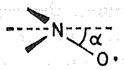
study of the temperature dependence of the h.f.s. values [11] and INDO calculations [12] it has been deduced that the angle α at nitrogen is *ca.* 30°, in contrast to the planar structure ($\alpha = 0°$) of the corresponding dimethyl nitroxide.[13]



The results of temperature-dependence studies for other fluorinated nitroxides are far from being well defined,[14] but it has been found that the replacement of one trifluoromethyl group by a SO_3^- group leads to a temperature-independent e.s.r. spectrum, suggesting planarity at the radical centre.[15] The e.s.r. spectra of some of the nitroxide radicals reported in this present work have been obtained over a range of temperatures, and the results for radicals (Ia) and (IVa) are summarised in Tables 3 and 4 respectively. Very similar

TABLE 3

Temperature dependence of the h.f.s. values of radical (Ia) in carbon tetrachloride

T/K	a_N / gauss	a_{CF_3} / gauss	$a_H(1)$ / gauss
293	10.50	10.70	2.54
273	10.49	10.79	2.50
253	10.45	10.80	2.44
233	10.43	10.87	2.39
223	10.41	10.89	2.37
213	10.39	10.91	2.34

TABLE 4

Temperature dependence of the h.f.s. values of radical (IVa) in carbon tetrachloride

T/K	a_N / gauss	a_{CF_3} / gauss	a_{CH_3} / gauss
313	7.225	8.255	0.35
303	7.185	8.260	0.35
293	7.155	8.270	0.35
273	7.055	8.405	0.35
253	6.955	8.515	0.35
233	6.855	8.635	0.35

variations were found for the other dioxo and acyl nitroxides of type (I) and (IV) respectively, while the e.s.r. spectra of the enol nitroxides (II) were found to be temperature independent over the range studied.

The temperature dependence of the parameters of the nitrogen atom and the trifluoromethyl group in (Ia) is very similar to that reported for bis(trifluoromethyl) nitroxide,[11] and assuming that a correlation exists between the two radicals it suggests that there is a deviation from planarity at the nitrogen atom of radical (Ia). The variation in the h.f.s. value of the β-methine proton does not give any useful information about the conformation of the diacetylmethyl group. The observed decrease with decreasing temperature is to be expected since the amplitude of the oscillations of the methine group will follow the same trend.

Similarly, the nitrogen and trifluoromethyl h.f.s. values of (IVa) show the same type of temperature dependence, and again non-planarity at the nitrogen atom is indicated. The lower values of these h.f.s. values compared to those of other nitroxides can be explained in terms of conjugation of the carbonyl group with the nitroxide function.[16] However, the value is still higher than might have been expected by analogy with the non-fluorinated analogues.* This relatively higher value of a_N for the acyl nitroxides studied in this work is paralleled by results obtained for sulphonyl nitroxides, $RN(\dot{O})\cdot SO_2Ar$,[18] where the nitrogen h.f.s. values are *ca.* 11 gauss, compared with *ca.* 8 gauss for the corresponding acyl nitroxides.[16] This higher value has been attributed to differences in configuration of the respective nitrogen atoms,[18,19] the sulphonyl nitroxides being more pyramidal. A similar argument can be used to explain the relatively higher value of a_N in the acyl nitroxides observed in this work, the assumption being that they assume a more pyramidal configuration around the nitrogen atom than does bis(trifluoromethyl) nitroxide, thus reducing the amount of conjugation between the nitroxide system and the carbonyl group.†

No temperature variation was found for the h.f.s. values of the iminoxy-radicals observed in this study. This is in contrast to the quite marked temperature dependence of the h.f.s. values of $(CF_3)_2C{:}N\cdot\dot{O}$, which also shows characteristic geometric isomerism.[20] This difference may well be due to a difference in spin transmission in these 'σ' type radicals; this type of interaction varies with the distance from the electron-bearing orbital.[21]

EXPERIMENTAL

E.s.r. spectra were obtained using a Varian E-9 spectrometer using 10 kHz modulation, and equipped with a Varian E-257 variable-temperature accessory. Splitting constants were measured to within ±0.05 gauss, the field sweep being calibrated against an aqueous solution of Fremy's salt ($a_N = 13.01$ gauss), which also served as a g-value standard ($g = 2.005\ 5$) when the dual-cavity configuration was employed. Carbon tetrachloride was dried over molecular sieves (type 4A) and de-oxygenated by bubbling dry, oxygen-free nitrogen through it.

