about 13 kcal/mole (the resonance energy of the allylic radical[3e]), thus leading to a predicted and observed activation energy for formation of an intermediate in the vinylcyclopropane isomerization of 50 kcal/mole. The diradical can cause geometrical isomerization of the deuterium label just as it does in cyclopropane. In addition this diradical can by redistribution of electrons and slight movement of some carbon and hydrogen nuclei rearrange to cyclopentene. We propose this scheme as a logically structured, and presently acceptable, mechanism. However, we would also point out that an alternative scheme that would consider cyclopentene formation and geometrical isomerization to be in separate energy manifolds is only so slightly different both conceptually and experimentally from the diradical mechanism that we cannot discount it without further, and more subtle, experiments.[8]

Acknowledgment. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

---

(8) A suggestion that this alternative explanation may be quite reasonable is provided by Hoffmann's calculations of the stereochemical course of the closure of trimethylene diradicals,[9] Crawford's observations on the behavior of these diradicals generated from pyrazoline pyrolysis,[10] and Rabinovitch, Setser, and Wiberg's expanded ring model for cyclopropane isomerization.[6a,7]

(9) R. Hoffmann, Abstracts of the 151st National Meeting of the American Chemical Society, Pittsburgh, Pa., March 1966, Paper 109K.

(10) R. J. Crawford and A. Mischra, *J. Am. Chem. Soc.*, **88**, 3963 (1966).

M. Robert Willcott, Virgil H. Cargle
Department of Chemistry, University of Houston
Houston, Texas 77004

Received October 31, 1966

Five-Coordinate Copper(II) in [Cu(tren)(NCS)](SCN)

Sir:

Raymond and Basolo[1] have recently reported the preparation of [Cu(tren)(NCS)](SCN)[2] and have suggested that one thiocyanate ion is coordinated to the copper(II) ion through the nitrogen atom and the other through the sulfur atom, in a *cis*-octahedral complex. Their conclusion was based upon two observations. First, the appearance of two C–N frequencies at 2094 and 2060 cm^{-1} and two C–S frequencies at 818 and 745 cm^{-1} in the infrared spectrum suggested that one thiocyanate is bonded to copper through the nitrogen atom and the other is either bonded through the sulfur atom or not coordinated to copper. Secondly, the similarity in cell dimensions and identity of space group of the crystalline copper and nickel compounds suggested that the two molecules have the same configuration, and Rasmussen[3] has shown $Ni(tren)(NCS)_2$ to have a *cis*-octahedral configuration.

Table I. Bond Lengths (in Angstroms) and Angles (in Degrees)

Cu–N(1)	2.04	N(1)–Cu–N(2)	84
Cu–N(2)	2.07	N(1)–Cu–N(3)	85
Cu–N(3)	2.16	N(1)–Cu–N(4)	85
Cu–N(4)	2.06	N(5)–Cu–N(2)	95
Cu–N(5)	1.95	N(5)–Cu–N(3)	98
		N(5)–Cu–N(4)	94
		N(1)–Cu–N(5)	177
		N(2)–Cu–N(3)	114
		N(2)–Cu–N(4)	130
		N(3)–Cu–N(4)	113

Professor Basolo kindly furnished us a sample of [Cu(tren)(NCS)](SCN), and we have determined its crystal structure. The cell has dimensions $a = 9.16$, $b = 14.00$, $c = 11.29$ A and contains four molecules. Systematic absence of $h00$, $0k0$, and $00l$ with odd indices indicates the space group $P2_12_12_1$. (The cell dimensions for the nickel compound are $a = 8.62$, $b = 14.72$, $c = 10.82$ A, and its space group is also $P2_12_12_1$.) Three-dimensional X-ray diffraction intensities were collected on a Picker single-crystal diffractometer with Mo Kα radiation, out to a limit of $2\theta = 55°$. The positions of the copper atoms were determined from a sharpened Patterson synthesis, and the other atoms were found in a series of Fourier syntheses. The structure has been refined by full-matrix least squares, with isotropic temperature factors and without introduction of hydrogen atoms, to a value of $R = 0.08$. The refinement is being continued and the final results will be published later.

The copper ion is surrounded by five nitrogen atoms from the tren molecule and one thiocyanate ion, in a somewhat distorted trigonal bipyramid, with the tertiary nitrogen atom, N(1), and the thiocyanate nitrogen atom, N(5), at the apices, and the three primary nitrogen atoms, N(2), N(3), N(4), in the equatorial positions. Bond lengths and angles in the coordination polyhedron are given in Table I. The nitrogen atom, N(6), of the second thiocyanate ion lies at a distance of 3.84 A from the copper ion in the equatorial plane of the trigonal bipyramid, near the bisector of the N(2)–Cu–N(3) angle. The Cu–N(6)–S(2) angle is 96°, bringing the S(2) atom to 3.7 A from N(3) but more than 5 A from Cu. The S(2) atom from another thiocyanate ion is 4.57 A from the copper ion, and this is the shortest Cu–S distance in the crystal. Thus the second thiocyanate ion is not coordinated to the copper ion.

