forming the ozonolyses. Ms. Mary McKenney Ulrich performed valuable preliminary experiments.

(17) Address correspondence to the author at the University of Texas at Dallas, Dallas, Texas 75230.

Richard A. Caldwell[17]
Department of Chemistry, Cornell University
Ithaca, New York 14850
Received September 15, 1972

Chemically Induced Dynamic Nuclear Polarization Detection of Selective Iron-Catalyzed Radical Formation from an Alkyl Halide in the Presence of Its Grignard Reagent

Sir:

It has long been recognized that the reaction between Grignard reagents and alkyl halides is catalyzed by the addition of salts of transition metals (the Kharasch reactions).[1] The role played by the catalytic species is, however, unknown. Kochi[2] has recently found the rate of the iron salt catalyzed reaction to be first order in the concentrations of halide and catalyst but independent of Grignard concentration. The evidence from deuterium labeling, which we present here, supports separate reaction pathways for the halide and Grignard reagent. Furthermore, we provide CIDNP data which allow us to draw mechanistic conclusions about these systems which are virtually unobtainable by product analysis alone.

The rapid ($t_{1/2} \simeq 3$ min) reaction of a tetrahydrofuran solution 0.7 *M* in 2-propylmagnesium bromide, 1.4 *M* in 2-deuterio-2-propyl bromide, and 7×10^{-6} *M* in either ferrous or ferric chloride[3] (reaction 1a) produces propene-d_0 and -d_1 in a ratio of approximately 3:2, propane-d_0 and -d_1, and smaller amounts of 2,3-dimethylbutane (Scheme I). In the absence of metal catalysts, less than 5% reaction occurs in 1 hr. Reversing the label (reaction 1b) produces the same products, although the deuteriopropene is now the favored alkene.

Scheme I

$$(CH_3)_2CHMgBr + (CH_3)_2CDBr \xrightarrow{FeCl_2} \underset{43\%}{CH_3CD{=}CH_2} + \underset{57\%}{CH_3CH{=}CH_2} + \text{propane (H + D)} + \text{coupling product} \quad \text{(1a)}$$

$$(CH_3)_2CDMgBr + (CH_3)_2CHBr \xrightarrow{FeCl_2} \underset{61\%}{CH_3CD{=}CH_2} + \underset{39\%}{CH_3CH{=}CH_2} + \text{propane (H + D)} + \text{coupling product} \quad \text{(1b)}$$

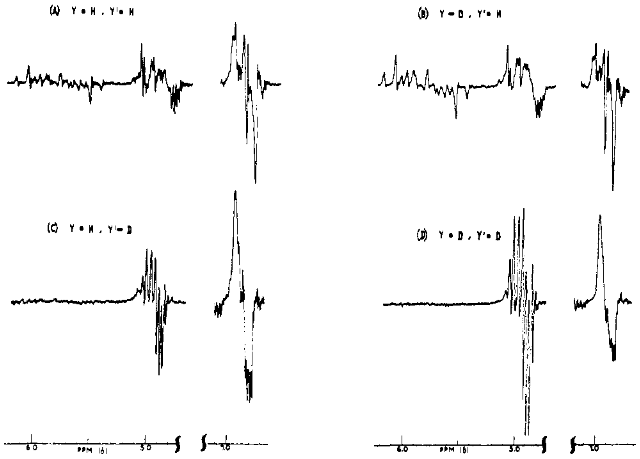

Figure 1. CIDNP spectra recorded during the ferrous chloride catalyzed reaction of $(CH_3)_2CYMgBr$ with $(CH_3)_2CY'Br$ in tetrahydrofuran. For Y = H and Y′ = H (A) and Y = D and Y′ = H (B), the multiplet at δ 0.9 is propane and the multiplets at δ 4.9 and 5.7 are the methylene and methyne protons of propene, respectively. For Y = H and Y′ = D (C) and Y = D and Y′ = D (D), the multiplet at δ 0.9 is 2-deuteriopropane and the multiplet at δ 4.9 is the methylene protons of 2-deuteriopropene.

When the above reactions were carried out in the probe of an A-60-A nmr spectrometer, large polarizations (AE) for the hydrocarbon products were observed. In reaction 1a, only 2-deuteriopropene and 2-deuteriopropane are polarized (Figure 1C), while in reaction 1b only undeuterated propane and propane are polarized (Figure 1B).[4]

Figures 1A and 1D display the polarization resulting from the reactions of undeuterated Grignard with undeuterated halide and deuterated Grignard with deuterated halide, respectively.

The polarization displayed in Figure 1B resembles closely that in Figure 1A, and likewise, Figure 1C resembles Figure 1D. No alkyl exchange between the Grignard reagent and labeled alkyl bromide was detectable by nmr, in either the presence or absence of catalyst.

