

7,12-Diphenylbenz[K]fluoranthene (IV).—(a) When 1.5 g. of the adduct was refluxed for 2 hours with 10 cc. of acetic acid, containing 1 cc. of aqueous 48% hydrobromic acid, a whitish powder separated. From butyl acetate or glacial acetic acid, silvery, fluorescent leaflets were obtained. The solutions of the substance, too, show intense violet fluorescence; m.p. 267° (brown-red melt).

(b) The mixture of 2 g. of acenaphthylene and 3 g. of diphenylisobenzofuran was heated at 160° for 24 hours. The solid reaction product was triturated with butanol and recrystallized repeatedly from the same solvent; m.p. 267°; yield, quantitative.

Anal. Calcd. for $C_{22}H_{20}$: C, 95.0; H, 5.0. Found: C, 95.0; H, 5.3.

Preparation of Acenaphthylene.—Kloetzel and Mertel⁸ have surveyed the known methods for the preparation of acenaphthylene. It has now been found that a most convenient method consists in the bromination of acenaphthene with NBS^{9,10} and treatment of the bromoacenaphthene formed, with pyridine. It has proved advisable to work with small batches (15 g.) of the parent hydrocarbon, from which a 28% yield of acenaphthylene is obtained.

The mixture of 15.4 g. of acenaphthene, 20 g. of N-bromosuccinimide and 100 cc. of carbon tetrachloride was refluxed for 6 hours, filtered and evaporated. The residue was boiled with 80 cc. of dry pyridine for 1 hour and poured out into ice-cold dilute sulfuric acid. The precipitate was isolated by extraction with ether and purified by distillation *in vacuo*; b.p. 156–160° (28 mm.). Trituration of the distillate with ice-cold methyl alcohol gave 4 g. of acenaphthylene, m.p. 94°.

(9) The claim of Ng. Ph. Buu-Hoi (*Ann.*, **556**, 1 (1944)) that acenaphthene is brominated by NBS in the 5-position, could not be substantiated.

(10) N-Chlorosuccinimide reacts analogously; M. F. Hebbelynck and R. H. Martin, *C. A.*, **45**, 2411 (1951).

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RECEIVED JULY 19, 1951

The Possible Use of 4f Orbitals in Bonding: the Enhanced Stability of the Higher Oxidation States of Iodine, Tellurium and Antimony; the Non-existence of Perbromic Acid

By Z. Z. HUGUS, JR.

Compared to bromine, selenium and arsenic, elements of the second long period: iodine, tellurium and antimony show enhanced stability in their higher oxidation states and the ability to bond to greater numbers of atoms, that is to say, maximum valency. Justification for this statement is found for example in the non-existence of arsenic pentachloride, arsenic pentabromide and perbromic acid, as well as the greater oxidizing power of the oxygen acids of arsenic(V) and selenium(VI) compared to those of antimony(V) and tellurium(VI).

The present idea is that this behavior is not due to a decreased stability of the compounds of elements of the first long period, but is due to the increased stability of the analogous compounds of elements of the second long period. The factor which stabilizes the latter compounds is the contribution of 4f atomic orbitals to bonding in these compounds.

To show that the f orbitals may contribute to the bonding in iodine, tellurium and antimony compounds, it is necessary to show that in the central field approximation upon which the designation of atomic orbitals as s, p, d, etc., is based, f orbitals have the requisite symmetry to be used in bond

formation in molecules of various symmetry types. By methods described by Wigner¹ and used by Kimball,² the irreducible representations of atomic f orbitals in a large number of symmetry point groups have been worked out. The results may be summarized here by stating that f orbitals may always be substituted for p orbitals in an hybridization complex, but only in particular symmetry groups may s and d orbitals be replaced by f orbitals. Octahedral bonding may occur with d^2sp^3 and d^2sf^3 , but not f^2sp^3 . According to Helmholtz³ the IO_6^{5-} group is almost octahedral in $(NH_4)_2H_3IO_6$ and the small deviation from the regular octahedral arrangement is presumably due to hydrogen bonding forces. It thus appears that the necessity for including d orbitals in the hybridization complexes cannot be obviated by introduction of f orbitals.

