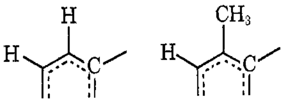
tons. On weak irradiation of the ring protons, each half of the doublet becomes a septet (J = 4.25 Hz) from the vicinal coupling to two adjacent methyl groups.

Discussion

Karabatsos and coworkers[16] have extended the valence-bond treatment of geminal proton–proton couplings[17] to geminal carbon–proton couplings. Such comparisons explain many trends in geminal and vicinal carbon–proton coupling in benzene[8] and the five-membered nitrogen heterocycles[9] if proper models are chosen. Some models and predicted and observed coupling constants are given in Table III. Although the quantitative agreement with Karabatsos' theory is best for benzene, the qualitative trends are correctly predicted throughout the heterocyclic series.

Vicinal carbon–proton couplings across a methyl group are approximately 0.9 times the corresponding couplings in compounds without the methyl. The ratio is the same as for the trans proton–proton couplings in ethylene (19.1 Hz)[18] and propene (16.8 Hz).[19]



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[16] G. J. Karabatsos, F. D. Graham, and F. M. Vane, *J. Amer. Chem. Soc.*, **84**, 37 (1962).

[17] H. S. Gutowsky, M. Karplus, and D. M. Grant, *J. Chem. Phys.*, **31**, 2278 (1959).

[18] R. M. Lynden-Bell, *Mol. Phys.*, **6**, 537 (1963).

[19] A. A. Bothner-By and C. Naar-Colin, *J. Amer. Chem. Soc.*, **83**, 231 (1961).

The Synthesis of Aryl Isocyanates from Nitro Compounds and Carbon Monoxide

F. J. WEIGERT

Contribution No. 1963 from the Central Research Department,
E. I. du Pont de Nemours and Company, Wilmington, Delaware 19898

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The $PdCl_2$-catalyzed reaction of nitrobenzenes and the thermal reaction of phenyl azides with CO show similar variations of isocyanate yields with pressure and similar by-products. The by-products from 4-fluoronitrobenzene, diphenylurea, triphenylbiuret, and an imidazolinone **3a** may arise from proton abstraction from a nitrene-like intermediate. Labelling of a phenyl with a 4-fluorine gives convenient quantitative analysis of crude reaction mixtures, but is unreliable as a single method for qualitative analysis.

The formation of phenyl isocyanate from nitrobenzene[1] or phenyl azide[2] and carbon monoxide in the presence of $PdCl_2$ is of both academic and practical interest.[3] The only by-products described have been diphenylurea and azobenzene, and the urea has been presumed to arise from reaction of the isocyanate with water.[1] The results presented here suggest that side reactions of nitrene-like intermediates are responsible for the by-products.[4]

$$ArNO_2 + 3CO \xrightarrow{PdCl_2} ArNCO + 2CO_2$$

Results

Over the range of 50–600 atm, the yield of 4-chlorophenyl isocyanate increases linearly with the square root of pressure (Table I). Yields are independent of temperature or palladium concentration (Table II). High pressure slows the reaction, but on extended heating the yield improvement is maintained.

The diphenylurea from pentadeuterionitrobenzene gave after sublimation infrared bands which were attributed to nitrogen–deuterium stretching vibrations.

An extensive study was made using 4-fluoronitrobenzene as substrate because ^{19}F nmr provided convenient analyses of the crude reaction mixtures. First, however, the various by-products were individually isolated by column chromatography over neutral SilicAR. In order of elution, the by-products isolated were 4,4-difluoroazobenzene, an imidazolinone **3a** discussed in detail below, 1,3,5-tris(4-fluorophenyl)biuret, and 1,3-bis(4-fluorophenyl)urea.

TABLE I

EFFECT OF CO PRESSURE ON THE REACTION OF 4-CHLORONITROBENZENE WITH CO[a]

CO, atm[b]	Time, hr	Conversion of $ArNO_2$, %	Yield of ArNCO, %
20	2	53[c]	7
75	2	97	13
150	2	90	35
300	2	97	46
600	2	30	72
600	4	97	68

[a] Charge: 4-chloronitrobenzene (5 mmol) in 2 ml of CH_3CN solution, NO_2/Pd ratio 5000/1. Run at 250° in 9-ml bomb. [b] At 25°. [c] Insufficient CO is present to react with all the nitrobenzene present.

