filtered Bausch and Lomb SP 200-W super pressure mercury lamp for periods of 10 sec to 2 min. Spectra were measured at room temperature with a Varian V-4500 epr spectrometer equipped with a 9-in. magnet. Sweep rates were calibrated by the spectrum of *p*-benzosemiquinone in aqueous ethanol.

Registry No.—Nitroxide from DPN + phenol, 34234-97-4; nitroxide from DPN + $Ph_3CN{=}NPh$, 34234-98-5; nitroxide from α-phenyl-*N*-*p*-chlorophenylnitrone + EtOH, 34234-99-6; nitroxide from α-phenyl-*N*-*p*-chlorophenyl nitrone + dimethylmercury, 34235-00-2; nitroxide from α-(*p*-methoxyphenyl)-*N*-phenylnitrone + EtOH, 34235-01-3; nitroxide from α-(*p*-methoxyphenyl)-*N*-phenylnitrone + Et_2Hg, 34235-02-4; nitroxide from α-phenyl-α-deuterio-*N*-phenylnitrone + EtOH, 34235-03-5; nitroxide from α-phenyl-α-deuterio-*N*-phenylnitrone + Et_2Hg, 34235-04-6; nitroxide from α-phenyl-α-cyano-*N*-phenylnitrone + *tert*-butyl peroxide, 34235-05-7; nitroxide from PNB + Ph_2Hg, 21572-75-8; nitroxide from DPN + Me_2Hg, 34235-07-9; nitroxide from DPN + Et_2Hg, 34235-08-0; nitroxide from DPN + Bu_4Pb, 34288-72-7.

Hydrogen Abstraction by the *p*-Nitrophenyl Radical[1,2]

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The relative reactivities of a series of organic hydrogen donors were measured toward *p*-nitrophenyl radicals generated from *p*-nitrophenylazotriphenylmethane (NAT). The relative rate constants k_H for hydrogen abstraction from the donors are reported as k_H/k_{Cl} values, where k_{Cl} is the rate constant for chlorine abstraction from CCl_4. The problems in calculation of k_H/k_{Cl} values are discussed. Some ArH is produced from the $ArN{=}NCPh_3$ type initiators even in pure CCl_4 as solvent, and higher yields are produced at higher viscosities. It is shown that ArH is not a cage product. The ArH yields result from hydrogen abstraction from reactive hydrogen donors produced by the reaction of the ambident trityl radicals with radicals present in the system. These donors include XH from the reaction of trityl with Ar radicals and ZH from the reaction of trityl with a second trityl radical (see structures in paper). Two mechanisms are suggested to rationalize the viscosity effect; the more likely one assumes that XH is a cage product and, therefore, that higher yields of XH are produced at higher viscosities.

One of the most useful methods for probing the reactivity, polar nature, steric sensitivity, and other identifying features of free radicals is to measure their relative rate constants for hydrogen abstraction from a series of typical organic hydrogen donors. This approach has been used, for example, in studies of the phenyl radical,[4,5] aromatic radicals,[6a] the methyl radical,[6b] and the hydrogen atom.[7] A convenient method for determining such a series of relative rate constants involves generating the radical in a mixture of the hydrogen donor RH and carbon tetrachloride (eq 1 and 2). In this paper we report data obtained in this way for the phenyl and *p*-nitrophenyl radicals.

$$RH + Ar\cdot \xrightarrow{k_H} R\cdot + ArH \qquad (1)$$

$$CCl_4 + Ar\cdot \xrightarrow{k_{Cl}} CCl_3\cdot + ArCl \qquad (2)$$

These radicals were generated by thermolysis at 60° of the appropriate phenylazotriphenylmethane (PAT) type of intiator, PAT itself for the phenyl radical and NAT, $p\text{-}NO_2C_6H_4N{=}NCPh_3$, for the *p*-nitrophenyl radical. We previously reported[6a] some data for phenyl, *p*-bromophenyl, *p*-methylphenyl, and *p*-nitrophenyl, and Bridger and Russell[8] have reported extensive data for the phenyl radical. We here wish to clarify the cage chemistry of PAT-type initiators and also to report additional relative rate constants for hydrogen atom abstraction by the *p*-nitrophenyl radical.

Results and Discussion

The Cage Chemistry of PAT and NAT.—Cage processes have been particularly troublesome to identify[9-10] for PAT and similar initiators. Previously[6a] we presented data on the yield of nitrobenzene (ArH) from NAT. We showed that the extrapolated yield of ArH appeared to be finite (~3%) at infinite dilution of NAT, in agreement with earlier reports on PAT,[8,10a] and that the thermolysis of NAT in solvents of higher viscosity led to higher yields of ArH. These facts seemed to imply that ArH is a cage product. Arguments against ArH being a cage product are based on the observation that carbon disulfide or a solution of iodine in CCl_4 results in the elimination of ArH.[11,12] It is now clear that the implication of these scavenging experiments is correct and that ArH is not a cage product.

