

served was unexpected. *N,N'*-Bisuccinimidyl was recovered quantitatively from a solution in chlorobenzene (b.p. 130°) containing a two molar excess of bromine and from a mixture of diphenyl ether and tetralin (3:1) (b.p. ca. 230°) in each case after refluxing for 24 hr. under irradiation with a 275-w. sun-lamp through a Pyrex flask. Also, *N,N'*-bisuccinimidyl was recovered in 95% yield after heating for 24 hr. in a sealed tube at 400–500°.⁹

The N–N bond energy in *N,N'*-bisuccinimidyl and closely related cyclic *N,N'*-diimides may be qualitatively represented as that of hydrazine less the difference between the resonance energies of the radical and the ground state dimer. While one might anticipate a cancellation of the resonance energy term for the radical by that due to the unshared pair on nitrogen in the dimer, the striking stability of the dimer suggests some extra stabilization in the ground state leading to a net increase in N–N bond energy. Experiments bearing on this question and that of the stability of the succinimidyl radical are currently in progress.

(9) It has been noted previously that *N,N'*-bipthalimidyl is an inefficient initiator for vinyl polymerization (C. Walling and A. N. Naglieri, *J. Am. Chem. Soc.*, **82**, 1820 (1960)).

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The Acidities of Weak Acids in Dimethyl Sulfoxide

Sir:

Price and Whiting¹ recently reported the use of a dimethyl sulfoxide solution of the sodium salt of dimethyl sulfoxide ("dimsylsodium")² as a reagent for titrating weak acids, such as alcohols, using triphenylmethane as an indicator. They obtained stoichiometric end points for all of the titratable acids tried except for glycerine (see Table I). We have likewise been using dimsyl reagents, as well as triphenylmethide reagents, to prepare alcohol-free alkoxide solutions. The method is advantageous in that the conversion of alcohol to alkoxide is practically instantaneous, strong reducing conditions do not prevail, and the equivalence point is readily observed because of the presence of the indicator. However, the method is limited as to the type of cation which may be used. Table I shows a comparison of titration data reported by Price and Whiting using dimsylsodium with data we obtained using dimsylpotassium. It may be seen that most acids having pK_a values lower than triphenylmethane's, with the exception of alcohols and amines, give stoichiometric end points with both ions. With alcohols, the triphenylmethyl anion becomes visible when only about one-half the calculated amount of dimsylpotassium has been added. Tetrahydrofuran solutions of triphenylmethides may be used to prepare both sodium and potassium alkoxides. In the latter case, however, end points occur when about 85% of the calculated amount of triphenylmethide solution has been added. With triphenylmethylcesium the method is not practical because the end point occurs when only about 50% of the calculated amount of base has been added.

The limitations in the titration method for preparing alkoxides are unexpected. The reported³ pK_a values of alcohols are 16–19 and of triphenylmethane, 33. This large difference between them means that the alcohols should be converted almost completely to alkoxides before a significant proportion of triphenylmethane will remain as its conjugate base. In contrast, our results show that significant quantities of

(1) G. G. Price and M. C. Whiting, *Chem. Ind. (London)*, 775 (1963).

(2) E. J. Corey and M. Chayakowski, *J. Am. Chem. Soc.*, **84**, 866 (1962).

TABLE I

Acid	Lit. pK_a^a	Moles of dimsyl ion per mole of acid to give visible concn. of Ph ₃ C ⁻	
		Na ⁺ ^b	K ⁺
Benzoic acid	4.2		1.01
Acetic acid	4.8	1.03	
2,4,6-Trichlorophenol	6.2		1.01
Phenol	9.9	1.02	0.99
Formanilide			[1.00] ^c
Glycerol		1.56	1.00
1-Methoxy-2-propanol			0.54
Dipropylene glycol methyl ether			.53
Tripolyene glycol methyl ether			.64
Water	15.7	1.00	.31
Ethanol	18		.45
<i>n</i> -Butyl alcohol		0.98	.33
<i>t</i> -Butyl alcohol	19	1.06	.97
Cyclopentadiene	17	0.99	.98
Indene	21	.98	1.00
Diphenylamine	23	.99	<0.01
Aniline	27	<.01	
Triphenylmethane	33		

^a See ref. 3. ^b See ref. 1. ^c Used to standardize the reagent.

triphenylmethide can exist in solutions having an alcohol-alkoxide ratio of one or more. The implication is that the two types of acids have approximately the same acidity. Furthermore, the very low acidities of alcohols under the conditions used here are not caused by some unique function of dimethyl sulfoxide, since comparable results are obtained in tetrahydrofuran solutions. The vast changes in the apparent acidity of alcohols as the medium and cation are varied have led us to undertake a detailed, quantitative study of these acid-base equilibria.