TABLE II

EFFECT OF REACTION VARIABLES ON ISOCYANATE YIELD[a]

CO, atm[b]	Temp, °C	Time, hr[c]	$ArNO_2$/Pd	Yield of ArNCO, %
100	225	10	10,000	15
100	275	1	10,000	10
300	200	2	200	45
300	250	2	200	46
400	225	15	10,000	44
400	275	2	10,000	50

[a] Charge: 5 mmol of 4-chloronitrobenzene + $PdCl_2$ in 2 ml of CH_3CN solution in 9-ml bomb. [b] At 25°. [c] The time is adjusted to give 100% conversion of nitrobenzene.

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[1] W. B. Hardy and R. P. Bennett, *Tetrahedron Lett.*, 961 (1967).

[2] R. P. Bennett and W. B. Hardy, *J. Amer. Chem. Soc.*, **90**, 3295 (1968).

[3] W. W. Prichard, U. S. Patent 3,576,836 to Du Pont; G. F. Ottmann, E. H. Kober, and D. F. Gavin, U. S. Patent 3,523,962 to Olin Matheson; W. B. Hardy and R. P. Bennett, U. S. Patent 3,461,149 to American Cyanamide.

[4] Similar conclusions have been advanced by F. L'Eplattenier, P. Matthys, and F. Calderazzo, *Inorg. Chem.*, **9**, 343 (1970), for the Ru-catalyzed reaction.

All except the imidazolinone were positively identified by comparison with samples prepared independently. Because identification of **3a** was difficult, the structure proof is presented in some detail.

Elemental analysis and high-resolution mass spectroscopy of **3a** gave the empirical formula $C_{20}H_{12}F_3N_3O_2$, or three phenyl nitrenes and two CO's. The infrared spectrum (Figure 1) showed an NH band at 3.12 μ and unusual carbonyl absorptions at 5.70 and 5.86 μ, which were assigned to an imide linkage. The ultraviolet spectrum showed typical benzenoid absorption at 242 nm (ϵ 32,900) with shoulders at 283 nm (ϵ 6670) and 288 (5630). The most significant feature of the 220-MHz pmr spectrum (Figure 2) was the doublet of doublets (J = 9, 5 Hz) at δ 8.21. The proton-decoupled ^{19}F nmr spectrum in CH_3CN showed three equal-intensity singlets at −112.8, −117.1, and −118.1 ppm.[5] With no proton decoupling, the resonance at −117 ppm was a doublet (J = 5 Hz) of triplets (J = 9 Hz) while the other two were triplets of triplets with the same splittings.

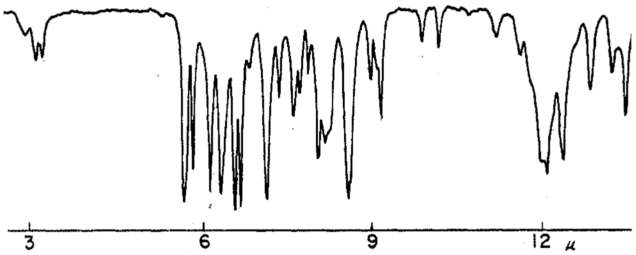


Figure 1.—Infrared spectrum of imidazolinone **3a**.

Reaction of **3a** with aqueous or ethanolic base at 80° caused loss of ArNCO rather than hydrolysis.

The infrared imide band was replaced by an amide band at 5.83 μ and the ^{19}F nmr spectrum showed two equal-intensity peaks at −114.3 and −121.6 ppm. The 220-MHz pmr spectrum showed a triplet (J = 9 Hz) and a doublet of doublets (J = 9, 5 Hz), 2 H each, attributed to a phenyl ring with para substituents, one of which is fluorine, and three single-intensity resonances assigned to a trisubstituted benzene ring. The low-field doublet of doublets in **3a** disappeared. The structure of the pyrolysis product, imidazolinone **2a**, is suggested by the general similarity of the high-frequency portion of its infrared spectrum to that of the unfluorinated material **2b** prepared from N-phenyl-o-phenylenediamine and phosgene, and the ^{19}F nmr spectrum.

