Measurements taken at 300°K. gave the following representative molar susceptibilities with field strengths in gauss given in parentheses: $+194 \times 10^{-6}$ ($4.2\text{–}4.3 \times 10^{3}$), $+165 \times 10^{-6}$ (5.2×10^{3}), $+93 \times 10^{6}$ (5.9×10^{3}).

Acknowledgment.—We are indebted to Mr. T. Porro of the Perkin–Elmer Corporation for assisting us in the determination of some of the near infrared spectra.

[Contribution from the Department of Chemistry, University of California, Berkeley 4, California]

Secondary Isotope Effects in Solvolysis of Various Deuterated Benzhydryl Chlorides[1]

By A. Streitwieser, Jr., and H. S. Klein[2]

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Solvolysis kinetics were determined for various deuterated benzhydryl chlorides in 80 and 70% aqueous acetone at 25.00°. Ring deuteriums cause rate accelerations of the following magnitude per D: *ortho*, 1.9%; *meta*, 1.5%; *para*, 1.0%. These unusual positional effects are discussed, but no unambiguous interpretation is possible at this time. Benzhydryl-α-*d* chloride shows a normal α-D rate depression of 12%.

Various observations show that deuterium has a significant electron-donating inductive effect relative to hydrogen.[3] The effect of deuterium on the acidity of carboxylic acids depends on the position of attachment down the chain in much the same way as the normal inductive effect of nonisotope substituents.[4,5] Comparable electron-donating effects have been established for deuterium substituted on a benzene ring in the acidities of benzoic acid[5] and anilinium ions[6] and in the formation of diphenylmethyl[7] and triphenylmethyl cations.[8] In the present study, we report the details of the *o*-, *m*-, and *p*-substitution of deuterium in solvolysis of benzhydryl chloride.

Results and Discussion

Various deuterated bromobenzenes were prepared as follows: Bromination of benzene-d_6 gave bromobenzene-d_5. *p*-Dibromobenzene was converted to the mono-Grignard reagent and decomposed with deuterium oxide to give bromobenzene-d_5. Repeated exchanges of aniline with DCl–D_2O gave aniline-2,4,6-d_3 which, by the Sandmeyer reaction, gave bromobenzene-2,4,6-d_3. Nitration of bromobenzene-2,4,6-d_3 gave the *p*-nitro compound which, on reduction and deamination, gave bromobenzene-2,6-d_2. Bromination of acetanilide-2,4,6-d_3, hydrolysis, and deamination gave bromobenzene-3,5-d_2. Benzhydrols were prepared from each bromobenzene by Grignard reaction with ethyl formate. Benzhydrol-α-*d* was prepared by reduction of benzophenone with lithium aluminum deuteride. The benzhydrols so obtained analyzed for >90% of the required deuterium. Benzhydryl chlorides were prepared by treatment of the benzhydrols with hydrogen chloride and were stored in Dry Ice–acetone under nitrogen until used. The infrared spectrum of benzhydryl-2,3,4,5,6,2′,3′,4′,5′,6′-d_{10} chloride showed that no hydrogen–deuterium exchange occurred on storage.

Solvolysis kinetics were run on each benzhydryl chloride in 70 and 80% aqueous acetone by following conductometrically the decrease in resistance of the solution as HCl was generated. Each reaction was followed for several half-lives during which about 80 readings were taken. The usual integrated first-order rate equation was applied to each point using an infinity point taken after about 20 half-lives. For each solvent, a calibration curve of resistance *vs.* concentration was determined. Second-, third-, and fourth-order polynomial equations in conductance were fitted to the data. A third-order polynomial (eq. 1) gave the best results in 80% acetone, whereas in 70% acetone the assumption that the concentration is proportional to conductance gave results equal to the best polynomial fit.

$$(\text{HCl in } 80\% \text{ acetone}) = -659{,}330(1/R)^3 + 1828.9(1/R)^2 + 5.6040(1/R) - 0.000012697 \qquad (1)$$

