Eliminations promoted by Weak Bases. Part 8.[1] Kinetics and Mechanisms of Reactions of Cyclohexyl Toluene-*p*-sulphonate with Thiourea in Various Solvents

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Cyclohexyl tosylate decomposes in the presence of thiourea to cyclohexene and cyclohexylisothiuronium tosylate, the product proportions depending on the solvent. In acetone and dimethylformamide, the substitution route is dominant and first-order kinetics are observed. The rate coefficients are increased relatively mildly on increasing the thiourea concentration. In acetone, the rate-determining step appears to be ionization, with thiourea consequently partitioning an intermediate between elimination and substitution pathways. In dimethylformamide, the rate-determining step is the same, but thiourea appears not to be kinetically active in producing cyclohexene. In the protic solvents ethanol and t-butyl alcohol, thiourea acts as if it is a weak anionic base, and the substitution : elimination ratio is almost 1 : 1, with second-order kinetics prevailing. Reasons for the anion-like behaviour of thiourea in these solvents are given, with reference to the *E*2C elimination mechanism.

IN the preceding paper [1] we have discussed an approach to the determination of the structure of the *E*2C transition state for bimolecular elimination from loose substrates, induced by weak bases which are also strong carbon nucleophiles.[2] The conclusion was that neutral bases in this category are less effective than anions, and an important transition state stabilization factor, namely electrostatic interaction between an anionic base and electron deficient C_α, was identified.[2e]

The weak neutral base employed was triphenylphosphine. We now turn our attention to the reaction of another weak neutral base, thiourea, with cyclohexyl tosylate ($C_6H_{11}OTs$). Like triphenylphosphine, thiourea is a strong carbon nucleophile under favourable circumstances, namely with tighter S_N2 substrates, *e.g.* MeI, in protic solvents. In methanol it is four times more reactive than Et_3N towards MeI, but the two nucleophiles are almost equally reactive towards MeOTs, a looser substrate, in the same solvent.[3] Reasons for this have been discussed [1,4] and, by analogy with Ph_3P, one would expect the relative S_N2 reactivity of thiourea (a 'soft' nucleophile) to be further diminished in 'softer' dipolar aprotic solvents.

RESULTS

As before,[1] reactions were conducted under pseudo-first-order conditions, with $[\text{base}]_0 > [C_6H_{11}OTs]_0$, and the fraction of cyclohexene produced, f_E, was assayed by g.l.c. The observed first-order rate coefficients, k_ψ, invariably increased in a linear fashion with increases in thiourea (or urea) concentration. Results are shown in Table 1, together with data for the non-basic and non-nucleophilic salt $LiClO_4$.[5] Analysis of these results is deferred to the following section, but at this point we tabulate in Table 2 the solute-induced increases in k_ψ in the form of *b* parameters from the Winstein–Fainberg equation,[6] equation (1). Here, $k_\psi{}^0$ is the solvolysis rate coefficient in the absence of all solutes.

$$k_\psi = k_\psi{}^0(1 + b[\text{solute}]) \qquad (1)$$

Cyclohexylisothiuronium tosylate as isolated from product samples (acetone solvent) and prepared by an unambiguous method differed from the claimed example resulting from the reaction of $C_6H_{11}OTs$ with thiourea in ethanol.[7] The latter is a 1 : 1 mixture of the desired salt and isothiuronium tosylate, as the f_E value of 0.56 (Table 1) suggests.

TABLE 1

First-order rate coefficients and olefin fractions for the decomposition of cyclohexyl tosylate (*ca.* 0.015M) in the presence of various solutes, in various solvents, at 75°

