trast to this trend. The solvent effects are complemented by enhanced stereoselectivity of the chloro analog **1c**.

Since the presence of heavy atoms is manifested in the stereoselectivity of photocyclization, the effect may be attributed to an enhanced rate of intersystem crossing in the conversion of the reactive n,π^* triplet carbonyl to cyclized products. In this event, it follows that facile intersystem crossing allows a highly stereoselective formation of the *cis*-2-phenyl-3-hydroxy isomer and, furthermore, that the loss of this specificity occurs in competition with the crossing process. These conclusions are particularly pertinent to the nature of solvent effects on the stereochemical course of this process. Whereas the previous results might have been explicable solely in terms of solvation of a biradical intermediate and the cyclization thereof, the high order of stereoselectivity in the polar heavy atom solvents is inconsistent with this possibility. Rather, in the event that a biradical intermediate is involved, the results indicate that stereochemical control is established in its formation, which clearly implicates a favored geometry for abstraction. Thus, both the stereochemistry of abstraction and cyclization are important considerations. These factors have been discussed previously[7] with reference to this system as well as the analogous case of *o*-benzyloxybenzaldehyde.[8]

The loss of specificity may well occur by solvent-dependent rotational relaxation of an intermediate triplet biradical in competition with intersystem crossing and cyclization. A similar argument has been advanced to explain a heavy atom effect on the quantum yield of sensitized photodimerization of coumarin.[9] In this view, the low order of stereoselectivity in polar solvents and the temperature effect in nonpolar media may reflect an enhanced rate of rotational equilibration of the triplet biradical or a diminished rate of intersystem crossing in its conversion to cyclized products.

In order to obtain evidence on the possible intermediacy of a biradical, irradiation of the mono- and dideuterated analogs **1a**-d_1 and -d_2, substituted at the benzyloxy carbon, was carried out in benzene and acetonitrile. Whereas the D:H ratio at the benzylic carbon of the cyclized products derived from **1a**-d_1 was found to be between 2 and 3:1 in both solvents, indicative of favored H abstraction, the quantum yields of product formation were found to be only slightly lower relative to the protiated parent (Table I). The quantum yields for **1a**-d_2 were somewhat lower still. Together, these results are indicative of an efficient abstraction process and serve as evidence against the importance of reverse hydrogen abstraction in this system, thereby neither implicating nor excluding the intermediacy of a biradical.[10]

In precluding the importance of inefficiency in abstraction and cyclization, the results do, however, support a recent study which correlates the low quantum yields in polar media with inefficient intersystem crossing in the population of the reactive triplet carbonyl.[11] Thus, the low quantum yields and the low order of stereoselectivity in polar solvents do not appear to be directly related. However, both effects are explicable in terms of reduced rates of intersystem crossing, the former in the formation of the reactive triplet carbonyl, the latter in its conversion to products. As such, both effects may reflect a reordering of energy levels in polar media.[12]

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(8) (a) S. P. Pappas and J. E. Blackwell, *Tetrahedron Lett.*, 1171 (1966); (b) S. P. Pappas, R. D. Zehr, and J. E. Alexander, *J. Heterocycl. Chem.*, 7, 1215 (1970).

(9) R. Hoffman, P. Wells, and H. Morrison, *J. Org. Chem.*, **36**, 102 (1971).

(10) D. R. Coulson and N. C. Yang, *J. Amer. Chem. Soc.*, **88**, 4511 (1966); (b) P. J. Wagner, *ibid.*, **89**, 5898 (1967).

(11) S. P. Pappas, R. D. Zehr, J. E. Alexander, and G. L. Long, *Chem. Commun.*, 318 (1971).

(12) J. Jortner, S. A. Rice, and R. M. Hochstrasser, *Advan. Photochem.*, 7, 149 (1969).

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Transition Metal Promoted Reductive Decyanation of Alkyl Nitriles

Sir:

In the hope that the reaction may find synthetic utility, we wish to describe the convenient, transition metal promoted reductive decyanation of alkyl nitriles to

$$\text{R—CN} \longrightarrow \text{R—H}$$

hydrocarbons. In representative cases, the transformation was carried out in 58–100% yields by the action of Fe(acac)$_3$–Na or, in lower yields, by means of "titanocene" ($C_{20}H_{20}Ti_2$), prepared and utilized *in situ*.[1]

Products and yields listed in Table I resulted from use of the following procedure. Under an argon atmosphere,[2] Fe(acac)$_3$ (10 mmol), organic cyanide (10 mmol), and sodium sand (20 mg-atoms) were stirred in 25 ml of