The standard procedure for carrying out the reactions was to make up a 0.1M-solution of the diketone in carbon tetrachloride, and a 0.5 cm³ aliquot of this solution was then placed into a thin-walled glass tube. The required amount of trifluoronitrosomethane was then distilled into this tube from a vacuum system, before the tube was sealed under vacuum. The e.s.r. spectrum of the sample was then recorded.

Thanks are due to the S.R.C. for a research studentship grant to one of us (R. G. G. H.), and to Dr. A. R. Thompson of this Department for providing us with the sample of diethyl-2-methyl-3-oxosuccinate.

[5/2089 *Received*, 27*th October*, 1975]

* In $Bu^tN(\dot{O})\cdot CH_3$ $a_N = 16.4$ gauss,[17] and in $Bu^tN(\dot{O})\cdot CO\cdot CH_3$ $a_N = 8.0$ gauss,[16] whereas in $CF_3\cdot N(\dot{O})\cdot CF_3$ $a_N = 9.4$ gauss,[10] and in $CF_3\cdot N(\dot{O})\cdot CO\cdot CF_3$ $a_N = 7.0$ gauss.

† Preliminary INDO calculations have confirmed this assumption, but optimisation of the bond lengths and hence the amount of conjugation is at present incomplete.

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[15] R. E. Banks, D. J. Edge, J. Freear, and R. N. Haszeldine, *J.C.S. Perkin I*, 1974, 721.
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[20] D. R. Choudhury, D. J. Edge, and R. N. Haszeldine, unpublished observations.
[21] B. C. Gilbert and R. O. C. Norman, *J. Chem. Soc.* (*B*), 1966, 86.

Catalysed Prototropic Rearrangements. Part 3.[1] Metal Carbonyl-catalysed Isomerization of *N*-Allylsulphonamides to *N*-Prop-2-enyl and *N*-Propylidene Derivatives

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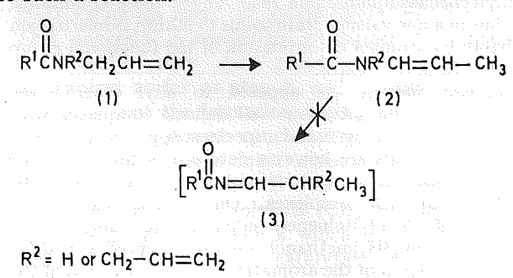
N-Allylsulphonamides (4) are readily isomerized in the presence of pentacarbonyliron upon irradiation by u.v. light. *N*-Prop-2-enyl derivatives (5) are obtained, and further isomerization under suitable conditions leads to *N*-propylidenesulphonamides (6). The last reaction proceeds by a specific 1,3-proton migration involving an N–H group as shown by isotopic labelling experiments.

IN Part 2 [1] we reported on the high efficiency of Asinger and Fell's procedure for the isomerization of *N*-allylamides (1) to *N*-prop-1-enylamides (2). We have now extended the reaction to *N*-allylsulphonamides. To date, isomerization of *N*-allylamides (1) stopped after formation of the corresponding enamides (2); further isomerization to the imides (3) had not been observed under these conditions. Thermal equilibrium between some particular imines and the corresponding enamines is a well documented phenomenon,[2,3] but to our knowledge transition metal catalysis had not yet been applied to such a reaction.



RESULTS

The Solvent.—The solvent plays a determinant role in this reaction as shown by experiments performed in benzene, acetone, or methanol. As reported earlier,[1] the reaction was run under argon because of the high sensitivity of the catalytic species to oxygen; isomerization was followed by n.m.r. spectroscopy (see Experimental section). *N*-Allylbenzenesulphonamide (4a) and *N*-allyltoluene-*p*-sulphonamide (4b) were readily isomerised to the corresponding propenyl derivatives (5a and b) in benzene or acetone as solvent. Typical curves for *N*-allylbenzenesulphonamide are shown in Figure 1 (curves a and b). Not only was the rate of the reaction much higher in benzene than in acetone, but the curves have a rather different shape as an induction period was detected in the latter case.