Solute	Solvent	[Solute]/M	10^5k_ψ/s^{-1}	f_E
	Me$_2$CO[a]		0.016 8[b]	1.00[b,c]
LiClO$_4$	Me$_2$CO[a]	0.032 6	0.054[b]	1.00[b,c]
Urea	Me$_2$CO[a]	0.056 1	0.067	>0.95
Urea	Me$_2$CO[a]	0.081 1	0.093	>0.95
Urea	Me$_2$CO[a]	0.103	0.107	>0.95
Thiourea	Me$_2$CO[a]	0.120	0.103	0.105
Thiourea	Me$_2$CO[a]	0.158	0.135	0.107
Thiourea	Me$_2$CO[a]	0.204	0.178	0.108
	DMF		0.59[d]	0.47[d]
Urea	DMF	0.102	0.76	0.492
Thiourea	DMF	0.099 3	0.72	0.395
Thiourea	DMF	0.152	0.78	0.364
Thiourea	DMF	0.208	0.87	0.340
Thiourea	DMF	0.257	0.89	0.316
	EtOH		2.64[e]	0.717[f]
Urea	EtOH	0.071 9	3.10	0.720
Urea	EtOH	0.128	3.64	0.742
Thiourea	EtOH	0.089 1	16.5	0.568
Thiourea	EtOH	0.116	20.7	0.562
Thiourea	EtOH	0.206	35.1	0.556
	Bu^{t}OH		0.12[g]	0.830[g]
Thiourea	Bu^{t}OH	0.070 0	3.56	0.619
Thiourea	Bu^{t}OH	0.085 0	4.22	0.615
Thiourea	Bu^{t}OH	0.100	5.04	0.619

[a] Contains 2,6-lutidine (*ca.* 0.015M). Values of k_ψ and f_E are independent of 2,6-lutidine concentration in the 0.01—0.03M range. [b] From ref. 5. [c] Assumed. [d] From ref. 12, extrapolated from results at other temperatures. [e] From S. Winstein and N. J. Holness, *J. Amer. Chem. Soc.*, 1955, **77**, 5562. [f] From W. Huckel, R. Bross, O. Fechtig, H. Felthamp, S. Geiger, M. Hanack, M. Heinzel, A. Hubele, J. Kurz, M. Maier, G. Naker, R. Neiddin, and R. B. Rashinghar, *Annalen*, 1959, **264**, 142. [g] See ref. 1.

No evidence for the presence of non-solvolytic substitution products in reactions conducted in the presence of

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[1] Part 7, D. J. McLennan, preceding paper.

[2] (*a*) A. J. Parker, *Chem. Tech.*, 1971, **1**, 297; (*b*) W. T. Ford, *Accounts Chem. Res.*, 1873, **6**, 410; (*c*) W. H. Saunders and A. F. Cockerill, 'Mechanisms of Elimination Reactions,' Wiley, New York, 1973, pp. 53, 69, 194; (*d*) J. F. Bunnett and D. L. Eck, *J. Amer. Chem. Soc.*, 1973, **95**, 1897, 1900; (*e*) D. J. McLennan, *Tetrahedron*, 1975, **31**, 2999.

[3] R. G. Pearson, H. Sobel, and J. Songstad, *J. Amer. Chem. Soc.*, 1968, **90**, 319; R. G. Pearson and J. Songstad, *J. Org. Chem.*, 1967, **32**, 2899.

[4] A. J. Parker, *Chem. Rev.*, 1969, **69**, 1.

[5] A. J. Parker, M. Ruane, G. Biale, and S. Winstein, *Tetrahedron Letters*, 1968, 2113.

[6] (*a*) S. Winstein and A. H. Fainberg, *J. Amer. Chem. Soc.*, 1956, **78**, 2763; (*b*) C. L. Perrin and J. Pressing, *ibid.*, 1971, **93**, 5705.

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urea was obtained. Urea has been assumed to be non-nucleophilic in some acetolyses [8] but this is not always the case.[9] Values of f_E for the decomposition of $C_6H_{11}OTs$ in the presence of urea in acetone were obtained from samples analysed before completion of reaction and are given as lower limits since up to 5% cyclohexene may be lost during removal of unchanged substrate. However, the olefin formation is quantitative in the practical sense.

TABLE 2

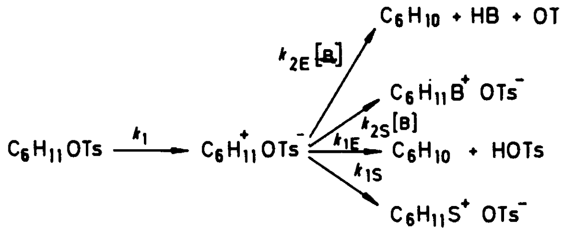
Parameters from the Winstein–Fainberg equation for the decomposition of cyclohexyl tosylate in the presence of various solutes at 75°

Solute	Solvent	*b*
$LiClO_4$	Me_2CO	67
Urea	Me_2CO	56
Thiourea	Me_2CO	44
Urea	DMF	2.8
Thiourea	DMF	2.2
Urea	EtOH	2.9
Thiourea	EtOH	59
Thiourea	Bu^tOH	407

DISCUSSION

Reactions in Acetone and Dimethylformamide.—The addition of thiourea accelerates the decomposition of the substrate. This could mean that second-order S_N2 and $E2$ reactions are competing with solvolysis, as is the case with Ph_3P.[1] However, we believe that this is not so, on two counts.

