were on hand from previous work.

1,4-Dimethyl-7-methoxy-1,2,3,4-tetrahydro-3,5,6-triphenyl-1,4-methanobenzene (IXa). A solution of 12.4 g. of the chloride VIIIa (m.p. 159–160°; previous value low) in 1 l. of methanol was refluxed for 34 hours, and chilled; 11 g. of the methyl ether (IXa) separated. It was recrystallized from benzene-hexane; m.p., 207–207.5°.

Anal. Calc'd for $C_{34}H_{32}O$: C, 89.4; H, 7.1.

Found: C, 89.4; H, 7.2.

The *ethyl ether* (IXb) was similarly prepared; m.p., 115°, from ligroin.

Anal. Calc'd for $C_{35}H_{34}O$: C, 89.4; H, 7.2.

Found: C, 89.1; H, 6.9.

The *methyl ether* (VI) was obtained by a 2-hr. refluxing of 4 g. of the carbinol (IV) in 150 ml. of methanol which had been saturated with hydrogen chloride (sulfuric acid was also satisfactory). The initial green color disappeared when the reaction was complete. The ether, m.p. 286°, was recrystallized from xylene. It could also be obtained by refluxing a methanolic solution of the chloride, Va.

Anal. Calc'd for $C_{41}H_{32}O_2$: C, 88.4; H, 5.8.

Found: C, 88.5; H, 5.8.

The *phenylurethan* of the carbinol (IV) resulted on refluxing a mixture of 1.8 g. of the carbinol, 2 ml. of xylene, and 2 ml. of phenyl isocyanate. After recrystallization from xylene, it had a melting point of 268°.

Anal. Calc'd for $C_{47}H_{35}NO_3$: C, 85.3; H, 5.3.

Found: C, 85.3; H, 5.5.

SUMMARY

From an examination of the infrared absorption spectra, it appears that endocarbinols instead of indenols result when carbonyl bridge compounds in the indene series are treated with Grignard reagents. A mechanism to account for their conversion to known polyarylated indenes by heat is proposed.

ROCHESTER 4, NEW YORK

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