Because to a zeroth approximation molecules are made out of atoms and because the largest amount of our computational experience has been with atoms, this theory treats molecular formation from the standpoint of slightly perturbed atoms. It may be noted that the theory of directed valence in carbon compounds proceeds from a similar atomic viewpoint. On the other hand we need a description which more completely reflects characteristic molecular features. There is little direct computational experience to guide us here but there is a great deal of chemical information which can be cast in quantum mechanical language and aid in establishing the geometry and other properties of molecules.[3]

To describe XeF_4 in this language twelve electrons are assumed to participate in molecular binding. The outer octet of xenon yields eight electrons and each fluorine supplies one. Alternatively we may start with Xe^{+4} and four F^- ions obtaining four electrons from the xenon ion and two from each F^-. Both of these are equally valid because the molecule represents a considerable distortion of its atomic constituents and we do not concern ourselves with the detailed process of molecule formation. These twelve electrons form six electron pairs. From classical electrostatic arguments the electron pairs will point toward the vertices of a regular octahedron. A fluorine atom will be located at each corner of a square centered on the xenon atom with a lone pair above and a lone pair below the plane defined by the square and each perpendicular to it. This configuration is the minimum energy way of arranging two lone pairs and four bond pairs because it minimizes the large electrostatic interaction energy between lone pairs. If we employ one-electron atomic-like basis functions of the highest possible symmetry mounted on the xenon center to form a set of directed orbitals, group theory specifies a configuration sp^3d^2. This merely states that basis functions of this symmetry on the xenon center plus p-like functions on the fluorine center with lobes pointed toward the xenon form convenient symmetry orbitals for XeF_4. Without extensive computational experiments it cannot tell us anything about the radial form of the atomic-like basis functions, their one-electron energies, the bond energies or bond lengths. However, the simple conventional nature of our picture implicitly predicts a conventional length for the xenon (analogy to iodine) fluorine bond[4]

$$1.33 + 0.64 = 1.97\text{Å}.$$

The planar structure predicted for XeF_4 is also suggested by the ICl_4^- ion which is isoelectronic for the binding electrons and is known to be planar.[5] Preliminary Raman spectra on the solid[1] support a planar configuration. Hexafluorides are unlikely because this would require fourteen valence electrons. A general rule from chemical experience is that stable molecules with an odd number of electrons are extremely rare and so no xenon compounds with an odd number of fluorines are predicted. Identical predictions (except for the bond length) but from a more physical viewpoint were made by the perturbed atom theory.[2]

An oxygen atom can complete its outer shell by attachment to a lone pair and so an XeF_4O molecule in the form of a tetragonal pyramid and an XeF_4O_2 molecule with tetragonal bipyramid structure potentially exist. The prediction of geometrical forms for XeF_4O and XeF_4O_2 is easier and less uncertain in this model than in the perturbed atom theory because the asymmetry introduced by oxygen makes molecular bond predictions difficult from data based primarily on atomic calculations.[6] In our present model XeF_3O is eliminated because it has an odd number of electrons.

XeF_2 is also known to exist[1] and molecular binding involves ten electrons—either eight from xenon and two from the fluorines or four from each. Five electron pairs are formed. The same reasoning employed for XeF_4 leads to a trigonal bipyramid with three triangularly arranged lone pairs in a plane and fluorines associated in bonds above and below the plane and perpendicular to the lone pairs. Orbital symmetry around xenon can be designated as sp^3d or spd^3. XeF_2O, XeF_2O_2, XeF_2O_3 are all predicted with equal *a priori* probability. In place of an oxygen atom BF_3 or another Lewis acid might be attached in either the XeF_2 or XeF_4 series.

It is a comment on the present state of our understanding of chemical structure that neither computational nor chemical experience have yet given us enough knowledge to have made a confident *a priori* prediction of the stability of XeF_4 or XeF_2.

