$Re(CO)_4L_2$ radical by direct comparison of the experimental spectrum with line shapes calculated for a wide variety of hyperfine parameters. The *g* value ($g = 2.0033$) of radical complex is still close to the free electron value. This means that the unpaired electron resides at the ligand, and the radical is considered as the 18 electron anion complex in which rhenium is surrounded by four carbonyl groups and a negatively charge diphosphine ligand. The next question still remains as to whether the radical is 17- or 19-electron complex. The IR spectrum of the radical complex in THF shows four absorption bands at 2078, 2009, 1900, and 1975 cm^{-1} in the carbonyl region, as expected from C_{2v} symmetry group $(2A_1 + B_1 + B_2)$. The peaks are very similar to those of the known $Mn(CO)_4L_2$ complex.[4]

Since it is known that the 19-electron complex is substitutionally labile, we attempted to react $Re(CO)_4L_2$ with phosphite ligand in THF. Unexpectedly, the product was turned out to be a diamagnetic compound rather than one substituted phosphite product. The ESR spectrum, immediately taken from the addition of $Re(CO)_4L_2$ and $P(OMe)_3$ at room temperature is shown in Figure 5. The ESR spectrum taken after leaving the mixture for one hour, is completely silent, indicating that the product is diamagnetic due presumbly to the formaiton of dimer. This is in striking contrast with the substitution reactions of the $Co(CO)_3L_2$ with phosphines.[9]

From these results, we could draw three salient aspects:

a) 19-electron complex of a stable $Re(CO)_4L_2$ can be obtained *via* a homolytic splitting of the metal-metal bond, although it is difficult to obtain the radical complex under a mild condition.
b) The unpaired electron essentially resides on the ligand.
c) The radical complex is substitutionally unstable, decomposing to the formation of dimer.

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Reactions of α,β-Dinitroolefins with *p*-Toluenethiol

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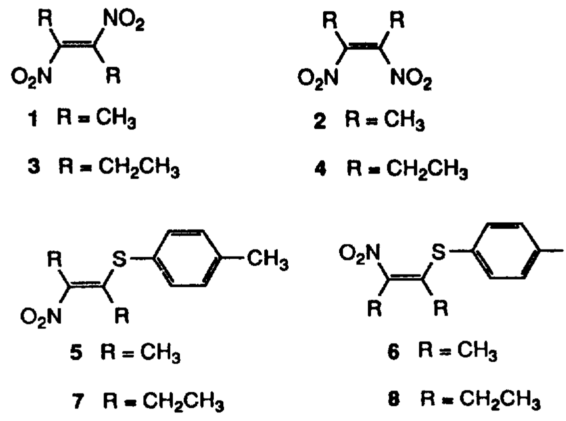
α,β-Dinitroolefins as a group of compounds have not been extensively investigated though they have been known for more than 30 years. They are generally synthesized by three synthetic routes: 1) dimerization of germinal halo-nitroalkanes by base,[1] 2) addition of nitrogen tetroxide on acetylene[2], and 3) addition of one mole halogen on disodium salt of vicinal dinitroalkanes[3]. Nitration of acetylene by nitrogen tetroxide produces predominantly *E* dinitroolefins with *Z* isomers as minor components[2]. Dimerization of germinal haloalkanes, on the other hand, was known to produce only *Z* products[1]. However, in this work some *E* isomers were found in the reaction mixture from the previously discarded low boiling fractions[4]. We also found that *E* isomer could be obtained by isomerization of *Z* isomer in the presence of hydrobromic acid or bromine in ethanol[5].

One of the two nitro groups is easily replaced by nucleophiles such as azide[6], ammonia[7], aniline[7] and mercaptans[6] giving furoxans, α-amino-, α-phenylamino-, and α-mercapto-β-nitroolefins. The mechanism of nucleophilic vinylic substitution reactions has drawn some interest for sometimes. One of the major tools to investigate this reaction has been the comparison of configuration of starting olefins and products[8]. Convergence of stereochemistry, meaning the same ratio of *E*/*Z* products or in the extreme case a single product starting from either *E* or *Z* olefin, strongly supports multi-step mechanism.

