576. *The Solvolysis of Arylmethyl Chlorides. Part II.* A Molecular-orbital Treatment and Further Experimental Evidence of the Transition from the Limiting to the Fully Nucleophil-assisted Mechanism.*

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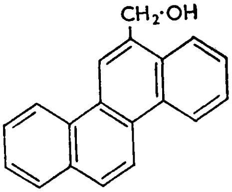
The rates of solvolysis of 2-chloromethylchrysene and 2-chloromethyltriphenylene, and a revised value for that of benzyl chloride in moist formic acid at 25°, have been obtained. The rates of solvolysis of a number of arylmethyl chlorides in 80% ethanol at 50° are reported.

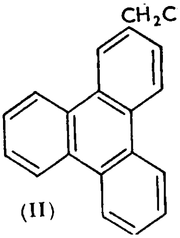
A molecular-orbital treatment for the transition from the limiting to the fully nucleophil-assisted mechanism is given and shown to agree qualitatively with experiment. There is some experimental evidence that in a fixed solvent, giving rise to a transition mechanism, those arylmethyl chlorides of higher reactivity accept less nucleophilic assistance. An explanation of this behaviour, based on the same molecular orbital treatment, is advanced.

EXPERIMENTAL

Starting Materials.—*2-Hydroxymethylchrysene* (I). 2-Acetylchrysene [1] (1·00 g.) was stirred with dioxan † (50 ml.), sodium hypochlorite solution (2·5% of available chlorine; 50 ml.) and benzene (5 ml.) under reflux on a boiling-water bath. A further 50 ml. of sodium hypochlorite solution were added during 90 min., and refluxing was then continued for 4 hr. The benzene was boiled off and excess of solid sodium hydrogen sulphite was added to the cooled solution. The precipitate was collected, boiled with 0·5N-hydrochloric acid, and filtered off. The resultant chrysene-2-carboxylic acid (0·92 g., 92%) recrystallized from dioxan in white needles, m. p. >300° (lit., 314°); on treatment in chloroform with diazomethane it yielded *methyl chrysene-2-carboxylate*, needles, m. p. 148° (from ethanol) (Found : C, 83·6; H, 5·0. $C_{20}H_{14}O_2$ requires C, 83·9; H, 4·9%). This ester (1·34 g.), dissolved in boiling ether (1 l.), was treated with lithium aluminium hydride (0·4 g.) in ether. Working up in the normal manner gave an almost quantitative yield of *2-hydroxymethylchrysene* which recrystallized from benzene in needles, m. p. 207—207·5° (Found : C, 88·2; H, 5·5. $C_{19}H_{14}O$ requires C, 88·3; H, 5·5%).



(I)



(II)

2-Chloromethylchrysene.—The foregoing alcohol (0·10 g.) was refluxed in benzene (50 ml.) with thionyl chloride (2 ml.) for 1 hr. Most of the solvent was distilled off, and *2-chloromethylchrysene* crystallized as needles, m. p. 202—203·5°, from benzene (Found : C, 82·5; H, 5·1; Cl, 12·8. $C_{19}H_{13}Cl$ requires C, 82·4; H, 4·7; Cl, 12·8%).

2-Chloromethyltriphenylene (II).—Methyl triphenylene-2-carboxylate (obtained in the same manner as the chrysene analogue) recrystallized from ethanol in needles, m. p. 174° (lit., 171—172°). Reduction, as for the chrysene analogue, gave *2-hydroxymethyltriphenylenylene*, prisms, m. p. 149·5—151° [from benzene–light petroleum (b. p. 60—80°)] (Found: C, 88·3; H, 5·7. $C_{19}H_{14}O$ requires C, 88·3; H, 5·7%). This was treated with thionyl chloride as above, except that refluxing was for 2 hr. The solvent and excess of thionyl chloride were evaporated at

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* The paper by Dewar and Sampson (*J.*, 1956, 2789) is to be regarded as Part I.

† Dioxan (" AnalaR ") was stirred with one-fifth of its volume of sodium hypochlorite solution (10% of available chlorine) on a boiling-water bath for 2 hr. After cooling, the organic layer was separated and distilled, reduction to low bulk being avoided.

