Tetrahedron Letters No.32, pp. 3801-3804, 1966. Pergamon Press Ltd.
Printed in Great Britain.

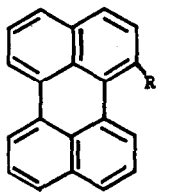
THE ALKYLATION OF PERYLENE WITH METHYLLITHIUM

Herman E.Zieger and Edward M.Laski*

Department of Chemistry, Brooklyn College of the City University of New York, Brooklyn , New York 11210

(Received 27 May 1966)

Certain aromatic hydrocarbons like phenanthrene undergo nucleophilic methylation with methylsulfinyl carbanion to afford methyl arenes in good yields (1-3). The alkylation of aromatic hydrocarbons with various butyllithium isomers has been reported (4). One case of ethylation by ethyllithium is known (5). A preliminary report concerning mechanism indicates that a lithium alkyldihydroaromatic intermediate is formed (6). Upon heating, the intermediate eliminates lithium hydride to form an alkyl aromatic hydrocarbon. Hydrolysis of runs having short reaction times afforded alkyldihydro aromatic hydrocarbons. In the ethylation (5) and butylation (7) of perylene (I a), we were unable to isolate such intermediates.



I (a) R = H-

(b) R = CH_3-

* National Science Foundation Undergraduate Research Participant 1965-66

In the methylation of perylene in benzene at 80° for 24 hr. with methyllithium - ether and a stoichiometric amount of N,N,N',N'-tetramethylethylene diamine, crystalline methyldihydroperylenes were formed (33 % crude, m.p. 160-165°). Two recrystallizations (i,hexane; ii, ethanol) afforded an analytical sample (5.6 %, m.p. 161.6-163.8°) whose ultraviolet spectrum (Table 1) showed that the characteristic perylene absorptions in the visible region had been shifted to 314, 329 and 345 mμ. Dehydrogenation of a sample of this methyldihydro-

TABLE 1

Methyl(1,x)dihydroperylene		1-Methylperylene	
λ mμ	log ε	λ mμ	log ε
230	4.86		
237	4.85	248.0	4.69
253	5.12	255.8	4.44
314	3.44	264 (infl.)	4.92
329	3.13		
345	3.45	382.0	4.49
401 *	3.85	404.0	4.16
426 *	3.78	427.0	4.01

* absorptions due to perylene (9.0 %) impurity

perylene (m.p. 155-159°) over 5 % palladium-carbon gave 1-methylperylene, yellow plates of m.p. 119-121°, not in agreement with the literature (8) m.p., 258-260°. (9) The infrared and ultraviolet spectra compare favorably with spectra for the homologous 1-n-butylperylene (7) and 1-ethylperylene (5). Confirmation that the methyl group is at C-1 was provided by the proton n.m.r. spectrum which has three methyl protons at 7.28 τ, a complex multiplet of eight A-B type aromatic protons from

2.45- 2.74τ and three X-type protons (at C_6,C_7 and C_{12}) as two doublets centered at 2.07 and 1.91τ. The low voltage (12 ev.) high resolution mass spectrum has a parent peak at mass 266 (90.1 %) and impurities at masses 280 (0.3 % of a dimethylperylene) and 252 (9.1 % of perylene). The P + 2 signal may arise from trace amounts of methyldihydroperylene as well as from normal isotope effects. Whether the perylene impurity was formed during the dehydrogenation over Pd-C by de-methylation or was present as an impurity in the sample of methyldihydroperylene is uncertain.

Methylation of perylene with the methylsulfinyl carbanion (1-3) in dry dimethylsulfoxide (DMSO) at 70.0 $\pm$ 0.1° for three hours produced only 1.0 % of 1-methylperylene (22 mg., m.p. 112.2-117.8 ° from methanol) and 87.6 % recovered perylene. Treatment of phenanthrene in a parellel experiment afforded 9-methylphenanthrene in 62 % yield as described by Russell (2) and Schriesheim (1). Interestingly, treatment of phenanthrene with methyllithium-ether in boiling benzene gave no methylphenanthrene and 99 % recovery of phenanthrene.

Acknowledgement: This work has been supported in part by the National Science Foundation through its Undergraduate Science Education Program. We thank Dr.T.F.Yen of the Mellon Institute for the high resolution mass spectrogram.

REFERENCES

1. P.A.Argabright,J.E.Hofmann and A.Schriesheim, J.Org.Chem., 30,3233 (1965).

2. G.A.Russell and S.A.Wiener, ibid, 31, 248 (1966).

3. H.Nozaki,Y.Yamamoto and R.Noyori, Tetrahedron Letters, 1123 (1966).

4. J.A.Dixon and D.H.Fishman, J.Am.Chem.Soc., 85, 1356 (1963).

5. H.E.Zieger, J.Org.Chem., 31, in press

6. J.A.Dixon,D.H.Fishman and R.Dudinyak, Tetrahedron Letters, 613 (1964).

7. H.E.Zieger and J.E.Rosenkranz, J.Org.Chem., 29, 2469 (1964).

8. A.D.Campbell,R.S.Elder and C.W.Emerson, J.Chem.Soc., 3526 (1959).

9. The ultraviolet spectrum reported[8] for 1-methylperylene indicates that the earlier researchers secured impure perylene (30 mg., 1.0 %). Possibly they too experienced substantial de-methylation during cyclodehydrogenation over Pd-C. Perylene crystallizes in two different forms[10] and we have obtained a lower melting form of our 1-methylperylene in numerous runs (m.p. 110-111°). with CH_3Li .

10. J.Tanaka, Bull.Chem. Soc.Japan , 36, 1237 (1963); (b) B.J.Mulder, Rec.trav.chim., 84, 713 (1965).