First, thiourea accelerates the decomposition to a lesser extent than do the non-nucleophilic polar solutes urea and $LiClO_4$. Differences in *b* values between acetone and DMF probably reflect the differing solvent dielectric constants.[6,10] It is thus reasonable to suppose that the accelerations arise from solute-induced assistance to substrate ionization, to at least the intimate ion-pair stage. The second point is that, if this is the case for all added solutes, the accelerations should be a function of the dipole moment of the solute.[6b] One would then expect thiourea (μ 4.89 D in dioxan) [11] to give rise to a greater acceleration than the less polar Ph_3P, but this is not observed.[1] The two neutral bases clearly behave differently, with only the latter reacting directly with the un-ionized substrate.*

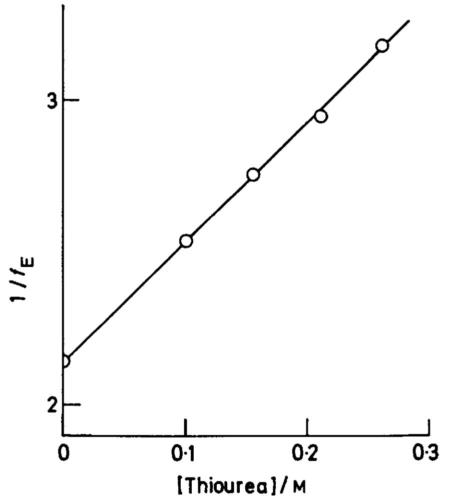


SCHEME

An ionization pathway of minimum complexity is shown in the Scheme. The k_2 steps depict base-induced decomposition of the ion-pair, formed in the rate-determining k_1 step, and the k_{1E} and k_{1S} steps respectively depict spontaneous decomposition induced by 2,6-lutidine.

The thiourea–acetone results can be accounted for by assuming that, in the presence of thiourea (>0.03M) $k_{1E} = k_{1S} = 0$. Values of f_E independent of [thiourea] are then expected, and found (Table 1). The ratio k_{2E}/k_{2S} is then $f_E/(1 - f_E)$ and is equal to 0.12. When urea is the added solute, it is likely that k_{2S} is also zero.

The same basic scheme can accommodate the DMF results. However, k_{1S} (no lutidine present) must now be finite because cyclohexyl formate, resulting from solvent attack, is a product of solvolysis.[12] The proportion of olefin decreases as [thiourea] increases, which could be taken to mean that $k_{1E} \gg k_{2E}[B]$. This is reasonable since DMF is reasonably basic [4] and might well act as a deprotonating agent. If this is so, kinetic analysis of the Scheme with $k_{2E} = 0$ leads to the prediction that a plot of $1/f_E$ against [thiourea] should be linear, with slope k_{2S}/k_{1E} and intercept $1/f_E^0$, where f_E^0 is the (known) [12] olefin fraction from solvolysis. As is shown by the Figure, a satisfactory plot is obtained, and k_{2S}/k_{1E} is found to be 4.05 l mol⁻¹. When urea is present, it appears to act as neither nucleophile nor base.



Plot of $1/f_E$ against [thiourea] for the solvolysis of $C_6H_{11}OTs$ in DMF, in the presence of thiourea

In acetone and DMF, Ph_3P behaves differently in that it is sufficiently reactive to engage in what are apparently S_N2 and $E2$ reactions with the un-ionized substrate,[1] which is clearly not attacked by thiourea.

Two lines of rationalization may be employed. The first is that Ph_3P may well be a stronger base in dipolar aprotic solvents than thiourea. On the basis of aqueous pK_a values [13] and the neutral base assumptions given in

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* A point for bimolecular S_N2 and $E2$ attack of thiourea on un-ionized $C_6H_{11}OTs$ is shown in Figure 1 of ref. 2*e*. We have since discovered that this point was based on min^{-1} as the time unit rather than s^{-1}, as pertains to the other points. The thiourea point must thus be deleted but the conclusions, resting on the behaviour of Ph_3P, remain unaltered.