[1] Carruthers, *J.*, 1953, 3486.

reduced pressure, and the resultant solid was passed in benzene through alumina (2 × 2 cm.), then recrystallized from light petroleum (b. p. 100—120°) as needles, m. p. 120—122° (decomp.) (Found: C, 82·6; H, 4·7; Cl, 12·7. $C_{19}H_{13}Cl$ requires C, 82·4; H, 4·7; Cl, 12·8%).

Benzyl chloride[2] had b. p. 70°/12 mm., n_D^8 1·5441 (lit., $n_D^{15\cdot4}$ 1·5415) (Found: C, 66·4; H, 5·7; Cl, 28·0. Calc. for C_7H_7Cl: C, 66·4; H, 5·6; Cl, 28·0%).

The other materials were as previously described.[3]

Kinetics.—The rate constants, k_1, for the solvolysis in formic acid (water content 0·38M) of benzyl chloride and 2-chloromethyltriphenylene were obtained from the initial rates of increase in electrical conductance as previously described.[3] 2-Chloromethylchrysene was not perceptibly soluble in this solvent. However the experimental values of K and k, determined from the equilibrium and the approach to equilibrium, when 2-hydroxymethylchrysene was dissolved in the formic acid containing hydrogen chloride, permitted calculation of the value of k_1 by using the equations: $k = k_1 + k_2[\mathrm{HCl}]$; and $K = k_2[\mathrm{H_2O}]/k_1$. The symbols have the meanings previously defined.[3]

TABLE 1. *Rate constants for solvolysis in moist formic acid* (0·38M *in water*) *at* 25°.

Ar in Ar·CH_2Cl	$2a_{or}$	k_1 (sec.$^{-1}$)
Phenyl	1·51	1·1(5) × 10^{-6}
2-Triphenylenyl	1·46	3·7 × 10^{-6}
2-Chrysenyl	1·28	1·3 × 10^{-3}

The rate for benzyl chloride is much smaller than that (2·9 × 10^{-7}) reported by Evans and Hamann.[4] Using carefully fractionated commercial benzyl chlorides we obtained an initial rate of formation of hydrogen chloride corresponding approximately to their rate constant, but the rate of generation of hydrogen chloride fell off more rapidly with time than expected. We believe this behaviour to be due to traces of an impurity (probably Ph·$CHCl_2$), not entirely removed by fractionation, in the commercial product.

80% Aqueous ethanol was obtained by weighing, as described by Winstein, Grunwald, and Jones.[5] Kinetic runs in this solvent were performed at 50·0° in an oil-filled thermostat which maintained a temperature constant within ±0·02°. In a run a weighed amount of the arylmethyl chloride was added to a flask (with a B14 neck) containing the solvent. Generally concentrations of about 10^{-2}M were used, but the limited solubilities of some compounds (*e.g.*, 2-chloromethylchrysene) necessitated the use of concentrations down to about 3 × 10^{-4}M. The flask was swirled until the arylmethyl chloride has dissolved. At recorded times 10 ml. portions of the solution were withdrawn by pipette, discharged into acetone (35 ml.) containing lacmoid, and titrated with a solution of triethylamine (concentrations varying from M/40 to M/160 in different runs) in toluene. Runs were followed for at least two half-lives, and infinity readings were taken after about 10 half-lives. Values of k_1, calculated in the normal manner, remained constant in each run within experimental error. In general two runs were performed on each substance, and the rate constants from independent runs differed by less than 2% from the mean.

TABLE 2. *Rate constants for solvolysis of arylmethyl chlorides in* 80% *ethanol at* 50°.

Ar in ArCl	$2a_{or}$	10^6k_1 (sec.$^{-1}$)	Ar in ArCl	$2a_{or}$	10^6k_1 (sec.$^{-1}$)
Phenyl	1·51	2·2 *	1-Phenanthryl	1·36	6·9
2-Phenanthryl	1·47	3·9	1-Naphthyl	1·34	9·4
2-Naphthyl	1·46	4·3	9-Phenanthryl	1·34	7·9
2-Triphenylenyl	1·46	4·2	6-Chrysenyl	1·28	42
3-Phenanthryl	1·43	6·9			

* Taken from Winstein, Grunwald, and Jones.[5]

RELATIVE RATES OF NUCLEOPHIL-ASSISTED REPLACEMENTS ON ARYLMETHYL CHLORIDES

The customarily postulated transition state for the S_N2-type replacement is shown in Fig. 1. The group Ar·CH_2 is planar, and the line joining the incoming nucleophil,

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[2] "Organic Reactions," Vol. I, p. 67.

