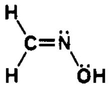
J. Org. Chem. 1982, *47*, 245–248



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izing iminodiazonium ions **2a** and **2b**. Any equilibration of these two ions, as in the hydrolysis of vinyl azides, must involve reversible addition of water (or sulfuric acid) to yield a tetrahedral intermediate. If the rate of this equilibration is slow, compared to the rate of rearrangement, then the ratio of products formed will depend on steric effects, whereas if the rate of equilibration is fast, the product will depend on the migratory aptitude and charge-stabilizing ability of the groups R_1 and R_2. Direct rearrangement of the tetrahedral intermediate 1 may occur if dehydration is unfavorable due to steric or other reasons. This study not only has resolved an important question concerning the mechanism of the Schmidt reaction but also has heightened our knowledge of the effect of the direction of polarization of multiple bonds attached to imino nitrogen on the inversion barrier to isomerism of imines.

Acknowledgment. We gratefully acknowledge support from the National Science Foundation (Grant No. CHE-80-06520) and the National Institutes of Health (Grant No. ES00761-08).

Registry No. 9, 43730-26-3; **12**, 79827-95-5; (*E*)-**15**, 79827-96-6; (*Z*)-**15**, 79827-97-7.

Theoretical Analysis of the Barrier to Nitrogen Inversion in *N*-Fluoroformimine and Formaldoxime

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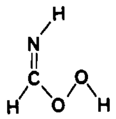
The barriers to nitrogen inversion in *N*-fluoroformimine and formaldoxime have been computed to be 77.4 and 59.5 kcal/mol, respectively, by employing a 6-31G basis set with full geometry optimization. A theoretical analysis of the origin of these barriers suggests that an "allyl type" MO containing the nitrogen lone pair is largely responsible for the increase in total energy in the transition state for planar nitrogen inversion.

In principle, inversion at planar nitrogen in imines may occur by rotation about the C=N double bond or by an in-plane lateral shift mechanism.[1] There is now a consensus of opinion that favors the latter process in most compounds. However, in specific cases heteroatom substitutents at the imino carbon may sufficiently perturb the C=N π system to lower the barrier to rotation, and a combined inversion–rotation mechanism may ensue.[2] In contrast, when the substitutent at imino nitrogen is a heteroatom bearing a lone pair of electrons (O, N, halogen), the inversion barrier usually increases. For example, the barrier to inversion in oximes is typically above 23 kcal/mol and isolation of epimers becomes feasible.[2]

A number of theoretical studies on the mechanism of syn–anti isomerism of oximes[3–5] agree that an inversion mechanism is lower in activation energy than a rotational process. Computed inversion barriers of 23.0 (Hückel),[5] 37.5 (CNDO),[4] 35.8 (FSGO),[3] and 50.6 (ab initio)[4] kcal/mol have been reported for formaldoxime (1). The origin of the increase in energy of the linear transition 1a has been attributed to the σ-electron-withdrawing effect of the electronegative substitutent and to the electron repulsion between the nitrogen lone-pair and the nonbonding electrons on heteroatom substitutents.[1,4] The transfer of electrons from a relatively diffuse 2s orbital to a more directed higher energy p orbital upon rehybridization ($sp^2 \rightarrow p$) at nitrogen also contributes to the barrier.[1a]

Our interest in nitrogen inversion stems from a theoretical study of syn–anti isomerism in peroxyformimidic acid (2). We demonstrated a pure inversion mechanism with no detectable torsional component to the *Z–E* isomerization pathway despite the heteroatom substitutent at carbon.[6] However, both the inversion and rotational barriers were diminished by the electronic influence of the lone pair on oxygen.



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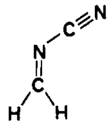

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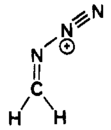

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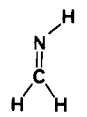

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In our related studies on the inversion barriers in *N*-cyano- and *N*-diazoformimine (**3** and **4**),[7] we found that a comparison between the frontier molecular orbitals in **3** and **4** to those in the simplest model substrate, methylenimine (**5**), provided us with considerable insight into the origin of the inversion barrier. With *N*-cyanoformimine (**3**), we observed good agreement between our computed barrier (14.5 kcal/mol) and the experimental barrier on the corresponding dimethyl analogue (18.9 kcal/mol)[8] when an extended 6-31G basis set was used. We now

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[1] For excellent reviews on this topic see: (a) Lehn, J. M. *Fortschr. Chem. Forsch.* **1970**, *15*, 311. (b) Kalinowski, H.-O.; Kessler, H. *Top. Stereochem.* **1973**, *7*, 295.