Three conclusions about the mechanism of the Kharasch reaction can be drawn from these observations. (1) The observation that unequal amounts of propene and deuterated propene are formed in these reactions indicates that a mechanism which involves disproportionation of an equal number of alkyl radicals derived from the organometallic reagent and the alkyl halide is not operative.[5] (2) The phase of the observed pure multiplet effect polarized (AE) indicates[6] that the hydrocarbon products are polarized during diffusive encounters of free radicals and is consistent with a free radical chain mechanism in which most radicals are not formed in pairs. (3) Free radicals are produced only from the alkyl halide since CIDNP is observed only in the products derived from the alkyl halide, although propane and propene are formed from both reactants.[7]

---

(1) M. S. Kharasch and O. Reinmuth, "Grignard Reactions of Non-Metallic Substances," Prentice-Hall, New York, N. Y., 1954, p 122 ff.

(2) M. Tamura and J. Kochi, *J. Organometal. Chem.*, 31, 289 (1971).

(3) Metallic impurities in the magnesium used to prepare the Grignard reagent apparently become catalytically active only if they are oxidized. This produces some interesting effects on the coupling reaction brought about by impurities in both the Grignard and alkyl halide; R. Allen, to be published.

(4) The polarized coupling product was difficult to observe due to the overlapping polarizations resulting from the methyl protons of the coupling product and propane. In reaction 1b, however, the polarized (AE) methyne protons of 2,3-dimethylbutane could be observed.

(5) A mechanism involving formation of radicals indiscriminately from both a halide and organometallic compound does, however, explain CIDNP data from the reaction of alkyllithium compounds with alkyl halides: see R. A. Cooper, H. R. Ward, and R. G. Lawler in "Chemically Induced Magnetic Polarization," G. L. Closs and A. R. Lepley, Ed., Wiley, New York, N. Y., 1972.

(6) H. R. Ward, *Accounts Chem. Res.*, 5, 18 (1972); R. G. Lawler, *ibid.*, 5, 25 (1972).

(7) The polarized propene lines are at least 30 times more intense than the corresponding lines of propene derived from the Grignard reagent. If free radicals are formed from the Grignard reagent they must therefore be quite ineffective in producing CIDNP. A tidier explanation is that they are simply absent.

The mechanism in Scheme II is consistent with the

Scheme II

$$R'Br + (Fe)^{red} \longrightarrow R'\cdot + (Fe)^{ox}Br \qquad (2)$$

$$2R'\cdot \xrightarrow{\text{CIDNP}} R'(H)^{*}, R'(-H)^{*} + R'R'^{*} \qquad (3)$$

$$2(Fe)^{ox}Br + 2RMgBr \xrightarrow[\text{process}]{\text{non-free-radical}} 2(Fe)^{red} + R(-H) + R(H) + 2MgBr_2 \qquad (4)$$

above conclusions.

In this mechanism a reduced iron species (Fe^{red}) reacts with the alkyl halide to form a free alkyl radical and an oxidized iron species (reaction 2). The free alkyl radicals can then diffuse together[8] and react to produce the polarized disproportionation or coupling products[9] (reaction 3). Finally the oxidized iron species is reduced by the Grignard reagent (reaction 4) to re-form the catalytically active iron species and hydrocarbons by a non-free-radical route.

Scheme II is similar to the mechanism for the Kharasch reaction suggested by Tamura and Kochi[2] in which reactions 2 and 4 proceed *via* the intermediacy of organoiron compounds.[10] Our results show, however, that the Grignard reagent and halide must produce different organoiron intermediates, if they are indeed formed, and that the intermediate formed from the Grignard reagent apparently does not decompose homolytically, as has been suggested for organocobalt reagents produced from Grignard reagents.[11]

An exception to the above mechanism appears to occur when the halide or Grignard can produce an especially stable radical. We have found, for example, that *tert*-butyl Grignard reacts with allyl and benzyl bromides in the absence of catalyst. The polarizations in these two systems, however, indicate a mechanism in which geminate radical pairs form *via* bimolecular reactions of the organomagnesium compound and halide (as is the case for the reactions of organolithium and halides).[5]

Work is presently underway to determine whether other catalysts such as cobalt or silver salts also produce separate reaction pathways for the Grignard reagent and halide.

Acknowledgments. This work was supported by grants from the National Science Foundation and the Petroleum Research Fund, administered by the American Chemical Society. H. R. W. is pleased to acknowledge a most helpful discussion with Professor H. O. House and correspondence with Professor J. K. Kochi.

---

[8] A paramagnetic iron-containing species, which might be a likely partner in a radical pair, would probably have a *g* factor different from that of an alkyl radical and be expected to product net enhancement,[6] rather than the observed multiplet effect, in reaction products.