[3] Dewar and Sampson, *J.*, 1956, 2789.

[4] Evans and Hamann, *Trans. Faraday Soc.*, 1951, **47**, 25.

[5] Winstein, Grunwald, and Jones, *J. Amer. Chem. Soc.*, 1951, **73**, 2700.

the carbon atom at which replacement is occurring, and the displaced group is perpendicular to the plane of the aromatic system.

In view of the considerations previously given [3] concerning the contributions to the free energy of activation by entropy and certain energy terms, the problem is the calculation of the variation of the energy of interaction of the nucleophil and the displaced group with the remainder of the system when (*a*) the configuration of the transition state (*i.e.*, the degree of nucleophilic participation) remains constant, but the nature of Ar varies, and (*b*) the configuration of the transition state varies also.

In treating the energetics of this system it is convenient to consider initially its isoconjugate hydrocarbon, in which both the incoming nucleophil and the displaced groups are methyl anions. All three species are then odd alternant hydrocarbons, and so each contains a non-bonding molecular orbital. The only first-order interactions will be between these orbitals.[6] The conjugation energy resulting from the interaction of those orbitals (ψ_2 and ψ_3) of the methyl anions with that (Ψ'_1) of the group Ar·CH$_2$ will stabilize the transition state. On the usual notation, the energies of the perturbed orbitals are related by the secular equation :

FIG. 1.

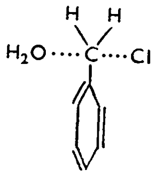
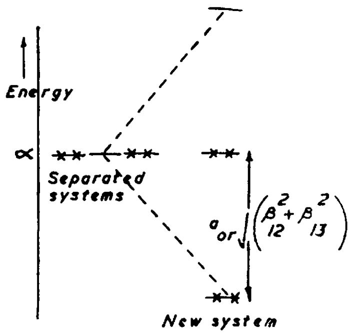


FIG. 2.



$$\det|H_{rs} - ES_{rs}| = 0 \qquad \text{. . . . .} \quad (1)$$

As is usual, the overlap and resonance integrals between non-adjacent atoms will be neglected, so that

$$S_{12} = S_{23} = S_{13} = 0; \ \ H_{23} = 0 \qquad \text{. . . . . . .} \quad (2)$$

Then, by solving equation (1) and writing α for the coulomb integral of carbon, so that $H_{ii} = \alpha$, the following results are obtained :

$$\alpha - E = 0; \ \ \alpha - E = \pm\sqrt{(H_{12}^2 + H_{13}^2)} \qquad \text{. . . .} \quad (3)$$

The non-bonding orbital, Ψ'_1, of Ar·CH$_2$, may be expanded in terms of its atomic orbitals :

$$\Psi'_1 = \sum a_{oi}\psi_i \qquad \text{. . . . .} \quad (4)$$

whence

$$H_{12} = \int\left(\sum a_{oi}\psi_i\right)H\psi_2 d\tau \qquad \text{. . . . . . .} \quad (5)$$

Since only *r*, the side-chain carbon atom, is adjacent to ψ_2, equation (5) reduces to

$$H_{12} = \int a_{or}\psi_r H\psi_2 d\tau = a_{or}\beta_{12} \qquad \text{. . . . . .} \quad (6)$$

where β_{12} is the resonance integral between the side-chain carbon atom and one methyl anion.

Similarly

$$H_{13} = a_{or}\beta_{13} \qquad \text{. . . . .} \quad (7)$$

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[6] Dewar, *J. Amer. Chem. Soc.*, 1952, **74**, 3341.