Because of the large quantity of data to be handled, a program was written for the IBM 7090 which took the input resistance and time data for each run, converted resistance to HCl concentration, and applied the first-order equation. A value for k was printed out to correspond to each point taken. This procedure was not perfect. The integrated first-order rate constants diminished during the course of a run by a few parts per thousand, undoubtedly because of the inadequacy of expressing concentration as a polynomial in reciprocal resistance. Theoretically, it would have been better to express $1/R$ as a polynomial in $\sqrt{c}$, but such a form is less desirable in machine computations where $1/R$ is given and c is to be found. In practice, all of the runs showed the same degree of decrease in k during the run; for greater consistency, an average value was taken at the same reaction time for each run. In general, this procedure gave rate constants reproducible to a few tenths per cent.

The results of the kinetics are summarized in Tables I and II. In addition, the equilibrium constant for the solvolysis in 80% aqueous acetone was determined by adding benzhydrol to a known amount of HCl and determining the resistance at equilibrium. Two determinations gave $K = 1.85 \pm 0.21$ moles/l.; hence, at the kinetic concentrations ($\sim 10^{-3}$ moles/l.), the solvolysis goes $\sim$99.9% to completion in qualitative agreement with an earlier report.[9]

The summary of the isotope effects in Table II shows

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[1] This research was supported in part by a grant from the National Science Foundation.

[2] National Science Foundation Predoctoral Fellow, 1959–1961; University of California Fellow, 1961–1962.

[3] E. A. Halevi, "Progress in Physical Organic Chemistry," Vol. 1, S. G. Cohen, A. Streitwieser, Jr., and R. W. Taft, Ed., Interscience Publishers, Inc., New York, N. Y., 1963, p. 109.

[4] E. A. Halevi, M. Nussim, and A. Ron, *J. Chem. Soc.*, 866 (1963).

[5] A. Streitwieser, Jr., and H. S. Klein, *J. Am. Chem. Soc.*, **85**, 2759 (1963).

[6] C. Bernasconi, W. Koch, and H. Zollinger, *Helv. Chim. Acta*, **46**, 1184 (1963).

[7] H. S. Klein and A. Streitwieser, Jr., *Chem. Ind.* (London), 180 (1961).

[8] A. J. Kresge, K. N. Rao, and N. N. Lichtin, *ibid.*, 53 (1961).

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TABLE I

SOLVOLYSIS OF DEUTERATED BENZHYDRYL CHLORIDES IN AQUEOUS ACETONE AT 25.00°

Position of deuteriums[a]	80% aq. acetone[b]		70% aq. acetone[d]	
	$10^5 k$, sec.$^{-1c}$	Acceleration, %	$10^5 k$, sec.$^{-1}$	Acceleration, %
None	(7.52), 7.37, 7.38	...	51.1, 51.2	...
2,6	(8.07), 7.86	(7.3), 6.7	55.15, 55.0	7.9, 7.4
3,5	(7.94), 7.81	(5.6), 6.0	54.1, 54.4	5.9, 6.2
4	(7.64), 7.55, 7.52, 7.54	(1.6), 2.4, 1.9, 2.2	52.2, 52.1	2.1, 1.7
2,4,6	(8.26), 8.04	(9.8), 9.1	56.0	9.5
2,3,4,5,6	(8.72), 8.54	(16.0), 15.9	59.8	17.0
α	(6.67), 6.46	(−11.3), −12.3	45.0	−12.0

[a] Benzhydryl chlorides are symmetrically substituted in both rings; positions of deuterium are shown for only one ring. [b] $d^{25}{}_4$ 0.8598. [c] Figures in parentheses are for a different batch of solvent of slightly more aqueous composition. [d] $d^{25}{}_{25}$ 0.88296.