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[8] McCarty, C. G.; Wieland, D. M. *Tetrahedron Lett.* **1969**, 1787.

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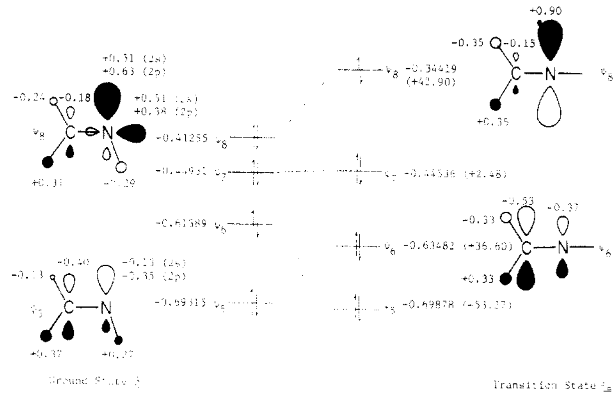


Figure 1. Frontier molecular orbital coefficients and energy levels (minimized, 6-31G (au)) with the net change in orbital energies (kcal/mol) for the ground state and transition state for inversion of formimine (5).

describe a comparable study that examines the π molecular orbital interactions of the imine functional group with electronegative oxygen and fluorine substitutents containing lone pairs adjacent to nitrogen.

Results and Discussion

The molecular orbital calculations were performed with the GAUSSIAN 70 series of programs.[9] The nitrogen inversion barrier in formaldoxime (1) was computed with a 6-31G basis set with full optimization on a geometry initially optimized[10] at the STO-3G level. The geometry of *N*-fluoroformimine (6) and its transition state for inversion **6a** were also both fully minimized with the extended 6-31G basis set. The computed structure and inversion barrier in methylenimine (5) have been reported previously.[7,11]

As noted in our prior paper,[7b] the nitrogen lone pair in **5** is mixed in a bonding and antibonding manner with the adjacent filled methylene fragment orbital. The resulting orbital splitting gives rise to two filled molecular orbitals containing the nitrogen lone pair as illustrated in Figure 1 for methylenimine (**5**). The π-type CH_2 fragment orbital, which is orthogonal to the π system of the carbon–nitrogen double bond, is constructed from an atomic 2p orbital on carbon and the two 1s orbitals of the hydrogen.[12] The HOMO in **5** (ψ_8) is largely comprised of the nitrogen lone pair (n) mixed in an out-of-phase fashion with a π_{CH_2} orbital (π_{CH_2} – n).[13] The lower lying bonding (π_{CH_2} + n) combination (ψ_5) contains a larger percentage of the π_{CH_2} fragment than the nitrogen lone pair. Both of these orbitals rise in energy during nitrogen inversion to afford ψ_6 and ψ_8 in the transition state **5a**. The C=N π orbital (ψ_7) shows only a slight elevation in energy (2.48 kcal/mol) upon inversion while the C—N and N—H σ bonds (ψ_6 in the ground state) decrease in energy by 53.3 kcal/mol (Figure 1) as a result of the shorter C=N bond length and the attendant increase in bonding in this linear array. The net change in these calculated frontier orbital energies (26.2 kcal/mol) compares remarkably well with the computed (6-31G) inversion barrier of 25.2 kcal/mol.[7] However, this may well be fortuitous since the same type of analysis does not provide a reliable barrier when substitutents on nitrogen other than hydrogen are involved. The same conclusion had been reached by Lehn,[1a] who felt that the energetic origin of the inversion barrier was delocalized over the entire molecule.

