

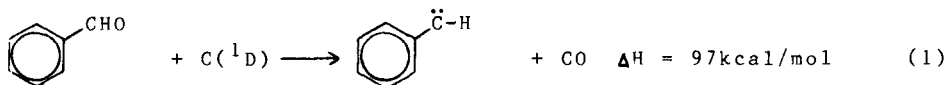
THE REARRANGEMENT OF CHEMICALLY ACTIVATED PHENYLMETHYLENES AT 77K

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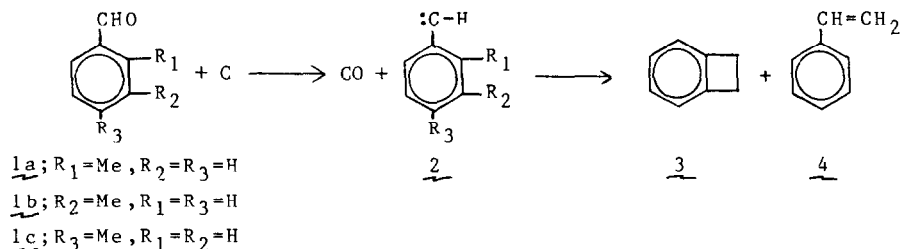
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Abstract. The cocondensation of atomic carbon with o, m and p-tolualdehyde at 77K results in deoxygenation to the o, m and p-tolylmethylenes which possess sufficient energy to rearrange to benzocyclobutene and styrene.

The reaction of atomic carbon with carbonyl compounds is known to result in deoxygenation with the concurrent formation of carbon monoxide and a carbene.¹ The high energy of atomic carbon coupled with stability of CO makes this an attractive method for generation of carbenes with excess energy.^{2,3} For example, the deoxygenation of benzaldehyde by C(¹D) to generate singlet phenylcarbene is exothermic by approximately 97 kcal/mol (eq 1).⁴



Since it is well known that phenylcarbenes with excess energy undergo the phenylcarbene rearrangement,⁵ we have investigated the deoxygenation of the o, m, and p-tolualdehydes (1a, b and c) to the corresponding tolylmethylenes (2a, b and c) and have observed the products resulting from their interconversion on a matrix at 77K. Thus, when arc generated atomic carbon is condensed at 77K with either 1a, b or c, the only isolable products are benzocyclobutene, 3 and styrene, 4.⁶



An interesting feature of the tolylcarbene rearrangement is the fact that the ratio of 3, which results from intramolecular trapping of 2a, to 4 is always greater for carbene precursors of 2a than for precursors of 2b and c.

In the present case, the ratio of 3:4 is 2.35±.08 from 2a while it is 0.94±.13 from 2b and 0.95±.04 from 2c. These ratios are similar to those obtained by other workers using diazo precursors to the tolylcarbenes.^{7,8} Although the reason for the higher ratio of 3:4 from 2a in the tolylcarbene rearrangement is not fully understood,^{7,8} it has been postulated that 2a may be formed in a geometry which is especially favorable for insertion or that insertion may occur via the diazo precursor to 2a.⁸ The present investigation, which does not use a diazo compound as a carbene precursor, rules out the latter possibility.

Although a recent report demonstrates that matrix photolysis of the isomeric triplet tolylmethylenes results in the phenylcarbene rearrangement,⁹ deoxygenation of carbonyl compounds by C(³P) has not been observed³ and we feel that triplet carbenes are not involved in the present reaction. The intermediacy of the triplet tolylmethylenes should lead to some products of hydrogen abstraction by these species. However, a careful search of the reaction products did not reveal the presence of the xylenes indicating that the interconversion and subsequent trapping of singlet 2a, b and c is rapid as compared to decay to the triplet ground state.

The deoxygenation of acetophenone by atomic carbon under similar conditions leads only to 4 (0.5%). This result indicates that 1-phenylethanylidene, 5, even though it has sufficient energy to undergo a phenylcarbene rearrangement, undergoes exclusive hydrogen migration to generate 4. Similar results are observed when 5 is generated from other precursors.^{5,7,9}

References and Notes

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