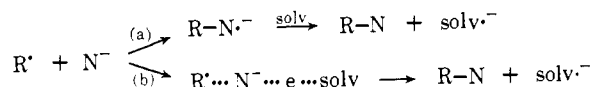


Coupling of Radicals with Nucleophiles. Scope of the Reaction¹

Sir:

There now exists substantial evidence for the coupling of radicals with nucleophiles to form products by way of intermediate radical ions.²⁻⁷ Most of this came from studies of systems which are uniquely structured to impart stability to the radical ion. These include nitroarenes,² nitroalkanes,³ and relatively simply substituted aromatics.⁴ Most recently, it was shown that a still simpler radical, 3-cyclohexenyl, couples rather efficiently with a variety of nucleophiles⁷ and the question thus posed was whether or not a radical ion is necessarily an intermediate, coupling reaction a, a



possible alternative being the transfer of an electron to solvent in the transition state (b). This appeared to be energetically unfavorable but could not be dismissed.⁸

We now report results of a study of the behavior of saturated radicals toward a number of saturated and unsaturated nucleophiles in solution. *tert*-Butyl radical and *n*-butyl radical were generated by the photodissociation of 2,2'-azobisisobutane and 1,1'-azobisbutane, respectively, in solutions of the appropriate nucleophile dissolved in hexamethylphosphoramide (HMPA).⁹ A filter was used to absorb irradiation of sufficiently short wavelength to excite either solvent or reaction products. Solutions contained approximately 1×10^{-3} mol of azo compound and between 5 and 6×10^{-3} mol of NaN or KN in 15 ml of HMPA.

Results are summarized in the following reaction schemes¹⁰ and expressed quantitatively in Tables I and II.

(1) This research was supported by the National Science Foundation.

(2) N. Kornblum, R. E. Michel, and R. C. Kerber, *J. Amer. Chem. Soc.*, **88**, 5660, 5662 (1966), and earlier papers cited therein; N. Kornblum, T. M. Davies, G. W. Earl, N. L. Holy, R. C. Kerber, M. T. Musser and D. H. Snow, *ibid.*, **89**, 725 (1967); N. Kornblum, T. M. Davies, G. W. Earl, G. S. Greene, N. L. Holy, R. C. Kerber, J. W. Manthey, M. T. Musser, and D. H. Snow, *ibid.*, **89**, 5714 (1967); N. Kornblum and F. W. Stuchal, *ibid.*, **92**, 1804 (1970); N. Kornblum, R. T. Swiger, G. W. Earl, H. W. Pinnick, and F. W. Stuchal, *ibid.*, **92**, 5513 (1970); M. Barreau and M. Julia, *Tetrahedron Lett.*, 1537 (1973).

(3) G. A. Russell and W. C. Danen, *J. Amer. Chem. Soc.*, **88**, 5663 (1966); G. A. Russell, R. K. Norris, and E. J. Panek, *ibid.*, **93**, 5839 (1971).

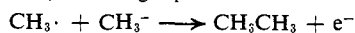
(4) J. F. Bunnett and C. C. Wamser, *J. Amer. Chem. Soc.*, **89**, 6712 (1967); J. K. Kim and J. F. Bunnett, *ibid.*, **92**, 7464 (1970); R. A. Rossi and J. F. Bunnett, *ibid.*, **94**, 683 (1972); *J. Org. Chem.*, **37**, 3570 (1972); **38**, 1407, 3020 (1973); J. A. Zoltewicz and T. M. Oestreich, *J. Amer. Chem. Soc.*, **95**, 6863 (1973). See also A. N. Frolov and O. V. Kul'bitskaya, *Zh. Org. Khim.*, No. 2, 432 (1972).

(5) J. G. Lawless and M. D. Hawley, *J. Electroanal. Chem.*, **21**, 365 (1969); D. E. Bartak, W. C. Danen, and M. D. Hawley, *J. Org. Chem.*, **35**, 1206 (1970).

(6) A good review of much of this work is presented by J. F. Garst in "Free Radicals," Vol. 1, J. K. Kochi, Ed., Wiley-Interscience, New York, N. Y., 1973, pp 503-546.

(7) D. Y. Myers, G. G. Stroebel, B. R. Ortiz de Montellano, and P. D. Gardner, *J. Amer. Chem. Soc.*, **95**, 5832 (1973).

(8) Note, however, that the gas-phase reaction




is reported to be exothermic by 60 kcal/mol, ref 6, p 539.

(9) HMPA was purified by fractional distillation under reduced pressure. Experiments using material which was further purified by distillation from calcium hydride gave the same results.

(10) The observed competing disproportionation in the case of *tert*-butyl radical and radical coupling in the case of *n*-butyl radical are consistent with other findings. For a recent discussion see M. J. Gibian and R. C. Corley, *Chem. Rev.*, **73**, 441 (1973).