On paper, inserting an aryl isocyanate back into imidazolinone **2** generates several alternate structures. Hydrazo compounds are eliminated by the ^{19}F nmr spectrum,[5] leaving **1** and **3** as plausible alternatives.

Chromatography of the by-products from nitrobenzene and CO gave analogous products but in different ratios. The imidazolinone **3b** was present in ~1% yield, while diphenylurea was the major by-product. The imidazolinone **3b** was identical with a sample prepared by $SnCl_4$-promoted condensation of **2b** with phenyl isocyanate. An isomeric product was obtained from the reaction of N-phenyl-o-phenylenediamine and phenyl isocyanate and was assigned the triazepinedione structure **1b**. Imidazolinone **3b** shows a low-field pmr resonance in CH_3CN solution, while triazepinedione **1b** shows no such resonance.

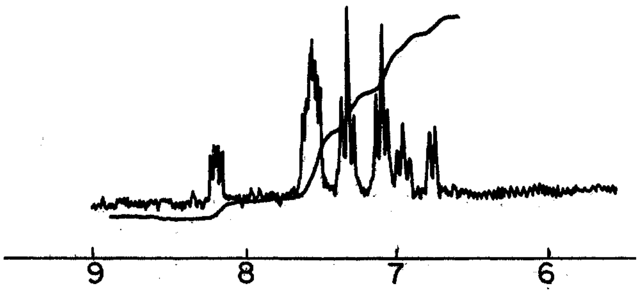
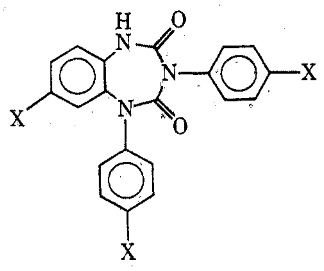
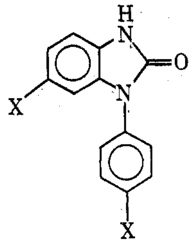


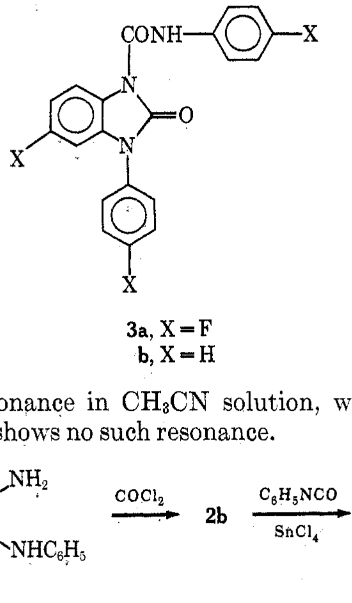
Figure 2.—220-MHz nmr spectrum of imidazolinone **3a**.



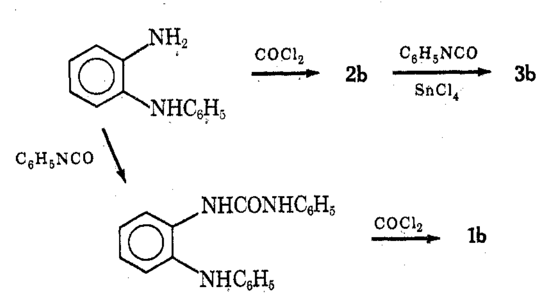
1a, X = F
b, X = H



2a, X = F
b, X = H



3a, X = F
b, X = H



Nitrenes, which are likely intermediates in these reactions,[2,4] are unambiguously produced by the thermolysis of aryl azides.[6] The yield of isocyanate from 4-fluorophenyl azide and CO increases with pressure; however, even at the highest pressure used, significant yield losses to urea and imidazolinone occurred (Table III). The product distributions from both nitrobenzenes and azides show similar pressure variations.

Discussion

Isolation of heptadeuterioaniline from the thermolysis of pentadeuteriophenyl azide suggested that the pro-

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(5) F. J. Weigert and W. A. Sheppard; the fluorine nmr studies of the model compounds used to identify the environment of these resonance will be published separately.

(6) P. A. S. Smith and J. H. Hall, *J. Amer. Chem. Soc.*, **84**, 480 (1962).

