

However, the recent discovery of fluoride formation by xenon,⁵ radon,⁶ and krypton⁷ suggests that under the circumstances of bond formation, neither electronegativity nor covalent radius of the "inert" elements need remain hypothetical.

According to the principle of electronegativity equalization and related concepts,¹ the electronegativity of XeF_4 is the geometric mean of the values of the component atoms before reaction. This is calculated to be 4.05, using the "compactness" scale of 5.75 for fluorine and 1.00 for xenon. By definition, this electronegativity is also equal to a ratio, r_1^3/r^3 , where r is the covalent radius of a combined atom in the molecule and r_1 the radius of the (usually) hypothetical iso-electronic inert atom. For xenon the inert atom is not hypothetical, and r_1 is 2.09 Å. The radius r of xenon in XeF_4 is determined as follows. The electronegativity of XeF_4 , 4.05, is equal to $2.09^3/r^3$, or $r = \sqrt[3]{9.13/4.05} = 1.31$ Å. The radius of fluorine in the same compound is similarly calculated to be 0.81 Å. The radius sum is thus 2.12 Å. In a comprehensive survey of bond lengths,⁸ single bonds to fluorine were found to be of length close to 0.92 times the sum of the radii-in-the-compound. This factor times 2.12 equals 1.95 Å., which is in reasonably close agreement with the reported² value of 1.92 ± 0.03 Å. The contraction of the xenon radius corresponds to a calculated positive charge of 1.36, and the increase in radius of fluorine to a partial negative charge of -0.34 (electron). In condition of fluorine, this would place XeF_4 between the fluorides of magnesium and aluminum. The fact that these xenon fluorides are quite volatile despite the indicated high polarity of the bonds can be explained in terms of the observation⁹ that outer vacant orbitals on the cationic atom appear to be an inherent essential in the usual condensation of metal salts to ionic or polymeric crystals. Such vacancies are relatively unavailable on the xenon.

This bond length calculation assumes a two-electron bond between xenon and fluorine, an assumption which must be regarded with caution since the bonding may be of some other type.¹⁰ However, the promotion of one electron from each of two xenon orbitals to outer d-orbitals, analogous to "expanding the octet" of phosphorus, would create the essentials for the four bonds observed. Furthermore, the presence of the two additional unshared electron pairs on the xenon would reasonably be expected to produce the observed² planarity of XeF_4 , these pairs then filling the fifth and sixth corners of an octahedron around the xenon. The bond length is at least consistent with that calculated for a two-electron covalent bond. The linearity⁵

of XeF_2 could be explained as the result of a trigonal bipyramidal structure with fluorines opposite and the three equatorial positions occupied by the three remaining unshared pairs of electrons of the xenon atom.¹⁰

A theory is neither validated nor invalidated by one bond length calculation, but the apparent consistency of the earlier selected¹ covalent radius and electronegativity of xenon with the experimental bond length in XeF_4 seems at least worthy of attention. We may await with interest other data which should permit better insight regarding the concepts of electronegativity and partial charge, and perhaps suggest a more conclusive answer to the question of whether covalent radii of the "rare gases" are larger^{1,3} or smaller¹¹ than those of the adjacent halogens. In anticipation of future measurements, the bond lengths in XeF_2 and KrF_4 are here predicted to be close to 2.11 and 1.84 Å., respectively.

(11) C. A. Coulson, "Valence," Clarendon Press, Oxford, 1952.

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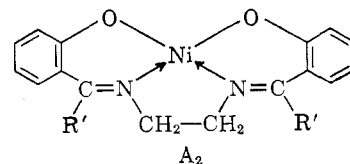
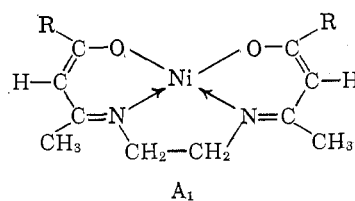
R. T. SANDERSON

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Amine-Catalyzed Condensation of β -Diketones Using a Metal-Chelate Template

Sir:

Compounds of type A_1 , A_2 have been prepared by a novel method which consists of the amine-catalyzed



$R = \text{CH}_3, \text{C}_6\text{H}_5$
 $R' = \text{H}, \text{CH}_3$

reaction of a β -diketone (or related compound) and tetrakis-(ethylenediamine)- μ -dichlorodinickel(II) chloride (B) which serves as a source of ethylenediamine and as a template¹ for the reaction.

It seems significant that the interaction of acetylacetone and B in the absence of pyridine results merely

(1) For a prior example of a metal-chelate compound functioning as a template, see M. C. Thompson and D. H. Busch, Abstracts of Papers, 142nd National Meeting of the American Chemical Society, Atlantic City, N. J., September, 1960, p. 13N.

(5) H. H. Claassen, H. Selig, and J. G. Malm, *J. Am. Chem. Soc.*, **84**, 3593 (1962); C. L. Chernick, *et al.*, *Science*, **138**, 136 (1962).

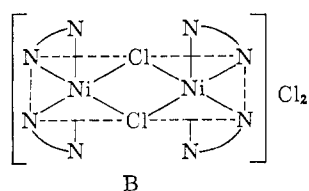
(6) P. R. Fields, L. Stein, and M. H. Zirin, *J. Am. Chem. Soc.*, **84**, 4164 (1962).

(7) A. V. Grosse, A. D. Kirshenbaum, A. G. Streng, and L. V. Streng, as reported in *Chem. Eng. News*, **41**, 47 (Jan. 7, 1963).