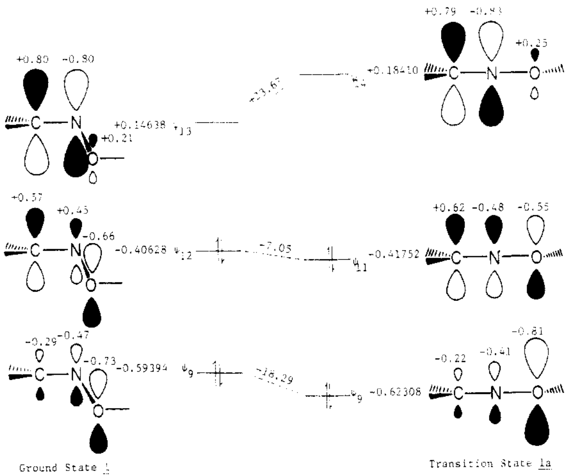
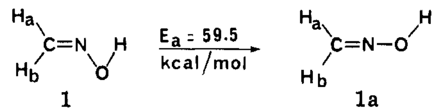


Figure 2. Calculated (6-31G) frontier orbital energies (au), eigenvectors, and the net change in orbital energies (kcal/mol) for the π molecular orbitals in formaldoxime (1) and its transition state for inversion, **1a**.

The computed barrier to inversion in formaldoxime (1) was 59.1 kcal/mol (6-31G) with the geometry minimized by STO-3G[10] while the transition state **1a** was 59.5 kcal/mol above the ground state with the optimized (6-31G) geometry given below (eq 1).



(1)

	1	1a
r_{CH_a}, Å	1.070	1.086
r_{CH_b}, Å	1.073	1.084
r_{CN}, Å	1.258	1.239
r_{NO}, Å	1.415	1.331
r_{OH}, Å	0.950	0.957
<H_a-C-N, deg	117.45	122.56
<H_b-C-N, deg	122.44	122.12
<C-N-O, deg	111.55	180.0
<N-O-H, deg	106.78	109.41
E_{tot}, au	−168.762 53	−168.667 73

The oxygen atom in **1** has two lone pairs that engage in intramolecular interactions with the orbitals of the imino moiety. The higher energy π-type[12] lone pair has the proper local symmetry to combine with the C=N π bond, and the two fragments afford a delocalized π system that is isoelectronic with the allyl anion (Figure 2). Interactions of the requisite oxygen lone pair (n) with both the π and π^* orbitals of the C=N bond afford the three molecular orbitals depicted in Figure 2. Upon nitrogen inversion the lower lying π orbital (ψ_9), which has the symmetry properties of ψ_1 in an allyl system, decreases in energy by 18.29 kcal/mol. This orbital has the largest contribution from oxygen since the lone pair is lower in energy than the C=N fragment. Conversely, the LUMO in **1** (ψ_{13}) is derived principally from the higher lying π^*C=N fragment orbital with only a small coefficient due to the oxygen lone pair. The orbital that is intermediate in energy of these three, ψ_{12}, is the HOMO in the molecule and contains one node. This occupied MO also decreases in energy (−7.05 kcal/

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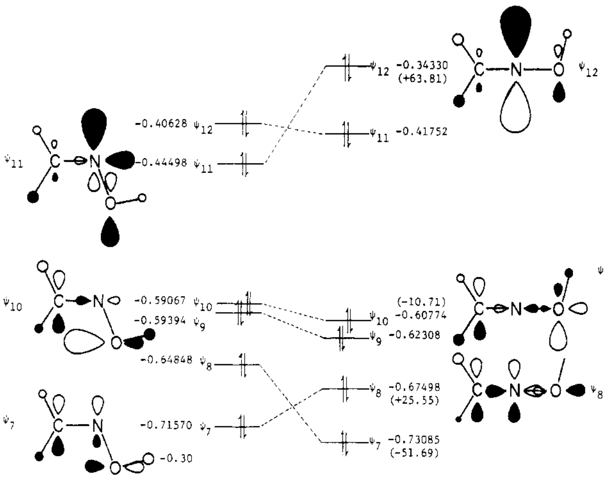
[11] Lehn, J. M.; Munsch, B.; Millie, P. H. *Theor. Chim. Acta* **1970**, *16*, 351.

[12] For a discussion see: Jorgensen, W. L.; Salem, L. "The Organic Chemist's Book of Orbitals"; Academic Press: New York, 1973; p 6.

[13] The C–N bond is placed along the *x* axis and the eigenvectors given for nitrogen are for the 2s and the p_x and p_z orbitals. The π orbitals of the C=N double bond are on the *y* axis.