TABLE II

SUMMARY OF ISOTOPE EFFECTS

Position of deuteriums	80% acetone		70% acetone	
	Av. k_D/k_H	$100(k_D/k_H - 1)$ per D	Av. k_D/k_H	$100(k_D/k_H - 1)$ per D
ortho	1.070 ± 0.003	1.8 ± 0.1	1.077 ± 0.003	1.9 ± 0.1
meta	1.057 ± .002	1.4 ± .05	1.060 ± .003	1.5 ± .1
para	1.020 ± .003	1.0 ± .2	1.019 ± .002	1.0 ± .1
ortho-para	1.094 ± .004		1.095	
ontho-meta-para	1.160 ± .001		1.170	
α	0.881 ± .005		0.880	

that to a close approximation the two solvent compositions used give the same results. The effect depends clearly on the position of substitution in the order: *ortho* > *meta* > *para*. Moreover, the effect is approximately additive. Using the % accelerations per D (*ortho*, 1.9; *meta*, 1.5; *para*, 1.0), the calculated and found % accelerations in 80 and 70% acetone are, respectively, 9.2, 9.4, and 9.5 for benzhydryl-2,4,6,2',4',6'-d_6 chloride and 15.2, 16.0, 17.0 for benzhydryl-2,3,4,5,6,2',3',4',5',6'-d_{10} chloride.

In these data, two features appear significant. One is that the effect in different positions is of comparable magnitude; the other is that the small variations which are observed do not correspond to those expected for normal substituent effects. The former point has also been made by Lichtin[10] in a related study of the ionization equilibria of deuterated triphenylmethyl chlorides in liquid sulfur dioxide. In this study, the following % enhancements of ionization were reported[10]: perdeuteriotriphenylmethyl chloride, 19.5[11]; tris(phenyl-*p*-*d*)-methyl chloride, 3.2; tris(phenyl-*m*-*d*)methyl chloride, 4.5. These numbers lead to % enhancements per position of: *ortho*, 1.2[12]; *meta*, 1.5; *para*, 1.1. The results for *meta* and *para* positions are in good accord with our results, but the effect calculated for the *ortho* position in the triarylmethyl chloride ionization is weaker than that which we find for benzhydryl chloride solvolysis, perhaps because of the cumulative errors associated with the former case. It would be interesting to have a direct determination of the ionization constant for tris(phenyl-*o*-*d*)methyl chloride. Nevertheless, the comparable magnitude of the directly measured effects in the two systems shows that the transition state for benzhydryl chloride solvolysis must be close in character to a "pure" carbonium ion.

We have shown previously[5] that the magnitude of the effect in the *meta* position is about that expected for an inductive effect; that is, a value for σ_m of about −0.0012 was estimated from acidities of deuterated aliphatic and benzoic acids. This value and a ρ of −4 for solvolysis of benzhydryl chlorides in aqueous acetone[13] lead to a predicted effect of log k_D/k_H = 1.011 for a single *m*-D, in reasonable agreement with the experimental value of 1.015. Because of the conjugation of positive charge to the *para* position, we might have anticipated a stronger effect for a *para* deuterium. The actual effect is weaker than at the *meta* position. No definite explanation can be given for this change; the system is far too complex for a detailed consideration of individual modes of vibration. Working hypotheses, however, can be offered which lead to generalizations subject to further experimental test. One such hypothesis is that these isotope effects measure inductive and field effect polarizations in the σ-bond system. It seems noteworthy that chemical shifts of ring protons in triphenylmethyl cation fall in the order[14] *para* > *meta* > *ortho* and may also reflect electron densities in the σ-bonds. In this interpretation, the stronger effect found in our study for the *ortho* position is consistent. If this hypothesis is sustained by future work, such isotope effects may be a useful probe of σ-electronic effects. One serious limitation, however, is the small magnitude of the effect. For example, the small isotope effects found experimentally for the p*K*'s of deuterated anilines had sufficient experimental error to be consistent with several hypotheses.[15]

An alternative hypothesis should be mentioned. Conceivably, the direct conjugation of the *para* position to the reacting center may cause vibrational changes that may weaken the strong effect normally anticipated for an electron-donating substituent in a *para* position; that is, the isotope effect may be such that the experimental σ^+ (*p*-D) is numerically smaller than the σ^+ anticipated in the absence of such perturbations. Tenuous grounds for such a thought derive from the knowledge that the difference in p*K* between HCOOH and DCOOH does not follow the same inductive order as deuterium substitution in higher carboxylic acids[3,5] and that the secondary isotope effect for protonation of *p*-chlorobenzaldehyde[16] is substantially less than might be expected from γ-deuterium isotope effects[17] in solvolysis reactions if these effects are interpreted as in-

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(10) N. N. Lichtin, ref. 3, p. 75.