Substituting results (6) and (7) in equation (3), and remembering that energies are reckoned relative to that (α) of a carbon $2p$ atomic orbital, we have:

$$E = 0;\ E = \pm a_{\mathrm{or}}\sqrt{(\beta_{12}^2 + \beta_{13}^2)} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

The four electrons contained in these new orbitals will doubly occupy the two orbitals of lowest energy and the change in delocalization energy (Fig. 2) is accordingly: $-2a_{\mathrm{or}}\sqrt{(\beta_{12}^2 + \beta_{13}^2)}$.

We have previously shown[3] that when an extracyclic carbon atom is placed in conjugation with an aryl system the change, ΔE_π, in π-energy is given by:

$$\Delta E_\pi = B + 2a_{\mathrm{or}}\beta \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

Hence the total change, $\Delta E_\pi{}^N$, in π-energy and delocalization energy for the solvolysis with nucleophilic assistance is:

$$\Delta E_\pi{}^N = B + 2a_{\mathrm{or}}\beta - 2a_{\mathrm{or}}\sqrt{(\beta_{12}^2 + \beta_{13}^2)} \quad . \quad . \quad . \quad . \quad (10)$$

$$i.e., \quad \Delta E_\pi{}^N = B + 2a_{\mathrm{or}}\{\beta - \sqrt{(\beta_{12}^2 + \beta_{13}^2)}\} \quad . \quad . \quad . \quad . \quad . \quad (11)$$

This equation may be written in the form:

$$\Delta E_\pi{}^N = B + 2a_{\mathrm{or}}\beta_{\mathrm{eff}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (12)$$

where

$$\beta_{\mathrm{eff}} = \beta - \sqrt{(\beta_{12}^2 + \beta_{13}^2)} \quad . \quad . \quad . \quad . \quad . \quad . \quad (13)$$

In our previous paper[3] we interpreted solvolysis results in terms of equation (9); it is now apparent that this equation, derived for a limiting process, should still hold in the nucleophil-assisted case, provided that β is replaced by a parameter β_{eff}, given by equation (13). Since β_{12} and β_{13} will increase with increasing nucleophilic assistance, β_{eff} will decrease. The maximum value of β_{eff} will be observed in a limiting reaction, and the decreases in the values of β_{eff} found for non-limiting reactions should be measures of the extent of nucleophilic participation.

The model we have been considering is of course oversimplified in that the entering and replaced groups are more electronegative than methyl anions. This will have an influence, the magnitude of which cannot at present be calculated. However, the qualitative conclusion should remain unaltered; that is, the greater the nucleophilic assistance, the smaller β_{eff}.

Comparison with Experiment.—Fig. 3 is a plot of the values of $2a_{\mathrm{or}}$ against $-\log k_1$ for the solvolysis of arylmethyl chlorides in moist formic acid (water 0·38M). The values for k_1 are taken from this and our previous paper.[3] The slope corresponds to the value $\beta_{\mathrm{eff}} = 33$ kcal. The distance between the lines for benzene-type and 1-naphthalene-type positions is 0·075 β_{eff}, and so the strain energy of the 1-naphthalene-type transition states is 2·5 kcal. There is no evidence of nucleophilic assistance for the solvolysis in this medium.

For the solvent: formic acid, 54·1; water, 6·1; dioxan, 39·8%; β_{eff} is 20 kcal.[3,7] We previously suggested that this fall was due to nucleophilic participation; this paper puts this idea on a sounder theoretical footing. That participation should take place here is not surprising since in comparison with moist formic acid the high proportion of dioxan will result in the solvent having a much reduced ionising power, and the relatively high water content will provide a potentially nucleophilic component. In this solvent the strain-energy of the 1-naphthalene-type transition states is 1·5 kcal. A possible explanation of the smallness of this strain energy compared with that (2·5 kcal.) in moist formic acid is that in the mixed solvent the transition state is not quite symmetrical, and the

