two ethylenes is quantitative rather than qualitative in character.

The suggested criterion is currently pertinent relative to the dehydrohalogenation reaction. Berry and Pimentel[1] have reported their observation of $HF^{(v)}$ and consequent lasing during the elimination of the halogen acid from nascent 1,1,1-trifluoroethane.

$$CF_3 + CH_3 \longrightarrow F_3C{-}CH_3^{(v)} \longrightarrow F_2C{=}CF_2 + HF^{(v)}$$

Accordingly we point to this as an operationally demonstrated example of a concerted bond-breaking process. One may anticipate a similar mechanism for the analogous reactions.

$$NH_3 + BX_3 \longrightarrow H_3N{:}BX_3^{(v)} \longrightarrow H_2NBX_2 + HX^{(v)}$$

The rates of association of ammonia with boron trihalides are of the order 10^{-2} of collision frequencies[2,3] and are not as exothermic as those of alkyl radical recombinations. However, they do have the distinct advantage that the reagents are individually stable and available in large quantities. A suitable flow reactor with appropriate temperature control is now being constructed in our laboratory.

Direct but limited study of the states of nascent products is possible *via* molecular beam techniques. For example, in an apparatus such as was described by Wilson,[4] a beam of 1-pyrazoline could be crossed by an intense flash of photolyzing radiation. Translational velocity analyses of the rays of nitrogen and cyclopropane which are ejected at measured angles relative to the beam axis will permit deduction of the partition of energy between translation, rotation, and vibration. In turn, the angular and linear momentum conservation conditions should permit the distinction between models wherein the final fission step was stepwise or concerted. This could be more easily ascertained for a decomposition which produces three particles, as does azomethane. Kinetic processes which are thermally initiated, in contrast to photolytic reactions, could be investigated in molecular beams for which the source is shock heated. The gas dynamics of back-reflected shock-driven molecular beams is under current development.[5]

Focus on the states of excitation of nascent products will sharpen as progress is made in the calculation of the shapes of potential energy surfaces for reacting systems. In highly exothermic, three-center displacement reactions $[A + BC \rightarrow (ABC)^{\ddagger} \rightarrow AB + C]$, Polanyi's computations[6] support his qualitative analysis that a strongly attractive potential favors the production of vibrationally excited $AB^{(v)}$. For the more complex four-center elimination reactions symmetry correlation criteria for the lowest energy reaction path[7-9] proved to be a powerful tool for predicting stereochemical features of the decomposition process. Computational experiments with models for vibrationally distorted structures should lead to predictions of the states of excitation of the nascent species, parallel to the current development of laboratory techniques for their characterization.

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A Novel Reduction by Diiron Nonacarbonyl

Sir:

We wish to report a novel and new reaction of diiron nonacarbonyl with an unsaturated hydrocarbon in which the latter suffers reduction after initial iron carbonyl complex formation.

Treatment of 1,2,5,6-tetrabromopyracene (I)[1] with 7 mole equiv of diiron nonacarbonyl in ether (6 ml) at 25° for 1 hr produces pyracylene (II)[1] in 95% yields (Scheme I).[2] If the reaction proceeds for 15 hr, a mixture of compounds is obtained. Separation by preparative thin layer chromatography[3] reveals the presence of three components. The fastest moving component (8% yield), a reddish black crystalline solid, has a molecular weight corresponding to the formula $C_{14}H_8 \cdot Fe_2(CO)_7$ by mass spectrometry. Unfortunately, attempts thus far to obtain either an nmr or epr spectrum have been unsuccessful.[4] The mass spectrum of the second component, formed in about 40% yield, shows a molecular ion at *m/e* 178 (base peak), with abundant peaks at *m/e* 177, 176, 152, 151, and 150. The nmr spectrum[5] consists of an AB pattern for 4 H (H_A at δ 7.65, H_B at δ 7.34, with $J_{AB} = 7$ Hz), a singlet (2 H) at δ 7.04, and a singlet (4 H) at δ 3.49. These data identify the compound as 1,2-dihydropyracylene (III). Its ultraviolet spectrum agrees with the published data.[6] Mass spectrometry shows the final product, formed in about 50% yield, to exhibit a molecular ion at *m/e* 354 with a base peak at *m/e* 177. High-resolution data indicate its formula to be $C_{28}H_{18}$. The nmr spectrum[5] shows an AB pattern for 8 H (H_A at δ 7.70, H_B at δ 7.46, with $J_{AB} = 8$ Hz), two singlets of unequal intensity at δ 7.01 and 6.98 totaling 4 H, a multiplet (2 H) at δ 4.59, and a very complex multiplet (4 H) centered at δ 2.90. The ultraviolet spectrum [$\lambda_{\max}^{\mathrm{EtOH}}$ 240 mμ (ϵ 78,270), 309 (9650), *ca.* 316 (sh; 12,060), 322 (17,790), *ca.* 328.5 (sh; 14,470), 345 (17,490), *ca.* 352 (sh; 12,970), and 360.5 (13,870)] is virtually superimposable on that of 1,2-dihydropyracyclene. This information supports the dimeric structure IV, present as a mixture of *meso* and *dl* isomers. Work-up of the reaction with D_2O leads