The general method of Stearns and Wheland^{3c} is being used with dimethyl sulfoxide as the solvent and di- and triphenylmethane as the indicators. McEwen^{3b} estimated the pK_a values of the indicators to be 35 and 33, respectively, but since the data are not precise we have chosen to use dimethyl sulfoxide as the reference acid. We find that the respective acidities of the indicators are approximately 0.6×10^3 and 13×10^3 times that of the solvent. The latter value does not agree with the estimated value of 21 as reported by Corey and Chayakowski,² which was obtained by treatment of an equilibrium mixture of dimsylsodium and triphenylmethane with D₂O and analysis of the resultant triphenylmethane for deuterium content. The reason for the large difference between the two values is not known, but we believe the present value is more reliable because it was obtained by direct measurement on the equilibrium mixture. The relative acidities of the indicators agree well with the estimates of McEwen.^{3b}

We have measured the acidities of *t*-butyl and *n*-butyl alcohols over a range of values for $[RO^-]/[ROH]$. At low $[RO^-]/[ROH]$, the acidity is relatively high. As $[RO^-]/[ROH]$ increases the acidity decreases rapidly and becomes constant at $[RO^-]/[ROH]$ greater than 2. The limiting value for the acidity is about 7×10^3 times that of dimethyl sulfoxide and is, within experimental error, the same for both alcohols. The alcohols are different in that the apparent acidity of *n*-butyl alcohol increases more rapidly as $[RO^-]/[ROH]$ decreases.

It is interesting to compare these data with a study by Stewart, O'Donnell, Cram, and Rickborn⁴ of the

(3) (a) P. S. Danner, *ibid.*, **44**, 2832 (1922); (b) W. K. McEwen, *ibid.*, **58**, 1124 (1936); (c) R. S. Stearns and G. W. Wheland, *ibid.*, **69**, 2025 (1947); (d) J. Hine and M. Hine, *ibid.*, **74**, 5266 (1952). (e) A. Streitwieser, Jr., *Tetrahedron Letters*, No. 6, 23 (1960).

(4) R. Stewart, J. P. O'Donnell, D. J. Cram, and B. Rickborn, *Tetrahedron*, **18**, 917 (1962).

acidity function (H_-) of 0.025 *M* sodium methoxide in mixtures of methanol and dimethyl sulfoxide. They found that H_- varied from 12 to 19 as the mole ratio of methanol in the solvent was decreased from 100 to 5%. In our system the mole ratio of alcohol is about 0.02% and the H_- about 33 if McEwen's^{5b} pK_a values are valid in this system. Hence, removal of the last 5% of alcohol increases the basicity of the medium by a factor of 10^{14} .

In order to explain the foregoing results, we suggest that the inherent acidity of alcohols is very low—less than that of triphenylmethane—and that the apparent acidity is increased drastically by materials which can reduce the activity of the alkoxide. Alcohols can do this by hydrogen bonding and cations by coordination or by forming incompletely ionized alkoxides as has been discussed by Cram⁵ and his co-workers.

(5) D. J. Cram, C. A. Kingsbury, and B. Rickborn, *J. Am. Chem. Soc.*, **83**, 3688 (1961).

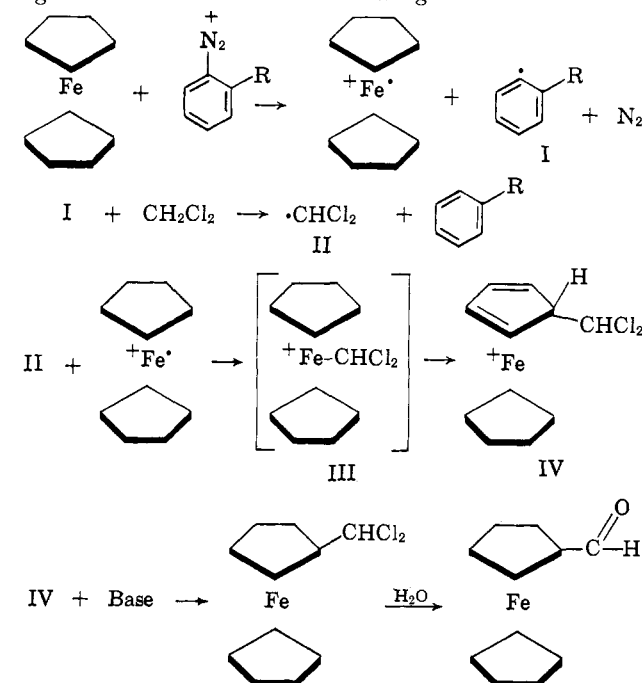
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A Novel Side Reaction Accompanying the Arylation of Ferrocene. An Example of Free Radical Substitution

Sir:

In the course of preparing a series of *o*-substituted phenylferrocenes, we have encountered an unusual side reaction with certain benzenediazonium salts and ferrocene in halohydrocarbon solvents. For example, the diazonium salts derived from *o*-toluidine, *o*-ethyl-aniline, 2,6-xylydine, and mesidine, formed in sulfuric acid and added to a mixture of an aqueous sodium acetate buffer and a solution of ferrocene in methylene chloride or added as dry diazonium fluoroborates to ferrocene in methylene chloride, followed by an aqueous work-up procedure, yielded principally recovered ferrocene and significant amounts of ferrocene monoaldehyde. The formation of the aldehyde can be explained in terms of an attack of the dichloromethyl radical, produced from the solvent, on the ferrocene nucleus, followed by hydrolysis to the aldehyde according to a scheme such as the following.