[9] Reaction of 1 mol each of Grignard reagent and alkyl halide produces 0.08 mol (8% yield) of 2,3-dimethylbutane. This is considerably lower than the 35% yield reportedly obtained from two isopropyl free radicals generated by photolysis of diisobutyryl peroxide [R. A. Sheldon and J. K. Kochi, *J. Amer. Chem. Soc.*, **92**, 4395 (1970)]. If, however, it is assumed that the coupling product is formed exclusively from free radicals derived from the alkyl halides, *i.e.*, that the Grignard reagent forms intermediates which give only propene and propane, the calculated yield is 16%. Although this is still low, the difference lies within the range of medium effects on coupling–disproportionation ratios [A. Stefani, *J. Amer. Chem. Soc.*, **90**, 1694 (1968)] and probably makes it unnecessary to postulate more than one pathway for reaction of the alkyl halide in this case, although a competitive pathway involving organoiron intermediates derived from the halide could also account for the results.

[10] The specific mechanism is shown below.

$$Fe + R'Br \longrightarrow FeBr + R'\cdot$$

$$R'\cdot + Fe \longrightarrow R'Fe$$

$$RMgBr + FeBr \longrightarrow RFe + MgBr_2$$

$$RFe, R'Fe \longrightarrow [R(H), R'(H), R(-H)', R'(-H)] + 2Fe, \text{etc.}$$

[11] A summary of the various mechanisms proposed for the Kharasch reaction is presented by M. H. Abraham and M. J. Hogarth, *J. Organometal. Chem.*, **12**, 497 (1968).

[12] Alfred P. Sloan Research Fellow, 1969–1971.

Richard B. Allen, Ronald G. Lawler,*[12] Harold R. Ward[12]
Metcalf Research Laboratories, Brown University
Providence, Rhode Island 02912

Received October 24, 1972

Oxidative Photoaddition of *p*-Benzoquinone to Cyclooctatetraene. A Chemical Application of the Laser

Sir:

During the course of an exploratory investigation intended to appraise the photochemical potential of the laser, we have studied the photocycloaddition of *p*-benzoquinone to cyclooctatetraene (COT).[1] A 6-W argon ion laser was used to selectively promote the *p*-benzoquinone to its n,π* excited state.[2] The ensuing photochemistry has been observed to be profoundly influenced by solvent acidity and the presence of oxygen.

In the absence of oxygen, irradiation of COT and *p*-benzoquinone affords a single product (**1**) (Scheme I). This sensitive substance is apparently the same as the material previously observed,[1] except that in this instance it could be readily isolated in crystalline form, mp 67–72° dec, from the uncomplicated laser reaction mixture. The adduct exhibits two single proton triplets in the nmr [δ 2.74 ppm (J = 8 Hz) and 4.67 ppm (J = 5 Hz)], which are not coupled to each other. Hydrogenation (Pd/C) of this adduct yields a phenolic alcohol **2**, mp 136.8–137.2°, which is not the same as the phenolic alcohol **3**, mp 120–121°, obtained from the hydrogenation (Pd/C) of the oxetane derived from cyclooctene and *p*-benzoquinone. These data together with the further chemistry of **1**, *vide infra*, strongly suggest that this substance is the 1,4-adduct **1** and not the 1,2-adduct **4** as proposed originally.[3] Irradiation of COT and *p*-benzoquinone in acetic acid either in the presence or absence of oxygen leads to two new substances as the only products: **5** [oil; nmr (60 MHz) δ 2.02 (s, 3 H), 2.30 (q, 1 H, J = 6 Hz), 5.42 (m, 2 H), 6.22 (m, 2 H), and 6.65 (m, 8 H)] and **6** [mp 81.5–82.5°, nmr (60 MHz) δ 5.48 (d, 1 H, J = 7 Hz), 6.48 (d, 1H, J = 7 Hz), and 6.65–7.75 (m, 10 H)]. These same materials are formed when the adduct **1** is warmed in acetic acid. Prolonged heating results in the complete conversion of both **1** and **5** to **6**. Similar acid catalyzed rearrangements have been observed with the epoxide of COT and certain cycloheptatriene derivatives.[4]

---

[1] D. Bryce-Smith, A. Gilbert, and M. G. Johnson, *J. Chem. Soc. C*, 383 (1967).

[2] A Coherent Radiation Model 53A argon ion laser with lines at 514.5 nm (2.5 W), 501.7 (0.5), 496.5 (0.7), 488.0 (1.5), 476.5 (0.6), and 457.9 (0.2) was used. At these wavelengths COT has an extinction coefficient of approximately ϵ 10^{-5}, and *p*-benzoquinone has λ_{max}^{hexane} 458 nm (ϵ 21) and 479 (ϵ 11).

[3] In the photoaddition of quinone carbonyls to conjugated dienes, 1,4 addition appears to be favored over the more usual 1,2 addition: J. M. Bruce, *Quart. Rev. Chem. Soc.*, **21**, 405 (1967).

[4] C. R. Ganellin and R. Pettit, *J. Chem. Soc.*, 576 (1958).