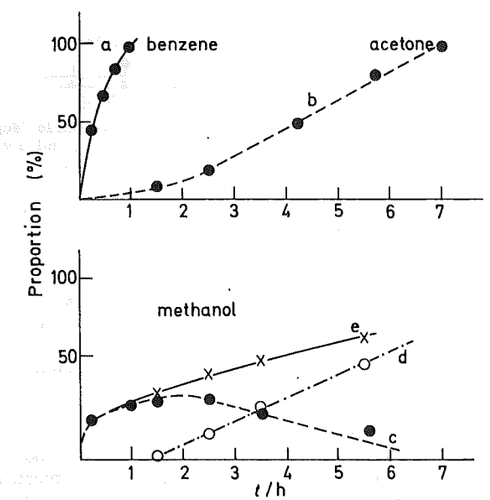


FIGURE 1 Isomerization of *N*-allylbenzenesulphonamide (4a) at 20° in the presence of 10% $Fe(CO)_5$ and u.v. light: ●, (5a); ○, (6a); ×, sum of isomerized material

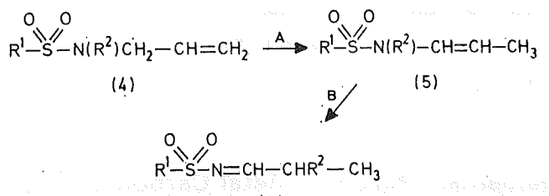
For reactions in methanol, a second migration of the double bond took place leading to the formation of an *N*-sulphonylimine which was detected by n.m.r. spectroscopy. A typical pattern is shown in Figure 1 (curves c and d).

When the isomerization of the methanesulphonamide (4c) was studied in [$^2H_4$]methanol, the reaction proceeded as

[1] Part 2, A. J. Hubert, Ph. Moniotte, G. Goebbels, R. Warin, and Ph. Teyssié, *J.C.S. Perkin II*, 1973, 1954.

[2] G. O. Dudek and R. H. Holm, *J. Amer. Chem. Soc.*, 1962, **84**, 2691.
[3] J. Dabrowski and J. Terpinski, *Tetrahedron Letters*, 1965, 1363.

for the aromatic sulphonamides (4a and b), and the imine (6c) was formed (Figure 2). Moreover the rate of formation of both products (5) and (6) was practically the same for all the investigated sulphonamides (4a—c) in methanol [Figure 1 (curves c and d), see also Figure 2 (curves f and g)].



a; $R^1 = C_6H_5$, $R^2 = H(D)$
b; $R^1 = p\text{-}CH_3C_6H_4$, $R^2 = H$ (D)
c; $R^1 = CH_3$, $R^2 = H$ (D)
d; $R^1 = C_6H_5$, $R^2 = CH_3$
e; $R^1 = C_6H_5$, $R^2 = CH_2\text{-}CH{=}CH_2$

SCHEME 1

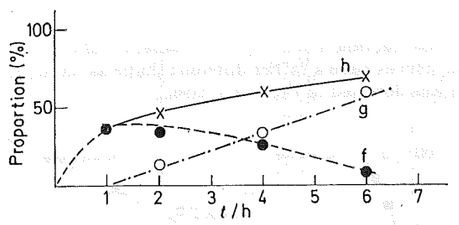


FIGURE 2 Isomerization of *N*-allylmethanesulphonamide (4c) at 20° in methanol in the presence of 10% $Fe(CO)_5$ and u.v. light: ● (5c); ○, (6c); ×, sum of isomerized material.

Isotopic Labelling.—In [$^2H_4$]methanol, exchange between the NH group and OD takes place readily and the sulphonamides (4a—c; $R^2 = D$) are formed.

When isomerization B takes place, it is therefore possible to localize the deuterium in the resulting imine (6; $R^2 = D$). In fact, no incorporation of deuterium into the propenyl group of (5) occurs during migration A whereas deuterium is found on C_β of the propylidene group of the imine (6; $R^2 = D$) after migration B in [$^2H_4$]methanol.

In fact, H_β gives a complex signal centred at δ 1.5 in [$^2H_4$]methanol. This results from the superposition of a doublet of doublets from the γ-methyl group of the propenyl derivative (5) still present in the solution with the expected signals. The methyl group of (6) absorbs as a doublet (^3J 7 Hz) at δ 0.74. The α-H signal appears as a doublet (^3J 6.2 Hz) at δ 4.39. However, a triplet at δ 4.38 shrouded by this doublet is still detected and originates from spin–spin (^3J 6.0 Hz) coupling of α-H with β-CH_2 (isotopic impurity). An isomerization experiment in [$^1H_4$]methanol supports this interpretation as the triplet at δ 4.38 is observed exclusively. The localization of the deuterium atom on β-C is therefore conclusively established by the observation that the expected triplet (which is effectively observed in the absence of deuterium) is changed into a doublet for reactions in the deuteriated solvent.

[4] E. Koerner von Gustorf and F. W. Grevels, *Fortschr. Chem. Forsch.*, 1969, **13**, 366.