[8] (*a*) W. S. Trahanovsky, M. P. Doyle, and P. D. Bartlett, *J. Org. Chem.*, 1967, **32**, 150; (*b*) M. S. Newman and L. K. Lala, *Tetrahedron Letters*, 1967, 3267.

[9] B. L. Johnson, personal communication.

[10] C. K. Ingold, 'Structure and Mechanism in Organic Chemistry,' Bell, London, 1969, 2nd edn., p. 486.

[11] W. D. Kumler and G. M. Fohlen, *J. Amer. Chem. Soc.*, 1942, **64**, 1944.

[12] G. E. Reinert, Ph.D. Thesis, University of Delaware, 1972.

[13] D. D. Perrin, 'Dissociation Constants of Organic Bases in Solution,' Butterworths, London, 1965.

the preceding paper,[1] Ph_3P may be up to four pK_a units more basic. And while basicity is not the dominant reactivity factor in *E*2C eliminations,[14] it must assume importance when nucleophiles having similar properties are compared. Secondly, thiourea is more soluble than is Ph_3P in acetone and DMF (see Experimental section) and thus the initial state for possible thiourea-induced reactions of un-ionized $C_6H_{11}OTs$ will be stabilized relative to that for Ph_3P. If transition state energies are comparable, this leads to the latter being the more reactive. However, the solubility difference corresponds to only 0.14 kcal mol^{-1} stabilization of thiourea relative to Ph_3P in acetone, which in turn is equivalent to the small rate factor of 1.26 in favour of Ph_3P on these grounds alone. Other factors are clearly of greater importance.

Reactions in Protic Solvents.—A dramatic change in the behaviour of thiourea is observed when the protic solvents EtOH and Bu^tOH are employed. Inspection of Table 2 reveals that larger rate accelerations, clearly inexplicable in terms of electrostatic assistance to ionization, result from the addition of thiourea. The data may be treated in terms of concurrent second-order substitution and elimination reactions accompanied by a small amount of solvolysis. On assuming no dependence of the solvolysis rate coefficient on the thiourea concentration, second-order rate coefficients may be calculated (Table 3), together with f_{2E}, the fraction of olefin arising from second-order reactions. These values are independent of solute concentration as required, and as is the case for Ph_3P.[1] The solvolysis assumption is reasonable since the urea *b* value is small, and in any case, solvolysis accounts for no more than 5.6% of products.* In fact, for the EtOH case, just as impressive agreement is obtained if the solvolysis rate coefficient is empirically adjusted using the urea *b* value.

TABLE 3

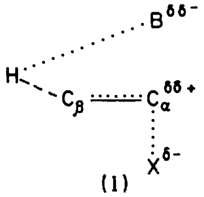
Dissected second-order rate constants and olefin fractions from thiourea data in Table 1 (EtOH and Bu^tOH)

Solvent	[Thiourea]/M	10^5k_{2E} [a]	10^5k_{2S} [a]	f_{2E}
EtOH	0.089 1	84.0 [b]	71.6 [b]	0.540
EtOH	0.116	84.0 [b]	70.6 [b]	0.543
EtOH	0.206	85.5 [b]	72.0 [b]	0.543
EtOH	0.089 1	78.5 [c]	69.5 [c]	0.530
EtOH	0.116	78.5 [c]	69.6 [c]	0.530
EtOH	0.206	80.0 [c]	69.9 [c]	0.534
Bu^tOH	0.070 0	30.0	19.1	0.612
Bu^tOH	0.085 0	29.4	18.5	0.609
Bu^tOH	0.100	30.2	19.0	0.613

[a] In l mol^{-1} s^{-1}, from equations (1) or (2) of ref. 1. [b] $10^5k\psi^0 = 2.64$ s^{-1} has been assumed. [c] $10^5k\psi^0 = 2.64(1 + 2.9[\text{thiourea}])$ s^{-1} has been assumed.

Thus, as with Ph_3P, the predominant reactions are S_N2 and *E*2 processes. Leaving aside the *E*2 reactivities for the moment, it is found that Ph_3P is a slightly better S_N2 reagent towards $C_6H_{11}OTs$ than is thiourea, unlike the MeI and MeOTs cases.[3] However, the rate difference is too small to warrant discussion. The fact that thiourea is more reactive towards un-ionized $C_6H_{11}OTs$ in protic solvents than in acetone and DMF can be partly rationalized by considering the solubilities (see Experimental section), which run in the order DMF $>$ $Me_2CO \gg$ EtOH $\approx$ Bu^tOH. Initial state solvation by the dipolar aprotic solvents is more stabilizing, so that mutual polarizability interactions in the case of thiourea are of more importance than specific hydrogen bond donation and acceptance by this zwitterion-like molecule. Furthermore, the protic solvents may stabilize the transition state by hydrogen bond donation to the well-severed and significantly charged leaving group (see later). Although DMF is a good cation solvator, the transition states we consider in the following paragraphs have their areas of charge deficiency somewhat buried, and so DMF is not at an advantage on this count.

