

The Use of Mixed Grignard Reagents in the Double Bradsher Reaction

S. D. SARAF,

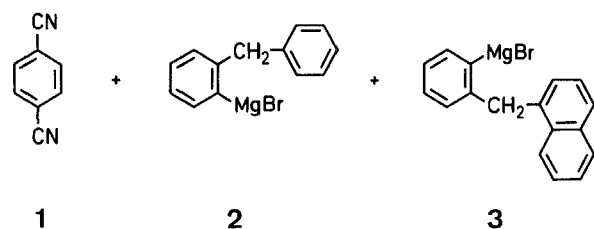
Institute of Chemistry, University of Islamabad, Rawalpindi,
West Pakistan

and

F. A. VINGIELLO,

Chemistry Department, Northeast Louisiana University, Monroe,
Louisiana, U. S. A.

In an earlier communication¹, we reported the use of a double Bradsher reaction to prepare polycyclic aromatic hydrocarbons. This method produces higher yields than Pschorr and Elbs reactions, with no rearrangements at all. In the present communication, we report details of the earlier work¹ and the preparation of an unsymmetrical starting material (4) of the double Bradsher reaction. The diketone 4 is obtained as a single product in moderate yield by reaction of 1,4-dicyanobenzene (1) with a mixed Grignard reagent (2+3). Acid cyclization of 4 affords the unsymmetrical hydrocarbon 5:



1,4-Bis-[2-benzylbenzoyl]-benzene: A Grignard reagent was prepared from 2-bromodiphenylmethane² (50.6 g, 0.205 mol) and magnesium (4.8 g, 0.2 g-atom) in dry ether (300 ml). When the reaction was complete, the ether was distilled and dry benzene (200 ml) was added. A solution of 1,4-dicyanobenzene (12.8 g, 0.1 mol) in benzene (200 ml) was added over a period of 30 min. The mixture was heated under reflux and stirred for 18 hr, then cooled to room temperature and decomposed with 20% aqueous ammonium chloride. The organic layer was separated, washed with water, dried, and added to an ethereal solution of hydrogen chloride. The precipitated solid was isolated by filtration, washed with little water, and hydrolyzed in a sealed tube containing 10 g of ketimine, 30 ml of water, and 5 ml of conc. hydrochloric acid at 200° for 4 hr. The product thus obtained was recrystallized from ethanol; yield: 45%; m. p. 134–135°, pale yellow plates.

$C_{34}H_{26}O_2$ calc. C 87.5 H 5.58
found 87.3 5.40

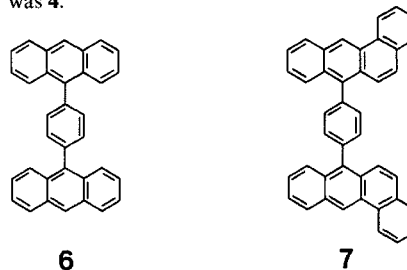
Similarly, **1,4-bis-[2-(1-naphthylmethyl)-benzoyl]-benzene** was prepared in 42% yield. The product crystallized from 10% ethanol/benzene as deep-yellow plates; m. p. 189–190°.

$C_{42}H_{30}O_2$ calc. C 89.0 H 5.3
found 88.9 5.3

1-(2-Benzylbenzoyl)-4-[2-(1-naphthylmethyl)-benzoyl]-benzene (4) was prepared by adding a mixture of a Grignard solution of 2-bromodiphenylmethane and 2-(1-naphthylmethyl)-bromobenzene (1:1) to a solution of 1,4-dicyanobenzene in benzene. Work-up as described above gave ketone 4 in 22% yield. It was recrystallized from benzene/ethanol; light-yellow needles, m. p. 184–185°.

$C_{38}H_{28}O_2$ calc. C 88.4 H 5.4
found 88.3 5.3

The crude reaction product of 1,4-dicyanobenzene and the mixed Grignard reagents was a mixture of six compounds, as evidenced by T. L. C., but the only product which crystallized was 4.

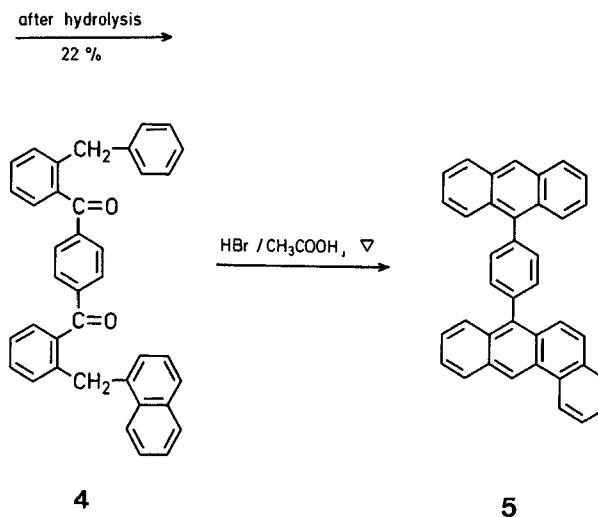


1,4-Bis-[9-anthryl]-benzene (6): A mixture of 1,4-bis-[2-benzylbenzoyl]-benzene (3.0 g), 48% hydrobromic acid (15 ml), and glacial acetic acid (30 ml) was heated in a sealed tube at 230° for 4 hr; on cooling, a solid precipitated; this was isolated and recrystallized from xylene; yield: 76%; m. p. 375–376°.

$C_{30}H_{22}$ calc. C 94.7 H 5.3 U. V.: λ_{max} , 385, 360, 347 m μ .
found 95.0 5.2

1,4-Bis-(7-benzo[a]anthryl)-benzene (7) was obtained analogously using hydrobromic acid/acetic acid at reflux temperature (4 hr); yield: 86%; m. p. 315–316°.

$C_{42}H_{26}$ calc. C 95.0 H 5.0 U. V.: λ_{max} , 291, 280, 270 m μ .
found 95.1 5.0



1-(9-Anthryl)-4-(7-benzo[a]anthryl)-benzene (5) was obtained analogously using hydrobromic acid/acetic acid at reflux temperature (4 hr); yield: 80%; m. p. 310–311°.

$C_{38}H_{24}$ calc. C 95.0 H 5.0
found 94.7 5.0

U. V.: λ_{max} , 385, 371, 352, 291, 281 m μ .

Compound 5 did not contain any impurities as evidenced by T. L. C. and G. L. C.

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¹ S. D. SARAF, F. A. VINGIELLO, *Chem. & Ind.* **1967**, 2145.

² F. A. VINGIELLO, M. M. SCHLECHTER, *J. Org. Chem.* **28**, 2448 (1963).