654. *Hydrogen Transfer. Part XVIII.*[1] *Homogeneous Hydrogen Transfer Between Nitrogenous Heterocycles.*

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Hydrogen transfer from dihydrides of nitrogenous heterocycles to higher aromatic members of the homologous nitrogenous heterocyclic series has been detected, thus allowing a partial scale of covalent hydrogen affinity to be established, in many ways analogous to the ionic redox scale.

The sequence dihydropyridine, dihydroquinoline, dihydroacridine, shows decreasing hydrogen-donor potential in homogeneous solution in purely organic systems. The "Hantzsch ester," a dihydropyridine, is capable of reducing both quinoline and acridine, and 1,2-dihydroquinoline can reduce acridine but not the dehydrogenated "Hantzsch ester." In such transfers between heterocycles the rôle of hydrogen donor is probably determined by the net gain in resonance energy involved in the transfer.

In any hydrogen-donor series derived from one nitrogen heterocycle, variation in the free-energy change of the dehydrogenation will depend upon the substituents in the molecule, and it may be predicted that pairs of energetically similar compounds will be found for which the hydrogen transfer will proceed to an equilibrium value.

	Acceptor	Temp.	Time	Oxidn. of donor (%)	Redn. of acceptor (%)
	Donor: *diethyl* 1,4-*dihydro*-2,6-*dimethylpyridine*-3,5-*dicarboxylate*.				
1	Quinoline *	172°	2 hr.	95	>36 Tetrahydro
2	Isoquinoline †	,,	24 hr.	66	<17 Tetrahydro
3	1,2-Dihydroquinoline	,,	2 hr.	93	⩾28 Tetrahydro
4	Acridine	20—78	3 hr.	100	⩾62 Probably quantitative
5	Phenanthridine	172	24 hr.	75	>27
	* 1 mol. of donor used. † 2 mol. of donor used.				
	Donor: 1,2-*dihydroquinoline*.				
6	Acridine	20°	4 min.	?	>80 Probably quantitative
7	Diethyl 2,6-dimethylpyridine-3,5-dicarboxylate	,,	4 days	?	0
	Donor: 9,10-*dihydroacridine*.				
8	Diethyl 2,6-dimethylpyridine-3,5-dicarboxylate	80	20 hr.	?	0

Both quinoline and 1,2-dihydroquinoline are reduced to 1,2,3,4-tetrahydroquinoline by the Hantzsch ester. The reduction of 1,2-dihydroquinoline would formally suggest that it is the first example of a simple unactivated olefin to be reduced under such conditions (cf. Part XVII [1]). However, at the high reaction temperature, it is possible that the unfavoured rearrangement to the isomeric 1,4-dihydroquinoline may be emphasised by rapid reduction of this form to the tetrahydro-level. One other possibility of thermal disproportionation was discounted in Part XVI,[1] and the remaining alternative appears to be thermal dehydrogenation of 1,2-dihydroquinoline to quinoline followed by homogeneous reduction to the tetrahydro-compound, either directly or in two stages, *via* the 1,4-dihydro-intermediate.

In Part XVI, it was necessary to postulate some 1,4-addition of hydrogen in the reduction of quinoline by lithium aluminium hydride to account for the presence of at least 3% of 1,2,3,4-tetrahydroquinoline in the product: in contrast, at least 16% of 1,2,3,4-tetrahydroisoquinoline was formed in the analogous reduction of isoquinoline. Quinoline and isoquinoline have now been found to be reduced to the tetrahydro-level by the Hantzsch ester, and quinoline is by far the more active acceptor. (In neither case was any dihydro-intermediate isolated.) Such a reversal of ease of reduction has been

[1] Parts XVI and XVII, preceding papers.

reported in Part XVII [1] for unsaturated imides and anhydrides when homogeneous hydrogen transfer is compared with catalytic hydrogenation; it occurs also with simple olefins and acetylenes when homogeneous transfer is compared with catalysed transfer from cyclohexene.

Experimental

General procedures are given in Part XVII.[1] Microanalyses were carried out in the microanalytical laboratory (Miss J. Cuckney) of this Department.

1. *Hantzsch Ester–Quinoline.*—Donor, 18·60 g., 1·0 mol.; acceptor, 10·00 g., 1·0 mol.; phenetole, 40 ml.; 172°; 2 hr. No unchanged donor crystallised from the cold reaction mixture. Acetic anhydride (12·8 ml., 1·2 mol.) was added and the solution was boiled (156°) under reflux for 15 min. Two drops of concentrated sulphuric acid were added to the hot solution which was then allowed to cool. After dilution with light petroleum, basic material was removed by extraction with dilute acid. The neutral acetylated amine, isolated by fractional distillation (twice) (2·41 g., 36% based on 1 mol. of donor), had b. p. 97°/0·1 mm., n_D^{24} 1·5742 (Found: C, 74·9; H, 7·4; N, 8·0. Calc. for $C_{11}H_{13}NO$: C, 75·4; H, 7·5; N, 8·0. Calc. for $C_{11}H_{11}NO$: C, 76·3; H, 6·4; N, 8·1%) (1-acetyl-1,2,3,4-tetrahydroquinoline, n_D^{25} 1·5740; 1-acetyl-1,2-dihydroquinoline, n_D^{23} 1·6028).

