

*Hydrogen Transfer. Part V.\* Dehydrogenation Reactions with Diphenylpicrylhydrazyl.*

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[Reprint Order No. 5156.]

Homolytic hydrogen transfer between various donors and the "stable" free radical, diphenylpicrylhydrazyl, has been investigated. Hydroaromatic donors such as the dihydrobenzenes react rapidly at 60–100°; the sequence of reactivity is the same as in heterolytic dehydrogenation by quinones (*e.g.*, 1 : 4-dihydronaphthalene > 9 : 10-dihydroanthracene > 1 : 2-dihydronaphthalene > acenaphthene) but the energies of activation are rather larger.

Dibenzyl does not react appreciably with diphenylpicrylhydrazyl at 80°, whereas benzylaniline is readily dehydrogenated to benzyldeneaniline and hydrazobenzene is converted into azobenzene almost instantaneously at room temperature. The radical can also be "titrated" with diethyl 1 : 4-dihydro-lutidine-3 : 5-dicarboxylate. It is suggested that the very pronounced and quite generally encountered difference in reactivity between donors containing C–H and N–H bonds has a stereochemical cause and is due to the fact that nitrogen passes much more readily than carbon from a tetrahedral to a planar, trigonal configuration.

WHEREAS numerous reactions are known involving the abstraction of hydrogen atoms, particularly from C–H, N–H, and O–H bonds, by free radicals of short life (*cf.* Waters, "The Chemistry of Free Radicals, Oxford Univ. Press, 1946; Steacie, "Atom and Free Radical Reactions," Reinhold Publ. Corp., New York, 1946; Trotman-Dickinson, *Quart. Reviews*, 1953, **7**, 198; Kooyman and Strang, *Rec. Trav. chim.*, 1953, **72**, 330, 342), very few cases have been described of homolytic hydrogen transfer to "stable" free radicals. Although stable radicals will be intrinsically less reactive hydrogen acceptors than are "unstable" radicals, in practice the difference will be considerably reduced by the very much higher concentrations of stable radicals which are attainable. For quantitative investigations, stable radicals have the additional advantage that their concentrations are readily and directly measurable.

For a preliminary study, we chose diphenylpicrylhydrazyl (Goldschmidt and Renn, *Ber.*, 1922, **55**, 628) which has been shown by magnetic measurements to exist mainly as the monomeric radical both in the solid state and in solution (Müller, Müller-Rodloff, and Bunge, *Annalen*, 1935, **520**, 235; Allen and Sugden, *J.*, 1936, 440), although the quantitative significance of the data is rendered somewhat uncertain by the unknown diamagnetic contribution (Selwood and Dobres, *J. Amer. Chem. Soc.*, 1950, **72**, 3860). The strong hydrogen-acceptor properties of diphenylpicrylhydrazyl are indicated by the instantaneous conversion of quinol into benzoquinone (Goldschmidt and Renn, *loc. cit.*), a reaction also exhibited by other stable free radicals, such as triphenylmethyl (Goldschmidt and Wurzschnitt, *Ber.*, 1922, **55**, 3217). Diphenylpicrylhydrazyl similarly dehydrogenates tetrachloro-

\* Part IV, preceding paper.

quinol, tetrachlorocatechol, and tetrachloro-4 : 4'-dihydroxydiphenyl to the corresponding quinones; with the first two, as with quinol, the reaction is instantaneous under the conditions used (in chloroform solution at room temperature), but with the diphenyl derivative a just perceptible reaction period of a few seconds can be observed. This accords with the fact that the diphenoquinone has the highest oxidation-reduction potential (*ca.* 1.0 v; Part IV) and leads to the deduction that the "potential" of the diphenylpicrylhydrazyl-diphenylpicrylhydrazine system is of the order of 1.2 v, intermediate between those of diphenoquinone and of quadrivalent lead (1.7 v) which is used in the preparative oxidation of the hydrazine.

The main results of experiments on hydrogen transfer between diphenylpicrylhydrazyl and hydroaromatic donors are shown in Table 1. The two dihydrobenzenes, 1 : 2- and 1 : 4-dihydronaphthalene, and 9 : 10-dihydroanthracene all react fairly rapidly in boiling chloroform or carbon tetrachloride solution, giving the hydrazine and benzene, naphthalene, or anthracene in almost quantitative yields. Under similar conditions, little or no reaction is observed with tetralin, acenaphthene, 9 : 10-dihydrophenanthrene, or dibenzyl, although some dehydrogenation is observed with acenaphthene at higher temperatures.

