274. *Homolytic Reactions of Aromatic Side-chains. Part III.*[1] *The Effect of the Solvent on the Relative Rates of α-Hydrogen Abstraction by t-Butoxy-radicals.*

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The effect of changes in solvent composition on the relative rates of α-hydrogen abstraction from toluene and γ-picoline, and cyclohexane and γ-picoline, have been investigated. No observable solvent effect exists for the former pair of substances; and, while the reaction with the latter pair is complicated by the transfer reaction of cyclohexyl radicals with γ-picoline, it is probable that solvent effects, if they exist at all, are small in this system also.

IN Part II,[1] the reactivities of a number of toluene derivatives towards α-hydrogen abstraction by t-butoxy-radicals were measured by means of competitive experiments with mixed solvents, and were shown to be influenced by both polar and resonance effects. In view of Russell's demonstration [2] that considerable solvent effects on relative rates of hydrogen abstraction by chlorine atoms exist when these are determined mainly by resonance effects, but not when they are determined largely by polar influences, the effect of solvent changes on relative rates of hydrogen abstraction by t-butoxy-radicals in systems analogous to those investigated in Part II has now been studied.

Toluene and γ-picoline were chosen as a pair of solvents whose difference in reactivity towards α-hydrogen abstraction is attributable mainly to polar influences, since it was shown in Part II [1] that the difference in reactivity between them is due mainly to the inductive effect of the nitrogen. Since Russell's results [2] indicate that the ability of an aromatic solvent to solvate the free chlorine atom is enhanced by an increase in the electron density at the aromatic nucleus, and since the t-butoxy-radical has an electronegativity which, while less than that of the chlorine atom, is still appreciable, γ-picoline might be expected to solvate this radical less efficiently than toluene. A series of competitive experiments was therefore conducted in which t-butyl peroxide was allowed to react with a large excess of mixtures of toluene and γ-picoline in varying proportions. The effect of the addition of benzene was also observed. The results, given in Table 1, indicate the absence of an appreciable solvent effect, and the results obtained with nuclear substituted toluene derivatives, which were reported in Part II, are independent of the solvent. The constancy of k_{rel} for γ-picoline over the range of solvent compositions also supports the conclusion, reached in Part II, that radical-transfer reactions are unimportant when both solvents are analogues of toluene, and therefore give rise to unreactive benzyl-type radicals by hydrogen abstraction.

TABLE 1.

Effect of variation in the composition of the solvent on the relative reactivity of toluene and γ-picoline.

Toluene (mole fraction)	γ-Picoline (mole fraction)	Relative reactivity γ-Picoline/Toluene (k_{rel}) Expt. 1	Expt. 2	k_{rel} of γ-picoline
0·5	0·5	0·39	0·39	0·39
0·5 *	0·5	0·41	0·41	0·41
0·75	0·25	0·41	0·40	0·41
0·25	0·75	0·40	—	0·40

* In the presence of benzene (0·5 mole).

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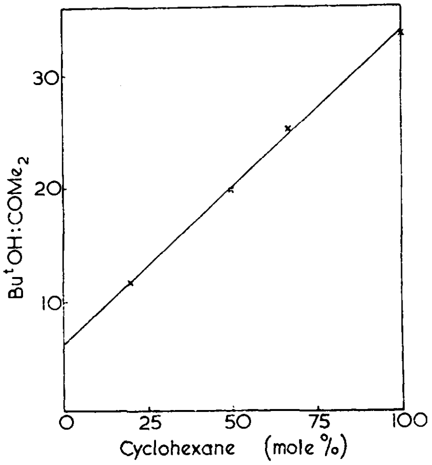
[1] Part II, Johnston and Williams, *J.*, 1960, 1446.

[2] Russell, *J. Amer. Chem. Soc.*, 1958, **80**, 4987, 4997, 5002.

Cyclohexane and γ-picoline were chosen as a pair of solvents which differ in reactivity towards t-butoxy-radicals at least partly because of the widely different degrees of resonance-stabilisation of their transition states for hydrogen abstraction. The possible existence of solvent effects in analogous systems has been investigated by Russell[3] and by Brook and Glazebrook[4] by measurement of the relative amounts of t-butyl alcohol and acetone formed. If it can be assumed that only the abstraction, and not the decomposition of t-butoxy-radicals to methyl radicals and acetone, is influenced by the solvent, then any difference between the ratio of the yields of t-butyl alcohol to acetone obtained from the reaction in a mixed solvent to that expected from the decomposition in the pure solvents, may be attributed to a solvent effect. Rather small differences were observed, although Brook and Glazebrook did not consider the existence of a solvent effect to have been definitely established. This test has now been applied to cyclohexane–γ-picoline mixtures, and the results, given in Table 2 and the Figure, indicate that the t-BuOH : Me_2CO ratio varies in a strictly linear manner with the molar composition of the solvent. The operation of a solvent effect is, therefore, not indicated by these measurements, except in the unlikely event that its influence on the rate of decomposition of t-butoxy-radicals exactly counterbalances the solvent effect on abstraction.



