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STUDIES OF ACENAPHTHENE DERIVATIVES. XVIII.(1)
THE NOVEL REACTION OF BENZYLIDENEACENAPHTHENONES WITH GRIGNARD REAGENTS

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The addition of Grignard reagents to α,β-unsaturated carbonyl compounds has been the subject of many investigations. Kohler et al.(2) have reported that ethyl cinnamate gives exclusively the 1,2-addition product with methylmagnesium iodide, but predominantly the 1,4-adduct with phenylmagnesium bromide. It is also known that chalcone reacted with phenylmagnesium bromide to give di-addition product, accompanying with the 1,4-adduct.(3)

In this communication we wish to report the novel reaction of benzylideneacenaphthenones (I) with Grignard reagents.

When Ia (R=H) was treated with phenylmagnesium bromide (IIa) in ethyl ether-benzene, white needles (IIIa), m.p. 184-185°, and yellow needles (IVa), m.p. 103-104°, were obtained in yields of 31 and 29% respectively. The compound IIIa was confirmed to be the expected 1,4-adduct, 2-benzhydrylacenaphthenone, on the basis of the following evidences. The compound IIIa was in agreement with the formula $C_{25}H_{18}O$ and its mass spectrum showed the parent peak at m/e 334. The IR spectrum exhibited the band at 1718 cm^{-1} and NMR spectrum in $CDCl_3$ showed peaks at τ 5.0, 4.6 (each 1H, doublet, J=6 cps) and 2.5 (16H, multiplet).

On the other hand, the molecular formula of IVa did not agree with an 1:1-adduct, but it agreed with $C_{27}H_{22}O$. The mass spectrum of IVa showed the parent peak at m/e 362 and IR spectrum exhibited the band assignable to ether group at 1070 cm^{-1}, but there was no absorption due to a hydroxyl or carbonyl group.

As illustrated in Fig. 1, the NMR spectrum of IVa in $CDCl_3$ exhibits peaks at τ 8.75 (3H, triplet), 6.24, 6.17 (2H, double quartet, J=4 cps), 3.85 (1H, singlet) and 2.5 (16H, multiplet).

