Mechanism and Inverse Primary Kinetic Isotope Effect in the Reaction of Fluorenylidene with 3-Deuteriocyclohexene

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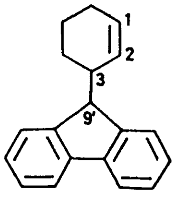
Summary 3-(9′-Fluorenyl)cyclohexene from the reaction of fluorenylidene with cyclohexene is formed by way of the fluorenyl–cyclohexenyl geminate radical pair, for the hydrogen abstraction leading to this radical pair, $k_H/k_D \simeq 0{\cdot}78$

CARBENES generated in the presence of olefins may give both allylic insertion and cyclopropane products[1] For the fluorenylidene–cyclohexene system, the apparent insertion reaction has now been shown to go by way of a geminate radical pair

9-Diazofluorene, from the nickel peroxide-catalysed oxidation of 9-fluorenone hydrazone,[2] was photolysed at 17° in neat, deaerated cyclohexene using a 450 W Hanovia medium-pressure mercury vapour lamp. The major product, a heat- and air-sensitive hydrocarbon identified as 3-(9′-fluorenyl)cyclohexene (I),† was isolated in 54% yield by preparative t.l.c.‡ The structural assignment was confirmed through an independent synthesis from sodium fluorenylide and 3-bromocyclohexene.[3]



(I)

Photolysis of the carbene precursor in neat, deaerated 3-deuteriocyclohexene[4,5] led to a deuterium labelled product, [$^2H_1$]-(I), 6·8% $^2H_0$, 90·9% $^2H_1$, 2·3% $^2H_2$. The fluorenyl fragment in the mass spectrum at *m/e* 165 (base peak) and peaks at 166 and 167 indicated an isotopic composition of 70·3%$^2H_0$, 27·2%$^2H_1$, 2·5% $^2H_2$. The deuterium in the cyclohexyl moiety was distributed at vinylic, allylic, and homoallylic positions in a 1:3:2 ratio, as shown by ^1H and ^2H n.m.r. spectroscopic analyses.§ The 3-deuteriocyclohexene solvent retained its isotopic integrity during the photolytic reaction.

These results are incompatible with direct allylic C–H insertion,[6] which leads to none of the original label at a vinylic carbon, and with a concerted $[\omega_s^2 + \pi_s^2 + \sigma_s^2]$ ene type of cycloreaction,[7] involving synchronous double bond migration and hydrogen atom transfer: the latter mechanism leads to a vinylic:allylic:homoallylic deuterium distribution, in the absence of significant secondary isotope effects, of 1:0:2.

The experimental findings are quantitatively consistent with a mechanism involving abstraction of allylic hydrogen from cyclohexene by triplet fluorenylidene[8] and subsequent collapse of the geminate pair. In the abstraction, 27·2% of the possible 90·9% $^2H_1$ label is transferred from [3-^{2}H]-cyclohexene to the fluorenylidene species: the ratio $[90{\cdot}9 - 27{\cdot}2]/27{\cdot}2 = 2{\cdot}34$ corresponds to (k_H/k_D), the primary isotope effect rate constant ratio for abstraction, times $[2 + (k_H/k_D)^{-1}{}_{\mathrm{secondary}}]$, and since the secondary isotope effect would be approximately 1·0,[9] the primary effect must be inverse: $(k_H/k_D)_{\mathrm{primary}} \simeq 0{\cdot}78$.

Insertion of methylene generated photolytically from keten into the allylic C–H bond of *cis*-but-2-ene has k_H/k_D 1·96;[10] another apparent carbene insertion reaction, involving the C–H bonds of cyclohexane, has been reported to have $(k_H/k_D)^{12} = 0{\cdot}7$, or $k_H/k_D \approx 0{\cdot}97$.[11]

Such small normal and inverse primary kinetic isotope effects reflect nonlinearity in the transition state, causing C–H bending modes in addition to stretching modes to determine the observed k_H/k_D values.[12]

Unusually severe nonlinearity may be present in the transition state leading to the geminate radical pair precursor of (I). Appreciable transfer of electronic charge from cyclohexene to fluorenylidene accompanied by a stabilizing superposition of the resulting partially ionic pair of reactants would favour a triangular transition state for abstraction. Or, if singlet–triplet interconversion is relatively slow, the favourable orientation for the "ene" singlet path may establish the geometry at which crossing to the triplet surface leading directly to the geminate pair may take place.

Experiments with *singlet* bivalent carbon species, designed to assay what propensity they may have to react as one-centre, high-energy olefin analogues in concerted cycloreactions, are in progress.

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† Hydrocarbon (I) had M^+ at *m/e* 246 and the expected n.m.r. spectrum: τ 2·2—2·9 (aromatic, m, 8H), 4·22 (vinyl, s, 2H), 6·01 (C-9′, d, 3Hz, 1H), 8·0—8·3 (allyl, m, 3H), and 8·4—8·9 (homoallyl, m, 4H).

‡ Minor products include fluorene, 3,3′-bicyclohexenyl (authentic sample provided by Professor T. Koenig), 9-fluorenone azine 9,9′-bifluorenyl, and 9,9′-bifluorenylidene.

§ ^2H n.m.r. spectra were obtained by R. Thrift, University of Illinois, Urbana.

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[4] *Cf.* J. E. Baldwin and R. H. Greeley, *J. Amer. Chem. Soc.*, 1965, **87**, 4514.

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[12] R. A. More O'Ferrall, *J. Chem. Soc.* (*B*), 1970, 785, and references therein.