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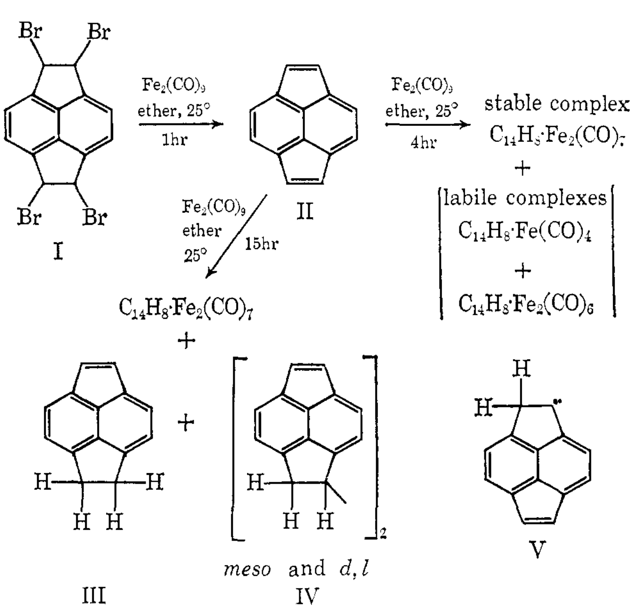
(1) (a) B. M. Trost and G. M. Bright, *J. Am. Chem. Soc.*, **89**, 4244 (1967). (b) This reaction has been carried out under both nitrogen and argon. Degassing the solution by the freeze–thaw technique has no effect on the course of the reaction. If the reaction is carried out in pentane, no reduction products are obtained; only the iron carbonyl complexes are produced.
(2) *Cf.* R. Pettit, G. Emerson, and L. Watts, *ibid.*, **87**, 131 (1965); W. R. Roth and J. D. Meier, *Tetrahedron Letters*, 2053 (1967).
(3) Preparative thin layer separations were achieved using deactivated silica gel G plates with hexane elution.
(4) A structure similar to that of diiron nonacarbonyl in which two of the bridging carbons have been replaced by pyracylene can be rejected as the infrared spectrum reveals the absence of bridging carbonyls.
(5) Determined as a solution in carbon tetrachloride.
(6) A. G. Anderson and R. G. Anderson, *J. Org. Chem.*, **23**, 517 (1968).

to no deuterium incorporation in either III or IV—a fact suggesting the ethereal solvent as the hydrogen source.

While treatment of pyracylene itself with diiron nonacarbonyl for 15-hr periods under similar conditions produces the $C_{14}H_8 \cdot Fe_2(CO)_7$ complex and reduction products III and IV, a mixture containing only organic iron carbonyl complexes is observed if the reaction is allowed to proceed just 4 hr. Preparative thin layer chromatography separates this mixture into two fractions, the fastest moving fraction containing a single component, the previously observed $C_{14}H_8 \cdot Fe_2(CO)_7$ complex. The second fraction consists of several very labile complexes, two major components having molecular formulas $C_{14}H_8 \cdot Fe(CO)_4$ and $C_{14}H_8 \cdot Fe_2(CO)_6$ by mass spectrometry.[7] Whereas the $C_{14}H_8 \cdot Fe_2(CO)_7$ complex remains unchanged when subjected for 20-hr periods to the reaction conditions of Scheme I, experiments with the mixture of iron tetracarbonyl and diiron hexacarbonyl complexes indicate that one or both of these unstable materials is responsible for reduction products III and IV. Upon standing in organic solvents, decomposition of the complexes occurs generating the observed products.