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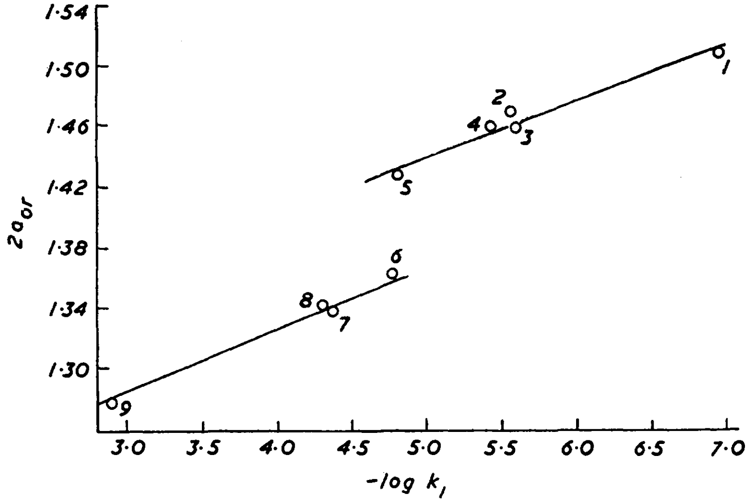
[7] Fierens, Hannaert, Van Rysselberge, and Martin, *Helv. Chim. Acta*, 1955, **38**, 2009.

Ar·CH$_2$ portion not quite planar, and so not subject to such intense strain. If this is the case the full energy gain expected on the assumption that Ar·CH$_2$ is planar will not be achieved in the transition state. This presumably would in turn contribute to the lowness of the magnitude of β_{eff}.

FIG. 3. *Relation between* $2a_{0r}$ *and the logarithm of the solvolysis rates of arylmethyl chlorides in moist formic acid* (*water* 0·38M), *at* 25°.



Ar = 1, Ph; 2, 2-*phenanthryl*; 3, 2-*naphthyl*; 4, 2-*triphenylenyl*; 5, 3-*phenanthryl*; 6, 1-*phenanthryl*; 7, 1-*naphthyl*; 8, 9-*phenanthryl*; 9, 2-*chrysenyl*.

FIG. 4. *Solvolysis of arylmethyl chlorides in* 80% *ethanol at* 50°. (*Key as Fig.* 3.)

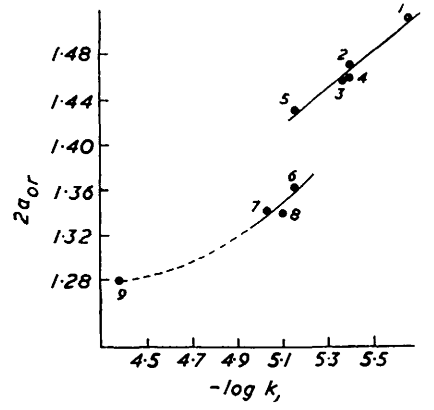
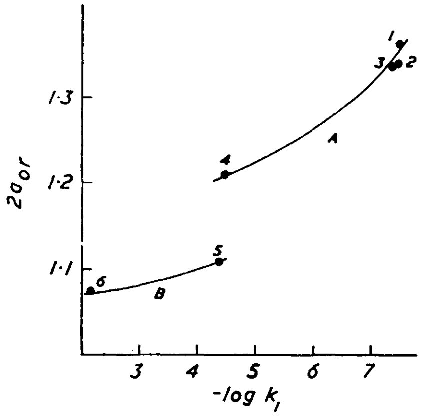


FIG. 5. *Solvolysis of arylmethyl chlorides in the system*: *water*, 5·8; *formic acid*, 34·0; *dioxan*, 60·2%; *at* 25°.



Ar = 1, 1-*phenanthryl*; 2-, 9-*phenanthryl*; 3, 1-*naphthyl*; 4, 3-*pyrenyl*; 5, 1 : 2-*benzo*-10-*anthryl*; 6, 9-*anthryl*.

A, 1-*Naphthalene type*. *B*, 9-*Anthracene type*.

Fig. 4 is the plot of $2a_{0r}$ against $-\log k_1$ for the solvolysis in 80% ethanol. Here β_{eff} falls even lower, to 9·5 kcal., suggesting that nucleophilic participation is even stronger, as one would expect. The strain of the 1-naphthalene-type transition states is only 0·7 kcal. The remarks concerning the magnitude of this strain in the previous solvent apply equally well here.

