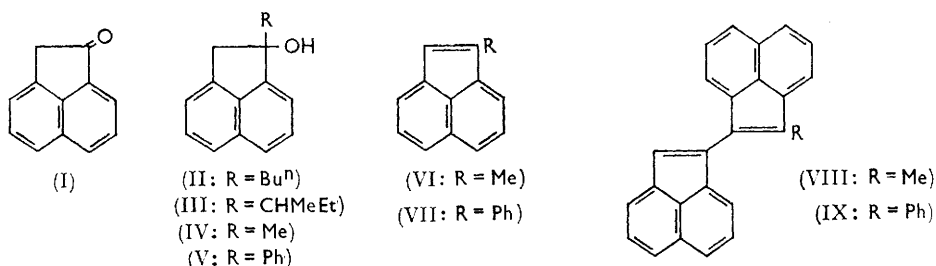


540. The Addition of Grignard Reagents to Acenaphthenone.

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Grignard reactions of acenaphthen-1-one lead variously to acenaphthen-1-ols, acenaphthylenes, and 1,1'-biacenaphthenyl or 1,1'-biacenaphthylenyl derivatives.

It has been reported that formation of a magnesium enolate interferes with the normal addition of Grignard reagents to the carbonyl group of acenaphthenone (I), though tertiary alcohols (II) and (III) resulting from such addition were isolated.¹ By using methylmagnesium iodide and phenylmagnesium bromide, 1-methyl- (VI) and 1-phenyl-



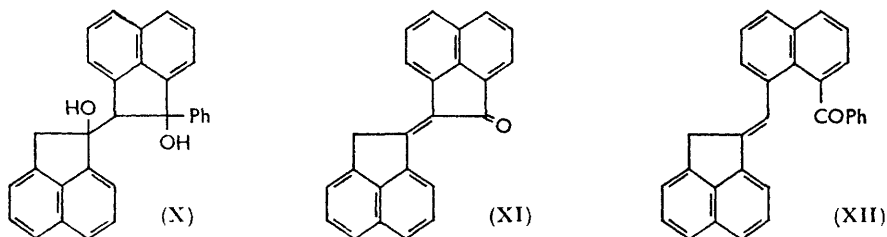
acenaphthylene (VII) were obtained on dehydration of the initial products with picric acid; distillation of the hydrocarbon (VI) produced in this way was said to leave a red residue of polymer.² We have chromatographed this residue and find it to contain the orange-red hydrocarbon, 2-methyl-1,1'-biacenaphthylenyl (VIII). Also by crystallisation of the original Grignard product, without dehydration, the tertiary alcohol (IV) was isolated.

The reaction of phenylmagnesium bromide with acenaphthenone has been studied in more detail. Decomposition of the original Grignard product with ammonium chloride gave a mixture which was separated by chromatography into 1-phenylacenaphthen-1-ol (V) (73%) and 2'-phenyl-1,1'-biacenaphthenyl-1,2'-diol (X) (27%). The former compound was dehydrated quantitatively to 1-phenylacenaphthylene (VII) in refluxing acetic acid. The diol (X) presumably arises because base-catalysed self-condensation of acenaphthenone precedes addition of Grignard reagent to the carbonyl group. By adding phenylmagnesium bromide to acenaphthenone (inverse procedure), the diol (X) becomes the main product (yield 80%). Its structure was confirmed by acidic dehydration: in refluxing acetic acid it gave two products, a red hydrocarbon, and a yellow ketone. The hydrocarbon was shown to be 2-phenyl-1,1'-biacenaphthylenyl (IX), which was also synthesised by treating 1,1'-biacenaphthyliden-2-one (XI)³ with phenylmagnesium

¹ Ghigi, *Gazzetta*, 1943, **73**, 71.

² Brown and Hammick, *J.*, 1948, 1395.

³ Graebe and Jequier, *Annalen*, 1896, **290**, 195.



bromide. The ketonic dehydration product can be identified as 1-(8-benzoyl-1-naphthyl)-methylideneacenaphthene (XII), resulting from a reaction analogous to the acidic fission of phenyl-substituted 1,3-diols described by English and Brucher.⁴

EXPERIMENTAL

Addition of Methylmagnesium Iodide to Acenaphthenone.—Acenaphthenone (11 g.), dissolved in benzene (150 c.c.), was added during 30 min. to a stirred Grignard reagent, prepared from magnesium (4 g.) and methyl iodide (6 c.c.) in ether (150 c.c.). The mixture was stirred for 30 min., then decomposed with dilute hydrochloric acid. The product, isolated with ether, was crystallised from benzene, affording 1-methylacenaphthen-1-ol (2.64 g.) as colourless prisms, m. p. 103—104° (Found: C, 84.5; H, 6.4. $C_{13}H_{12}O$ requires C, 84.8; H, 6.6%).