Table I. Reductive Cleavage of Nitriles (RCN) to Hydrocarbons by Fe(acac)$_3$–Na^0 (1:2)

Starting material, R =	Product	Yield, %
Methyl	Methane	98
n-Octyl	*n*-Octane	100
tert-Butyl	Isobutane	58
	Isobutylene	40
Cyclopentyl	Cyclopentane	77
Δ^3-Cyclohexenyl	Cyclohexene	80
Benzyl	Toluene	56
Δ^1-Cyclohexenylmethyl	1-Methylcyclohexene	43
Allyl	Propylene	40
Phenyl[a]	Benzene	46
1,1′-Dicyanobicyclohexyl	Bicyclohexyl	76

[a] Toluene solvent.

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(1) Formation of hydrocarbon by reductive cleavage of nitriles results from the action of Na or Li in liquid NH$_3$ or C$_2$H$_5$NH$_2$, or by electrolysis in C$_2$H$_5$NH$_2$. See: P. G. Arapakos, *J. Amer. Chem. Soc.*, **89**, 6794 (1967); P. G. Arapakos and M. K. Scott, *Tetrahedron Lett.*, 1975 (1968); and P. G. Arapakos, M. K. Scott, and F. E. Huber, Jr., *J. Amer. Chem. Soc.*, **91**, 2059 (1969). It is pertinent that, in contrast to the present findings, yields in the alkali metal–amine reductions were optimal with trityl, benzhydryl, benzyl, phenyl, and *tert*-alkyl cyanides, while in primary–secondary alkyl cases, the expected hydrocarbon products were generated in 35–49% and were accompanied by considerable amounts of organic amine and hydrocarbons resulting from carbon skeletal rearrangements. The entire body of results points to intrinsic mechanistic differences between the transition metal promoted and nontransition metal promoted processes, in keeping with the view of Arapakos and coworkers that ther system involves a stepwise, two (solvated) electron transfer to nitrile with formation of radical and carbanion, followed by protonation of the latter.

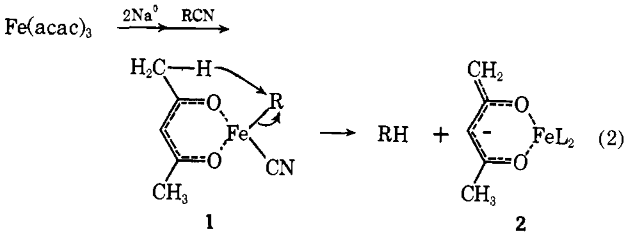
(2) In one octyl cyanide run, wherein the reactants were weighed, and the reaction started, in air, the yield fell from 100 to 71%.

dry benzene at room temperature for 50–70 hr. After the addition of 0.5 ml of water, the reaction mixture was analyzed for hydrocarbon content by vpc means (10 ft long, $^1/_4$ in. Porapak S or 10% Carbowax column at 100–120°). It is of interest that the best yields (58–100%) are obtained with saturated primary, secondary, and tertiary cyanides. The lower yields (40–46%) observed in the allyl and phenyl cases may be a consequence of alternative behavior patterns of the more stable allyl and phenyl radicals. Yields (per cent) of *n*-octane from *n*-octyl cyanide decreased markedly when the same, or a similar, procedure was employed, but with different transition metal–reducing agent combinations, *e.g.*: $TiCl_3$–Mg (2.5), $FeCl_3$–Mg (5), $CoCl_2$–Mg (3.5), $Ti(O\text{-}i\text{-}C_3H_7)_4$–K(25), $Fe(acac)_3$–Mg(0.0–0.5), $Fe(acac)_3$–Zn(0). With $Mo(acac)_3$–Na or NaNp, yields for the octyl cyanide case fell in the range 14–71%. Reductive decyanations with "titanocene" ($C_{20}H_{20}Ti_2$) (in toluene for 2 days at room temperature) are noteworthy in that although yields in preliminary experiments were lower than with the $Fe(acac)_3$–Na system, no external reducing agent need accompany the transition metal reagent.[3]