The double migration is observed exclusively in methanol and not in solvents without hydroxy-groups.

Products.—Attempts to isolate the pure enamides (5a—c) as well as the imines (6a—c) failed up to now; benzamide and propanol were the sole products observed. Isolation of (5a), however, seems possible by assuring the exclusion of water (see Experimental section).

When the sulphonamido-group is disubstituted [*e.g.* (4d)], isomerization A of the allyl to the propenyl group took place readily, but further isomerization to the imine is unlikely as an alkyl group is required to migrate. In fact the reaction stopped at the propenyl stage (after 150 min) and was practically quantitative as shown by n.m.r. spectroscopy. The signals of the $CH_2{=}CH$ group (δ 4.8 and 5.2) disappeared and were replaced by absorptions for a $CH_3\text{-}CH{=}CH\text{-}N$ function which appears as an AMX_3 system with coupling constants consistent with the *trans*-isomer (J_{AM} 14 Hz) (see Experimental section). In this case, it was possible to isolate the pure enamide (5d) by t.l.c. by contrast with the above examples.

When R^2 = allyl [(4e)] the reaction proceeded very sluggishly; only 20% conversion was observed after irradiation for 15 h. The monopropenyl derivative (5e) is therefore probably the main product.

Geometrical Isomerism.—The *cis* : *trans* ratio for the propenylsulphonamides (5a and b) was 30 : 70 when the toluene-*p*-sulphonamide (4b) was isomerised in the presence of much pentacarbonyliron (amide : catalyst = 2 : 1) whereas a 40 : 60 ratio was found for the benzenesulphonamide (4a). This *cis* : *trans* ratio could be estimated by n.m.r. spectroscopy from signals typical of an olefinic proton vicinal to a methyl group: the *cis*- and *trans*-isomers absorb respectively at δ 4.99 ($J_{cis} = J_{=CHCH_3} \simeq 7$ Hz) and 4.62 (J_{trans} 13.5, $J_{=CHCH_3}$ 7 Hz) as doublets of doublets in [$^2H_6$]acetone. Surprisingly, *N*-allyl-*N*-methylbenzenesulphonamide (4d) gave exclusively the *trans*-isomer (5d).

Oxidation State of the Sulphur Atom.—The isomerization is specific for sulphonamides as neither diallyl sulphide nor *N*-allylbenzenesulphinamide react under these conditions. Sulphur in a low valence state seems to inhibit isomerization probably by stronger co-ordination of the functional group with the catalytic centre.

Catalytic Species.—As opposed to allyl ethers,[4] the sulphonamides do not show well defined complexes with pentacarboxyliron by n.m.r. spectroscopy. Some weak, ill resolved signals are however detected in the δ 2.4—3.0 region in benzene or acetone and they may possibly be attributed to such complexes. On working with a 2 : 1 mixture of *N*-allyltoluene-*p*-sulphonamide and pentacarbonyliron in [$^2H_4$]methanol, we also observed a modification of the signal of the aromatic protons at the end of the reaction; this can be attributed to the formation of an iron complex with the product.

DISCUSSION

N-Allylsulphonamides are not isomerized in the presence of bases. However, we have shown[1] that transition metal catalysis can be applied successfully to the isomerization of various amides. We have now observed the formation of unsaturated sulphonamides in high yield by applying the Asinger procedure to the isomerization of *N*-allylsulphonamides. The mechanism generally accepted for such olefin isomerizations consists in the co-ordination of the substrate with formation of a

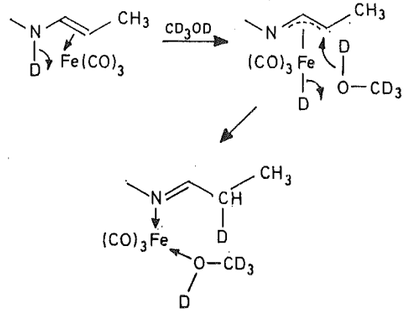
π-complex such as $Fe(CO)_4$(alkene).[4] Recent studies[5] postulate a further transformation of the complex to $Fe(CO)_3(alkene)_2$ which would be the precursor of a hydrido-π-allyl intermediate. This mechanism leads to a 1,3 hydrogen shift. We clearly observed the formation of a π-complex in the case of allyl ethers,[6] but spectroscopic methods were unable to detect unambiguously catalytic intermediates in the case of amides. This may be related to competitive co-ordination of the sulphonamido-group and the olefinic system to the metal which prevents detection of well characterized intermediates.