(11) Also reported earlier: A. J. Kresge, K. N. Rao, and N. N. Lichtin, *Chem. Ind.* (London), 53 (1961).

(12) This figure is calculated assuming additivity of the effects; Lichtin[10] calculates 0.9 for the *ortho* position from the same numbers.

(13) Y. Okamoto and H. C. Brown, *J. Org. Chem.*, **22**, 485 (1957); V. J. Shiner and C. V. Verbanic, *J. Am. Chem. Soc.*, **79**, 369 (1957); L. Verbit and E. Berliner, *J. Am. Chem. Soc.*, **86**, 3307 (1964).

(14) T. Schaefer and W. G. Schneider, *Can. J. Chem.*, **41**, 966 (1963).

(15) C. Bernasconi, W. Koch, and H. Zollinger, *Helv. Chim. Acta*, **46**, 1184 (1963).

(16) R. Stewart, A. L. Gatzke, M. Mocek, and K. Yates, *Chem. Ind.* (London), 331 (1959).

(17) K. T. Leffek, J. A. Llewellyn, and R. E. Robertson, *J. Am. Chem. Soc.*, **82**, 6315 (1960).

ductive effects.[5] In this hypothesis, we would also expect a weaker effect for the *ortho* positions. The stronger effect actually found would then require still a further superimposed effect, namely, the decreased steric effect of deuteriums. The effectively smaller deuteriums would cause less strain in the *ortho* position of a planar benzhydryl cation, or, for the case that a normal benzhydryl cation is somewhat twisted, would allow a somewhat smaller angle of twist and greater conjugation. This hypothesis requires a separate effect for each position, and, if true, suggests that secondary isotope effects of ring deuteriums of this sort will not become useful tools.

Finally, we may mention that the α-deuterium isotope effect of 12% retardation of rate is in the normal range for such α-D effects.[3,18]

Experimental[19]

Bromobenzene-4-*d*.—The Grignard reagent prepared from 95 g. (0.4 mole) of *p*-dibromobenzene and 12.2 g. of crystalline magnesium in dry ether was quenched with D_2O and worked up as usual to yield 22 g. of bromobenzene-4-*d*, $n^{25}D$ 1.5538. The infrared spectrum showed <5% of undeuterated bromobenzene (strong bromobenzene bands at 6.90 and 11.05 μ absent in the 4-*d* compound).

Bromobenzene-2,4,6-d_3.—About 33 g. of aniline hydrochloride was refluxed overnight with 50 ml. of D_2O in a flask equipped with a reflux condenser equipped with take-off and drying tube. The spent D_2O was distilled into a second such apparatus and refluxed with a second batch of aniline hydrochloride. The first batch was refluxed with fresh D_2O, and the process was repeated a total of six times. Each volume of D_2O was used with a total of six batches of aniline hydrochloride, but a final exchange was run with fresh D_2O in each case. The combined deuteriochloride was treated with sodium hydroxide to give 144 g. of aniline-2,4,6-d_3. One hundred grams of the amine was converted to the diazonium salt and treated with cuprous bromide in a normal Sandmeyer reaction to give 77 g. of bromobenzene-2,4,6-d_3, b.p. 150–152.5°, $n^{25}D$ 1.5563. A measure of the isotopic purity is shown by the infrared spectrum in which the virtual absence of absorption at 11.40 and 12.20 μ indicates the presence of <1% of bromobenzene-2,6-d_2.