Our evidence indicating that ArH is not a cage product can be summarized as follows. (1) Using a new, more sensitive gas chromatograph, we have been able

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[1] Reactions of Radicals. 42.

[2] This work was supported in part by a U. S. Public Health Service Grant GM-11908 from the National Institue of Health.

[3] (a) John Simon Guggenheim Fellow, 1970–1971; (b) postdoctoral student on an NIH grant, 1965; (c) Research Participant in an Atomic Energy Commission Research Participation Program, summer 1966.

[4] W. A. Pryor, "Free Radicals," McGraw-Hill, New York, N. Y., 1966, Chapter 12.

[5] A. F. Trotman-Dickenson, *Advan. Free Radical Chem.*, **1**, (1965).

[6] (a) W. A. Pryor, J. T. Echols, Jr., and K. Smith, *J. Amer. Chem. Soc.*, **88**, 1189 (1966); (b) W. A. Pryor, D. F. Fuller, and J. P. Stanley, *ibid.*, in press.

[7] W. A. Pryor, J. P. Stanley, and M. G. Griffith, *Science*, **169**, 181 (1970); W. A. Pryor and J. P. Stanley, *J. Amer. Chem. Soc.*, **93**, 1412 (1971); W. A. Pryor and R. W. Henderson, *ibid.*, **92**, 7234 (1970).

[8] R. F. Bridger and G. A. Russell, *ibid.*, **85**, 3754 (1963).

[9] (a) E. L. Eliel, M. Eberhardt, O. Simamura, and S. Meyerson, *Tetrahedron Lett.*, 749 (1962); (b) D. H. Hey, M. J. Perkins, and G. H. Williams, *ibid.*, 445 (1963); (c) J. G. Garst and R. S. Cole, *ibid.*, 679 (1963); (d) G. A. Russell and R. F. Bridger, *ibid.*, 737 (1963).

[10] (a) W. A. Pryor and H. Guard, *J. Amer. Chem. Soc.*, **86**, 1150 (1964); (b) W. A. Pryor and K. Smith, *ibid.*, **89**, 1741 (1967).

[11] Figure 3 of ref 6a.

[12] It is possible that a trace (<0.1%) of ArH is formed under these circumstances, but the amount is too small to estimate accurately.

to show that graphs of the yield of ArH *vs.* initial concentration of PAT and NAT break sharply toward zero at very low concentrations (see Figure 1). (2) Iodine in toluene reduces the yield of ArH to <0.1%. Iodine or CBr_4 in CCl_4 reduces the yield of ArH to zero for NAT and for PAT, and this is true even when silicone oils are present as thickeners.

These facts establish that ArH is not a cage product. the production of ArH from PAT or NAT in pure CCl_4 and the increased yields of ArH at higher viscosity, therefore, must be explained. In addition, the question arises of whether there are any cage products from PAT. Any cage products which are formed are produced only in low yields; the data of Table I show that the recovery of Ar groups is always <100% but is very high.

TABLE I

SCAVENGING EXPERIMENTS WITH PAT AT 60°

		% yield			
Solvent	Scavenger	ArH	ArCl	ArX[a]	Total
CCl_4	0.12 *M* I_2	<0.5	11	79	90[b]
CCl_4	Variable I_2	<0.5	14	79	93[c]
Toluene	0.15 *M* CBr_4			88	
Toluene	Variable CBr_4			85	
CCl_4	0.15 *M* CBr_4	<0.5	6	90	96[d]
CCl_4	Variable CBr_4	<0.5	6	88	94[c]

[a] ArI or ArBr depending on whether I_2 or CBr_4 is the scavenger. [b] The total yield was studied for a range of PAT initial concentrations and was found to be approximately independent of this variable. [c] Using 0.05 *M* $[PAT]_0$, various scavenger concentrations were examined. The total yield was roughly independent of the initial scavenger concentration, although, of course, the product mixture changes drastically as the scavenger concentration is varied. [d] The yield of ArBr decreases as $[PAT]_0$ is increased, presumably owing to competition between trityl and CBr_4. This is the maximum value, obtained at 0.02 *M* $[PAT]_0$.