Evaporation of the benzene mother-liquor left a waxy semi-solid product (9.0 g.). A portion of this (8.0 g.) and picric acid (12 g.) were boiled under reflux in methanol for 10 min., then cooled. The crystals resulting were collected, washed with cold methanol, then decomposed with sodium carbonate solution. The product was isolated with benzene, as an orange oil. Distillation afforded 1-methylacenaphthylene (4.7 g.), b. p. 84—94°/0.1 mm. The red distillation residue was extracted with benzene and chromatographed on alumina. Benzene (10%) in light petroleum eluted 2-methyl-1,1'-biacenaphthylenyl. This recrystallised from ether-pentane as red-orange prisms, m. p. 91—97° (0.57 g.). Two further recrystallisations from the same solvents failed to raise this m. p. (Found: C, 94.8; H, 5.2. $C_{25}H_{18}$ requires C, 94.9; H, 5.1%).

Addition of Phenylmagnesium Bromide to Acenaphthenone.—*Method (a).* Acenaphthenone (5 g.) in ether (400 c.c.) was added gradually under nitrogen to a stirred Grignard reagent, prepared from magnesium (1.2 g.) and bromobenzene (6.0 g.) in ether. The mixture was stirred for 2 hr., then poured into aqueous ammonium chloride. The product was isolated with ether, dissolved in benzene, and chromatographed on neutral alumina. 1:1 Ether-benzene eluted 1-phenylacenaphthen-1-ol (5.6 g.), m. p. 97—99° (from benzene) (Found: C, 87.4; H, 5.6. $C_{18}H_{14}O$ requires C, 87.8; H, 5.7%). 1:1 Methanol-ether eluted 2'-phenyl-1,1'-biacenaphthényl-1,2'-diol (1.7 g.), m. p. 198—200° (from benzene) (Found: C, 87.0; H, 5.6. $C_{30}H_{22}O_2$ requires C, 87.0; H, 5.4%).

Method (b). Acenaphthenone (1 g.) in ether (100 c.c.) was boiled under nitrogen, and treated dropwise during 30 min. with a Grignard reagent prepared from magnesium (0.2 g.) and bromobenzene (1.05 g.) in ether. After further boiling for 90 min. the mixture was poured into aqueous ammonium chloride. The product was isolated with ether and chromatographed in benzene on neutral alumina. 1:1 Methanol-ether eluted 2'-phenyl-1,1'-biacenaphthényl-1,2'-diol (0.99 g.), identical with that prepared by method (a).

Dehydration of 1-Phenylacenaphthen-1-ol (V).—This compound (0.25 g.) was boiled under reflux in glacial acetic acid for 1 hr. The mixture was poured into water and extracted with ether. The extract, after filtration through a column of alumina, afforded on evaporation orange 1-phenylacenaphthylene (0.22 g.), m. p. 56—58° (from methanol) (cf. lit.,² m. p. 57—58°).

Dehydration of 2'-Phenyl-1,1'-biacenaphthényl-1,2'-diol (X).—This compound (444 mg.) was boiled in glacial acetic acid for 1 hr. The mixture was poured into water, and the product isolated with ether and chromatographed on neutral alumina in benzene. Benzene eluted 2-phenyl-1,1'-biacenaphthényl (167 mg.), red prisms (from ethyl acetate-ethanol), m. p. 151—155° [Found: C, 95.0; H, 5.1%; *M* (mass spectrogram), 378. $C_{30}H_{18}$ requires C, 95.2; H,

⁴ English and Brucher, *J. Amer. Chem. Soc.*, 1952, **74**, 4279.

4.8%; *M*, 378]. 1; 9 Ether-benzene eluted a yellow gum (219 mg.). Recrystallisation from ethanol afforded 1-(8-benzoyl-1-naphthyl)methylideneacenaphthene, m. p. 135–137°, λ_{max} 350 m μ (ϵ 13,200) with shoulders at 240, 325 m μ (ϵ 33,200, 11,300), ν_{max} 1670 cm.⁻¹ (C=O stretching) (Found: C, 90.9; H, 5.0. C₃₀H₂₀O requires C, 90.9; H, 5.1%).

2-Phenyl-1,1'-biacenaphthylenyl.—1,1'-Biacenaphthyliden-2-one (300 mg.) in benzene (150 c.c.) was treated dropwise with a Grignard reagent prepared from magnesium and bromobenzene (220 mg.) in ether. The mixture was heated under reflux for 90 min., then poured into aqueous ammonium chloride. The organic layer was separated and filtered through a column of alumina in benzene. Concentration of the filtrate left a red gum (60 mg.) which after two recrystallisations from methanol afforded 2-phenyl-1,1'-biacenaphthylenyl, m. p. 146–149°, identical with that obtained by dehydrating the diol (X).

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