Better information on the mechanism came from isotopic labelling experiments. Isomerization of sulphonamides (4; $R^2 = D$) to the imines (6; $R^2 = D$) in [$^2H_4$]methanol leads to *specific* incorporation of a deuterium atom in the β-position of the propylidene group. This observation is best explained by assuming a 1,3-shift of deuterium from N to β-C. Moreover this result allows rejection of a 1,2 addition–elimination mechanism as no deuterium exchange takes place on α-C and no incorporation of deuterium is observed during step A of Scheme 1.

A concerted 1,3-shift cannot be distinguished from a π–π-allyl mechanism by the isotopic labelling experiments. In fact, such specific 1,3 migrations are generally explained by postulating π-allyl type intermediates[5-7] and according to Whitesides and Nerlan[7] there is no necessity to postulate any sigmatropic migration of hydrogen as the results are explicable in terms of known intermediates. Moreover the absence of incorporation of deuterium in the propenyl compounds (5) during step A when the reaction is run in [$^2H_4$]methanol requires intramolecular migration of hydrogen within the co-ordination sphere of the metal without any H–D exchange from the intermediate π-allyl complex. This suggests a concerted mechanism.* Therefore, our results may be explained by Wrighton's mechanism as far as step A and possibly step B are concerned but the formation of a hydrido-π-allyl intermediate does not seem conclusively established. Moreover, the mechanism must account for the observed solvent effects as reaction B is unambiguously observed only in hydroxylated solvents (CD_3OD, CH_3OH). We therefore propose Scheme 2 which implies the participation of solvent at the catalytic centre. Scheme 2 explains the selective migration of deuterium onto β-C and takes account of the solvent requirement for the process.

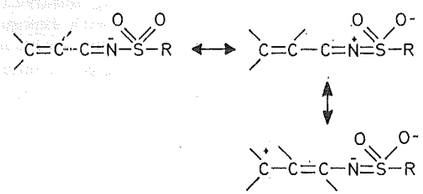
The influence of the solvent on the rate of the overall isomerization process (Figure 2) can be best explained by competition between the solvent and the substrate for the catalytic centre. Acetone and methanol would be more effective than benzene. Moreover, the rate of formation of the catalytic species decreases in acetone as shown by the induction period (Figure 2).

At first it might seem unexpected that imines (6) are formed from the enamides (5), as it is established that a sulphonyl group destabilizes a double bond by its inductive effect.[8] It must be realized however that,



SCHEME 2

besides some shielding of the inductive effect of the sulphonyl group due to the nitrogen atom, the presence of the electron pair on the nitrogen atom is an additional factor which helps to stabilize the conjugated isomer (6) by the contribution of mesomeric forms which are not possible with a C=C double bond directly connected to the sulphonyl group.



Conclusions.—Isomerization of *N*-allylsulphonamides exposure to the $Fe(CO)_5$–u.v. light system gives, besides the usual propenyl derivatives, the formation of iminosulphonamides. The first process is observed in benzene or acetone as solvent whereas the second reaction takes place exclusively in methanol. The use of isotopic labelling shows that the second step corresponds to a 1,3 hydrogen shift from the amine-group of the propenyl derivative which is an intermediate for the formation of (6). This result agrees with the usual π–π-allyl mechanism (though a concerted 1,3 shift mechanism explains some of the observations). From the preparative point of view, the formation of the olefins (5) in good yield leads to the availability of the ene-sulphonamides as intermediates in organic synthesis. However, the great difficulties encountered during purification shows that they should be used *in situ*.

* *Note added in proof:* H–D exchange seems to be a relatively slow process in hydrido-π-allyl complexes. The absence of isotopic exchange therefore does not constitute evidence in favour of a concerted process (J. A. Osborn, personal communication).

[5] M. A. Schroeder and M. S. Wrighton, *J. Amer. Chem. Soc.*, 1976, **98**, 551 and references therein.

[6] A. J. Hubert, A. Georis, R. Warin, and Ph. Teyssié, *J.C.S. Perkin II*, 1972, 366.

[7] T. H. Whitesides and J. P. Neilan, *J. Amer. Chem. Soc.*, 1976, **98**, 63.

[8] D. Cram, 'Fundamentals of Carbanion Chemistry,' Academic Press, New York, 1965, p. 203.

EXPERIMENTAL

Starting Materials.—Sulphonamides were prepared from the corresponding acid chlorides and amines by classical procedures.[9] *N*-Allyl-*N*-methylbenzenesulphonamide was prepared by methylation of *N*-allylbenzenesulphonamide with methyl iodide in the presence of base.