Ground State 1 | Transition State 1a

		H_a	H_b	C_{2pz}	N_{2s}	N_{2px}	N_{2pz}	O_{2s}	O_{2px}	O_{2pz}	H
	ψ_{11}	-0.15	+0.25	-0.12	+0.43	+0.37	+0.58	+0.19	-0.16	-0.48	-0.15
1	ψ_{10}	-0.38	+0.24	-0.40	+0.01	-0.16	+0.10	-0.28	+0.46	+0.02	+0.36
	ψ_8	-0.19	+0.26	-0.38	-0.18	0.0	-0.34	+0.13	-0.41	+0.04	-0.30
	ψ_{12}	-0.34	+0.33	-0.13	-0.03	-0.03	+0.88	+0.19	+0.08	-0.24	-0.23
1a	ψ_{10}	-0.21	+0.31	-0.37	+0.08	+0.20	-0.02	-0.38	-0.30	+0.50	+0.24
	ψ_8	-0.33	+0.09	-0.37	-0.04	-0.31	-0.35	+0.22	+0.33	-0.16	+0.02

Figure 3. Calculated (6-31G) frontier orbital energies (au), eigenvectors, and the net change in orbital energies (kcal/mol) for the molecular orbitals containing the nitrogen lone pair in formaldoxime (1) and its transition state for inversion, **1a**.

mol) in the inversion process (Figure 2). The lack of symmetry and orbital degeneracy in this MO is reflected in the relatively large coefficient on the central nitrogen atom compared to that in the classical allyl anion, where the central coefficient is zero. Significantly, *the occupied molecular orbitals derived from the C=N π system make make no positive contribution to the observed barrier to inversion in oximes since both decrease in energy.*

The second oxygen σ-type lone pair[12] that possesses more s character is orthogonal to the above π system and lies in the same plane as the nitrogen lone pair. As a consequence, this lone pair combines with the two filled (π_{CH_2} ± n) molecular orbitals previously discussed for methylenimine (Figure 1) to afford three additional "allylic" orbitals as depicted in Figure 3. The lowest energy bonding MO (ψ_7) and the higher lying antibonding combination (ψ_{11}) both contain coefficients from the central nitrogen atom. The intermediate "allylic" MO (ψ_{10} in the ground state) has virtually no contribution from nitrogen.

The most striking change in orbital energy (63.8 kcal/mol) upon inversion is in the NHOMO (ψ_{11}) which contains the lone pair on the imino nitrogen interacting in an antibonding manner with both the π_{CH_2} fragment and the σ-type lone pair on oxygen (Figure 3). This orbital, which is ψ_{12} in the transition state, has the nitrogen lone pair highly localized in an atomic p orbital on nitrogen in **1a**. The corresponding bonding combination of this orbital (ψ_7) also increases in energy by 25.5 kcal/mol. This behavior is reminescent of the orbital increases in methylenimine upon inversion. Similarly, we observe a substantial decrease in the energy of the σ-bonding MO (ψ_8) by an amount comparable to that calculated for **5** (Figure 1). By analogy to **5**, *we attribute the high barrier in oxime 1 to the sharp energy increase in the two (π_{CH_2} ± n) molecular orbitals containing the nitrogen lone pair.*

Inclusion of *N*-fluoroformimine (**6**) in this study provides an extreme test on the effect of electronegativity on the inversion barrier. As anticipated, the computed (6-31G) barrier for inversion (**6** → **6a**) was further increased to 77.4 kcal/mol (eq 2). We observed the expected attendant decrease in C=N and N—F bond distances and lengthening of the C—H bond distances.

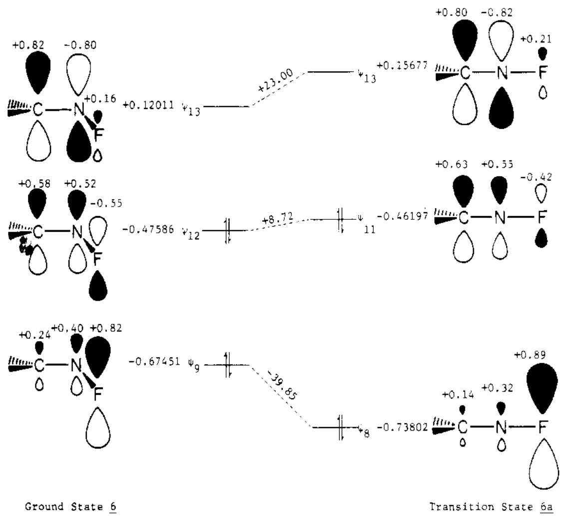
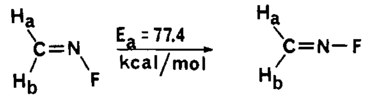