2. *Hantzsch Ester–Isoquinoline.*—Donor, 1·960 g., 2·0 mol.; acceptor, 0·500 g., 1·0 mol.; phenetole, 8 ml.; 172°; 24 hr. Unchanged donor (0·659 g., 34%) crystallised from the cold solution, the separation being completed by addition of light petroleum (50 ml.). Basic material was extracted from the phenetole–petroleum filtrate with dilute hydrochloric acid and was recovered as a yellow oil (1·703 g.), which was dissolved in pyridine (5 ml.), treated with benzenesulphonyl chloride (0·68 ml., 1·2 mol.) at 100° for 10 min., then cooled; the neutral product was isolated as a sticky off-white solid (0·118 g., 17%). Repeated crystallisation from ethanol afforded 1-benzenesulphonyl-1,2,3,4-tetrahydroisoquinoline (0·041 g.), m. p. and mixed m. p. 152·5—154°.

3. *Hantzsch Ester–1,2-Dihydroquinoline.*—Donor, 1·930 g., 1·0 mol.; acceptor, 1·000 g., 1·0 mol.; phenetole, 10 ml.; 172°; 2 hr. The mixture was worked up as in reaction no. 2 to give unchanged donor (0·134 g., 7%), and the mixed basic components as a viscous yellow oil (2·68 g.). The latter was heated in pyridine (5 ml.) with acetyl chloride (0·68 ml., 1·25 mol.) at 100° for 5 min., then cooled, and the neutral product isolated as a yellow oil (0·780 g., 58%), n_D^{25} 1·5479. Fractional distillation gave a colourless oil (0·370 g., 28%), b. p. 103°/0·13 mm., n_D^{25} 1·5740 (Found: C, 75·2; H, 7·6; N, 8·1%). The poor recovery in the distillation was due largely to the mechanical hold-up of the apparatus.

4. *Hantzsch Ester–Acridine.*—Donor, 0·707 g., 1·0 mol.; acceptor, 0·500 g., 1·0 mol.; ethanol, 12 ml. The mixture was homogeneous when hot and was boiled for 1 min., then allowed to cool in a sealed vessel. The cold solution deposited a large quantity of unchanged donor. In 2 hr. at room temperature there was no change in appearance. The solid was therefore redissolved by heating the mixture to the b. p. again for 1 min. On this occasion the deep yellow solution remained homogeneous on being cooled to room temperature. In ~1 hr., crystals separated and filtration afforded 9,10-dihydroacridine (0·312 g., 62%), m. p. and mixed m. p. 171—172°. The filtrate was not further worked up, but its complete lack of colour suggests that the transfer was quantitative.

5. *Hantzsch Ester–Phenanthridine.*—Donor, 0·707 g., 1·0 mol.; acceptor, 0·500 g., 1·0 mol.; phenetole, 8 ml.; 172°; 24 hr. The mixture was worked up as in reaction no. 2 to give unchanged donor (0·179 g., 25%), and the mixed basic components as a yellow oil (1·010 g.). As before, the latter fraction was dissolved in pyridine and treated with benzenesulphonyl chloride. Crystallisation of the neutral product from ethanol gave 1-benzenesulphonyl-1,2-dihydrophenanthridine (0·239 g., 27%), m. p. 113·5—115°. Repeated crystallisation from ethanol raised the m. p. to 114·5—115° (Found: C, 71·0; H, 5·0; N, 4·4. $C_{19}H_{15}NO_2S$ requires C, 71·0; N, 4·7; N, 4·4%).

6. *1,2-Dihydroquinoline–Acridine.*—A colourless solution of 1,2-dihydroquinoline (0·366 g., 1·0 mol.) in the minimum volume of cold ethanol (3·5 + 1·0 ml.) was quickly added to a pale yellow solution of acridine (0·500 g., 1·0 mol.) in cold ethanol (4·5 ml.). The mixture was at once sealed under nitrogen. An intense orange colour was immediately produced in the clear solution. The colour quickly faded and, ~80 seconds after mixing, crystals began to separate from the colourless solution. After about 4 min. no further change could be observed. The

mixture was chilled to 0° and filtered, yielding 9,10-dihydroacridine (0·325 g.), m. p. and mixed m. p. 170—171·5°. Concentration of the filtrate afforded a second crop (0·081 g.), m. p. 166—172°.

7. *1,2-Dihydroquinoline–Diethyl 2,6-Dimethylpyridine-3,5-dicarboxylate.*—1,2-Dihydroquinoline (0·261 g., 1·0 mol.) and the ester (0·500 g., 1·0 mol.) were dissolved in benzene (6 ml.)., diluted with light petroleum (6 ml.), sealed under nitrogen, and set aside at room temperature for 4 days. The solution remained clear and colourless, showing no sign of the bright yellow, insoluble Hantzsch ester.

8. *9,10-Dihydroacridine–Diethyl 2,6-Dimethylpyridime-3,5-dicarboxylate.*—A solution of 9,10-dihydroacridine (0·195 g., 1·0 mol.) and the pyridine ester (0·271 g., 1·0 mol.) in light petroleum (b. p. 60—80°) (20 ml.) was boiled under nitrogen for 20 hr. As in reaction no. 7 the solution remained clear and completely colourless.

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