Technique of Isomerization.—The isomerizations were performed at 20 °C, as previously reported.[1,6] In some cases, [$^2H_6$]acetone was used instead of [$^2H_6$]benzene or [$^2H_4$]methanol. The course of the reaction was followed by n.m.r. spectroscopy by monitoring the characteristic absorptions of the allyl, propenyl, and propylidene groups. As shown in Figures 1 and 2, the yields of isomerization product are practically quantitative in most cases at least as far as step A is concerned in benzene or acetone as solvent. Isolation is generally not possible except in the case of (4d) (see below).

Isolation of the Isomerization Products.—*Isomerization of compound* (4a). This reaction was carried out in benzene (0.5 ml) in the presence of 5 mol % $Fe(CO)_5$ [relative to the substrate (100 mg)] by cooling at 15 °C with exposure to Pyrex-filtered u.v. irradiation, and was followed by n.m.r. spectroscopy. The solution of the isomerized material was filtered in air to separate the precipitate of $Fe_2(CO)_9$. The solution slowly deposited crystals which were identified as benzamide. The solution also contains propanol which was identified by g.l.c. on a Porapak column at 100 °C. T.l.c. performed on a silica gel plate thoroughly dried at 110 °C, working in a dry atmosphere and using carefully dried solvents (benzene–ether 75 : 25) allowed the isolation of a sample of isomerized material; it was identified as the corresponding *N*-propenylamide by n.m.r. spectroscopy. However, starting material was still present in the compound, and the mixture was not suitable for elemental analysis.

Isomerization of compounds (4b, c, *and* e). The isomerizations were performed as above, but the compounds were identified by n.m.r. spectroscopy only which shows practically transformation in benzene or acetone as solvent.

Physical data for allylsulphonamides (4) and propenylsulphonamides (5)

Compound	B.p. (°C) [*p*/mmHg]	M.p. (°C)	Yield (%)	Formula	Found (%) C	Found (%) H	Found (%) N	Calculated (%) C	Calculated (%) H	Calculated (%) N
(4a)	110 [0.001]	38	71	$C_9H_{11}NO_2S$	54.9	5.5	7.3	54.8	5.6	7.1
(4b)		62	80	$C_{10}H_{13}NO_2S$	57.0	6.2	6.5	56.8	6.2	6.6
(4c)	100 [0.01]		73	$C_4H_9NO_2S$	34.9	7.1	11.5	35.5	6.7	10.4
(4d)	120 [0.001]		64	$C_{10}H_{13}NO_2S$	56.8	6.1	6.8	56.8	6.2	6.6
(4e)	138 [0.001]		70	$C_{12}H_{15}NO_2$	61.0	6.5	6.0	60.8	6.3	5.9
(5d)			*a*	$C_{10}H_{13}NO_2S$	56.8	6.2	6.5	56.8	6.2	6.6

[a] Isolated by t.l.c. Quantitative yield as shown by n.m.r. spectroscopy.

Isomerization of compound (4d). The isomerization was carried out in benzene as above but the filtered solution was stable in air and no amide nor propanol were formed. The isomerized material (quantitative transformation as shown by n.m.r. spectroscopy) was separated from the catalyst by preparative t.l.c. on silica gel as in the previous example. The isomerized material was collected as a slightly yellowish oil and was identified as the *trans*-propenylsulphonamide (5d) by n.m.r. spectroscopy, δ (C_6D_6) 6.71 (dd, α-H), 4.28 (6 ill-defined peaks, β-H), 2.45 (NMe), and 1.32 (dd, γ-H_3). The propenyl group appears as an AMX_3 system (J_{AM} 14, J_{AX} 1, J_{MX} 6.8 Hz), *m/e* 211 (M^+) 211.

Isomerization of compound (4f). As this compound could be only partially isomerized (20% conversion at most), the formation of propenyl groups was only detected by n.m.r. spectroscopy.

Attempted isolation of compound (6a). Any attempt to isolate (6a) by preparative t.l.c. led to a mixture of benzenesulphonamide and enamide (5a), together with some (6a) as demonstrated by n.m.r. spectroscopy and t.l.c. Obviously this compound is very readily hydrolysed during purification on silica gel.

[5/2278 *Received, 21st November,* 1975]

[9] A. Vogel, 'Practical Organic Chemistry,' Longman, London, 1958, 653.