Figure 4. Calculated (6-31G) frontier orbital energies (au), eigenvectors, and the net change in orbital energies (kcal/mol) for the π molecular orbitals in *N*-fluoroformimine (**6**) and its transition state for inversion, **6a**.



(2)

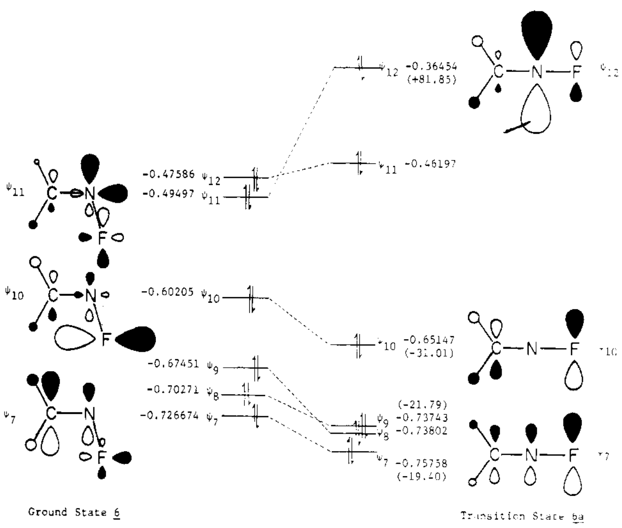
6 **6a**

	6	6a
r_{CH_a}, Å	1.069	1.084
r_{CH_b}, Å	1.071	1.084
r_{CN}, Å	1.258	1.239
r_{NF}, Å	1.435	1.334
<H_a-C-N, deg	116.40	121.85
<H_b-C-N, deg	123.12	121.85
<C-N-F, deg	108.72	180.0
E_{tot}, au	-192.748 44	-192.624 50

The three π-type molecular orbitals derived from the C=N double bond and a lone pair on fluorine exhibited the same trend as the oxime. The lower energy MO (ψ_9) is largely fluorine, and the antibonding MO (ψ_{13}) contains mostly the π* C=N orbital. In this instance, the bonding MO decreases in energy on inversion while the second occupied MO (ψ_{12}) slightly increases (Figure 4).

The symmetry of the additional three "allyl type" molecular orbitals, which are derived from the π_{CH_2} orbital, a nitrogen lone pair and the eclipsed fluorine lone-pair,[12] is particularly evident in transition state **6a** (Figure 5). Thus, ψ_7 contains no nodes, ψ_{10} has no contribution from the central nitrogen, and ψ_{12}, containing two nodes, mostly consists of an atomic p orbital on nitrogen. The very large increase in energy (81.9 kcal/mol) of the NHOMO orbital (ψ_{11} → ψ_{12}) is particularly revealing and obviously makes the major contribution to the barrier to nitrogen inversion.

As we pointed out earlier, the lack of predictability in the relative change in frontier orbital energies makes an exact analysis of the origin of the barrier quite difficult. For example, the π_{CH_2} + n bonding combination (ψ_7) shows a *decrease* in energy upon inversion in **6**. There does, however, appear to be one consistent trend in the inversion process. In our analyses of the origin of the inversion barrier, we have attempted to single out the "culprit" frontier orbital that appears to be largely responsible for the increase in total energy of the molecule in the tran-



		H_a	H_b	C_{2pz}	N_{2s}	N_{2px}	N_{2pz}	F_{2s}	F_{2px}	F_{2pz}
6	ψ_{11}	-0.13	+0.24	-0.11	+0.45	+0.40	+0.54	+0.04	-0.31	-0.45
	ψ_{10}	-0.28	+0.17	-0.25	0.0	-0.13	+0.24	+0.09	+0.82	-0.11
	ψ_7	+0.30	-0.37	+0.50	+0.09	+0.03	+0.30	-0.15	+0.28	-0.14
6a	ψ_{12}	-0.32	+0.32	-0.12	0.0	0.0	+0.89	0.0	0.0	-0.39
	ψ_{10}	-0.30	+0.30	-0.44	0.0	0.0	-0.05	0.0	0.0	+0.67
	ψ_7	+0.18	-0.18	+0.33	0.0	0.0	+0.43	0.0	0.0	+0.64