Relative yields of t-butyl alcohol and acetone in competitive reactions of cyclohexane and γ-picoline with t-butoxy-radicals.

TABLE 2.

Reaction of t-butyl peroxide with mixtures of cyclohexane and γ-picoline.

Reactants Molar propns. Peroxide : cyclohexane : γ-picoline	Products Molar ratio, $Bu^tOH/COMe_2$	Products Molar ratio, cyclohexyl/γ-picolyl groups in products	Apparent rel. reactivity, cyclohexane/γ-picoline
1 : 4 : 16	11·5	1·18	4·70
1 : 3 : 9	—	1·31	3·93
1 : 4 : 8	—	1·08	2·16
1 : 4 : 4	19·8	0·75	0·75
1 : 8 : 4	25·4	1·14	0·57
1 : 9 : 3	—	1·06	0·35
1 : 4 : 0	33·8	—	—

The observed variation in the apparent reactivity of cyclohexane relative to γ-picoline,

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[3] Russell, *J. Org. Chem.*, 1959, **24**, 300.
[4] Brook and Glazebrook, *Trans. Faraday Soc.*, 1960, **56**, 1014.

as calculated from the product composition, arises from the incursion of the known radical-transfer reaction [5] of cyclohexyl radicals with γ-picoline. These variations do not, therefore, indicate a solvent effect.

The comparative unimportance of solvent effects in the hydrogen-abstraction reactions of t-butoxy-radicals is probably attributable to two factors: (i) the lower intrinsic reactivity, and hence greater selectivity, of t-butoxy-radicals, even in the absence of complex-forming solvents, than of chlorine atoms, in whose analogous reactions solvent effects are important; and (ii) the lower effective electronegativity, and correspondingly lower tendency to form complexes with electron-rich solvents, of t-butoxy-radicals than of chlorine atoms.

EXPERIMENTAL

Solvents were purified as described in Part I.[6] t-Butyl peroxide (Light and Co.) was used without further purification (cf. Part I).

Competitive Experiments with Toluene and γ-Picoline.—t-Butyl peroxide (4·0 g., 0·027 mole) was allowed to decompose in a mixture of toluene and γ-picoline for 72 hr. at 110° (thermostat). The reactions were conducted and the products worked up and analysed as described in Part II. The relative reactivity of the two solvents was calculated, as before, from the ratio of the amount of material derived from each solvent found in the dehydrogeno-dimer fraction and the higher-boiling fraction, which was assumed to consist mainly of dehydrogeno-trimers. A suitable statistical factor was applied when the solvents were not present in equimolar proportions. The results are given in Table 1.

Competitive Experiments with Cyclohexane and γ-Picoline.—A solution was prepared from t-butyl peroxide, cyclohexane, and γ-picoline in the required molar proportions, and aliquot portions (~5 ml.) were transferred to thick-walled glass tubes. The tubes were cooled in liquid air, evacuated, and sealed while under vacuum. They were heated at 110° (thermostat) for 72 hr., then cooled in liquid air and opened. The low-boiling products, unused peroxide, and solvent were removed by vacuum-distillation at room temperature and were collected in a receiver cooled in liquid air. The relative amounts of t-butyl alcohol and acetone present in the low-boiling fraction were determined by gas-chromatography with a Perkin-Elmer model 116 vapour fractometer. The stationary phase was 10% w/w silicone elastomer on Celite, and nitrogen was used as carrier gas. The column temperature was 52°. The material remaining after the vacuum-distillation, which was assumed to consist mainly of dehydrogeno-dimers and -trimers of the two solvents, was analysed for γ-picolyl groups by potentiometric titration with a Cambridge pH meter, with glass and calomel electrodes. The results of these experiments are given in Table 2.

In order to check this procedure an equimolar solution of toluene and γ-picoline was allowed to react with t-butyl peroxide in a sealed tube and analysed as described above. The value found for the relative reactivity (0·38) is in good agreement with those given in Table 1.

We thank the Department of Scientific and Industrial Research for the award of a maintenance grant to W. V. S.

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[*Received, July 26th,* 1962.]

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[5] Sherman and Williams, unpublished observations.

[6] Johnston and Williams, *J.*, 1960, 1168.