Bromobenzene-3,5-d_2.—Acetanilide-2,4,6-d_3, prepared from 32 g. of aniline-2,4-6-d_3 and acetic anhydride, was dissolved in acetic acid and treated with 21.6 ml. of bromine in acetic acid at room temperature. The crude *p*-bromoacetanilide-2,6-d_2 (containing some *ortho* isomer) was hydrolyzed with ethanolic KOH to yield 36 g. of crude *p*-bromoaniline-2,6-d_2. This product was mixed with 65 ml. of 48% hydrobromic acid and treated successively with 15.4 g. of sodium nitrite and 110 ml. of hypophosphorous acid at 0–5°. After several days in a refrigerator, the separated heavy oil was taken into ether, washed, dried, and distilled to give 16 g. of bromobenzene-3,5-d_2, b.p. 150–152.5°, $n^{25}D$ 1.5560. Note that deamination of the *o*-bromoaniline-4,6-d_2 also present yields the same bromobenzene-3,5-d_2.

Bromobenzene-2,6-d_2.—Fifty-seven grams of bromobenzene-2,4,6-d_3 was nitrated with a mixture of 70 ml. of concentrated nitric acid and 70 ml. of concentrated sulfuric acid at 50–60°. After a further 0.5 hr. on the steam bath, the product was poured into cold water and recrystallized from ethanol yielding 36 g., m.p. 123–124°. Reduction with iron filings and hydrochloric acid gave 27 g. of *p*-bromoaniline-3,5-d_2, m.p. 64.6°. This product was diazotized and deaminated with hypophosphorous acid as above, yielding 14.2 g. of bromobenzene-2,6-d_2, b.p. 150–152°, $n^{25}D$ 1.5566.

Infrared Spectra.—Each of the bromobenzenes discussed in this paper have prominent peaks in the infrared not shared by the others. Some of these characteristic bands are: bromobenzene, 11.05, 13.6 (broad), 14.88 μ; 4-*d*, 10.13, 14.17 μ; 3,5-d_2, 11.9, 11.81, 15.28 μ; 2,6-d_2, 7.72, 10.22, 13.76 μ; 2,4,6-d_3, 7.25, 11.97, 13.31, 14.29 μ; 2,3,4,5,6-d_5, 7.45, 7.60, 15.54 μ.

Benzhydrols.—Each of the deuterated benzhydrols was prepared by adding to the Grignard reagent prepared from about 7 g. of the deuterated bromobenzene and 1.05 g. of crystalline magnesium in dry ether 1.65 g. of ethyl formate previously purified by drying with potassium carbonate and distilling from phosphorus pentoxide. The benzhydrol was isolated from the ether solution in the usual way and crystallized from hexane. Yields were 2.2–2.8 g. Benzhydrol-α-*d* was prepared by reduction of benzophenone with lithium aluminum deuteride in the usual way. Deuterium analyses were run by determination of the density of combustion water by a drop suspension method.[19] At the time these analyses were done, this method usually gave low results for compounds of high deuterium content. Results are summarized in Table III.

TABLE III

PROPERTIES OF DEUTERATED BENZHYDROLS

Deuterium positions	Uncor. m.p., °C.	—Deuterium, %— Calcd.	Found	Isotopic purity (min.,) %
None	66.4–67.0			
4,4'-d_2	66.0–66.6	16.6	15.8	95
3,5,3',5'-d_4	66.8–67.4	33.3	31.5	95
2,6,2',6'-d_4	67.8–68.3	33.3	32.8, 33.1	99
2,4,6,2',4',6'-d_6	67.0–67.8	50.0	46.2, 46.6	93
2,3,4,5,6,2',3',4',5',6'-d_{10}	66.6–67.0	83.3	73.9, 75.4	90
α-*d*	66.8–67.2	8.3	8.5	100

Benzhydryl Chlorides.—Dry hydrogen chloride was passed into a solution of 1 g. of the benzhydrol in 15 ml. of 1:1 benzene–petroleum ether in the presence of anhydrous calcium chloride. After 2 hr., the hydrogen chloride flow was stopped and most of the solvent was distilled. On vacuum distillation, benzhydryl chloride was collected at 103–105° (0.2–0.3 mm.) and was stored frozen in Dry Ice–acetone under nitrogen until used. An infrared spectrum of benzhydryl-2,3,4,5,6-2',3',4',5',6'-d_{10} chloride showed that no hydrogen–deuterium exchange had occurred.