TABLE III
PRODUCT DISTRIBUTION FROM THE THERMAL DECOMPOSITION OF 4-FLUOROPHENYL AZIDE IN A CO ATMOSPHERE[a]

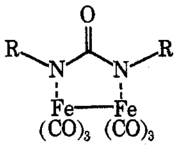
CO pressure, atm[b]	Isocyanate yield (gc), %	By-products yield (nmr), %		
		Azobenzene	Urea	**3a**
25	0	(7)[c]	(12)[c]	0
50	16			
100	30	10	25	6
200	50	0	10	15
300	60			
400	78	0	8	14

[a] 180°/1 hr, 133 mg azide, 1.5 ml CH_3CN, 0.5 g *o*-$C_6H_4Cl_2$. [b] Pressure at 25°. [c] Relative yields only; absolute yields very low.

tons attached to the nitrogen came from ring abstraction.[7] In the presence of isocyanate, any aniline

$$C_6D_5N_3 \longrightarrow C_6D_6N \longrightarrow C_6D_5ND_2$$

formed would be converted to urea. Pyrolysis of phenyl azide with iron carbonyl gave a product **4** which



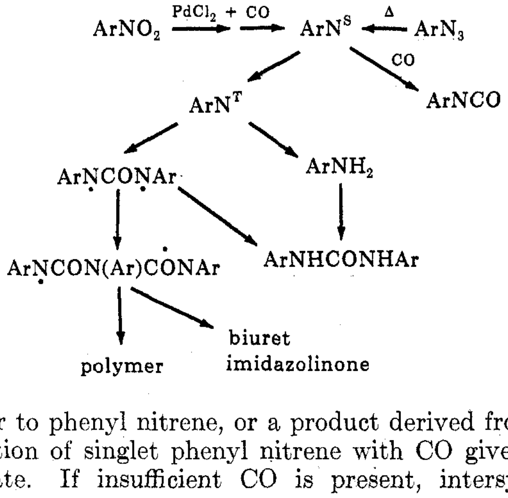
4

formally is the result of trapping the diradical of diphenylurea.[8] Proton abstraction by a similar species could also lead to urea. The biuret may result from the reaction of urea with more isocyanate, or by proton abstraction of a diradical analogous to **4**.

Isocyanate may be formed from singlet nitrene and singlet CO, while a triplet nitrene would abstract hydrogen.[9] Because the nitrene ground state is the triplet,[10] CO must intercept the initially formed excited singlet state; hence the high pressure required for efficient isocyanate formation.

Chart I suggests a mechanism to account for the products of this reaction. Azobenzene may be a precursor to phenyl nitrene, or a product derived from it. Reaction of singlet phenyl nitrene with CO gives isocyanate. If insufficient CO is present, intersystem crossing occurs, giving the triplet which can abstract protons to give aniline or react with isocyanate to give a diradical which can abstract protons to form urea or add another isocyanate to give a second diradical. This diradical can abstract protons to give biuret or cyclize to give imidazolinone **3**. Proton abstraction from the other terminal ring would have led to triazepinedione **1**. Continued reaction of the diradical with isocyanate leads to polymeric species which are always produced.

CHART I



The product distribution from thermal decomposition of substituted aryl azides varies widely with substituent.[6] Similarly, from nitrobenzene and CO, imidazolinone **3** accounts for 10% of the yield from 4-fluoronitrobenzene, less than 1% from nitrobenzene, and none from 4-chloronitrobenzene.

Chart I is drawn from the viewpoint of the organic chemist. Nowhere is the function of the palladium catalyst illustrated; yet it is vital to the success of the reaction. We have no knowledge of the structure of any possible metal-containing intermediates and do not wish to speculate on this phase of the mechanism, in spite of its importance.

Experimental Section

Proton nmr spectra were determined on Varian A-60 and HR-220 instruments, the latter using Fourier transform techniques. Fluorine nmr spectra were determined on a Varian HA-100 using external oscillators for locking and observing sidebands and proton noise decoupling. Ir spectra were determined on a Perkin-Elmer 21, uv spectra on a Cary 14, and mass spectra on a Du Pont CEC-21-110B. Melting points are uncorrected. Gas chromatography was done on a Hewlett-Packard Model 700 operating isothermally at 160° with a 6 ft × 0.25 in. stainless steel column packed with 20% SE-30 (methyl) silicon gum rubber on Chromosorb W. Correction factors for the disc integrator were determined by injecting mixtures with known proportions. Area per cent was directly proportional to mole per cent.