TABLE 1. *Dehydrogenations with diphenylpicrylhydrazyl.*

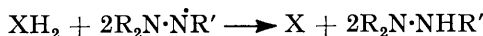
Donor	Solvent *	Time (hr.)	Total yield (%)	Dehydrogen. (%)
1 : 2-Dihydrobenzene	CCl <sub>4</sub>	3	—	> 50
1 : 4-Dihydrobenzene	"	1	—	> 50
1 : 2-Dihydronaphthalene	"	5	68	100
1 : 4-Dihydronaphthalene	CHCl <sub>3</sub>	1	74	100
9 : 10-Dihydroanthracene	CCl <sub>4</sub>	3	56	95
Tetralin	CHCl <sub>3</sub>	3	73	< 10
Acenaphthene	C <sub>6</sub> H <sub>6</sub>	16	50	18
9 : 10-Dihydrophenanthrene	CHCl <sub>3</sub>	20	40	< 10
Dibenzyl	"	24	76	< 2
Benzylaniline	" †	6	90	100
Hydrazobenzene	" ‡	0.2	96	100
Diethyl 1 : 4-dihydrolutidine-3 : 5-dicarboxylate	" ‡	0.2	95	100

\* At the b. p. of *ca.* 1M-solutions with respect to donor and hydrazyl, except where otherwise stated. For details, see experimental section.

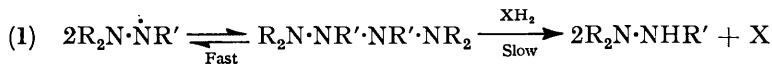
† At 40°.

‡ At 20°.

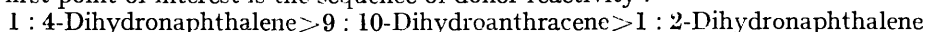
A preliminary kinetic investigation of some of the above reactions in dioxan was carried out by following the rate of disappearance of the hydrazyl spectrometrically. The results are of a low order of accuracy owing to several complicating factors, particularly the thermal instability of the hydrazyl solution under the conditions employed, but suffice to show that the reactions obey approximately the third-order rate law,  $v = k_3[\text{donor}][\text{hydrazyl}]^2$ , as expected from the equation :



As with other homogeneous, third-order processes, the reaction almost certainly involves a fast, reversible association of two of the reacting species followed by a rate-determining attack on this intermediate by the third component. The initial association could occur either (1) between two hydrazyl radicals to form the tetrazan, or (2) between a tetrazyl radical and the hydrocarbon to form a molecular complex. Although we cannot yet distinguish between these two possibilities, the second appears the more probable, particularly since complex formation will be assisted by the picryl group.



Rate constants and energies of activation for three of the donors are given in Table 2. The first point of interest is the sequence of donor reactivity :



which is the same as that found in hydrogen transfer to quinone acceptors (Part III). This parallelism is not unexpected, since the relative rates will be governed by the same factor—the stabilisation of the transition state arising from the gain in resonance energy accompanying dehydrogenation—independently of whether the C–H bond fission is heterolytic or homolytic. A second point of interest is the magnitude of the energies of activation, which are considerably higher than those found in the dehydrogenation of quinones (cf. Part III). Thus, whereas the reaction of 1:4-dihydronaphthalene with diphenylpicrylhydrazyl has  $E_A = 26$  kcal./mole, the corresponding reaction with tetrachloro-1:2-benzoquinone which proceeds with comparable rates under similar conditions has  $E_A = 13$  kcal./mole (unpublished work by J. S. Shannon). This difference will be partly due to the fact that the observed  $E_A$  for the radical reaction includes the enthalpy change of the pre-equilibrium, but this is unlikely to amount to as much as 13 kcal./mole. It is probable that the high value of  $E_A$  for the radical reaction is predominantly due to the fact that in hydrogen transfer to the radical there is a gain in resonance energy in the donor but a loss of resonance energy in the acceptor, whereas in hydrogen transfer to the quinone there is a gain in resonance energy in both donor and acceptor, and consequently a greater stabilisation of the transition state. A third point of interest is the fairly large positive value of the entropy of activation which is typical of free-radical reactions, though the observed value will again include any entropy change accompanying the postulated pre-equilibrium.