Before consideration of these questions, one relatively trivial point needs clarification. There is a possibility that the spuriously low yields of ArI in scavenging experiments result from the radical-initiated destruction of ArI. We eliminated this by showing that reaction 3 occurs without loss of total organic iodide product (Table II).[13]

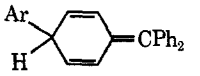
TABLE II

THE EXCHANGE OF IODIDE BY RADICALS IN CCl_4 AT 60°

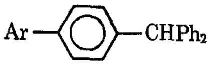
	Concentrations, *M*			
	Expt 1		Expt 2	
Compd	Initial	Final	Initial	Final
PAT	0.0468	0	0.0508	0
Iodobenzene [PhI]	0	0.0016	0	0.0011
p-Nitroiodobenzene [ArI]	0.0095	0.0082	0.0095	0.0083
Total [iodine derivatives]	0.0095	0.0098	0.0095	0.0094

$$Ph\cdot + ArI \longrightarrow PhI + Ar\cdot \qquad (3)$$

It appears reasonable to assume that any cage products which are formed from PAT-type initiators result exclusively from the coupling of the Ar· and trityl radicals. Only radical disproportionation and combination reactions might be expected to compete with diffusion from the cage, and disproportionation is not possible for Ar· and trityl. The trityl radical is ambident[14] and can be expected to couple with Ar· radicals to give both $ArCPh_3$ and XH and, perhaps, the ortho analog of XH. If XH were formed, the aromatized derivative



XH



YH

YH might be detectible by gas chromatography (gc). In fact, Table III shows that YH can be detected from PAT decompositions in pure CCl_4 both in the presence and the absence of iodine as scavenger. Ordinarily, this would be taken as *prima facie* evidence that XH is a cage product and that an additional amount is formed in free solution. However, in this case, the identification of $ArCPh_3$ and XH in the presence of a radical scavenger is not necessarily conclusive evidence that these products are produced in the cage because of the exceptional stability of the trityl radical.

TABLE III

YIELDS OF COUPLING PRODUCTS IN THE PRESENCE AND ABSENCE OF SCAVENGERS[a]

	% yield	
Solvent	CPh_4	YH
CCl_4	1.5	0.51
$CCl_4 + I_2$[b]	0.70	0.28

[a] 0.0720 *M* PAT. [b] 0.104 *M* iodine initially.

Trityl is a stable radical and a good radical scavenger. In fact, this was why the PAT series of initiators were adopted for kinetic studies. It was hoped that trityl would "mop up" secondary radicals and prohibit chain processes,[6,8,9] and, in contrast with acetyl radicals, trityl does appear to serve this role.[15] An electron spin resonance (esr) study of PAT decompositions shows that trityl radicals reach a maximum concentration after 2 half-lives of PAT and that the concentration decreases quite slowly after that. The trityl concentration is still high after 4 half-lives, and the esr signal persists for months. The possibility exists, therefore, that coupling products from Ar· and trityl are formed in the presence of iodine because trityl is able to compete with iodine as a scavenger.[16] In addition, there is considerable evidence that PAT-type initiators decompose in two steps and that the aryldiazenyl radical is stable enough to diffuse from the cage.[17] This suggests

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(13) After we had concluded this work, J. F. Bunnett and C. C. Wamser [*J. Amer. Chem. Soc.*, **88**, 5534 (1966)] published similar data which led to the same conclusion.

(14) Para coupling products from trityl radicals have previously been reported. (a) J. A. Kampmeier, R. P. Geer, J. A. Meskin, and R. M. D'Silva [*ibid.*, **88**, 1257 (1966)] identified *p*-$C_6H_5C_6H_4C(SC_4H_9)(C_6H_5)_2$, as well as tetraphenyl- and triphenylmethane, from the reaction of PAT with *tert*-butyl sulfide. (b) J. P. Lorand and P. D. Bartlett [*ibid.*, **88**, 3294 (1966)] isolated *p-tert*-$BuOC_6H_4CH(C_6H_5)_2$ from the decomposition of *tert*-butyl triphenylperacetate. (c) S. F. Nelson and P. D. Bartlett [*ibid.*, **88**, 137 (1966)] have shown that cumyl also is ambident and couples at the para position. (d) Also see H. Lankamp, W. T. Nanta, and C. MacLeon, *Tetrahedron Lett.*, 249 (1968); D. H. Hey, M. J. Perkins and G. H. Williams, *J. Chem. Soc.*, 110 (1965); D. H. Hey and R. Tewfik, *ibid.*, 2402 (1965).

(15) W. A. Pryor, U. Tonellato, D. L. Fuller, and S. Jumonville, *J. Org. Chem.*, **34**, 2018 (1969).

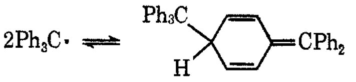
(16) The ratio of coupling at the center carbon to form $ArCPh_3$ and at the para position to give XH is roughly the same in the presence and absence of iodine, but this cannot be taken as evidence that the products are all formed in free solution. Ambident radicals undergo coupling at two positions with a similar ratio whether the reaction takes place in the cage or in free solution. See G. S. Hammond, C. S. Wu, O. D. Trapp, J. Warkentin, and R. T. Keys, *J. Amer. Chem. Soc.*, **82**, 5394 (1960).

(17) H. van Zwet and E. C. Kooyman, *Recl. Trav. Chim. Pays-Bas*, 1143 (1967).

that cage products should be formed only in low yields if at all.