Scheme I. Reaction of Pyracylene with Diiron Nonacarbonyl



The anhydrous experimental conditions and the absence of deuterium in III and IV when D_2O is used in workup suggest the absence of proton-abstracting intermediates such as the free pyracylene radical anion or dianion. Furthermore, the absence of higher oligomers indicates the absence of free pyracylene radical anion. A most reasonable explanation for the formation of reduction products III and IV requires that in the intermediate pyracylene–iron carbonyl complex(es) involved in the reduction, the highest occupied orbital having primarily metal character and the lowest lying vacant orbital having mainly ligand character be of similar energy. Thus, a thermally accessible triplet state could be realized by the transfer of an electron from the highest occupied "metal orbital" to the vacant lowest lying "ligand orbital."[8] Hydrogen abstraction from solvent by this triplet species would produce radical V, either free or, more likely, complexed with iron.[9] Hydrogen abstraction from solvent by V would produce III, whereas an attack on a pyracylene molecule, with subsequent hydrogen abstraction from solvent, would lead to the dimeric product IV. This example represents the first reported case of a hydrocarbon ligand reduction by an iron carbonyl.

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[7] The nmr spectrum of this second thin layer fraction is consistent with reasonable structures for complexes having these molecular formulas. The mass spectrum shows peaks at *m/e* 344, 316, 288, 260, 232, 176, and 150 for the iron tetracarbonyl complex and peaks at *m/e* 456, 428, 400, 373, 344, 316, 288, 260, 232, 176, and 150 for the diiron hexacarbonyl complex. However the extreme lability of these complexes has thus far precluded their separation and complete characterization.

(8) For a discussion of current theories regarding the bonding in arene and olefin-metal carbonyl complexes see F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry," 2nd ed, Interscience Publishers, New York, N. Y., 1966, Chapters 26–28.

(9) The absence of high polymers suggests that these radicals (*i.e.*, V) are not free, but are bonded in some manners to iron.

(10) Alfred P. Sloan Foundation Fellow.

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Kinetics of Photoreduction of Aromatic Ketones by Primary, Secondary, and Tertiary Aliphatic Amines

Sir:

We have previously studied the kinetics of photoreduction of benzophenone by a primary amine, 2-butylamine, in benzene and have reported[1] values for k_{ir} and k_d, the rate constants for interaction of the excited triplet ketone with the amine and that for decay of the triplet, respectively. We were unable to carry out such studies with secondary and tertiary amines because of formation of light-absorbing products. This difficulty was avoided in aqueous medium, in which secondary and tertiary amines were very effective photoreducing agents.[2] Kinetic constants have now been determined for photoreduction of the 4-benzoylbenzoate anion by the three classes of amines in aqueous medium. Reaction with tertiary amines is exceedingly rapid.

Solutions of 0.10 *M* 4-benzoylbenzoic acid, 0.12 *N* NaOH, and 0.050–1.0 *M* amine in 1:1 water–pyridine were degassed and irradiated under argon in Pyrex tubes on a turntable with a G.E. H-85 W-A3 lamp. Photoreduction of the ketone was followed by measurement at 338 nm of the absorbance of aliquots diluted with acidified 2-propanol. Rates of photoreduction of 0.10 *M* ketone by 1.0 *M* amine in the same medium were determined as a function of concentration (0.0050–0.080 *M*) of a quencher, naphthalene. Linear plots of inverse rate against inverse concentration of amine, and of inverse rate against concentration of naphthalene, led to values of k_{ir}/k_d and k_q/k_{ir}. Some results are summarized in Table I. Data for photoreduction of this ketone and of benzophenone by 1 *M* 2-propanol are included.

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