TABLE 2. *Extrapolated third-order rate constants ( $k_3$ ,  $l.^2$  mole $^{-2}$  min. $^{-1}$ ), energies of activation ( $E_A$ , kcal./mole), and entropies of activation ( $\Delta S$ , e.u.) for the reaction between hydrocarbons and diphenylpicrylhydrazyl in dioxan.*

Hydrocarbon	$t$	$k_3$	$E_A$	$\Delta S_{80}$
1:4-Dihydronaphthalene .....	56°	0.8	26	12
	80	12		
1:2-Dihydronaphthalene .....	56	0.04	33	27
	80	1.2		
9:10-Dihydroanthracene .....	56	0.1	29	14
	80	2.0		

In marked contrast to dibenzyl, its aza-analogue, benzylaniline, reacts even at 40° to give benzylideneaniline, while the diaza-analogue, hydrazobenzene, is rapidly converted into azobenzene at room temperature. The much greater ease of dehydrogenation of systems containing N–H in place of C–H bonds is also illustrated by diethyl 1:4-dihydrolutidine-3:5-dicarboxylate which is dehydrogenated almost instantaneously and can be “titrated” with diphenylpicrylhydrazyl at room temperature in chloroform. The high reactivity of N–H bonds in hydrogen transfer appears to be a general phenomenon, which is reflected in the prominent part played by nitrogen-containing heterocycles in biological systems (cf. Waters, *op. cit.*, Chap. XII), and deserves some comment. The bond energies and bond dissociation energies of C–H and N–H, as well as the resonance energies of unsaturated systems containing C=C or C=N, are very similar (cf. Szwarc, *Chem. Reviews*, 1950, 47, 75; Wheland, “The Theory of Resonance,” Wiley, New York, 1944), so that such thermodynamic differences cannot be responsible for the difference in reactivity. The explanation is most probably to be sought in the much greater ease with which nitrogen can pass from the tetrahedral to a planar configuration, as is indicated by, *inter alia*, the failure to resolve compounds of trivalent nitrogen (for summaries, see Shriner, Adams, and Fuson in Gilman, “Organic Chemistry,” Wiley, New York, 1943, p. 402; Maitland, *Ann. Reports*, 1939, 36, 239), except in one case where inversion is structurally precluded (Prelog and Wieland, *Helv. Chim. Acta*, 1944, 27, 1127), and by spectroscopic evidence (cf. Herzberg, “Infra-red and Raman Spectra,” Van Nostrand, New York, 1945; Walsh, *J.*, 1953, 2296). At a carbon atom, planarity will therefore be established only concurrently with the fission of the C–H bond and any resonance stabilisation of the resulting intermediate will become effective only at a fairly advanced stage of the dehydrogenation. At a nitrogen atom, on the other hand, planarity can be established even in the tervalent state at the expense of a relatively small amount of energy (*ca.* 10 kcal.; Maitland, *loc. cit.*), and fission of the N–H bond will be assisted by resonance stabilisation well before the transition

state is reached, with a consequent lowering of the energy of activation. This difference between the reactivity of C-H and N-H bonds should exist independently of whether the hydrogen is removed heterolytically as a hydride anion (as postulated in dehydrogenation by quinones) or homolytically as a hydrogen atom (as in dehydrogenation by free radicals); in either case the resulting intermediate cation or radical will adopt a planar configuration at the carbon or nitrogen atom concerned and be stabilised by charge resonance or electron resonance.

## EXPERIMENTAL

*Dehydrogenations.*—The preparative experiments were carried out as described in the preceding paper. *NN*-Diphenylpicrylhydrazyl, m. p. 137—138°, was prepared according to Goldschmidt and Renn (*Ber.*, 1922, 55, 628; cf. *Annalen*, 1924, 437, 194) except that in the final stage, 2 parts by weight of specially reactive lead dioxide obtained by hydrolysis of lead tetraacetate (Kuhn and Hammer, *Ber.*, 1950, 83, 413) were employed, instead of 15 parts by weight of ordinary lead dioxide. Solutions approx. 1M with respect to the hydrazyl and the donor were refluxed under dry nitrogen for the appropriate time (see Table 1). During the reactions, the colour changed from deep violet to red and finally pale orange. The solutions were then diluted with 10 volumes of light petroleum (b. p. 40—60°) which resulted in almost quantitative precipitation of crystalline diphenylpicrylhydrazine (smaller volumes of petroleum tend to give a gummy precipitate). After filtration, the solutions were passed through a short column of alumina, the product was eluted with more solvent and the eluates were evaporated. With the *cyclohexadienes*, the procedure was modified by directly distilling the reaction mixture and estimating benzene spectrometrically in the distillate. Details of some typical experiments are given below.

(a) 1 : 4-Dihydronaphthalene (0.26 g.), hydrazyl (3.94 g.), and chloroform (5 ml.) were refluxed for 1 hr. Light petroleum (50 ml.) was added and the hydrazine (3.2 g.), m. p. 163—165°, was filtered off. The solution was passed through alumina and evaporated, giving naphthalene (0.19 g., 74%), m. p. and mixed m. p. 80°.