Figure 5. Calculated (6-31G) frontier orbital energies (au), eigenvectors, and the net change in orbital energies (kcal/mol) for the molecular orbitals containing the nitrogen lone pair in *N*-fluoroformimine (**6**) and its transition state for inversion, **6a**. (See ref 13.)

sition state for nitrogen inversion. In all three model compounds the lone pair on nitrogen resides principally in an sp^2 orbital as seen by the eigenvectors for the HOMO (ψ_8) in **5** and the NHOMO (ψ_{11}) in **1** and **6**. When the nitrogen lone pair is directed along the *x* axis the magnitude of the coefficients reflects the relative contribution of the substitutent on nitrogen to these particular molecular orbitals.

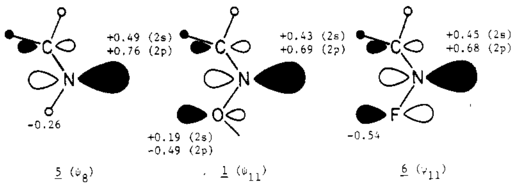


Table I. Computed (6-31G) Inversion Barriers for $CH_2{=}N{-}X$ and the Increase in Orbital Energies upon Nitrogen Inversion

compd	X	inversion barrier, kcal/mol	ΔE for $\pi_{CH_2} - n$	ΔE for $\pi_{CH_2} + n$
3	CN	14.4	35.55	12.96
5	H	25.2	42.90	36.60
4	$^+N{\equiv}N{:}$	28.2	79.57	20.24
1	OH	59.5	63.81	25.55
6	F	77.4	81.85	-21.79

A similar observation was made for the corresponding $\pi_{CH_2} - n$ orbitals in the *N*-cyano and *N*-diazoformimines **3** and **4**.[7b] In all five model substrates that we have studied using the extended 6-31G basis set, this particular molecular orbital consistently exhibits the largest increase in energy on going to the transition state. The lower energy ($\pi_{CH_2} + n$) bonding combination of this MO, that also contains the nitrogen lone-pair, shows an increase in orbital energy (Table I) with the exception of the fluoro derivative. The anomalously high increase in orbital energy noted for the diazo derivative **4** is presumably due to its unusually strong σ inductive effect and to the fact that the diazo portion of the molecule is nonlinear in the ground state, decreasing its effectiveness to extend the conjugation by resonance delocalization.

In summary, we have corroborated earlier suggestions[1] that electron-withdrawing substituents at nitrogen markedly increase the inversion barrier, and we have identified the molecular orbital that contributes most significantly to the activation energy as an "allyl type" MO containing the nitrogen lone pair.

Acknowledgment. We gratefully acknowledge support from the National Institutes of Health (Grant No. ES 00761-08) and the National Science Foundation (Grant No. CHE-80-06520).

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On the Mechanism of the Titanium-Induced Reductive Coupling of Ketones to Olefins

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The reductive coupling of ketones, induced by low-valent titanium, was studied by using benzophenone and cyclohexanone as model compounds. The reaction conditions were optimized. It is essential that $TiCl_3$ is reduced completely before addition of the ketone. The reaction mechanism is deduced from ESR measurements. Both the inorganic and organic part of the radical reaction are discussed. Various techniques were invoked to obtain a model for the actual coupling site. The coupling reaction occurs on the surface of an active titanium specimen.

In the early seventies three groups of investigators[2-4] established that low-valent Ti, prepared by the action of strong reducing agents on $TiCl_3$ or $TiCl_4$ in THF, can abstract oxygen from ketones, leading to the formation of

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[1] On leave from Polish Academy of Sciences, Institute of Organic Chemistry, Kasprzaka 44/52, Warszawa, Poland.

[2] S. Tyrlik and I. Wolochowicz, *Bull. Soc. Chim. Fr.*, 2147 (1973).

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