In addition to possessing the proper symmetry properties, the radial portion of the f wave function must have a reasonable magnitude at the observed interatomic distances in a molecule, if f orbitals are to contribute to bonding in that molecule. The only evidence bearing on this point is the calculation of Mayer⁴ using the Fermi-Thomas statistical model of the atom. She showed that the curve of the "effective potential energy" of an f electron as a function of the distance to the nucleus shows two minima, a broad outer minimum in the range 5–6 Å., and a much narrower inner minimum at about 0.2 Å., which falls very rapidly as the nuclear charge (Z) increases in the region of Z = 57. Evidently the outer minimum is too remote to lead to bonding at customary interatomic separations, although it might conceivably lead to rather weak long range forces in a condensed phase. In elements of Z greater than 57 the potential energy becomes positive at distances considerably smaller than the crystal radii of these elements, thus the contribution of f electrons to bonding would be expected to be nil.

In the elements preceding the rare earths the inner minimum is rather well developed. As valence electrons are removed the radius of the atom shrinks, and simultaneously the potential energy curve will fall in the region where shielding of f electrons by the valence electrons is appreciable. These effects will then cooperate to provide increasing f bonding as the degree of ionization increases. The net result is then a preferential stabilization of the higher oxidation states of the central atom.

Potential energy curves and qualitative eigenfunctions (based on the Fermi-Thomas model) indicate the possibility of a moderately large overlap integral of an f eigenfunction on iodine and a p eigenfunction on oxygen, for example.

One factor which would appear to limit the use of f orbitals in bonding is the rather large energy required to promote the valence electrons to a configuration involving f electrons. On this account one would think that rather than the hy-

(1) E. Wigner, "Gruppentheorie und ihre Anwendung auf die Quantenmechanik der Atomspektren," Vieweg, Braunschweig, 1931.

(2) G. E. Kimball, *J. Chem. Phys.*, **8**, 188 (1940).

(3) L. Helmholtz, *This Journal*, **59**, 2036 (1937).

(4) M. G. Mayer, *Phys. Rev.*, **80**, 184 (1941).

bridization complex sf^3 occurring in the tetrahedral IO_4^- group, a small amount of f character would be conferred to the p orbitals of an sp^3 complex giving effectively a $sp^{3-\epsilon}f^\epsilon$ complex, where ϵ is supposed to be small. For a given problem ϵ could then be found by minimization of the energy eigenvalue by a variational treatment.

It thus appears that f electrons may contribute to bonding in compounds of the elements immediately preceding the rare earths, and that thereby certain chemical properties of these elements may be explained. In particular, the preferential stabilization of the higher oxidation states of these elements may be accounted for.

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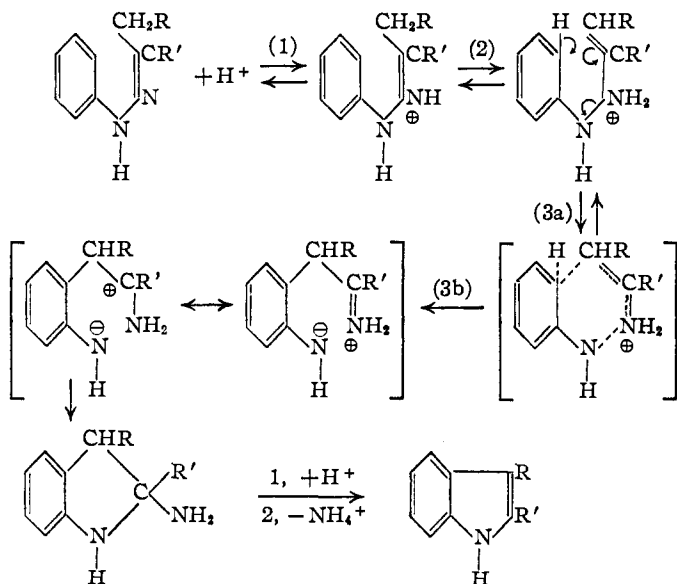
RECEIVED OCTOBER 1, 1951

