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A NOVEL PREPARATION OF TRITIUM- AND TRIMETHYLSILYL-LABELLED AROMATICS

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Our attempts to label aromatics *via* hydrolysis of organometallic intermediates with tritiated water have occasionally been frustrated in that we have obtained the correct hydrocarbon, but containing *no tritium*. Examples of the starting materials and conditions are: 2-chloroanthracene, Grignard, T.H.F; 2-bromo-11,11-difluoro-1,6-methano-[10]annulene, Grignard, Et_2O; 2- and 4-bromo-*p*-terphenyl, n-butyllithium, Et_2O. Two reasons can be postulated for these curious results: [1] The organometallic intermediate reacts with traces of water in the solvent. [2] The intermediate abstracts hydrogen from the solvent.

The former possibility is intuitively more attractive and may be a contributory factor when small quantities of halogenoaromatic are used in very dilute ethereal solutions. However it is not decisive for the following reasons: [a] Sodium dried solvents were used so that the quantity of water remaining was unlikely to be sufficient to cause complete destruction of the intermediate. [b] If sufficient quantities of water were present, the Grignard reagents would almost certainly not have formed in the first place. [c] The results are reproducible and are different for isomeric halogenoaromatics *eg*. 2-chloroanthracene consistently yielded inactive anthracene whereas 1-chloroanthracene gave the tritium-labelled derivative without difficulty.[1]

Other examples of formation of the parent hydrocarbon may be cited. Cross-metallation of 9-bromoanthracene (n-BuLi) followed by carbonation gave only anthracene[2] as did reaction of this bromo compound with Mg/Et_2O followed by $SiMe_3Cl$.[2] Attempts to prepare 2-trimethylsilyl-11,11-difluoro-1,6-methano-[10]annulene by cross-metallation of the bromo precursor (n-BuLi) followed by reaction with $SiMe_3Cl$ also gave only the parent hydrocarbon. In the case of anthracene the failure to produce the required products is due to rapid abstrac tion of hydrogen from the solvent. n-Butyllithium was added to 9-bromoanthracene[3] in sodium-dried ether and the mixture analysed (within 5 minutes) on g.l.c.-linked to mass spectrometry. Large quantities of anthracene (absent in the bromo compound) were present. This was shown not to arise from the presence of water traces by changing the order of reagent addition. n-Butyllithium was added to sodium-dried ether (this would destroy any moisture traces) and then (after ca. 1 minute) solid 9-bromoanthracene was added; anthracene was again found to be present and in a similar quantity.

In order to compete with these very rapid hydrogen abstractions it is necessary for the hydrolysing or coupling reagent to be in situ before addition of n-butyllithium. Accordingly we have been able to obtain the required tritiated compounds by wetting sodium-dried ether with tritiated water, dissolving the halogenoaromatic in this, cooling to ca. -70° and then adding n-butyllithium. Reaction is virtually instantaneous and high incorporation of tritium results. For trimethylsilyl compounds the technique is to dissolve $SiMe_3Cl$ and halogenoaromatic in sodium-dried ether, cool to ca. -70° and then add n-BuLi; reaction is again very rapid. In this way we have successfully prepared 2-trimethylsilyl-11,11-difluoro-1,6-methano[10]annulene in ca. 70% yield and reaction was complete in less than a minute. The technique appears to have general applicability and we have used it to make trimethylsilylbenzene, an example of a compound that can also be made by the conventional technique; we have also found that the abstraction of hydrogen also takes place with hydrocarbon solvents.

It follows from the above that the cross-metallation reaction (1) must be at least as fast and most probably faster than the reaction of n-butyllithium

$$\text{ArHal} + \text{nBuLi} \rightarrow \text{ArLi} + \text{nBuHal} \qquad (1)$$

with either water or trimethylsilyl chloride.

REFERENCES

1. R. Taylor, G.J. Wright, and A.J. Homes, J. Chem. Soc (B), 1967, 780.
2. J.A. Sperry, Ph.D. Thesis, University of Leicester, 1960; private communication from C. Eaborn.
3. Kindly donated by Dr. H. Bouas-Laurent, University of Bordeaux.