Table I. Yields of Products and Conversion Levels for the Reaction of *tert*-Butyl Radical with Various Nucleophiles^a

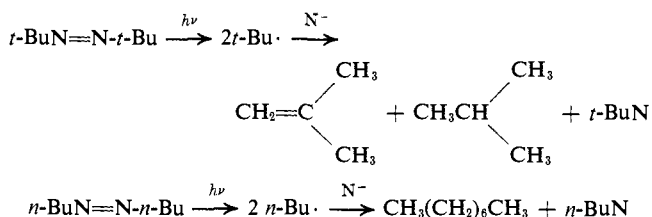
Nucleophile (N ⁻)	Alkane (%)	Alkene (%)	<i>t</i> -BuN (%)	Conversion (%)
None	59	39	0	81
AcO ⁻	37	35	29	79
CN ⁻	45	42	0.6	79
N ₃ ⁻		11 ^b	17 ^c	100
	42	21	~0 ^{d,e}	88 ^f
EtO ⁻		38 ^b	~0 ^d	100 ^f

^a Yields and conversions were determined by glc using appropriate internal standards. Yields are based on unrecovered starting material and expressed to account for two radicals/molecule of azo compound. The limit of accuracy is $\pm 2\%$. ^b Per cent of combined alkane and alkene. ^c Determined as the amine after reduction with NaBH₄. ^d Not detectable by glc. ^e A small amount (3%) of dimer resulting from radical coupling was also observed. Pyrrolidine rather than HMPA was used as the solvent in this experiment. ^f Considerable resin was formed which was shown from blank runs to be derived from solvent.

Table II. Yields of Products and Conversion Levels for the Reaction of *n*-Butyl Radical with Various Nucleophiles^a

Nucleophile (N ⁻)	<i>n</i> -Octane (%)	<i>n</i> -BuN (%)	Conversion (%)
None	10	0	100
AcO ⁻	4	29	85
CN ⁻	3	2	86
N ₃ ⁻	3	16	100

^a See footnote a in Table I for a description of general analytical procedures and the expression of data. The use of 1,1'-azobisbutane as a radical source for reaction with basic nucleophiles is precluded by its facile base-induced isomerization.



Data in Tables I and II show that saturated radicals do indeed couple with nucleophiles although with widely varying degrees of efficiency. Highest yields of adducts with both *tert*-butyl and *n*-butyl radicals were observed in experiments employing acetate and azide ions. By contrast, experiments with pyrrolidine and ethoxide ion (Table I) failed to produce detectable quantities of adduct. These observations are rather significant in view of the fact that adducts derived from coupling with cyanide ion were easily detected and quantitated at levels as low as 0.6%. The failure of pyrrolidine or ethoxide ion to couple with *tert*-butyl radical suggests that the presence of an unsaturation site in the nucleophile is a requisite for the reaction. To determine if this must be adjacent to the atom at which bonding occurs, attempts were made to couple *tert*-butyl radical with the salt of allyl alcohol. No adduct could be detected.

The behavior of each radical in HMPA in the absence of a nucleophile was examined to obtain base line data. The ratio of isobutane to isobutylene (59/39) shown for *tert*-butyl radical in Table I indicates that 78% of the radicals produced from the azo precursor

disproportionate and that about 20% of them abstract hydrogen from HMPA. The higher ratio (42/21) observed from the reaction using pyrrolidine as both nucleophile and solvent merely reflects the relative ability of pyrrolidine and HMPA to donate hydrogen atoms to radicals. The production of essentially equimolar amounts of alkane and alkene in the reaction using acetate ion makes it clear that radical-nucleophile coupling leading to *tert*-butyl acetate occurs virtually to the exclusion of the hydrogen abstraction process. Further, the similar alkane/alkene ratio in the reaction using cyanide ion suggests that radical-nucleophile coupling is a major competing reaction in this case as well even though this is not reflected in the yield of coupling product. The possible further reaction of *t*-BuCN with its radical ion to give higher molecular weight products is being explored.

These results, examined with earlier findings,⁷ indicate that the coupling of radicals with nucleophiles is a general reaction if *either* of the two reactants has a site of unsaturation which may be as simple as an isolated multiple bond. They also suggest, however, that the multiple bond must be adjacent to the atom being bonded. The mechanistic implication is that reaction will occur only if a reasonably low-lying antibonding orbital is available at the reaction site, a strong argument for the intermediacy of an adduct radical ion. The fate of the electron has not yet been determined although it is clear that its capture by R· is not an important process when HMPA is used as a solvent. It is very likely transferred to solvent, as noted in the reaction scheme, and leads ultimately to solvent decomposition products.¹¹

It appeared reasonable that the variation in yields of RN might reflect the relative stabilities of RN radical ions, a postulate which in principle could be explored with polarographic measurements. Unfortunately, all three classes of compound require higher negative voltages for reduction than can be successfully applied with presently available solvents and supporting electrolytes.