In view of these facts, we suggest two different mechanisms to explain the ArH yields and viscosity dependence. The first assumes that both $ArCPh_3$ and XH are produced in the cage. If ArH *itself* is not a cage product, then the most obvious explanation of the increased yields of ArH at higher viscosities is to assume that the hydrogen donor which is the *precursor* of ArH is a cage product. Clearly, XH is a likely precursor. The cage yields of XH need not be large; we have presented evidence that a hydrocarbon hydrogen donor which is not unlike XH has an extraordinarily large transfer constant of the order of magnitude of those of thiols.[18]

The other mechanism, which can be formulated in two ways, allows the cage yield from PAT-type initiators to be zero, but assumes that the concentration of the unknown hydrogen donor is controlled such that its concentration increases at higher viscosity. One formulation envisions XH as the donor and postulates that the conversion of XH to YH is slower at higher viscosities. (It is clear that XH would have a much higher transfer constant than would YH.[18]) The second possibility uses ZH as the donor and postulates that the equilibrium[14d,19] between trityl radicals and ZH is shifted toward ZH at higher viscosities.



ZH

Thus, we can satisfactorily account for the formation of ArH in pure CCl_4, but we cannot formulate a unique mechanism which accounts for the viscosity dependence of the ArH yields. Of the two explanations for the viscosity effect which we have suggested, the mechanism which postulates that XH is the precursor to ArH and is a cage product has the advantage that it allows a straightforward interpretation of the production of YH and $ArCPh_3$ in the presence of scavengers (Table III). The mechanism which postulates that either a slower conversion of XH to YH or an equilibrium between trityl radicals and ZH increases the concentration of reactive hydrogen donors at higher viscosity is *ad hoc.* However, it has the advantage of being consistent with the assumption of zero cage yields from PAT-type initiators, an assumption which is attractive in view of the stability of $ArN_2\cdot$ radicals and the high yields of Ar fragments in our scavenging experiments (Table I). At present, we have no data which exclude either of these two mechanisms, but we favor the former. Although it is conceivable that the conversion of XH to YH is retarded by viscosity, there is no evidence that it is, and the equilibrium between ZH and trityl would more likely decrease the concentration of ZH at higher viscosities.

One further problem in the cage chemistry of PAT remains; it has been suggested that 9-phenylfluorene (9-PF) is a cage product from PAT.[8,9d] We could not detect this compound by gc analysis of decomposed solutions of PAT in CCl_4, even though the gc used in this work was sensitive enough to detect concentrations of 9-PF in standard solutions which would correspond to a yield of <0.1%. We conclude that 9-PF is neither a cage product nor a significant product in free solution in CCl_4 solvent.

TABLE IV

YIELDS OF NITROBENZENE AND *p*-CHLORONITROBENZENE AND THE RELATIVE RATE CONSTANTS FROM THE THERMOLYSIS OF 0.02 *M* *p*-NITROPHENYLAZOTRIPHENYLMETHANE

Hydrogen donor, RH (registry no.)	$[CCl_4]/[RH]$	% ArH	% ArCl	k_H/k_{Cl}[a]	$[ArH]_0$[b]
Heptane	3.9	56.35	25.32	8.1	3.9
(142-82-5)	31.0	19.12	58.20		
Octane	1.16	77.8	7.9	10.87	2.7
(111-65-9)	8.32	45.5	34.3		
	25.49	24.0	51.7		
	62.7	14.9	62.75		
3-Methylpentane	8.42	38.53	46.52	6.35	3.2
(96-14-0)	25.80	18.39	65.74		
	39.56	13.82	62.62		
	59.35	9.53	57.62		
2,3,4-Trimethylpentane	8.71	38.80	38.75	8.3	2.0
(565-75-3)	16.95	26.77	50.29		
	35.64	17.23	60.74		
	42.43	13.44	62.99		
	59.90	11.45	69.63		
2,3-Dimethylbutane	1.03	73.0	10.8	6.3	6.8
(79-29-8)	21.4	22.5	50.6		
	53.25	15.0	74.0		
Cyclohexane	1.50	70.0	10.2	9.5	3.7
(110-82-7)	7.99	43.8	34.0		
	9.80	41.5	40.0		
	29.4	21.9	58.4		
	63.8	13.6	61.0		
	66.4	13.5	65.0		
Cycloheptane	16.17	44.34	36.05	18.7	2.6
(291-64-5)	31.28	30.55	46.91		
	61.08	20.01	56.34		
Cyclooctane	24.71	45.62	29.7	26.9	1.8
(292-64-8)	32.77	36.65	42.87		
	41.15	31.67	45.3		
	61.59	24.04	51.34		
CCl_4		3.76	71.6		
(56-23-5)					

[a] From the slope of a plot of eq 5. [b] From the intercept of the plot of eq 5.