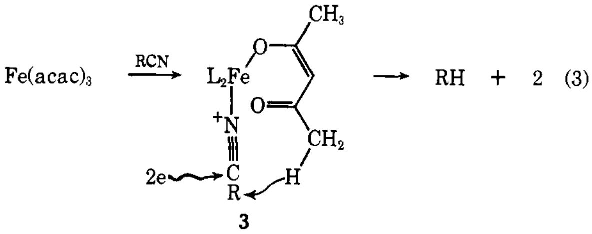
In connection with stoichiometric and mechanistic aspects, the following experiments were carried out. A series of reduction runs, in which the molar ratios of $Fe(acac)_3$ or metallic sodium were varied while other variables were held constant, revealed that 1 and 2 equiv, respectively, of these reagents are required for maximal yields of hydrocarbon product. Considerably decreased yields resulted when either $Fe(acac)_3$ was omitted from the reaction, or the sodium sand was allowed to stand in contact with the $Fe(acac)_3$ solution for 70 hr before starting nitrile was added. Although the exact fate of the transition metal reagent was not determined, the iron seemed to end up in the III state (red-reddish brown reaction solutions), while cyanide ion could be detected as silver cyanide on neutralization of the reaction product with dilute nitric acid. When benzene-d_6 replaced benzene-h_6 in a $Fe(acac)_3$–Na reduction of *n*-octyl cyanide, no incorporation (mass spectrum) of deuterium into the product *n*-octane could be detected. Since all of the *n*-octane is available *per se* at the end of the reduction reaction and before any proton source is added, the hydrogen incorporated into the alkane must derive from the $Fe(acac)_3$ reagent.[4] On the basis of the foregoing, an overall equation such as (1) would apply.

$$RCN + Fe(C_5H_7O_2)_3 + 2Na \longrightarrow RH + Fe(C_5H_7O_2)_2C_5H_6O_2^- + CN^- + 2Na^+ \quad (1)$$

The mechanism of the reduction might involve (a) oxidative addition of organic cyanide to an initially formed lower valent iron species,[5] giving *e.g.*, **1**, followed by proton transfer from the acac ligand to the organometallic moiety, thereby generating hydrocarbon (eq 2), or (b) initial coordination of nitrile with iron, generating, *e.g.*, **3**, followed by reductive cleavage of the nitrile 1,2 carbon–carbon bond, and proton transfer to the latter area (eq 3). Similarly, in the titanocene version, oxidative addition to the starting Ti(II) species would occur, but completion of the reaction would be achieved merely by supply of hydrogen to the alkyl residue from solvent or from a cyclopentadienide unit.[6]



1 **2**



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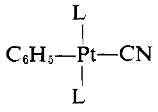
[3] An active form of titanocene was prepared, using the method of J. J. Salzman and P. Mosimann, *Helv. Chim. Acta*, **50**, 1831 (1967), and used *in situ* after removal by filtration of insoluble by-products.

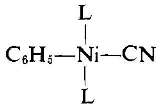
[4] That $Fe(acac)_3$ serves as more than a proton source in the reductive decyanation reaction is indicated by the finding that $Al(acac)_3$ does not increase the yield of octane from octyl cyanide beyond the level observed with metallic sodium alone.

[5] For oxidative additions of benzonitrile to Pt(0) and Ni(0) species to yield products i and ii, see J. L. Burmeister and L. M. Edwards,



$$C_6H_5-\overset{L}{\underset{L}{Pt}}-CN$$

i



$$C_6H_5-\overset{L}{\underset{L}{Ni}}-CN$$

ii

J. Chem. Soc. A, 1663 (1971); D. H. Gerlack, A. R. Kane, G. W. Parshall, J. P. Jesson, and E. L. Muetterties, *J. Amer. Chem. Soc.*, **93**, 3543 (1971).

[6] H. H. Brintzinger and J. E. Bercaw, *ibid.*, **92**, 6182 (1970).

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Oxidations of Hydroaromatic Systems. I.[1] The Oxidation of Tropilidene by Ceric Ammonium Nitrate

Sir:

The relative reactivities of oxidants toward carbon–hydrogen and carbon–carbon double bonds determine the course of hydrocarbon oxidations. Ceric ammonium nitrate (CAN) is known to oxidize toluenes in the side chain[2] in preference to reacting with the π-electron system of the aromatic ring. The purpose of our study was to examine whether CAN could also react with a carbon–hydrogen bond in preference to a nonaromatic unsaturated system.

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[1] (a) Support of this work by the U. S. Army Research Office–Durham is gratefully acknowledged. (b) Presented in part at the Third Great Lakes Regional Meeting of the American Chemical Society, DeKalb, Ill., June 1969.

[2] (a) W. S. Trahanovsky and L. B. Young, *J. Org. Chem.*, **31**, 2033 (1966); (b) R. Ramaswamy, M. S. Venkatachalapathy, and H. V. K. Udupa, *Bull. Chem. Soc. Jap.*, **35**, 1751 (1962); (c) L. A. Dust and E. W. Gill, *J. Chem. Soc. C*, 1630 (1970); (d) L. Syper, *Tetrahedron Lett.*, 4493 (1966).