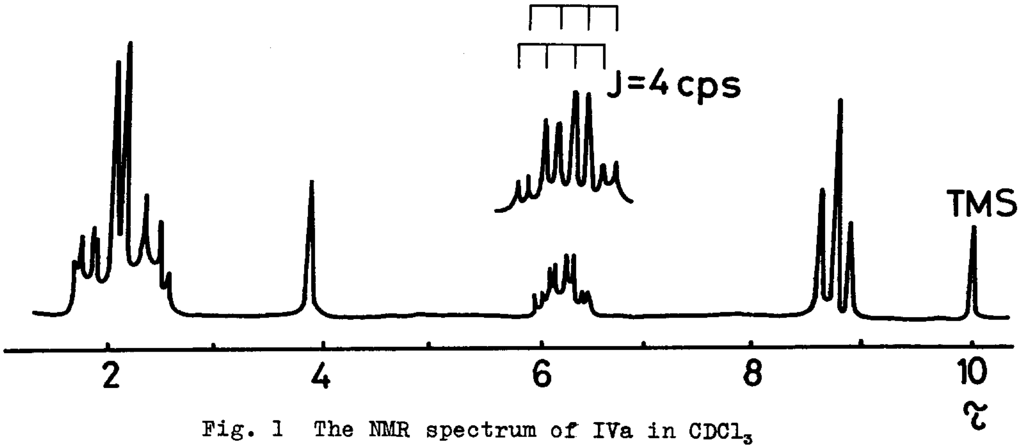


Fig. 1 The NMR spectrum of IVa in $CDCl_3$

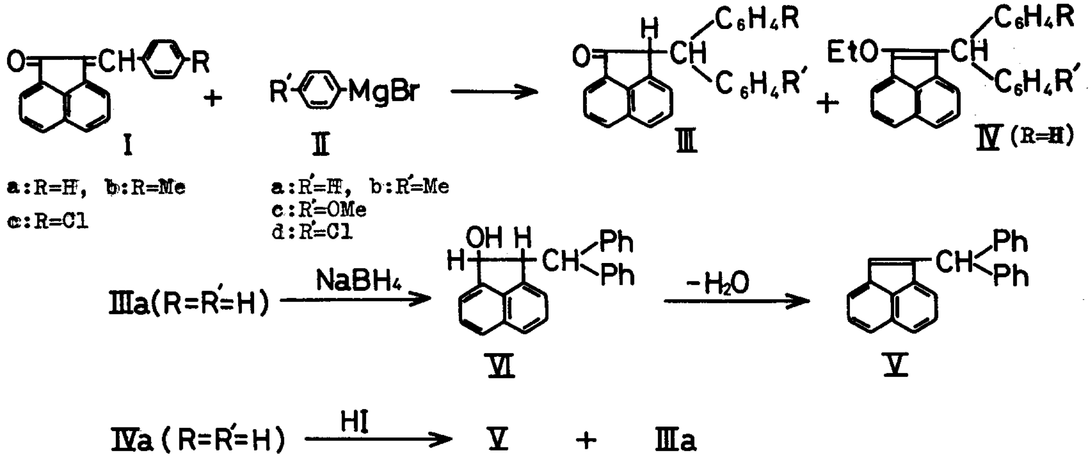
The above observations can be explained on the assumption that IVa is 1-ethoxy-2-benzhydrylacenaphthylene; hence, ethyl ether used as a solvent appears to be involved in the reaction. This structure was also confirmed by the following results. The treatment of IVa with hydriodic acid afforded 1-benzhydrylacenaphthylene (V), $C_{25}H_{18}$, m.p. 49-50°, yellow grains, in 80% yield, accompanying with a trace amount of IIIa.

When IIIa was reduced with $NaBH_4$ in ethanol at room temperature, 2-benzhydrylacenaphthenol (VI), m.p. 190-192°, white needles which, when treated with 35% sulfuric acid at 70°, suffered dehydration to V, was obtained in 89% yield.

The structures for V and VI were confirmed by elemental analyses, IR, NMR and mass spectra respectively.

Similar reactions of IIa with p-substituted phenylmagnesium bromides (IIb-IId) afforded the corresponding compounds III and IV respectively (Scheme 1).

The yields, physical properties and elemental analyses of III and IV are summarized in Table I.



Scheme 1

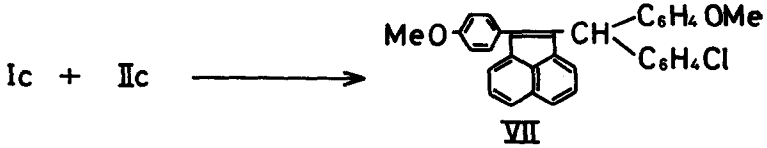
Interestingly, the reaction of Ia with IIa in *iso*propyl ether-benzene gave IIIa in 43% yield, accompanying with a trace amount of 1-*iso*propoxy-2-benzhydrylacenaphthylene, m.p. 113°, yellow needles.

TABLE I

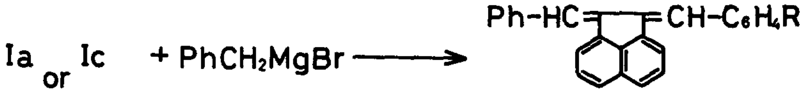
	R′	Yield	M.p.	IR, cm^{-1}		Found, %		Calc, %	
		%	°C	C=O	-C-O-C-	C	H	C	H
IIIa	H	31	184-185	1718	——	89.56	5.35	89.79	5.43
IVa	H	29	103-104	——	1070	89.66	6.13	89.47	6.12
IIIb	Me	15	153-154	1715	——	89.29	5.93	89.62	5.79
IVb	Me	20	103-104	——	1075	89.44	6.50	89.32	6.43
IIIc	OMe	15	225-226	1710	——	85.71	5.61	85.69	5.53
IVc	OMe	47	142-143	——	1070	85.80	6.24	85.68	6.16
IIId	Cl	6	140-142	1715	——	81.64	4.67	81.50	4.62
IVd	Cl	23	101-102	——	1080	81.81	5.43	81.75	5.30

III: white needles, IV: yellow needles.

In the reactions of Ib (R=Me) and Ic (R=Cl) with IIa, IIb and IId under similar conditions, the corresponding 1,4-adducts were only obtained, accompanying with a large amount of resinous material respectively. On the other hand, Ic reacted with IIc to give the di-addition product (VII), $C_{33}H_{25}O_2Cl$ (M^+=448), m.p. 72-73°, in 33% yield. The IR spectrum of VII did not reveal any bands for the carbonyl or hydroxyl group, and NMR spectrum in $CDCl_3$ exhibited peaks at τ 5.93 (6H, singlet), 3.34 (1H, singlet) and 2.5 (18H, multiplet).



VII



VIII

The reactions of Ia and Ic with benzylmagnesium bromide gave the corresponding bis-benzylideneacenaphthenes VIIIa (R=H) and VIIIc (R=Cl) in yields of 47 and 29% respectively.

VIIIa: $C_{26}H_{18}$ (M^+=330), m.p. 177-178°. VIIIc: $C_{26}H_{17}Cl$ (M^+=364), m.p. 171°.

The reaction courses are uncertain as yet. Further studies are in progress and the results will be reported shortly.

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