We now discuss the *E*2 reactivity of thiourea in protic solvents. If the *E*2C transition state for weak anionic bases which are also strong carbon nucleophiles can be represented by structure (I) as claimed previously [1,2e]



(I)

then weak neutral bases are at a disadvantage in that the stabilizing electrostatic interaction between the base and electron deficient C_α is not available. This is the case for Ph_3P which, relative to typical anionic weak bases, induces elimination from $C_6H_{11}OTs$ more slowly than substitution.[1] Were thiourea to behave similarly we would expect f_{2E} values significantly less than 0.5.

Yet this is not the case (Table 3). In fact thiourea mimics the behaviour of anionic bases in giving f_{2E} values in the 0.5—0.6 range. The comparison may be more easily perceived by noting that thiourea points are correlated, well within the statistical limits of uncertainty, by the log k_E *versus* log k_S linear free energy relationship generated by a range of anions in various solvents,[14] and illustrated in the preceding paper.

Two alternative conclusions are possible. The first is that transition state (I) is wrong. If so, the aberrant behaviour of Ph_3P must have origins other than those proposed.[1] The second is that thiourea, unlike Ph_3P, does not behave like a typical neutral base within the context of (I) as the *E*2C transition state.

The first possibility may be rejected on the grounds that convincing evidence for (I) may be adduced from a wide variety of mechanistic probes.[2e] The second possibility is more reasonable, for although Ph_3P and thiourea share the properties of high polarizability and low base strength, they are distinctly dissimilar. Triphenylphosphine is less dipolar in character than

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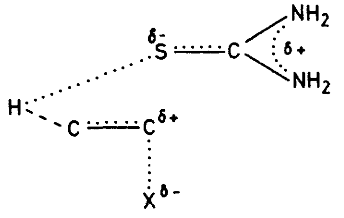
* This treatment does not give reasonable k_{2E}, k_{2S}, and f_{2E} values for DMF reactions nor for acetone as solvent once the solvolysis rate coefficient is adjusted using the urea *b* parameter. This is further testimony to the fact that these reactions do not have significant second-order components.

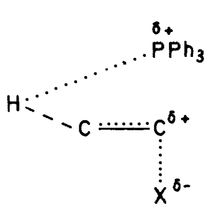
[14] P. Beltrame, G. Biale, D. J. Lloyd, A. J. Parker, M. Ruane, and S. Winstein, *J. Amer. Chem. Soc.*, 1972, **94**, 2240.

thiourea,[11,15] and the polarity of the former is due more to the lone pair of electrons on phosphorus [16] rather than resonance charge separation, which in any case would lower electron density at the nucleophilic atom. Thiourea on the other hand has a high resonance energy [17] and is distinctly zwitterionic in character.[18] Thus, while protonation or alkylation of Ph_3P places the positive charge on phosphorus, sulphur protonation [19] and alkylation of thiourea results in the positive charge being localised on nitrogen, two atoms removed from the nucleophilic atom. But for the presence of partially positively charged nitrogens, protonation of thiourea therefore resembles protonation of a thiolate anion. In this way we may visualize base–C_α electrostatic stabilization in *E*2C transition state (II) appropriate for thiourea, but this is not available in the Ph_3P transition state (III).

The analogy between thiolate ions and thiourea in protic solvents would be improved if a mechanism were available to delocalize the partial positive charges on nitrogen in transition state (II). Donation of hydrogen bonds by the nitrogen-bound protons to the solvent may help to smear these charges. Ethanol and Bu^{t}OH are good hydrogen bond acceptors,[20] and they could scarcely be worse than acetone in this respect.[14,21] This is confirmed semi-quantitatively by the donor number scale of solvent basicity.[22] But Ph_3P is a poorer acceptor of hydrogen bonds than even acetone [23] and so might be expected to behave similarly in protic and dipolar aprotic solvents. It does.[1]



(II)



(III)

In summary, the zwitterionic character of thiourea seemingly disqualifies it as a neutral base suitable for the examination of charge distribution in the *E*2C transition state. While the results in the present paper tell us little about the *E*2C transition state, they do not rule species (I) from contention. A result of practical significance arising from this and the preceding paper is that weak bases which are also strong carbon nucleophiles are effective eliminating agents towards loose substrates only when they are anionic, and the advantages the latter enjoy over such conventional reagents, *e.g.* OR^-–ROH, such as high yields of olefin in reactions that are more regioselective and stereoselective,[2a] are not shared by neutral weak bases.