The Kinetics of the Reactions of Picryl Chloride with Some Substituted Anilines. Part IV [1]

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Arrhenius parameters have been measured for the reactions of picryl chloride with the following substituted anilines in acetonitrile: 3-methoxyaniline, 3-X-5-nitroanilines (X = CF_3, SO_2Me, or OMe), 3-X-5-methoxyanilines (X = F, Cl, Br, I, CF_3, SO_2Me, or OMe), and 3-X-5-methylsulphonylanilines (X = Cl, Br, or I). In both the methoxy-halogeno- and methylsulphonyl-halogeno-aniline series, the span of the rate constants is small and log *A* increases with increasing activation energy. The effects of the substituents in 3-methylsulphonyl-5-nitroaniline and in 3-methylsulphonyl-, 3-methoxy-, 3-trifluoromethyl-, 3-fluoro-, and 3-iodo-5-methoxyanilines on the free energies of activation is not additive.

RECENTLY [1] we examined the additivity of substituent effects in the reactions of 3-halogeno-5-nitroanilines with picryl chloride in acetonitrile. We have now extended our investigations to the series 3-X-5-nitroanilines (X = CF_3, SO_2Me, or OMe), 3-X-5-methoxyanilines (X = F, Cl, Br, I, CF_3, SO_2Me, or OMe), and 3-X-5-methylsulphonylanilines (X = Cl, Br, or I). The Arrhenius parameters for the reaction of 3-methoxyaniline with picryl chloride in acetonitrile have also been determined. The reactions were followed by spectrophotometric estimation of the products with the amines in large enough excess to ensure first-order kinetics. In all cases the optical densities at infinity agreed with the theoretical ones, and the expected products were isolated from the reaction mixtures. Values of the Arrhenius parameters are tabulated.

[1] Part III, T. A. Emokpae, J. M. Dosunmu, and J. Hirst, *J.C.S. Perkin II*, 1974, 76.

The introduction of a 3-methoxy-group into aniline reduces the rate constant of the reaction by a factor of 2.29, and the introduction of a second methoxy-group at the 5-position gives a further 1.75 fold reduction in the rate constant. The same deactivating effect of a 3-methoxy-group was observed by Peacock and Singh [2] in the reaction of substituted anilines with 1-chloro-2,4-dinitrobenzene in ethyl alcohol. Similarly a comparison of the results for 5-methoxy-3-nitroaniline with those for 3-nitroaniline given in Part III [1] shows that the introduction of a 5-methoxy-group into the 3-nitroaniline series reduces the rate constant by a factor of 3. Hence the overall effect of a *meta*-methoxy-group in these reactions is an electron-withdrawing one, in contrast to its effect when it is present in the substrate of aromatic nucleophilic substitution reactions. Bevan, Hirst, and Una [3] have shown that in the methoxydefluorination of substituted 3-nitrofluorobenzenes a 5-methoxy-group is deactivating.

A comparison of the present results with those of Hirst and Rahman [4] shows that the introduction of 5-CF_3, 5-SO_2Me, and 5-NO_2 groups into 3-nitroaniline is powerfully deactivating, reducing the rate constants by factors between 80 and 540. The variation within the three groups, though, is fairly small, the rate constant ratios (5-CF_3 : 5-SO_2Me : 5-NO_2) are 1 : 0.24 : 0.15 at 25 °C, which are similar to those obtained when these groups are introduced into the 3-position of aniline. The rate constants give the expected $-I$ sequence $NO_2 > SO_2Me > CF_3$, but inspection of the Arrhenius parameters shows that this sequence is determined entirely by the entropy of activation and not the enthalpy. We have already [4] drawn attention to examples of this phenomenon and comparison of the present results with those reported in ref. 1 shows that when 5-NO_2 and 5-SO_2Me groups are introduced into 3-chloro- and 3-bromo-anilines, although the expected rate constant sequence $SO_2Me > NO_2$ is obtained, in both cases the sequence is due to the entropies of activation.

A comparison of the present results with those for the 3-halogenoanilines given in ref. 1 shows that the introduction of a 5-OMe group reduces the rate constant approximately two-fold (halogen = F, Cl, Br, or I) while the introduction of 5-SO_2Me reduces the value between 90- and 200-fold (halogen = Cl, Br, or I). In each series the span encompassed by the rate constants is small, and between 0—100 °C never exceeds a factor of three. The sequences of the rate constants are temperature variable, but are the same in both series, as is the sequence of activation energies, the magnitude of log *A* increasing with increase in activation energy. The general behaviour is the same as that previously observed [1] in the 3-halogeno- and 5-halogeno-3-nitroaniline series, and the sequence of activation energies, F > Br > Cl > I, is the same as that in the 3-halogenoaniline series, but different from the sequence in the 3-halogeno-5-nitroaniline series.