(b) Acenaphthene (0.49 g.), hydrazyl (2.55 g.), and benzene (7 ml.) were refluxed for 16 hr. Working up as under (a) gave 0.24 g. (50%) of recovered hydrocarbon, m. p. 78—82°. It showed  $E_{1\text{cm}}^{1\%}$  115 at 3230 Å, corresponding to an acenaphthylene content of 18%.

(c) Hydrazobenzene (0.2 g.) in chloroform (3 ml.) was added to the hydrazyl (0.84 g.) in chloroform (3 ml.). The colour of the radical immediately disappeared. On adding light petroleum, diphenylpicrylhydrazine (0.79 g., 94%), m. p. 165°, was precipitated. The solution was passed through alumina and evaporated, giving azobenzene (0.2 g.), m. p. and mixed m. p. 68°.

(d) A solution of diethyl 1 : 4-dihydrolutidine-3 : 5-dicarboxylate (1.7 g.) and hydrazyl (5.0 g.) in chloroform (25 ml.) was kept for 10 min. at 30° and then diluted with light petroleum (200 ml.). The bright red precipitate of diphenylpicrylhydrazine (4.9 g.) was filtered off and had m. p. 167—168° after one crystallisation from ethanol-chloroform. The petroleum solution was evaporated, leaving an almost colourless residue (1.7 g.) which was dissolved in light petroleum (b. p. 100—120°), poured on alumina, and eluted with benzene-chloroform (1 : 1), giving pure diethyl lutidine-3 : 5-dicarboxylate (1.3 g.), m. p. 73—74°.

*Rate Measurements.*—These were carried out in reaction vessels of the type described by Braude, Jones, and Stern (*J.*, 1946, 396), but of only 10-ml. capacity. 5 ml. of approx. 0.2M-solution of the hydrazyl were placed in the flask and, after thermal equilibrium was attained, a 0.1-ml. sample was withdrawn by means of a specially constructed long-stem pipette and dissolved in 25 ml. of carbon tetrachloride. The pipette was pre-warmed to the reaction temperature by keeping it in a jacketed pistol surrounded by boiling acetone or benzene. As soon as possible after the removal of the initial sample, the weighed amount of hydrocarbon to give a 0.5M-solution was dropped into the flask in a small capsule, and the vessel was vigorously shaken. Further samples were then taken at appropriate intervals.

The sample solutions were then diluted further with solvent (2 in 25 ml.), and the hydrazyl concentration was determined spectrometrically by means of a Unicam SP 500 instrument and a 1-cm. cell; extinction was measured at 5180 Å where the hydrazyl exhibits a maximum with  $\epsilon$  12000. [For chloroform solutions, Goldschmidt and Graef (*Ber.*, 1928, 61, 1858) give  $\lambda_{\text{max}}$  5300 Å,  $\epsilon$  6500, while Poirier, Kahler, and Benington (*J. Org. Chem.*, 1952, 17, 1437) give  $\lambda_{\text{max}}$  5300 Å,  $\epsilon$  14,500.] It was established that Beer's law is obeyed at the maximum in the range 0.1—1.5 *E*, and is little affected by the presence of diphenylpicrylhydrazine which has  $\epsilon$  ca. 500 at 5180 Å.

The third-order rate constants were calculated from the standard equation :

$$k_3 = (1/t)(a - 2b)^2[2x(2b - a)/a(a - 2x) + \ln b(a - 2x)/a(b - x)]$$

where  $t$  = time (min.),  $a$  = initial concentration of hydrazyl (mole/l.),  $b$  = initial concentration of hydrocarbon, and  $2x$  = change in hydrazyl concentration at  $t$ . Details of two typical runs are given below.

(i) Hydrazyl and dihydroanthracene (0.450 g.; 0.5M) in dioxan (5 ml.) at 56°. Samples diluted 2 : 625.

$t$	0	7	15	35	60	120	360
$E$ (5180 Å) .....	0.739	0.643	0.573	0.457	0.358	0.214	0.037
$a$ (calc.) .....	0.190	0.165	0.147	0.118	0.092	0.055	---
$k_3$ .....	—	0.114	0.104	0.097	0.097	0.119	---

(ii) Reagents as above, at 80°.

$t$	0	2	6	10	28	90
$E$ (5180 Å) .....	0.557	0.355	0.244	0.149	0.103	0.035
$a$ (calc.) .....	0.144	0.092	0.058	0.039	0.027	---
$k_3$ .....	—	2.02	1.81	2.02	1.86	---

Grateful acknowledgment is made to the Nuffield Foundation for a Fellowship (A. G. B.).

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[Received, February 24th, 1954.]