

AN UNUSUAL NUCLEOPHILIC AROMATIC SUBSTITUTION REACTION

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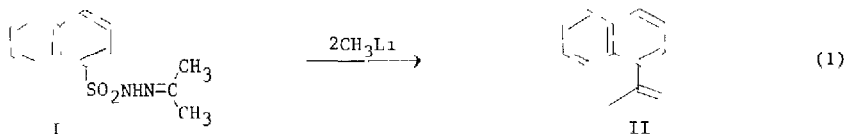
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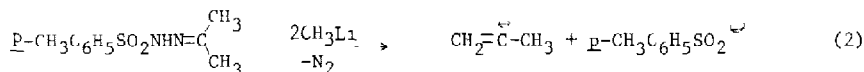
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In the course of another study we had reason to treat the 1-naphthalenesulfonylhydrazone (1-nasylyhydrazone) of acetone (I)¹ with methyl lithium. We found as a major product (22%)^{2a} 1-isopropenylnaphthalene, (II)^{2b}, (eqn 1)



The reaction of aryl hydrazones of ketones with alkyl lithium reagents yields olefins through the intermediacy of alkenyl anions (eqn 2)³



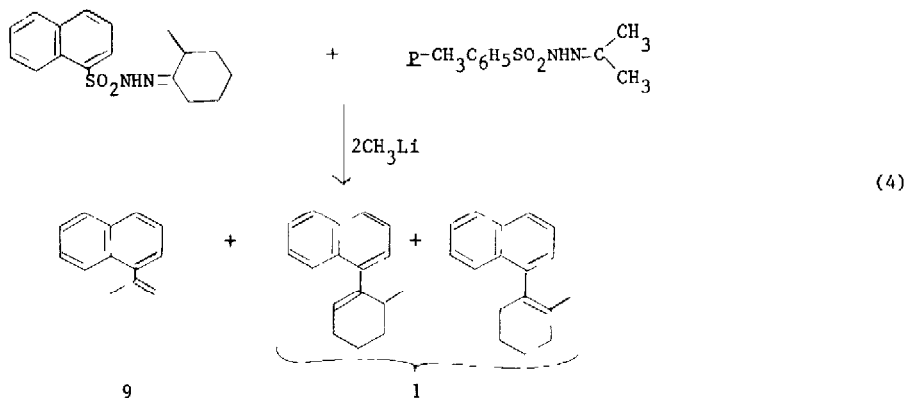
The formation of II appears to involve the displacement of the sulfinate dianion from the naphthalenesulfinate by the isopropenyl anion (eqn 3)



Although nucleophilic displacements on aromatic systems are under intensive investigation very few reactions are known in which the leaving group is a dianion. The classical textbook example of this type of reaction is the reaction of sodium naphthalenesulfonates with hydroxide or ammonia derivatives to yield the corresponding naphthol or naphthylamine⁴. The conditions, however, under which these reactions occur are quite vigorous. W. Burkhardt and Th. Kauffman have observed the displacement of both sulfite and sulfinate dianions from aryl sulfonates and sulfonates by the sodium salt of hydrazine under mild conditions⁵. Shapiro and Tomer have also observed the photochemically induced nucleophilic displacement of sulfinate dianion from lithium p-toluenesulfinate by methyl lithium⁶. It should be pointed out that even in the presence of a large excess of methyl lithium less than 1% 1-methylnaphthalene is observed.

The relatively negligible amounts of substitution by methyl relative to substitution by isopropenyl is consistent with either 1) the nucleophilic substitution occurring prior to formation of the free anions, or 2) the more easily polarizable isopropenyl anion being more nucleophilic than the less polarizable methyl anion ⁷

To investigate the former possibility a 1:6 mixture of the 1-naphthylhydrazone of 2-methylcyclohexanone (III) (m.p. 124-126 C D) and the tosylhydrazone of acetone was reacted with excess methyl lithium. If the mechanism does not involve the free anions no 1-isopropenyl-naphthalene should be observed. 1-Isopropenyl-naphthalene was, however, observed to be the major nucleophilic substitution product (eqn. 4) ⁸



Thus the difference in reactivities between the isopropenyl anion and the methyl anion appear to be due to the difference in their polarizability

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