Reactions of Nitrobenzenes and Carbon Monoxide.—In a 10-ml Hastelloy bomb was placed an acetonitrile solution of $(CH_3CN)_2PdCl_2$, nitro compound, and *o*-dichlorobenzene (internal standard for gc). The bomb was pressured at room temperature with carbon monoxide and heated for the desired period. Pressure was vented and the liquid contents were assayed by gc. Residual oxygen in the bomb was consumed during the reaction forming CO_2 and was not detrimental to the catalytic process.

Reaction of 4-Fluorophenyl Azide and CO.—A solution of 4-$FC_6H_4N_3$, *o*-$C_6H_4Cl_2$ (internal standard for GC), and C_6H_5F (internal standard for nmr) in CH_3CN was heated in an atmosphere of CO at 180° for 1 hr. The solution was analyzed for isocyanate by gc and by-products by nmr.

Isolation of By-Products from 4-Fluoronitrobenzene and CO.—In a 200-ml Hastelloy bomb was placed 20 g of 4-$FC_6H_4NO_2$, 20 ml of CH_3CN, and 0.1 g of $PdCl_2$. After evacuation, the bomb was pressured to 150 atm with CO and heated at 250° for 2 hr. The bomb was cooled and vented, and the contents were decanted. The volatile fractions consisting of CH_3CN and 4-FC_6H_4NCO were distilled at room temperature and 0.3 mm. The brown residue was dissolved in THF, preadsorbed on 20 g of SilicAR CC-7, and chromatographed. Pentane eluted a small amount of orange solid (~200 mg) identified by ir and ^{19}F nmr as 4,4′-difluoroazobenzene. Benzene–pentane (1:1) eluted 2 g of imidazolinone **3a**. Benzene eluted a small amount of 1,3,5-tris-(4-fluorophenyl)biuret. Continued elution with methylene chloride, ether, acetone, tetrahydrofuran, and methanol produced dark solids which were 1,3-bis(4-fluorophenyl)urea by ir, ^{19}F nmr, and elemental analyses.

1,3,5-Tris(4-fluorophenyl)biuret.—To 2.0 g of 4-fluorophenyl isocyanate in 50 ml of benzene was added 3.0 g of 4-fluoroaniline. A white precipitate of the urea formed immediately. After 15 min at room temperature, 7.8 g of anhydrous stannic chloride was added, forming more precipitate. 4-Flurophenyl isocyanate (2.1 g) was added and the suspension was stirred for 2 hr under

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[7] J. H. Hall, J. W. Hill, and J. Fargher, 156th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept 8–13, 1968, Paper ORGN 39.

[8] M. Dekker and G. R. Knox, *Chem. Commun.*, 1243 (1967).

[9] J. W. Hall, J. W. Hill, and J. Fargher, *J. Amer. Chem. Soc.*, **90**, 5313 (1968).

[10] E. Wasserman, G. Smolinsky, and W. A. Yager, *ibid.*, **86**, 3166 (1964).

nitrogen. The solid was filtered and addition of petroleum ether (bp 30–60°) gave a second crop. The solid was recrystallized twice from methanol to remove tin salts, giving 3.8 g of biuret as a white solid, mp 175.5–179°. *Anal.* Calcd for $C_{20}H_{14}F_3N_3O_2$: C, 62.4; H, 3.7; N, 11.2. Found: C, 62.1; H, 3.6; N, 10.9. Ir 2.96, 3.16 (NH), 3.25 (=CH), 5.85, 6.02 (C=O), 6.23, 6.45, 6.58, 6.65 (C=C and amide II), ~8 (CF), 11.93, 12.08, 12.36, 12.43 μ (para-disubstituted aromatic); ^{19}F nmr (CH_3CN) −112.8 (1 F), −117.7 (2 F).