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(3) N. Sidgwick and H. Powell, *Proc. Roy. Soc.* (*London*), **A176**, 153 (1940); R. Gillespie and R. Nyholm, *Quant. Rev.*, **11**, 339 (1957); "Progress in Stereochemistry," Vol. 2, Chapter 8, Academic Press, New York, N. Y., 1962); R. Gillespie, *Canad. J. Chem.*, **38**, 818 (1960).

(4) Data from L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 3rd Ed., 1960.

(5) R. C. L. Mooney, *Z. Krist.*, **98**, 377 (1938).

(6) Unfortunately there have been no *ab initio* molecular calculations that directly relate to this geometry.

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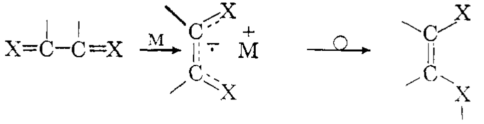
RECEIVED OCTOBER 22, 1962

STEREOCHEMISTRY OF METAL ADDITION TO CONJUGATED SYSTEMS. I. BENZIL

Sir:

We wish to report evidence that the addition of metals, either monovalent or divalent, as a heterogeneous phase or in solution, to conjugated systems X=C—C=X exhibits a pronounced *cis* stereochemical preference, ultimately yielding products thermodynamically rich in or exclusively composed of the less stable *cis* olefinic isomer (1). Furthermore the *trans* content can be varied from vanishingly small to slightly predominant by regulating the reaction medium. This communication submits extensive data for a system (benzil) with



(1)

X = O. A subsequent communication will report similar data for some systems with X = C.

The addition of two moles of potassium to benzil in refluxing benzene solution has been reported[1] to occur in discrete stages (2), the first product being the radical anion (1). Addition of excess benzoyl chloride to the dianion suspension gave two stilbenediol dibenzoate isomers (3). The predominant isomer has been established recently, in another connection, to be the *cis* isomer.[2] We have isolated both isomers in pure form and found them to be readily distinguishable by infrared analysis. Infrared spectrophotometric analyses of the *cis–trans* content of the stilbenediol dibenzoate produced in various reaction systems are compiled in Table I.

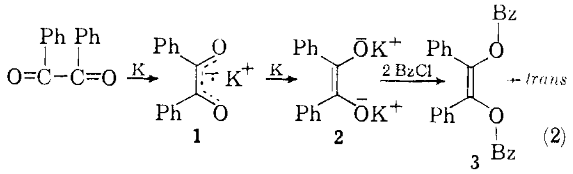


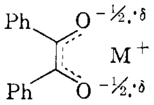
TABLE I

Metal	Solvent	Yield, %	% *cis* (±5)
Mg	Benzene	62	100
Mg	Ether	62	95
Mg	THF	79	80
Mg	Diglyme	45	80
Mg	CH_3CN	67	80
K	Benzene	60	90–95
K	THF	60	75
Na	N-Methylpyrrolidone	30	35
Na	NH_3(l)	30	35
$Ni(CO)_4$	Hexane	50	95–100
$Ni(CO)_4$	THF	65	45

These data establish a pronounced *cis* preference for all metals studied which is especially accented in non-polar solvents. We assert that the *cis–trans* analysis of **3** represents the percentage of *cis* and *trans* addition in the reaction's first stage. This follows because the stereochemistry is fixed at the anion radical stage. Addition of a second electron in a subsequent step necessarily produces the dianion of the same stereochemistry as its anion radical progenitor, and similarly for the diester produced by dibenzoylation of the dianion.

We propose to account for the observed stereospecificity in terms of the structures (**4** and **5**, respectively) of the *cis* and *trans* anion radicals. Owing to the symmetry of the anion radical roughly one half of the negative charge resides at a position remote from the stabilizing metal counterion in the *trans* isomer. This is not true of the cyclic *cis* isomer, which is therefore more stable and more likely to be formed. Since the stereochemistry is fixed at this stage subsequent addition of the second electron affords the selfsame excess of *cis* dianion even though the latter probably is the less stable isomer as a consequence of coulombic repulsions which are more serious in the *cis* than in the *trans* dianion (but are nonexistent in either radical anion).