Studies on the Fischer Indole Synthesis. III. Mechanism

By ROBERT B. CARLIN

A proposed¹ mechanism for the Fischer indole synthesis has been criticized recently on the basis of a kinetics study.² It is the purpose of this paper to show not only that the criticism is invalid but also that a reaction sequence essentially identical with that previously proposed¹ does account satisfactorily for the data given by Pausacker and Schubert as well as for certain other established facts about this transformation.

The following reaction sequence appears to embody the principal features of the Robinson-



Robinson mechanism,³ of the ring closure mechanism first suggested by Allen and Wilson,⁴ and of our proposed mechanism.¹ Examination of these formulations discloses that no fundamental changes

- (1) R. B. Carlin and E. E. Fisher, *THIS JOURNAL*, **70**, 3421 (1948).
- (2) K. H. Pausacker and C. I. Schubert, *J. Chem. Soc.*, 1814 (1950).
- (3) G. M. Robinson and R. Robinson, *ibid.*, **113**, 639 (1918); 827 (1924).
- (4) C. F. H. Allen and C. V. Wilson, *THIS JOURNAL*, **65**, 611 (1943).

are required if the proton is accepted by the other nitrogen atom in step (1). Pausacker and Schubert argued that a similar reaction sequence¹ could not be reconciled with their rate data for the reason that the effects on the observed rate constants of introducing certain substituents into the aromatic ring of the phenylhydrazone were not those to be expected on the rates of the rearrangement step (3) in the reaction sequence above. However, the rate constants measured by Pausacker and Schubert cannot be the simple rate constants for the rearrangement step (3) alone; furthermore, there need be no relationship between changes in measured rate and changes in the rate of step (3) which result from structural alterations, as the authors implicitly assume in making their criticism. In fact, in order to account for their observed kinetics, Pausacker and Schubert assumed that the rate-determining step in the sequence is the reaction of the phenylhydrazones with a proton (step 1, above). If this assumption were to prove correct, then the observed effects of structural variations on the experimental rate constants should parallel the effects of structure on the base strengths of the phenylhydrazones; and, indeed, such a parallelism appears likely when the data of Pausacker and Schubert are examined. In any case, the effects of structure on the rate of the rearrangement step (3) should not be reflected in the experimental rate constant if this step is assumed not to be rate determining.

However, it is not necessary to assume that step 1 is rate determining in order to account for the kinetics observed by Pausacker and Schubert. If proton addition and tautomerization (steps 1 and 2) are assumed to be reversible and rapid compared to step 3, and if the succeeding steps are also rapid compared to step 3, then the following rate expression can be derived from the reaction sequence

$$\frac{dx}{dt} = \frac{k_3 K_1 K_2 (a - x) [H^+]}{1 + K_1 [H^+] + K_1 K_2 [H^+]}$$

in which K_1 , K_2 and k_3 are the equilibrium and rate constants for the first three steps, respectively, a is the initial phenylhydrazone concentration and x is the concentration of indole at time t . If $K_1 [H^+]$ and $K_1 K_2 [H^+]$ are small compared to 1, a likely condition, then the above expression becomes identical with the experimentally derived rate equation, where $k_{\text{expt}} = k_3 K_1 K_2$. Thus the experimental rate constant would be proportional to the first base constant for the phenylhydrazone and to the tautomerization equilibrium constant, as well as to the rate constant for the rearrangement step.

Since the tautomeric shift (step 2) is comparatively remote structurally from the benzene ring, substitution on the latter would be expected to affect K_2 to a smaller extent than K_1 or k_3 . If the introduction of the substituents selected by Pausacker and Schubert on the benzene ring causes much greater changes in K_1 than in k_3 , then the fact that the relative reaction rates of cyclohexanone, phenylhydrazone and three of its aromatic