We have no good estimate of the absolute efficiency of the coupling reaction. The fact that it competes favorably with disproportionation in the case of *tert*-butyl radical and with radical coupling and hydrogen abstraction in the case of *n*-butyl radical suggests that it is rather fast.

(11) G. Fraenkel, S. H. Ellis, and D. T. Dix, *J. Amer. Chem. Soc.*, **87**, 1406 (1965).

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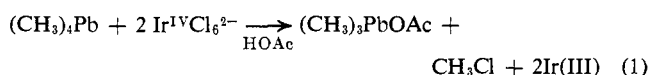
Alkyl Transfers from Organometallic Compounds by One-Electron Processes

Sir:

The formation and cleavage of alkyl-metal bonds play an important role in the chemistry of organometallic intermediates involved in catalytic processes of organic as well as biochemical substrates. We wish to demonstrate the importance of electron transfer pro-

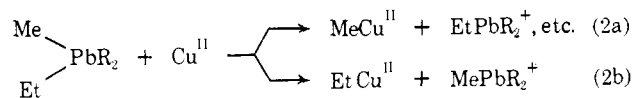
cesses as viable routes for reactions of alkyl-metals since charge transfer and other homolytic processes are little known¹ in contrast to the usual electrophilic mechanisms.²

As a model system, we examined alkyl transfers from a series of organoleads listed in Table I with hexachloroiridate(IV), which is known to participate in outer-sphere oxidations involving one-electron changes.³ For example, the oxidative cleavage of tetraethyllead by Ir^{IV}Cl₆²⁻ occurs rapidly at 25° with a 1:2 stoichiometry in acetic acid or acetonitrile solutions to afford ethyl chloride and chloroiridium(III). Similarly, only one alkyl group is readily cleaved from the other tetraalkylleads [PbMe_nEt_{4-n}]. The lead species from tetramethyllead in acetic acid can be identified as trimethyllead acetate by quantitative pmr analysis of the reaction mixture.



The rates were followed in acetonitrile by the disappearance of IrCl₆²⁻ spectrophotometrically and showed a first-order kinetic dependence on each reactant.

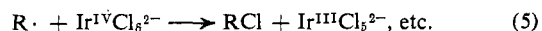
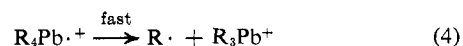
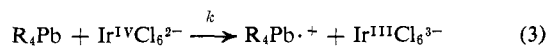
Two important criteria can be used to distinguish the reaction with Ir^{IV}Cl₆²⁻ from the more conventional electrophilic processes, *e.g.*, with Ag^I, Cu^I,¹¹ complexes, etc.⁴ First, the rate of reaction of PbMe_nEt_{4-n} with IrCl₆²⁻ increases successively as methyl is replaced by ethyl groups (see *n* = 4-0 in Table I, column 2). Second, a given ethyl group is cleaved approximately 25 times faster than a methyl group (column 5). Both of these reactivity trends are diametrically opposed to an electrophilic cleavage such as reaction 2 with chloro-



copper(II). Thus, preferential attack by the copper(II) electrophile occurs directly at the less hindered methyl site by a factor of 44.^{4b,d,e}

These results suggest that the rate-limiting step with IrCl₆²⁻ occurs prior to alkyl transfer, and we propose the mechanism given in Scheme I in which the slow step

Scheme I



(1) Cf. (a) P. Abley, E. R. Dockal, and J. Halpern, *J. Amer. Chem. Soc.*, **94**, 659 (1972); (b) J. H. Espenson and J. S. Shveima, *ibid.*, **95**, 4468 (1973); (c) A. van den Bergen and B. O. West, *Chem. Commun.*, **52**, (1971); (d) D. Dodd and M. D. Johnson, *J. Organometal. Chem.*, **52**, 1 (1973).

(2) M. H. Abraham in "Comprehensive Chemical Kinetics," Vol. 12, C. H. Bamford and C. F. Tipper, Ed., Elsevier, Amsterdam, 1972.

(3) J. Halpern, R. J. Legare, and R. Lumry, *J. Amer. Chem. Soc.*, **85**, 680 (1963); J. Halpern and M. Pribanić, *ibid.*, **90**, 5942 (1968); P. Abley and J. Halpern, *Chem. Commun.*, 1238 (1971).

(4) (a) N. Clinton and J. K. Kochi, *J. Organometal. Chem.*, **42**, 229 (1972); (b) *ibid.*, **56**, 243 (1973); (c) *ibid.*, **61**, 433 (1973); (d) *ibid.*, **56**, 227 (1973); (e) The stoichiometry of the reaction of tetraalkyllead with copper(II) chloride is the same as that for iridium(IV) in eq 1. Alkyl chlorides are formed subsequent to homolysis of the alkylcopper(II) intermediates in eq 2 by ligand transfer with copper(II) chloride, *e.g.*