Calculation of k_H/k_{Cl} for PAT Initiators.—Edwards and Mayo[20] who originally used the CCl_4 method for determining relative rate constants, as well as Bridger and Russell[8,9d] and ourselves,[6a] observed the formation of some ArH-type products even when the solvent was pure CCl_4. Clearly, some ArH is produced from reactions other than eq 1, and a technique must be developed to correct for this spurious ArH yield.

Correction Factor.—The correction for the spurious ArH can be made by subtracting a correction factor, $[ArH]_0$, from the yield of ArH observed in CCl_4–RH mixtures. The equation is

$$\frac{k_H}{k_{Cl}} = \left(\frac{[ArH] - [ArH]_0}{[ArCl]}\right)R \qquad (4)$$

where R is the solvent ratio of $[CCl_4]/[R]$ and is assumed to be constant throughout a run. Russell[8,9d] suggested evaluating $[ArH]_0$ by using a standard concentration of PAT, measuring the ArH yield in CCl_4 at that concentration, and subtracting this yield from the total ArH yields in CCl_4–RH mixtures. (Edwards and Mayo[20] used an

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[18] W. A. Pryor and J. H. Coco, *Macromolecules*, **3**, 500 (1970).

[19] A brief review is given by W. B. Smith, *J. Chem. Educ.*, **47**, 535 (1970).

[20] F. G. Edwards and F. R. Mayo, *J. Amer. Chem. Soc.*, **72**, 1265 (1950).

TABLE V

SUMMARY OF k_H/k_{Cl} VALUES FOR NAT IN VARIOUS SOLVENTS AT 60° [a]

Hydrogen donor, RH	k_H/k_{Cl}	$\pm\bar{X}$ [b]	No. of runs	$(k_H/k_{Cl})_{calcd}$ [c]
Alkanes and Alkylbenzenes				
Hexane	7.6	0.50	2	6.9
Heptane	8.4[d]	0.42	3	8.5
Octane	10.3[d]	0.29	7	9.7
Decane	12.8	0.60	2	11.7
2-Methylpentane	7.7		1	7.5
3-Methylpentane	8.0		1	7.5
2-Methylhexane	8.6	0.30	2	9.1
3-Methylhexane	8.8[d]		1	9.1
2,5-Dimethylhexane	9.7		1	11.4
2,4-Dimethylpentane	5.2	0.16	4	9.8
2,3-Dimethylbutane	8.9[d]	1.30	3	8.2
2,2,3-Trimethylbutane	6.2		1	4.9
2,3,4-Trimethylpentane	7.27[d]	0.48	7	12.1
2,2,4-Trimethylpentane	2.77	0.53	4	6.4
2,2,3,3-Tetramethylbutane	1.33	0.47	3	1.33
1,4-Di-*tert*-butylbenzene	1.0		1	1.33
Diphenylmethane	6.7		1	
Triphenylmethane	16.1		1	
Indan	23.5		1	
Cyclopentane	8.85	0.05	2	
Cyclohexane	9.14[d]	0.74	9	
Cycloheptane	18.35[d]	0.74	4	
Cyclooctane	24.62[d]	1.55	4	
Methylcyclohexane	13.9	0.88	3	
Alkenes				
1-Hexene	4.2	0.2	2	8.7
2-Hexene	14.5		1	10.8
3-Hexene	18.0	0.7	2	10.9
1-Heptene	10.35	0.25	2	10.3
2-Heptene	15.15	0.55	2	12.4
1-Octene	9.35	0.35	2	11.9
2-Octene	15.6		1	14.0
2-Methyl-2-butene	9.1		1	11.2
4-Methyl-1-pentene	6.4		1	9.4
2-Methyl-2-pentene	14.2		1	13.9
4-Methyl-2-pentene	5.75	0.15	2	
2,3-Dimethyl-2-butene	22.3		1	14.9
Cyclopentene	20.7		1	
Cyclohexene	30.3	0.54	3	
2,5-Dimethyl-2,4-hexadiene	19.4		1	
Haloalkanes				
1-Bromopropane	1.93		1	
2-Bromopropane	1.67	0.05	3	
Bromocyclopropane	0.32		1	
Bromoethane	0.75		1	
1-Bromobutane	2.53	0.12	3	
Methylene chloride	0.94	0.01	4	
Alkyl Sulfides				
Methyl phenyl sulfide	0.97		1	
Ethyl phenyl sulfide	5.1		1	
Isopropyl phenyl sulfide	8.0		1	
Heteroaromatics				
2-Methylpyrazine	0.32		1	
2-Methylpyridine	0.93	0.18	2	
2-Methylthiophene	1.5		1	
3-Methylthiophene	0.4		1	
Oxygen Compounds				
Ethyl acetate	0.8		1	
Methyl acetate	0.4		1	
Tetrahydrofuran	19.2	0.45	2	
tert-Butyl methyl ether	2.5		1	
Methanol	1.4		1	
3-Pentanone	5.2		1	
Dicyclopropyl ketone	1.1		1	
Nitrogen Compounds				
Nitromethane	0.05		1	
Nitroethane	0.43	0.02	2	
2-Nitropropane	0.6		1	
Hydrazobenzene	36.1		1	
Acetonitrile	0.23		1	
Methyl thiocyanate	0.16		1	
Miscellaneous Compounds				
Tetrahydrothiophene	32.1		1	
Tetramethylsilane	0.8		1	
Hexamethylbenzene	38.7	0.9	2	
Hexaethylbenzene	4.3	0.1	2	