The observed stereoelectronic control grows even more impressive upon pausing to reflect that a large steric factor (the opposition of two bulky phenyl groups in *cis*-**1**) acting on behalf of *trans* addition must be overcome in order for *cis* addition to even compete on an equal footing. It follows that if the stereoelectronic factor discussed previously were sufficiently attenuated the addition mode would be shifted to *trans*. This prediction is verified by the results in polar solvents. Ion pairs such as **1** are looser in more polar solvents and since the transition state for addition must resemble **1** somewhat, it too must be looser in these solvents and therefore less susceptible to the influence of the metal ion which engenders the stereoelectronic effect responsible for the *cis* preference. The *trans* content is seen to increase monotonically with solvent polarity and, indeed, in solvents liquid ammonia and N-methylpyrrolidone *trans* addition is actually slightly predominant.



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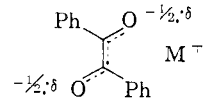

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In order to consolidate the adopted explanation involving contending stereoelectronic and steric factors, in preference to *ad hoc* explanations invoking heterogeneity effects, a soluble metal species, nickel carbonyl, was employed. Results (Table I) are even more dramatic than in the heterogeneous reactions. In hexane the same virtual exclusivity of *cis* addition prevailed but in the more polar solvent tetrahydrofuran the addition was 55% *trans*. It is suggested that solvation is materially obstructed in the surface reactions, retarding ion-pair loosening in all solvents, thus giving rise to a depressed scale of solvent effects.

Noteworthily, the preferred interpretation of the solvent dependence of the *cis/trans* ratio stresses ion pair loosening in the more polar solvents rather than a gradual transition from a heterogeneous to a homogeneous mechanism, the former favoring *cis* and the latter *trans* addition. The predominantly *trans* addition in liquid ammonia is clearly homogeneous, but fundamentally because of ion pair loosening (sodium, *e.g.*, exists as Na^+e^- in liquid ammonia). Thus the explanations are not mutually exclusive, but the adopted one is more basic. The explanations do differ in their predictions for an un-ionized, dissolved metal, a hypothetical species since ionization invariably accompanies dissolution of a pure metal. However, if complexing groups are countenanced a model, nickel carbonyl, is available. The pronounced solvent dependence for reactions of this species, all of which are homogeneous, tends to corroborate the ion pair loosening proposal.

The very similar behavior of the alkali and alkaline earth metals indicates the latter, as well as the former, are transferring a single electron in the transition state for addition.

Acknowledgment.—Generous support of this research by the National Science Foundation (Grant No. G22513) and the University of Texas Research

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[1] H. Staudinger and A. Binkert, *Helv. Chim. Acta*, **5**, 703 (1922).

[2] L. F. Fieser, *J. Chem. Ed.*, **31**, 291 (1954).

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RECEIVED JULY 30, 1962

STEREOCHEMISTRY OF METAL ADDITION TO CONJUGATED SYSTEMS. II. DIENES

Sir:

Evidence has been submitted[1] that metal additions to benzil, and presumably to α-diketones in general, consistently exhibit a pronounced *cis* stereochemical preference which is especially accentuated in nonpolar solvents and further that a novel stereoelectronic effect which should be operative to a greater or lesser extent in metal additions to all conjugated systems is responsible for the observed stereospecificity. This latter conclusion has now been reinforced with data for another common type of conjugated system, the 1,3-dienes.

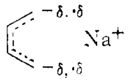
TABLE I

Diene	Temp., °C.	% *cis*-Olefin
Butadiene	−33	13
Butadiene	−78	50
1,3-Pentadiene	−33, −78	68

Table I contains v.p.c. analyses of the *cis–trans* composition of the olefin produced (in 60–75% yield) in the liquid ammonia reductions of butadiene and 1,3-pentadiene. Controls established the absence of olefin isomerization and also that any allylic sodium intermediates were configurationally stable. The latter was accomplished for the butadiene system by reducing *trans*-γ-methylallyl (crotyl) acetate in the media used in this study to essentially pure *trans*-2-butene. The intermediate butenyl sodium is involved in both this reduction and that of butadiene. Therefore a minimum conclusion is that no isomerization from *trans* to *cis* occurs and the *cis* olefin content accurately reflects the minimum percentage of *cis* addition to the diene.