We have examined a few cases of converged nucleophilic vinylic substitution of α,β-dinitroolefins. *E*- and *Z*-α,β-dinitroolefins separately or combined reacted with ammonia and primary amines as nucleophiles to yield single products. A few α-amino-β-nitroolefins were synthesized from either *E*- and *Z*-α,β-dinitroolefins and their *Z* configuration were deduced through spectral interpretation[9]. This configuration is the only one known for this type of compound. On the other hand, either *E*-(**3**) or *Z*-3,4-dinitro-3-hexene(**4**) was reacted with *p*-toluenethiol to produced the mixture of *E*-(**7**)



Scheme

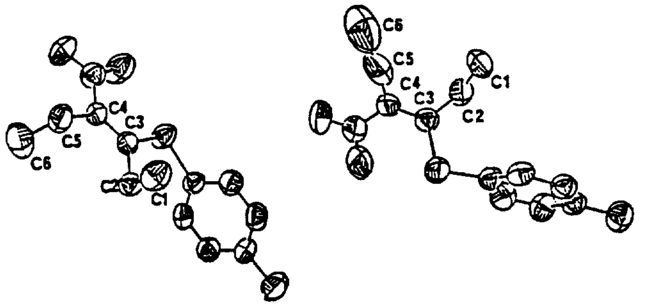


Figure 1. An ORTEP diagram of Z-3-*p*-toluenethio-4-nitro-3-hexene (**8**).

and *Z*-3-*p*-toluenethio-4-nitro-3-hexene(**8**). (Scheme)

Previously, Emmons and Freeman conducted similar reaction but did not isolate the primary product, instead they further oxidized it to sulfone which was presumed to be *E* configuration due to steric consideration but the configuration assigned is apparently in error[10]. Experiments were conducted by adding sodium carbonate (1.59g, 15 mmol) and *p*-toluenethiol(1.86g, 15 mmol) to *E* or *Z*-α,β-dinitroolefins (10 mmol) in 10 m*l* ethanol. The reaction mixture was stirred at room temperature. In a few minutes the starting material was completely consumed. From this reaction mixture, we were able to isolate both products by chromatography. The *Z* isomer was yellow crystalline solid whose structure was identified by spectroscopy[11] and X-ray crystallography[12,13] (Figure 1). It was oxidized further to its corresponding sulfone that Emmons and Freeman isolated and presumed to be *E* configuration[10]. The *E* isomer was an oil eluted before *Z* isomer in column chromatography with silica gel and completely characterized[14]. The ratio of *E* to *Z* isomer as the reactions product in ^{1}H NMR was determined to be 2:3 by comparision of the integration of separated peaks for methylene protons at C-2 and methyl protons attached to benzene ring irrespective of starting configuration. In the same manner each of *E*- and *Z*-isomers of 2,3-dinitro-2-butene(**1,2**) were reacted with *p*-toluenethiol to yield a mixture of *E* and *Z* isomers of 2-*p*-toluenethio-3-nitro-2-butene(**5,6**) in 1:3 ratio by comparision of methyl peaks of *E* and *Z* isomers of products in ^{1}H NMR[15].

This observation can be explained by the stepwise process of addition-elimination mechanism. Obviously the intermediate in the case of thiol is not efficiently stabilized as in those of amine where hydrogen bonding between nitrogen of amine and oxygen of nitro group exists in the transition state leading to a single *Z* product. Further study of vinylic substitution reactions of α,β-dinitroolefins with several different nucleophiles to clarify the mechanism is in progress.