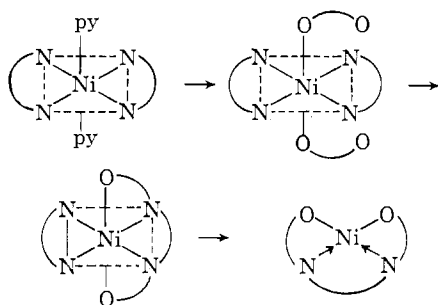
(8) R. T. Sanderson, *Science*, **114**, 670 (1951).

(9) R. T. Sanderson, *J. Chem. Educ.*, **38**, 382 (1961).

(10) L. C. Allen, *Science*, **138**, 892 (1962); L. C. Allen and W. D. Horrocks, Jr., *J. Am. Chem. Soc.*, **84**, 4344 (1962).



in the destruction of B. However, in view of the recent report² that B is actually a dimer with bridging chloride ions, it seems likely that treatment of B with pyridine would result in the formation of *trans*-[Ni(en)₂(py)₂]²⁺. An oxygen atom from each of two β-diketone molecules then could replace a molecule of pyridine and condense with an adjacent coordinated amino group.



This scheme may not represent the exact sequence of reaction steps, but it shows the template mechanism. It is supported by the observation that β-diketones do not condense with [Ni(en)₃]Cl₂.

It is worth noting that only catalytic amounts of pyridine are required and that the desired condensation does not occur if the base is added after B and the β-diketone are mixed. This is probably an indication that a labile proton from the β-diketone is combining with the base to nullify its catalytic properties. Moreover, no reaction is observed when aqueous solutions of B and sodium acetylacetonate are mixed. This suggests that the condensation does not involve direct removal of bridging chloride ions by a β-diketone or its conjugate base.

The preparation of compounds of type A₁, A₂ (Table I) is exemplified by the condensation of acetylacetonate and B. To a solution of B (2.49 g. or 0.005 mole in 20 ml. of water) was added two drops of pyridine followed by acetylacetonate (1.98 g., 0.02 mole). The mixture was allowed to reflux for 2 hr., during which time the product crystallized in quantitative yield. Even though some of the β-diketones studied do not dissolve in water, they readily take part in the condensation.

Condensation of acetylacetonate also was noted when butylamine or 2,4-lutidine was used as catalyst; 2,6-lutidine gave no reaction. The latter failure can be attributed to the steric hindrance of the two methyl groups on the base and would seem to indicate that replacement of the bridge chlorine atoms by a coordinating base is necessary for condensation to occur.

Further investigation of the scope, kinetics, and mechanism of the reaction is in progress.

(2) A. S. Antsyshkina and M. A. Porai-Koshits, *Dokl. Akad. Nauk USSR*, **143**, 105 (1962); *Chem. Abstr.*, **57**, 2954f (1962).

TABLE I

PROPERTIES OF COMPOUNDS OF THE TYPE A₁ AND A₂ PREPARED BY PYRIDINE-CATALYZED CONDENSATION OF β-DIKETONES AND RELATED COMPOUNDS WITH B

Ligands	M.p., °C.	Yield, %	Analysis ^a			Ref.
			C	H	N	
Acetylacetonate	198	82	51.25 ^b	6.4	9.97	^c
			51.75	6.44	9.69	
Benzoylacetone	290	86	65.23	5.44	6.92	^d
			64.53	5.44	6.96	
<i>o</i> -Hydroxyacetophenone	290	81	61.24	5.10	7.94	
Salicylaldehyde	350	94	61.72	5.47	8.27	
			58.83	4.31	8.62	^e
			58.39	4.24	8.64	

^a First line for each substance is calculated per cent; second found. ^b Analyses are for the crude products. ^c G. T. Morgan and J. D. Main Smith, *J. Chem. Soc.*, 920 (1926); m.p. 200°. ^d P. J. McCarthy, R. J. Hovey, K. Ueno, and A. E. Martell, *J. Am. Chem. Soc.*, **77**, 5820 (1955); m.p. 288–289°. ^e P. Pfeiffer, E. Buchholz, and O. Bauer, *J. Prakt. Chem.*, **129**, 163 (1931); no m.p. reported.

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Decomposition of the Electronically Excited Difluoramino Free Radical

Sir:

The ability of difluoramine to deaminate primary amines has been explained¹ by postulating the intermediate formation of fluorazene or fluoronitrene (NF). This intermediate species presumably arises by the loss of a fluoride ion from the initially formed unstable alkylammonium difluoramide.

We now have observed that photochemical activation (2537 Å.) of the difluoramino free radical² may also produce fluoronitrene by inducing loss of a fluorine radical. For example, irradiation of an equilibrium mixture of N₂F₄ and ·NF₂ at room temperature gave NF₃ and N₂F₂ along with N₂ and other products involving N₂F₂ decomposition in glass, N₂O, NO, and SiF₄.³ Coupling of fluoronitrene can give rise to N₂F₂, a reaction which other nitrenes undergo,⁴ and F· and ·NF₂ may combine to furnish NF₃. When SO₂ was introduced into the system (10 mmoles each of N₂F₄ and SO₂) a new compound, sulfonyl fluoride di-

(1) C. L. Bumgardner, K. J. Martin, and J. P. Freeman, *J. Am. Chem. Soc.*, **85**, 97 (1963).

(2) C. B. Colburn and F. A. Johnson, *J. Chem. Phys.*, **33**, 1869 (1960).

(3) C. B. Colburn, F. A. Johnson, A. Kennedy, K. McCallum, L. C. Metzger, and C. O. Parker, *J. Am. Chem. Soc.*, **81**, 6397 (1959).

(4) G. Smolinsky, *J. Org. Chem.*, **26**, 4108 (1961).