[a] [NAT], 0.01–0.05 *M*. [b] The average error of the mean. [c] The $(k_H/k_{Cl})_{calcd}$ values were calculated from the reactivities of the appropriate carbon–hydrogen bonds (see text). [d] See Table IV for values obtained from a plot of eq 5.

analogous method.) This technique cannot be exact, since the value of $[ArH]_0$ should vary with the solvent as well as with the initial concentration of PAT. Solvents which are more reactive will scavenge more Ar· radicals, and the Ar· + T· reaction will produce a smaller yield of XH.

To reduce this uncertainty in $[ArH]_0$, and under the erroneous impression that ArH was a cage product, we previously used a method which involved the extrapolation of runs to zero PAT concentration.[6a] In practice, this is tedious since at least five runs must be made for each hydrogen donor studied; the Russell method often is used with only a single run.

We now wish to propose an alternative method for the evaluation of $[ArH]_0$. Rearrangement of eq 4

$$[ArH] = \frac{k_H[ArCl]}{k_{Cl}R} + [ArH]_0 \qquad (5)$$

gives 5, where k_H/k_{Cl} is the slope and $[ArH]_0$ is the intercept of a plot of [ArH] *vs.* [ArCl]/*R*. The correction factor, $[ArH]_0$, is determined by studying the competition reactions at a given $[NAT]_0$ and various ratios of $[CCl_4]/[RH]$. Table IV lists our new data for the results of competition studies for eight hydrogen donors with CCl_4. The mean $[ArH]_0$ is $(3.3 \pm 1.1)\%$ [ArH] (excluding 2,3-dimethylbutane) at $(NAT)_0 = 0.02\ M$. This $[ArH]_0$ is comparable with the 3.7% ArH obtained from thermolysis of 0.02 *M* NAT in pure CCl_4. The data of Table IV do indicate, however, that there is a significant variation in $[ArH]_0$. As expected, solvents with large relative values of k_H tend to give small correction values, although 2,3-dimethylbutane appears to be anomolous. Despite this indication that a separate value of $[ArH]_0$ should be evaluated for each solvent, the effort involved in determining data by this technique appears to be unjustified for the increased precision available. We, therefore, have chosen to use the Russell method in which the correction factor is taken to be the yield of ArH in CCl_4 for a given initial concentration of NAT. These values can be read from

Figure 1. Table IV shows that the error in k_H due to an erroneous correction factor should be <10%.

Selectivity of the *p*-Nitrophenyl Radical.—Table V summarizes the relative rate constants determined for numerous hydrogen donor solvents. The table also shows calculated values of k_H/k_{Cl} based on the assumption that the relative reactivity of the *p*-nitrophenyl radical toward primary, secondary, and tertiary alkyl hydrogens is 0.074, 0.805, and 3.67, respectively. The reactivity of a primary alkyl hydrogen was calculated using the k_H/k_{Cl} value of hexamethylethane and that for a secondary hydrogen was calculated using the data for all the normal alkanes and the previously calculated reactivity of primary hydrogens. Reactivity of a tertiary alkyl hydrogen was calculated using the data for monomethylalkanes. Normalization leads to a selectivity series of 1:10.9:49 for primary, secondary, and tertiary alkane hydrogens.

The relative reactivities of the primary and secondary allylic hydrogens are 1.24 and 2.63. Normalization relative to the primary alkyl hydrogen gives a series of 16.8 to 35.6 for primary to secondary allylic hydrogens. The sequence of relative reactivities for cycloalkyl hydrogens is cyclooctane > cycloheptane > cyclopentane > cyclohexane. This reactivity sequence is consistent with that for the methyl,[6b] phenyl,[8] chlorine,[21] and trichloromethyl[22] radicals.

Table VI summarizes the reactivities of primary hydrogen atoms α to various functional groups and the data show that most substituents have small effects on the reactivities of hydrogen atoms toward *p*-nitrophenyl radicals. Table VII compares the relative reactivities of the phenyl and *p*-nitrophenyl radicals. The *p*-nitrophenyl radical appears to be slightly more selective.