The apparently reasonable, but incorrect, conclusions of Raymond and Basolo regarding the structure of [Cu(tren)(NCS)](SCN) illustrate the danger of drawing structural conclusions from comparisons of cell dimensions and the space group of crystals.

Acknowledgment. This work was supported in part by a grant from the National Science Foundation.

---

(1) K. N. Raymond and F. Basolo, *Inorg. Chem.*, **5**, 1632 (1966).

(2) tren = $N(CH_2CH_2NH_2)_3$.

(3) S. E. Rasmussen, *Acta Chem. Scand.*, 13, 2009 (1959).

Prem C. Jain, E. C. Lingafelter
Department of Chemistry, University of Washington
Seattle, Washington 98105

Received December 1, 1966

Arylation by Aromatic Nitro Compounds at High Temperatures

Sir:

Since Berthelot in 1887 established the explosiveness of nitroaromatics at high temperatures,[1] there has been an understandable reluctance on the part of chemists to study the reactions of these derivatives at 400° and higher. What scant literature exists is concerned with determination of safe temperature limits, *e.g.*, for hydrogenation of nitroxylenes to xylidines.[2]

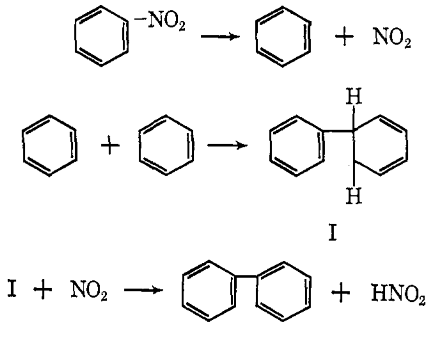
---

(1) M. Berthelot, *Compt. Rend.*, **105**, 1159 (1887).

(2) R. L. Datta and N. R. Chatterjee, *J. Chem. Soc.*, **115**, 1006 (1919); C. L. Brown, W. M. Smith, and W. G. Scharmann, *Ind. Eng. Chem.*, **40**, 1538 (1948); P. C. Condit and R. L. Haynor, *ibid.*, **41**, 1700 (1949).

We have discovered a new method for arylating aromatic compounds and heterocyclic compounds of aromatic character. This consists of heating mixtures of nitroaromatics and aromatics at 400–600° in a flow reactor for 2–30 sec. In a typical reaction, a mixture of 5.11 ml (0.05 mole) of nitrobenzene and 22.23 ml (0.25 mole) of benzene was passed through a Vycor tube filled with Vycor chips at 600° under dry nitrogen flowing at 45 cc/min, with a contact time of 9 sec. The vapors were condensed in a bulb at −60°. The condensate was distilled to recover 15.3 ml of benzene and give 8.8 g of product, which consisted of 62% biphenyl and 13.9% terphenyl.[3] Combined yield of biphenyl and terphenyl was 85 mole %. Under identical conditions the same amount of benzene alone gave 0.3 g of product, consisting of 90% biphenyl and 8% terphenyl.

The reaction of nitrobenzene with benzene, run under helium to determine the fate of the nitro group, indicated the course.[4]



$$2HNO_2 \longrightarrow H_2O + N_2O_3$$

The free-radical nature of the reaction was further shown by phenylation of pyridine with nitrobenzene at 600° in 72% yield. Isomer distribution, determined by gas chromatography, was (isomer, %): 2-, 63.6; 3-, 26.3; 4-, 10.1. This distribution is similar to that obtained at 80° by attack of phenyl radicals from the decomposition of benzoyl peroxide on pyridine (isomer, %): 2-, 58; 3-, 26; and 4-, 14.[5]

With thiophene, nitrobenzene (1:5 mole ratio) gave a 60 mole % yield of phenylthiophenes, of which 75% was 2-phenylthiophene and 25% 3-phenylthiophene.[6] Phenylation of thiophene with benzoyl peroxide and three other phenyl radical precursors has likewise led predominantly to 2-phenylthiophene, although the ratios varied over a wide range; the best yield of phenylthiophenes was only 3.75%.[7] The nitrobenzene reaction also gave 3.6 and 0.24%, respectively, of diphenylthiophene and triphenylthiophene or isomers (available data do not differentiate between further phenyl substitution on the phenyl and thienyl rings).