Kinetics.—Over periods of time, we noticed that the 80% aqueous acetone solvent changed significantly in composition; hence, an entire kinetic series was run within a space of a few days. Reproducibility of a sample at the start and end of the series showed no significant change. The 70% acetone solvent was stored in a ground-glass stoppered bottle which, itself, was stored in a container containing the solvent. Differential losses by evaporation were minimized by this method. In each run, 1 drop of the benzhydryl chloride was added to about 40 ml. of the aqueous acetone which had been equilibrated in the constant temperature bath maintained at 25.00 ± 0.01°. The solution was shaken and poured quickly into the thermostated conduc-

TABLE IV

SOLVOLYSIS RUN OF BENZHYDRYL-4,4'-d_2 CHLORIDE IN 80% AQUEOUS ACETONE AT 25°

Initial time = 3.00 min., initial resistance = 62,000 ohms, final resistance = 1790 ohms

Time, min.	Resistance, ohms	[HCl], 10^4 moles/l.	$10^5\ k$, sec.$^{-1}$
8	33,200	1.577	7.676
14	21,560	2.511	7.687
22	14,920	3.709	7.672
30	11,530	4.867	7.671
38	9,485	5.977	7.662
48	7,840	7.305	7.650
57	6,833	8.445	7.638
65	6,154	9.434	7,644
74	5,566	10.493	7.640
84	5,054	11.626	7.642
94	4,650	12.705	7.640
105	4,295	13.829	7.634
123	3,844	15.573	7.641
146	3,435	17.575	7.630
173	3,093	19.680	7.626
204	2,812	21.818	7.635

k (at t = 100) = 7.64×10^{-5} sec.$^{-1}$

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[18] A. Streitwieser, Jr., "Solvolytic Displacement Reactions," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p. 173.

[19] Analysis by the Microanalytical Laboratory of the Department of Chemistry, University of California.

tivity cell of conventional design. Resistance measurements were taken at 1–2-min. intervals with an Electro-Measurements, Inc., impedance bridge, Model 250-DA. A variable capacitor attached to the capacitance terminals of the bridge was used to maximize the sensitivity of the bridge. Infinity points were taken after at least 10 half-lives. Rate constants were calculated for each point using the usual integrated first-order rate equation with hydrochloric acid concentrations derived from the resistance measurements and previously determined calibrations. A typical run is shown in Table IV. Since this run contained 81 points, only every fifth point is reproduced.

The equilibrium constant was determined by adding a solution of hydrochloric acid in 80% aqueous acetone to weighed amounts of benzhydrol. The resistance of the acid solution was taken before and after the addition using equilibrium values in the 25.00° thermostat. The depression of the hydrochloric acid concentration was taken as the equilibrium concentration of benzhydryl chloride.

[CONTRIBUTION FROM THE CHEMISTRY DIVISION, ARGONNE NATIONAL LABORATORY, ARGONNE, ILLINOIS]

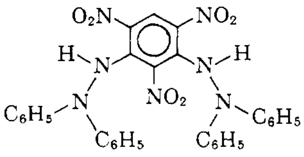
Dihydrazyl. Synthesis and Magnetic Properties[1]

BY JOACHIM HEIDBERG[2] AND JOHN A. WEIL

RECEIVED JUNE 1, 1964

Synthesis and characterization of the previously undescribed 1,3-bis(1,1-diphenylhydrazyl)-2,4,6-trinitrobenzene is described. Removal of the two hydrazinic hydrogen atoms by oxidation with PbO$_2$ proceeds in two steps, leading first to an unstable radical very similar to DPPH (e.p.r., color) and then yielding the (very unstable) "dihydrazyl" molecule. The latter was shown, by e.p.r. and n.m.r. measurements below $-30°$, to be a diamagnetic, spin-paired species.