TABLE VI

RELATIVE RATE CONSTANTS FOR THE REACTION OF THE CARBON–HYDROGEN BONDS α TO FUNCTION SUBSTITUENTS AT 60°

Substituent Z in ZCH_3	Relative reactivity
Alkyl	(1)
Phenyl	7.7
Vinyl	17.2
Hydroxy	6.5
Cyano	1.1
Methoxycarbonyl	1.8
Nitro	0.3
Thiophenyl	4.4
Thiocyanate	6.9

Experimental Section

Material.—Alkanes from Phillips Petroleum Co. and Columbia Organic Chemical Co. were purified using columns filled with silver nitrate on alumina as reported by Murray and Keller.[23] Alkenes were purified by passing them through a column of alumina W200 basic. Tetrahydrofuran, 1-bromobutane, and 2-bromobutane were purified by the methods suggested by Wiberg.[24] CCl_4 was Spectrograde and was further purified by passing it through a column packed with silica gel. The azo compound was synthesized employing the method of Cohen and Wang.[25] Spectrograde benzene was purchased from Eastman Kodak Co. and used without further purification. Reagent grade nitrobenzene was distilled at 53° (1 Torr). Reagent grade nitrochlorobenzene was recrystallized twice from ethyl alcohol and dried in a vacuum oven, mp 82.8°.

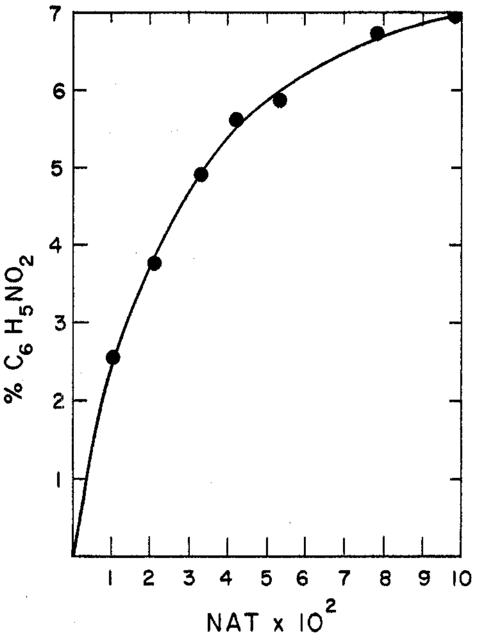

Figure 1.—Decomposition of NAT in carbon tetrachloride: effect of initial [NAT] on yields of nitrobenzene.

TABLE VII

RELATIVE REACTIVITIES OF VARIOUS TYPES OF CARBON–HYDROGEN BONDS TOWARD PHENYL AND NITROPHENYL RADICALS IN SOLUTION (RELATIVE TO THE α H ON TOLUENE)

Type of bond	Phenyl[a]	Nitrophenyl[b]
Primary alkyl	0.11–0.13	0.17
Secondary alkyl	1.01	1.8
Tertiary alkyl	4.8	8.3
Cyclopentane	1.15	2.1
Cyclohexane	1.0	1.7
Cycloheptane	1.8	2.9
Cyclooctane	2.0	4.6
Primary allylic	1.6	2.8
Secondary allylic	3.3	6.0
Tertiary allylic	13.3	
Cyclopentene (α)	9.7	10.4
Cyclohexene (α)	11.2	15.4
Toluene (α)	(1)	(1)
Ethylbenzene (α)	4.6	4.7
Cumene (α)	9.7	28.5
Diphenylmethane	7.7	7.6
Indan	8.0	11.7

[a] Reference 8. [b] Present work.

Procedure of Kinetic Runs.—A solution with a known ratio of hydrogen donor and carbon tetrachloride was prepared by weight. The NAT, 15.7 mg, was weighed into a 2-ml volumetric flask which was filled with the solution and then transferred to two 9-mm-o.d. Pyrex sample tubes. The ampoules were then degassed and sealed under vacuum and placed in a constant temperature bath at 60° for 10 half-lives (13 hr).[25] The samples were analyzed on a gas chromatograph equipped with a 6-ft, 0.25-in.-o.d. glass column packed with silicone XF-1150 (Nitrile) on Chromosorb W. The chromatograph was a Glowall 320 equipped with a flame-ionization detector, Varian Aerograph G-2010 recorder, and Disc Chart integrator. The experimental conditions follow: column temperature, 140°; detector temperature, 200°;

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[21] G. A. Russell, *J. Amer. Chem. Soc.*, **80**, 4997 (1958).

[22] E. S. Huyser, H. Schimke, and R. L. Burham, *J. Org. Chem.*, **28**, 2141 (1963).

[23] F. C. Murray and R. N. Keller, *ibid.*, **34**, 2234 (1969).

[24] K. B. Wiberg, "Laboratory Technique in Organic Chemistry," McGraw-Hill, New York, N. Y., 1960.