EXPERIMENTAL

Materials.—The substrate, thiourea, and the solvents were obtained as before.[1] Cyclohexylisothiuronium chloride was prepared from cyclohexanol, thiourea, and concentrated HCl as described [24] and had m.p. 229—232° (lit.,[24] 230—231°); picrate, m.p. 173.5—174.5 (lit.,[25] 173—174°). Isothiuronium tosylate was prepared by the method of Bauer and Gardella,[25] m.p. 172—174° (lit.,[25] 173—174°) (Found: C, 38.8; H, 4.8; N, 11.4. Calc. for $C_8H_{12}N_2O_3S_2$: C, 38.7; H, 4.9; N, 11.3%).

Cyclohexylisothiuronium tosylate was prepared from the chloride by the anion exchange method described previously. After recrystallization from water it had m.p. 173—174° (Found: C, 50.9; H, 6.6; N, 8.4. Calc. for $C_{14}H_{22}N_2O_3S_2$: C, 50.9; H, 6.7; N, 8.5%). The literature preparation,[7] involving the reaction of cyclohexyl tosylate with thiourea in ethanol, yielded a sample which, by microanalysis, i.r. spectrum, and g.l.c. analysis (Table 1), was a *ca.* 1 : 1 mixture of isothiuronium and cyclohexylisothiuronium tosylates. This mixture had the same decomposition temperature as that reported.[7]

Reaction Products.—Cyclohexene was assayed by g.l.c. as before.[1] Cyclohexylisothiuronium tosylate was recovered in 80% yield from kinetic infinity samples (acetone solvent). Mock infinity samples containing the latter, cyclohexene, thiourea, and isothiuronium tosylate in ethanol were stable with respect to cyclohexene and total cations for one month in ethanol at 75°, and for two months in acetone when 2,6-lutidine was present. In some of the slower solvolyses in the presence of urea, cyclohexene was estimated in samples that had only partially reacted. Unchanged substrate was removed by passage of n-pentane extracts through a short alumina column.[12] Control experiments showed no more than 5% of cyclohexene was lost.

Kinetics.—The cation exchange technique previously described [1,26a] was employed. Control experiments with mock infinity solutions demonstrated the effectiveness of the method. Rate constants were obtained as before, and are associated with uncertainties of *ca.* 3%.

Solubilities.—Saturated solutions of thiourea in acetone, EtOH, and Bu^{t}OH were prepared at 35°, and cooled to 30° in a thermostat. Samples were removed and titrated for thiourea by the bromate method.[26b] It was found necessary to remove acetone under vacuum before oxidation, otherwise a precipitate of elemental sulphur formed which interfered with the stoicheiometry and the end-point. A

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[24] J. M. Sprague and T. B. Johnson, *J. Amer. Chem. Soc.*, 1937, **59**, 1837.

[25] L. Bauer and L. A. Gardella, *J. Org. Chem.*, 1961, **26**, 82.

[26] H. M. R. Hoffmann and E. D. Hughes, *J. Chem. Soc.*, 1964 (*a*) 1262; (*b*) 1259.

saturated solution of thiourea in dimethylformamide corresponds almost to a 1 : 1 mole ratio of the two components, and what appeared to be a crystalline complex was formed. The molarities of saturated solutions of thiourea in the other solvents are: 2.07 (acetone); 0.592 (EtOH); 0.435 (Bu^tOH). For the two last-mentioned solvents, u.v. spectrophotometry at 236 nm of samples suitably diluted by water, confirmed these values. At this wavelength, thiourea has a molar absorbance of 1.01×10^4.

In determining the solubility of Ph_3P in the four solvents, an iodimetric method [27] was employed. The molar concentrations of saturated solutions are: 2.12 (DMF), 1.64 (acetone), 0.174 (EtOH), and 0.155 (Bu^tOH).

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