Aromatic compounds containing more than one nitro group can also be used as arylating agents; this greatly increases the versatility of the reaction. Thus, *m*-dinitrobenzene with benzene (1:10 mole ratio) at 450° gave a mixture (40% yield) of 3-nitrobiphenyl and *m*-terphenyl in the ratio 7:1. With increasing temperature at the same contact time (16 sec) this ratio decreased, and at 600° the ratio of the two products was 1:2. At 28-sec contact time and 600° no nitrobiphenyl survived, and *m*-terphenyl was the major product (37%).

Trinitrobenzene behaved similarly in its reaction with benzene at 450–600°. It gave the three products triphenylbenzene, nitroterphenyl, and dinitrobiphenyl in varying ratios that depended upon the temperatures and contact times.

This new reaction appears to be of wide scope and considerable synthetic utility. It has many advantages over present methods of generating free aryl radicals by thermal decomposition of aroyl peroxides[8] or photolysis of aryl iodides;[9] a great variety of nitroaromatics are readily and abundantly available, or easily made. Thus, for example, arylations have been achieved by such diverse nitroaromatics as 1-nitronaphthalene, *m*-nitrobenzotrifluoride, methyl *p*-nitrobenzoate, and 4-nitro-*o*-phenylenediamine. We are presently studying application of our new method in preparing many compounds hitherto unknown or difficult to make by conventional syntheses.

---

(3) Small amounts of phenol and naphthalene among the products from the reaction of nitrobenzene with benzene suggest parallels between the thermal processes and those occurring under electron impact. *Cf.* S. Meyerson, I. Puskas, and E. K. Fields, *J. Am. Chem. Soc.*, **88**, 4974 (1966). Such parallel behavior has been demonstrated in other systems: E. K. Fields and S. Meyerson, *Chem. Commun.*, 474 (1965); 275 (1966); *J. Org. Chem.*, **30**, 937 (1965); **31**, 3307 (1966); *J. Am. Chem. Soc.*, **88**, 2836 (1966); R. F. C. Brown and R. K. Solly, *Australian J. Chem.*, **19**, 1045 (1966); M. P. Cava, M. J. Mitchell, D. C. DeJongh, and R. Y. Van Fossen, *Tetrahedron Letters*, 2947 (1966).

(4) For the structure of nitrous acid in the gas phase and its dissociation products, see A. P. Cox and R. L. Kuczowski, *J. Am. Chem. Soc.*, **88**, 5071 (1966), and references cited therein.

(5) D. H. Hey and G. H. Williams, *Discussions Faraday Soc.*, **14**, 216 (1953); R. L. Dannley, E. C. Gregg, Jr., R. E. Phelps, and C. B. Coleman, *J. Am. Chem. Soc.*, **76**, 445 (1954); R. L. Dannley and E. C. Gregg, Jr., *ibid.*, **76**, 2997 (1954).

(6) Authentic 2- and 3-phenylthiophenes for standards in gas chromatographic analysis of the arylation products were synthesized according to J. L. Melles and H. S. Backer, *Rec. Trav. Chim.*, **72**, 325, 491 (1953).

(7) C. E. Griffin and K. R. Martin, *Chem. Commun.*, 154 (1965).

(8) G. H. Williams, "Homolytic Aromatic Substitutions," Pergamon Press, New York, N. Y., 1960, Chapter 3.

(9) W. Wolf and N. Kharasch, *J. Org. Chem.*, **26**, 283 (1961).

Ellis K. Fields
Research and Development Department
Amoco Chemicals Corporation, Whiting, Indiana
Seymour Meyerson
Research and Development Department
American Oil Company, Whiting, Indiana

Received December 27, 1966

New and Facile Substitution Reactions at Tertiary Carbon

Sir:

Few, if any, authentic SN2 displacements involving tertiary halides are known.[1] Instead, tertiary halides usually undergo substitution *via* the carbonium ion mechanism.

We wish to report a new type of substitution at tertiary carbon which is described by eq 1; a variety of anions are effective.

For example, the reaction of *p*-nitrocumyl chloride (I) with sodium thiophenoxide in DMF solution at 0° is complete in 2 hr and produces the pure tertiary sulfide II ($A = SC_6H_5$)[2] in 95% yield. That this result does not derive from an elimination reaction

---

(1) For example, the alleged SN2 Finkelstein substitutions of *t*-butyl bromide have been shown to be spurious by S. Winstein, S. Smith, and D. Darwish, *Tetrahedron Letters*, **16**, 24 (1959). See, however, U. Miotti and A. Fava, *J. Am. Chem. Soc.*, **88**, 4274 (1966).

(2) Satisfactory elemental analyses have been obtained for all new compounds and all structures have been confirmed by nmr.