Recently, a number of studies on the synthesis and magnetic properties of triplet molecules and biradicals have yielded detailed information about the electron correlation in these systems. Herein, an investigation of the potentially paramagnetic molecule 1,3-bis(1,1-diphenylhydrazylene)-2,4,6-trinitrobenzene (III, dihydrazyl) will be reported.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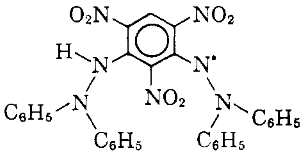
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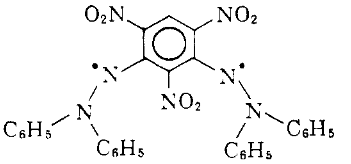
III

The previously undescribed substance 1,3-bis(1,1-diphenylhydrazyl)-2,4,6-trinitrobenzene (I), precursor to formation of the dihydrazyl, was prepared as follows.

Condensation of pyridinium styphnate with phosgene in acetone at 35° gave 1,3-dichloro-2,4,6-trinitrobenzene (IV) in 90% yield, m.p. 129°.[3] 1,1-Diphenylhydrazine (4.4 moles), m.p. 35°, which had been purified immediately before the reaction, and IV (1 mole) in boiling ethanol in 2 hr. yielded the dark red, crystalline dihydrazine I (yield 90%). Recrystallization from ethyl acetate and subsequent drying *in vacuo* at 60° afforded the pure product; I undergoes color changes when heated and melts with decomposition at 164°. *Anal.* Calcd.: C, 62.4; H, 4.0; N, 17.0. Found: C, 62.5; H, 4.0; N, 16.6. Compound I contains two acidic hydrogens and its molecular weight could be determined by potentiometric titration in pyridine with a 0.1 M solution of triethyl-n-butylammonium hydroxide in benzene using a glass electrode as indicator and a calomel electrode as reference[4]; mol. wt. calcd. 578, found 567 and 592. Further evidence for the structure of I was obtained by means of high-resolution proton magnetic resonance studies in methylene chloride at 60 Mc./sec. employing a Varian A-60 instrument. The weak peaks[5] at 314 and 240 c./sec. are attributed to the NH and picryl proton, respectively, and the strong doublet at 113 and 108 c./sec. to the phenyl protons. There is ample analogy for these assignments.[6]

Oxidation of I in methylene chloride or 2-methyltetrahydrofuran solution was effected by PbO$_2$ (well washed with acetone, then with the solvent to be used) freshly prepared by hydrolysis of Pb(CH$_3$COO)$_4$ in glacial acetic acid in the presence of CHCl$_3$.[7] Since the oxidation products II and III were found to be unstable at room temperature, all preparations and experiments with these were carried out at temperatures below $-30°$. The oxidation was followed by recording the e.p.r. spectra of the radical produced. The clearly resolved five-line spectrum of a deeply violet (mono) radical II appeared immediately; its intensity increased as the oxidation proceeded and then decreased markedly but could not be made to vanish entirely without irreversible decomposition. The g-value, nitrogen hyperfine-coupling constants A and A', and line-widths Δ measured in degassed 2-methyltetrahydrofuran solution at $-50°$ were found to be very similar for the radical II ($g = 2.0035 \pm 0.0003$, $A = 8.5 \pm 0.3$ oe. (oersted), $A' = 8.9 \pm 0.3$ oe., $\Delta = 5.5 \pm 0.1$ oe.) and 1,1-diphenyl-2-picrylhydrazyl (DPPH).[8]

When the PbO$_2$ was removed by centrifugation from the oxidized solution and an excess of dihydrazine (I) was added, the intensity of the e.p.r. signal from II increased to more than twice the maximum intensity observed during the course of the oxidation, whereas the spectral pattern remained unchanged.

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(1) Based on work performed under the auspices of the U. S. Atomic Energy Commission.

(2) Please address reprint requests to J. A. Weil. J. Heidberg on leave of absence from Institut für Physikalische Chemie, Frankfurt am Main.

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(5) Spectrum taken at $-60°$. Peak positions are relative to the CH$_2$Cl$_2$ peak. Conversion to the τ scale can be made using τ (CH$_2$Cl$_2$) = 4.67.

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