Similar reactions occurred in other halohydrocarbon solvents. In chloroform, ferrocenoic acid and ethyl ferrocenoate¹ were produced; in ethylidene chloride, acetylferrocene was formed; and in bromotrichloromethane, ferrocenoic acid was the major reaction product. In all cases, large amounts of ferrocene were recovered (from 36 to over 80%). Table I shows the results from typical experiments, with yields based on unrecovered ferrocene.

TABLE I
REACTION OF FERROCENE WITH SOLVENT RADICALS UNDER ARYLATION CONDITIONS

Diazonium salt employed	Solvent	Product	Yield, %
<i>o</i> -Toluenediazonium acetate	CH ₂ Cl ₂	FcCHO	16
Mesitylenediazonium acetate	CH ₂ Cl ₂	FcCHO	23
<i>o</i> -Toluenediazonium acetate	CHCl ₃	FcCO ₂ H	25
2,6-Dimethylbenzenediazonium fluoroborate	CHCl ₃	FcCO ₂ Et ^a	26
		FcCO ₂ H	Trace
2,6-Dimethylbenzenediazonium fluoroborate	CH ₃ CHCl ₂	FcCOCH ₃	10
<i>o</i> -Toluenediazonium fluoroborate	CH ₃ CHCl ₂	FcCOCH ₃	5
		<i>o</i> -CH ₃ C ₆ H ₅ Fc	64
2,6-Dimethylbenzenediazonium acetate	CCl ₃ Br	FcCO ₂ H	43

^a See ref. 1.

These reactions, while as yet of little synthetic value, are of interest in view of the evidence recently presented by Rosenblum² that neither ferrocene nor the ferricenium ion is susceptible to radical substitution. There seems to be no doubt that phenyl radicals are produced in the reaction between ferrocene and diazonium salts,^{2,3} and there are numerous reports of the reaction of phenyl radicals with halohydrocarbon solvents^{4,5} to produce solvent radicals. The usual order of abstraction in such reactions is Br > H > Cl,⁴ as observed here.⁶

While we have no evidence that the radical attack occurs on the ferricenium ion rather than on neutral ferrocene (both are present in the reaction mixture), Beckwith and Leydon³ have recently reported that azobisisobutyronitrile attacks the ferricenium ion, by a radical process, but does not react with neutral ferrocene under conditions that preclude the formation of the ferricenium ion. The existence of intermediate III has not been demonstrated, but it seems reasonable since the ferricenium ion contains an unpaired electron, and suggestions of the involvement of the metal atom in electrophilic substitution^{2,7,8} seem plausible. Direct attack on the carbocyclic ring⁹ remains a possibility, however.

The rapid hydrolysis of the intermediate chloroalkylferrocene (V) would be expected, since it is known

(1) Ethyl ferrocenoate was produced when dry diazonium fluoroborates were added to dry chloroform solutions of ferrocene. The chloroform used contained 0.5% of ethanol as a preservative. This amount was more than enough to account for the ethyl ester produced.

(2) M. Rosenblum, W. G. Howells, A. K. Banerjee, and C. Bennett, *J. Am. Chem. Soc.*, **84**, 2726 (1962).

(3) A. L. J. Beckwith and R. J. Leydon, *Tetrahedron Letters*, **6**, 385 (1963).

(4) For examples and references, see C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957, p. 247 ff.

(5) D. H. Hey and J. Peters, *J. Chem. Soc.*, 79 (1960).

(6) Hey and Peters⁵ have reported that sodium benzenediazoate at 0° and other phenyl radical sources, such as *N*-nitrosoacetanilide and benzoyl peroxide, at higher temperatures react with chloroform to form principally, and usually exclusively, CCl₃ radicals, but at 0° benzenediazonium acetate abstracts chlorine rather than hydrogen. We have looked carefully for ferrocenemonoaldehyde among the reaction products in chloroform solvent, but have not found this compound to be present.

(7) J. H. Richards, presented at the 135th National Meeting of the American Chemical Society, Boston, Mass. April, 1959; *cf.* Abstracts, p. 86-O.

(8) M. Rosenblum and W. G. Howells, *J. Am. Chem. Soc.*, **84**, 1167 (1962); M. Rosenblum, J. O. Santer, and W. G. Howells, *ibid.*, **85**, 1450 (1963).

(9) W. F. Little and A. K. Clark, *J. Org. Chem.*, **25**, 1979 (1960).