Arrhenius parameters for the reactions of picryl chloride with some substituted anilines in acetonitrile and a comparison of the rate constants (l mol^{-1} s^{-1}) at 25 °C calculated (i) on the assumption of additivity of the free energies of activation ($k_{calc.}$) and (ii) from the measured Arrhenius parameters (k_m)

Substituent	*E*/kcal mol^{-1} [a]	log *A*	$10^6k_{calc.}$	10^6k_m
3-CF_3-5-NO_2	14.3 ± 0.04	5.31	7.17 ± 0.06	6.76 ± 0.44
3-SO_2Me-5-NO_2	16.0 ± 0.06	5.94	3.85 ± 0.04	1.62 ± 0.16
3-OMe-5-NO_2	11.9 ± 0.09	5.12	2.46 ± 0.02 × 10^2	2.47 ± 0.38 × 10^2
3-Cl-5-SO_2Me	11.9 ± 0.10	4.43	4.43 ± 0.23 × 10	5.08 ± 0.86 × 10
3-Br-5-SO_2Me	12.9 ± 0.08	5.09	4.74 ± 0.56 × 10	4.29 ± 0.47 × 10
3-I-5-SO_2Me	10.9 ± 0.01	3.97	9.27 ± 1.57 × 10	9.53 ± 0.27 × 10
3-CF_3-5-OMe	10.9 ± 0.12	5.17	1.12 ± 0.01 × 10^3	1.51 ± 0.02 × 10^3 [b]
3-SO_2Me-5-OMe	11.6 ± 0.09	5.37	6.02 ± 0.07 × 10^2	7.37 ± 0.06 × 10^2 [b]
3-F-5-OMe	11.7 ± 0.10	6.21	3.40 ± 0.58 × 10^3	4.23 ± 0.11 × 10^3 [b]
3-Cl-5-OMe	11.2 ± 0.05	5.67	2.83 ± 0.13 × 10^3	2.96 ± 0.01 × 10^3 [b]
3-Br-5-OMe	11.5 ± 0.08	5.91	3.02 ± 0.36 × 10^3	3.01 ± 0.03 × 10^3 [b]
3-I-5-OMe	10.5 ± 0.08	5.37	5.97 ± 1.00 × 10^3	4.73 ± 0.03 × 10^3 [b]
3,5-$(OMe)_2$	9.9 ± 0.05	5.93	3.88 ± 0.03 × 10^4	5.08 ± 0.06 × 10^4 [b]
3-OMe	8.6 ± 0.07	5.25		8.89 ± 0.08 × 10^4 [b]
H	7.9 ± 0.27 [c]	5.06 [c]		

[a] The errors quoted are standard errors of the mean. [b] Values measured directly at 25°. [c] Values from ref. 4.

The sequences of the rate constants are temperature variable, but are the same in both series, as is the sequence of activation energies, the magnitude of log *A* increasing with increase in activation energy. The general behaviour is the same as that previously observed [1] in the 3-halogeno- and 5-halogeno-3-nitroaniline series, and the sequence of activation energies, F > Br > Cl > I, is the same as that in the 3-halogenoaniline series, but different from the sequence in the 3-halogeno-5-nitroaniline series.

The same criteria as used previously [4] have been applied to test the hypothesis of additivity of substituent effects on the free energies of activation. The rate constants and their statistical deviations at 25 °C for the 3,5-disubstituted anilines calculated on this hypothesis * together with the rate constants (and their statistical deviations) either obtained from direct

* The values of k_2 for trifluoromethylaniline (2.60 ± 0.04 × 10^{-3}), 3-methoxyaniline (8.89 ± 0.08 × 10^{-2}), and 3-methylsulphonylaniline (1.38 ± 0.01 × 10^{-3}) determined directly at 25 °C, together with the values for aniline and 3-nitroaniline given in ref. 1, were used in these calculations. The errors quoted are standard errors of the mean.

[2] D. H. Peacock and A. Singh, *J. Phys. Chem.*, 1936, **40**, 669.
[3] C. W. L. Bevan, J. Hirst, and S. J. Una, *Nigerian J. Sci.*, 1966, **1**, 27.
[4] J. Hirst and Khali-Ur Rahman, *J.C.S. Perkin II*, 1973, 2119.