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4. E-1,2-dinitro-2-butene(yield 18%) ^{1}H NMR (CCl$_4$) 2.40(s); IR 2924, 1545, 1443, 1383, 1128 cm^{-1}; Z-1,2-dinitro-2-butene(yield 46%) ^{1}H NMR(CCl$_4$) 2.47(s); IR 2896, 1682 1548, 1435, 1391 cm^{-1}; E-3,4-dinitro-3-hexene (yield 14%) ^{1}H NMR(CCl$_4$) 1.16(t, J=7.2Hz, 6H), 2.54(q, J=7.2Hz, 4H); IR 2986, 1545, 1461, 1438, 1352, 1273, 1119, 1062, 962, 929, 807 cm^{-1}; MS, *m/z* (relative intensity), 174(13, M$^+$), 81(241), 79(167), 77(78), 67(214), 65(112); Z-3,4-dinitro-3-hexene(yield 42%), ^{1}H NMR(CCl$_4$) 1.24(t, J=7.2Hz, 6H), 2.66(q, J=7.2Hz, 4H); IR 2987, 1667, 1544, 1461, 1429, 1362, 1273, 1202, 1120, 1063, 967, 903, 816 cm^{-1}; MS, *m/z* (relative intensity), 174(15, M$^+$), 81(500), 79(482), 77(128), 67(282), 65(169).
5. Isomerization of E and Z isomers of α,β-dinitroolefins was tried by using several different acids and salts in various solvents. Only hydrobromic acid or bromine in ethanol could isomerize either E or Z-dinitroolefins to the mixture of E and Z by 1:1 ratio. The mechanism of this isomerization is not clear at this moment.
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11. m.p. 56-58 °C, ^{1}H NMR(CDCl$_3$); 0.97(t, J=7.3Hz, 3H, H-1), 1.15(t, J=7.3Hz, 3H, H-6), 2.24(q, J=7.3Hz, 2H, H-5), 2.40(s, 3H, methyl), 2.72(q, J=7.3Hz, 2H, H-2), 7.27(d, J=7.8Hz, 2H), 7.41(d, J=7.8Hz, 2H); IR 1561, 1294 cm^{-1}; MS, *m/z*(relative intensity) 251(60, M$^+$), 221(67), 177(31), 163(100), 123(31), 119(50), 79(93).
12. Crystal data for 8: Monoclinic, space group P2$_1$/a, with a = 13.756Å, b = 9.310Å, C = 14.284Å, $\alpha = \gamma = 90°$, $\beta = 94.97°$. Data collected at 20 °C on a Nicolet R 3m diffractometer with MoK radiation. One asymmetric unit contains two independent molecules.

13. Work done by Prof. C. T. Ahn, Hankuk Univ. of Foreign Studies, Seoul, Korea.
14. ^{1}H NMR($CDCl_3$) 1.04(t, J = 7.3 Hz, 3H, H-1), 1.15(t, J = 7.3Hz, 3H, H-6), 2.24(q, J = 7.3Hz, 2H, H-5), 2.36(s, 3H, methyl), 2.89(q, J = 7.3Hz, 2H, H-2), 7.15(d, J = 7.8Hz, 2H), 7.26(d, J = 7.8Hz, 2H); IR 1501, 1313 cm^{-1}; MS, *m/z*(relative intensity), 251(84, M^+), 221(80), 177(35), 163(100), 123(32), 119(43), 79(64).
15. ^{1}H NMR($CDCl_3$) for E-2-*p*-toluenethio-3-nitro-2-butene, 2.04(s, 3H, methyl) 2.30(s, 3H, methyl), 2.39(s, 3H, methyl), 7.20(d, J = 8Hz, 2H), 7.36(d, J = 8Hz, 2H); for Z-2-*p*-toluenethio-3-nitro-2-butene, 1.91(s, 3H, methyl), 2.32(s, 3H, methyl), 2.39(s, 3H, methyl), 7.18(d, J = 8Hz, 2H), 7.42(d, J = 8Hz, 2H).

The Effect of Polarizability on Reactivity

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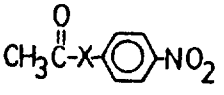
As many as 17 factors have been suggested to be important in influencing nucleophilic reactivity,[1] and numerous relationships have been established to correlate nucleophilicity with one or more properties of the nucleophiles.[2] Polarizability has also been recognized as an important factors in determining nucleophilicity[3]. The best known description based on polarizability is Pearson's concept of hard and soft acids and bases, the so-called HSAB principle.[4]

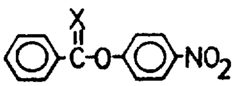
The discovery that acylated coenzyme A, an intermediate in many biochemical reactions, is a thiol ester has accelerated the kinetic and spectroscopic investigations of thiol esters.[5] However, thionesters have not been studied intensively yet, largely due to their inaccessibility.[6] Recently the development of synthetic methods for the thiocarbonyl compounds has encouraged their systematic investigation.[7]

The replacement of oxygen atom by sulfur either in the carbonyl oxygen or in the ether-like oxygen in carboxylic esters has been reported to cause a significant increase in polarizability of the reaction center, and consequently to cause great differences in reactivity.[8] Although scattered information on the effect of polarizability on reactivity is available,[9,10] systematic studies have been lacking.