In every instance the *cis* content exceeds that expected on the basis of the low (3–7% at room temperature[2]) *cis* conformer population of the diene (assuming indiscriminate addition). The results for butadiene are especially telling. Though reduction at the boiling point of ammonia (−33°) was rather indiscriminate, giving but 13% *cis* addition, that at −78° produced 50% *cis* addition, *i.e.*, completely overcame the large adverse conformational factor, which is *ca.* 10^2 at −78°, the stabler *trans* conformer being "frozen in" at low temperatures.

These facts demonstrate a temperature dependent factor acting to promote *cis* addition. Undoubtedly this is the same factor suggested to account for the *cis* stereospecificity of diketone additions, namely, preferential stabilization of the *cis*-anion radical (1) relative to its *trans* counterpart (2).



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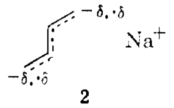

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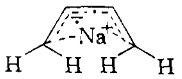
It is especially noteworthy that the *cis*-directing effect, shown earlier to be maximal in nonpolar solvents, already has reached a magnitude sufficient to nullify the adverse conformational effect in one of the least favorable solvents, ammonia (though at −78°). The implication is that, just as in the diketone case, addition should be *cis* specific in nonpolar solvents, though it is doubtful that diene reductions should have the same high specificity as those of diketones for reasons easily gleaned from a more detailed picture of the *cis* anion radicals of the two systems (**3** and **4**). Ion pair interaction is optimum in **4** but in **3** the Na^+ is displaced from the ideal location (midway between the termini of the system and coplanar with it) it occupies in **4** by the two inside hydrogens. The distinction should become more apparent the more intimate the ion pair, *i.e.*, the less polar the solvent. Consequently the limit of practically attainable specificity may be somewhat lower for systems **3** than **4**. Unfortunately the data necessary to test this surmise could not be obtained since mainly polymerization occurs in aprotic media and pertinent polymer stereostudies on butadiene are not yet available.



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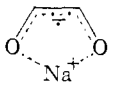

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Reduction in nonpolar media using added proton donors is only a partial solution to the problem. Ziegler, *et al.*,[3] reported the reduction of butadiene by lithium in ether with added N-ethylaniline to furnish mainly *cis*-2-butene, but no quantitative measure of the olefin composition was ascertained. Our v.p.c. measurements for the same reaction in THF solvent (ether interfered with the analysis) indicated only a very slight (50–60%) *cis* excess. Even so, this confirms the expected greater stereospecificity in more nonpolar solvents since even at −33°, the ammonia reduction was 87% *trans*. Very probably, then, metal additions in pure aprotic solvents will be at least somewhat more *cis*-stereospecific.

Results for 1,3-pentadiene were similar. The more specific (68% *cis*) reduction is ascribed to a combination of a selectivity–reactivity effect (pentadiene should be less reactive than butadiene) and the circumstance that *trans* addition to the (25%) *cis* component of our pentadiene (*i.e.*, addition to the *trans* conformer of *cis*-1,3-pentadiene) can lead to some *cis* olefin. Finally, the absence of a perceptible temperature dependency in this case is noted as curious.

It appears, then, that the formation of a cyclic anion radical renders *cis* additions to 1,3-systems generally more apt than would otherwise be anticipated and in the majority of solvents actually dominant over or exclusive of *trans* addition.

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(1) Part I of this series, *J. Am. Chem. Soc.*, **84**, 4345 (1962).

(2) W. B. Smith and J. L. Masingill, *ibid.*, **83**, 4301 (1961), and references cited therein.

(3) K. Ziegler, F. Hoffner and H. Grimm, *Ann.*, **528**, 101 (1937).