[25] S. C. Cohen and C. H. Wang, *J. Amer. Chem. Soc.*, **75**, 5504 (1953).

injection temperature, 200°; flow rate, ~30 cc/min. The relative retention for CCl_4, $C_6H_5NO_2$, p-$O_2NC_6H_4Cl$ was 1:20:24, respectively.

To determine the yield of $C_6H_4NO_2$ and p-$O_2NC_6H_4Cl$, standard solutions of $C_6H_5NO_2$ and p-$O_2NC_6H_4Cl$ dissolved in CCl_4 were prepared and stored in sealed 1-ml glass vials. These standards were analyzed in triplicate prior to and following the reaction samples.

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Formation of Radical Anions from Vicinal Diamines and Strong Bases[1]

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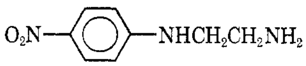
Ethylenediamine (EDA) reacts with butyllithium to form the pyrazine radical anion. On standing, in the presence of EDA and N-lithioethylenediamine, this radical is slowly converted to a dihydropyrazine radical. Other vicinal diamines were also found to yield pyrazine-type radicals when treated with strong base. The large amounts of hydrogen gas evolved during these reactions is attributed to loss of metal hydride from the metalated EDA.

In the course of the kinetic study of the reaction mechanism of the prototropic propargylic rearrangement of 3-hexyne with sodium amide in ethylenediamine (EDA) at room temperature,[3] the rate of rearrangement was found to be dependent on the time given to the interaction of sodium amide with EDA before introduction of the hexyne. The suspension of sodium amide in EDA gradually changes color from gray to purple to deep blue. Subsequent investigation by electron paramagnetic resonance (epr) revealed the presence of organic radicals in this and other reactions involving strong bases and vicinal diamines. Although further research has indicated that the rearrangement may not be related to the formation of these radicals,[4] the radicals themselves are of sufficient interest to warrant separate presentation.

Results

A. Detection of Radicals in Base-Treated Vicinal Diamines.—When strong bases [$NaNH_2$, $LiNH_2$, LiH, or butyllithium (BuLi)] are treated with excess EDA (a 10:1 molar ratio of diamine to base was commonly used) in a drybox at room temperature, intense blue solutions are obtained. Regardless of the base used, identical epr spectra resulted (Figure 1). The radical concentration was estimated to be 0.005 M by comparison with a standard solution of diphenylpicrylhydrazyl. Additional hyperfine structure was observed when tetrahydrofuran (THF) solvent was added to the EDA–BuLi mixture. Fully deuterated EDA, on treatment with BuLi, gave a five-line spectrum (Figure 2).

The reaction between EDA and BuLi results in a golden yellow color (no λ_{max} in the visible region 400–800 nm) if air is very carefully excluded using vacuum line techniques. Exposure to a trace of oxygen results in a gradual color change from yellow to purple (λ_{max} 585 nm) with little or no change in the epr signal. Extensive degassing does not reverse the color change. Excess oxygen, however, destroys the purple color as well as the radical signal. The radical signal can also be quenched by the addition of nitrobenzene, which results in formation of the nitrobenzene radical anion and N-(p-nitrophenyl)ethylenediamine (1).



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If either the yellow or the blue solution containing the radical (produced from EDA and BuLi) are allowed to stand for several days (under vacuum at room temperature) a different epr spectrum gradually develops (Figure 3).

Other diamines were also treated with strong base and examined by epr. The results are tabulated in Table I.

B. Formation of a Radical on Treatment of Pyrazine with Butyllithium.—Treatment of a dilute solution of

TABLE I

BASE-TREATED DIAMINES WHICH WERE ANALYZED BY EPR[a]

Diamine	Color	Epr signal
EDA	Blue[b]	Figure 1[c]
EDA-d_8	Blue	Figure 2
Propylenediamine	Red	Yes
N,N'-Dimethylethylenediamine	Green	Figure 4
2-Methyl-1,2-diaminopropane	Brown	Yes
N-Methylethylenediamine	Green	Yes
o-Phenylenediamine	Blue	Yes
cis-1,2-Diaminocyclohexane	Red-brown	Yes
trans-1,2-Diaminocyclohexane	Cloudy white	No
1,3-Diaminopropane	Cloudy white	No
N,N-Dimethylethylenediamine	Yellow	No

[a] A 10:1 molar ratio of diamine to BuLi was used. [b] The color is golden yellow if air is very carefully excluded. [c] Upon standing the spectrum gradually changes (Figure 3).

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[1] Presented, in part, at the 161st National Meeting of the American Chemical Society, Los Angeles, Calif., March 28–April 2, 1971.

[2] Postdoctoral Research Associate, 1970–1971.

[3] J. H. Wotiz, W. E. Billups, and D. T. Christian, *J. Org. Chem.*, **31**, 2069 (1966).

[4] P. Barelski, Ph.D. Thesis, Southern Illinois University, 1971.