Using the data of Fierens, Hannaert, Van Rysselberge, and Martin[7] we previously showed[3] that the value of β_{eff} for the exchange by arylmethyl chlorides of chloride for iodide in anhydrous acetone is 5 kcal. This solvent deters ionization to such an extent, and the iodide ion is such a strong nucleophil, that there can be no doubt that this reaction is typically S_N2, with full nucleophilic assistance. The variation of β_{eff} is thus in full agreement with theory.

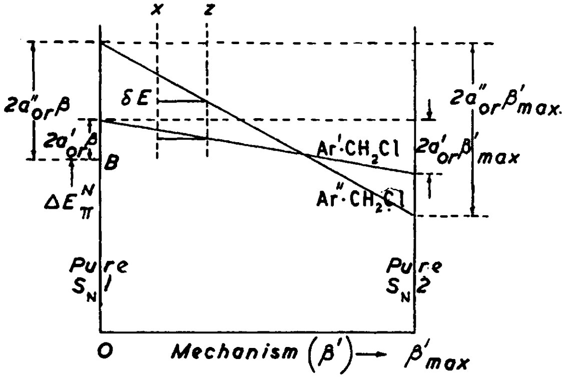
Table 3 summarizes the above findings.

TABLE 3.

Reaction environment	k_1 (kcal.)	Strain energy of 1-naphthalene-type transition states	Character of reaction
Moist formic acid	33	2·5	Limiting
Water 6·1; formic acid 54·1; dioxan 39·8%	20	1·5	Transitional
Ethanol 80%; water 20%	9·5	0·7	,,
Iodide ions in anhyd. acetone	5	—	Fully assisted

Evidence for the Change of Mechanism in a Fixed Solvent.—In this discussion[3] of the solvolysis in formic acid it was mentioned that there is no evidence for change of mechanism along the series. Fig. 4 shows that solvolysis of 2-chloromethylchrysene in 80% ethanol is faster than would be expected. Moreover, Fierens *et al.*[7] measured the rates of solvolysis of a number of arylmethyl chlorides, including the highly reactive 3-pyrenyl, 1 : 2-benzo-10-anthryl and 9-anthryl compounds, in the solvent: water, 5·8; formic acid, 34·0; dioxan, 60·2%. The logarithms of their rate constants are plotted against the corresponding values of $2a_{\text{or}}$ in Fig. 5. Once again the theory breaks down, for the more reactive compounds undergo solvolysis faster than expected. Similar deviations occur when arylmethyl chlorides of a wide range of reactivity are solvolyzed in water–dioxan.[8] Evidently β_{eff} for a given solvent is greater for more reactive compounds than for less reactive compounds.

FIG. 6.



If $\sqrt{(\beta_{12}^2 + \beta_{13}^2)}$ is written as β', this equation (10) becomes:

$$\Delta E_{\pi}^{N} = B + 2a_{\text{or}}\beta - 2a_{\text{or}}\beta' \quad . \quad . \quad . \quad . \quad . \quad . \quad (14)$$

The terms of this equation are shown diagrammatically for the two compounds Ar′·CH$_2$Cl (highly reactive) and Ar″·CH$_2$Cl (relatively inert) in Fig. 6, which is a plot of ΔE_{π}^{N} against β' (*i.e.*, against mechanism). Suppose in a given environment the combined effects of ionizing power and nucleophilicity make (for the less reactive compound) the energetically most favourable mechanism that corresponding to $\beta' = z$. Slightly less nucleophilic assistance ($\beta' = x$) would results in a large loss, δE, of stabilizing energy for this compound.

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[8] From data personally communicated by Fierens and Martin.

For the more reactive compound, however, the diagram shows that the corresponding loss would be considerably smaller, and could be compensated by the accompanying favourable change in solvation energy (which for a given mechanism and environment is assumed to be independent of the arylmethyl chloride). It is immediately clear that less reactive compounds should be more susceptible to nucleophilic assistance than the more reactive compounds. We have seen that this is borne out by experiment.

The term $2a_{or}\beta'$ of equation (14) represents the energy of nucleophilic assistance. In view of the above discussion it is now apparent that the factor $2a_{or}$ is a measure of the susceptibility of the compound towards nucleophilic assistance, and the factor β' is a function of the environment which represents the latter's nucleophilic power.

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