Thus we have prepared the following 4 esters (I, II, III, and IV) and performed kinetic studies of these esters with various nucleophiles of different nucleophilic atoms. Such a systematic change in the structure has been suggested to cause a significant difference in polarizability of the reaction center.[8] Thus any reactivity change upon the systematic structural change would be interpreted as an effect of polarizability on reactivity.



I: X = O, PNPA (*p*-nitrophenyl acetate)
II: X = S, PNTPA (*p*-nitrothiophenyl acetate)



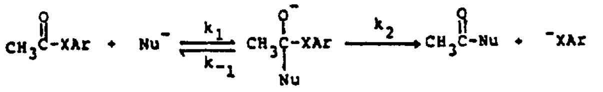
III: X = O, PNPB (*p*-nitrophenyl benzoate)
IV: X = S, PNPTB (*p*-nitrophenyl thionbenzoate)

Table 1. The second order rate constants (k, $M^{-1}s^{-1}$) for the reactions of the esters (I, II, III, and IV) with various types of nucleophiles at 25.0 °C

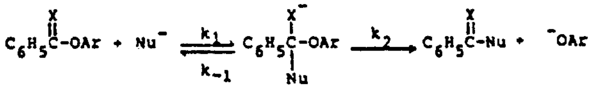
Nu^-	pKa (NuH)[a]	k, $M^{-1}s^{-1}$			
		I	II	III[d]	IV[d]
N_3^-	4.0	0.0342	0.853	0.00288	10.1
CN^-	9.3	0.164	0.174	0.0698	0.0852
p-ClPhO$^-$	9.38	0.683[b]	3.27[b]	0.144	2.20
PhO$^-$	9.95	0.967[b]	3.77[b]	0.303	2.30
OH^-	15.7	12.0	6.01	6.3 1.45[c]	0.71 0.172[c]
p-ClPhS$^-$	7.50	0.143	42.7	0.02-0.03[e]	342
PhS$^-$	7.80	0.36[b]	36[b]		

[a] reference 13. [b] reference 9. [c] reference 10(a). [d] The reactions for III and IV were performed in 10 mole % DMSO-H_2O mixture due to a solubility problem. [e] A large error might be expected due to a long reaction time which caused the oxidation of thiophenoxide to disulfide.

In Table 1 is presented a summary of the second-order rate constants for the nucleophilic substitution reactions, as shown in the following equation 1 and 2. The reaction mechanism of the present system has generally been suggested as a two-step reaction, *i.e.* the formation of a tetrahedral intermediate followed by the breakdown of it.[2b-c,9,10]



$$\mathrm{CH_3\overset{O}{\overset{\|}{C}}-XAr} + \mathrm{Nu^-} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{CH_3\underset{\underset{Nu}{|}}{\overset{\overset{O^-}{|}}{C}}-XAr} \xrightarrow{k_2} \mathrm{CH_3\overset{O}{\overset{\|}{C}}-Nu} + \mathrm{{}^-XAr} \quad (1)$$



$$\mathrm{C_6H_5\overset{X}{\overset{\|}{C}}-OAr} + \mathrm{Nu^-} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{C_6H_5\underset{\underset{Nu}{|}}{\overset{\overset{X^-}{|}}{C}}-OAr} \xrightarrow{k_2} \mathrm{C_6H_5\overset{X}{\overset{\|}{C}}-Nu} + \mathrm{{}^-OAr} \quad (2)$$

It is clearly demonstrated in Table 1 that the effect of polarizability on the substrate reactivity is strongly dependent on the polarizability of nucleophiles. The reactivity of the sulfur containing substrates toward HO^- ion is decreased by two to ten folds when the substrate changes from I to II and from III to IV, respectively. On the contrary, the thiol