7-Fluoro-1-(4-fluorophenyl)-3-(4-fluorophenylcarbamoyl)-2-benzimidazolinone (3a), had mp 201.5–203° (CH_3CN). *Anal.* Calcd for $C_{20}H_{12}F_3N_3O_2$: C, 62.6; H, 3.1; N, 10.9. Found: C, 62.5; H, 3.3; N, 11.1. Uv max (THF) 242 nm (ϵ 32,800), sh 283 (6570), 288 (5620); ir (KBr) 3.12 (NH), 3.23 (CH), 5.70, 5.86 (C=O), 6.16, 6.35, 6.60, 6.75 (C=C and amide II), 12.07 μ (para aromatic); pmr (DMSO) δ 6.79 (d, d, 1, J = 9, 2 Hz), 6.97 (d, t, 1, J = 2, 9 Hz), 7.12 (t, 2, J = 9 Hz), 7.35 (t, 2, J = 9 Hz), 7.57 (m, 4), 8.21 (d, d, 1, J = 9.5 Hz), 10.73 (broad s, NH); ^{19}F nmr (CH_3CN) δ −112.2 (t, t, 1, J = 5, 9 Hz,) −117.1 (d, t, 1, J = 5, 9 Hz), −118.1 (t, t, 1, J = 5, 9 Hz); mass spectrum (calcd for $C_{20}H_{12}F_3N_3O_2$, 383.0881) 383.0885, (calcd for $C_{13}H_8F_2N_2O$, 246.0604) 246.0608, 217.0556 ($C_{12}H_7F_2N_2$), 137 (C_7H_4FNO).

Pyrolysis of Imidazolinone 3a.—A solution of 200 mg of imidazolinone **3a** and 3 ml of a 10% potassium hydroxide solution was refluxed under nitrogen for 2 hr. On cooling a yellow solid formed and was extracted into ether and dried, the ether was removed on a rotary evaporator, and the product was recrystallized from acetonitrile to give 50 mg of white needles, mp 224–225°. *Anal.* (HRMS). Calcd for $C_{13}H_8F_2N_2O$: mol wt, 246. Found: mol wt, 246 (mass spectrum). Ir 3.13, 3.23, 5.83, 6.18, 6.25, 6.60, 6.69, 8–9, 12.04, 12.51 μ; uv (THF) 293 nm (ϵ 7960), 250 (6030); pmr (CH_3CN) δ 6.80 (d, d, 1, J = 9, 2 Hz), 6.85 (d, t, 1, J = 2, 9 Hz), 7.08 (d, 1, J = 9 Hz), 7.32 (t, 2, J = 9 Hz), 7.57 (d, d, 2, J = 9, 5 Hz), 8.8 (broad, 1, NH); ^{19}F nmr (CH_3CN) δ −114.3 (1 F), −121.6 (1 F).

1-Phenyl-2-benzimidazolinone was prepared by the reaction of phosgene with *N*-phenyl-*o*-phenylenediamine.[11]

2-Anilinocarbanilide was prepared by the reaction of phenyl isocyanate with *N*-phenyl-*o*-phenylenediamine.[12]

1,3-Diphenyl-1*H*,3*H*,5*H*-1,3,5-benzotriazepine-2,4-dione (1b).—To 100 ml of phosgene-saturated *o*-dichlorobenzene at 10° was added dropwise a solution of 5 g of 2-anilinocarbanilide in 30 ml of THF. After the addition was complete, the solution was warmed to room temperature, and excess phosgene was allowed to escape. Solvent was removed at reduced pressure, leaving a residue which was recrystallized from DMSO–H_2O, giving 1.3 g of triazepinedione as a white solid, mp 197–200°. *Anal.* Calcd for $C_{20}H_{15}N_3O_2$: C, 72.9; H, 4.6; N, 12.8. Found: C, 73.0; H, 4.7; N, 12.9. Ir 5.88, 6.21, 6.26, 6.66, 6.74 μ; nmr (DMSO-d_6–TMS) δ 11.05 (s, NH), 7.52 (s, 8 H), 7.05 (m, 6 H).

1-Phenyl-3-phenylcarbamoyl-2-benzimidazolinone (3b).—A slurry of 4 g of benzimidazolinone **2b**, 2.5 g of phenyl isocyanate, and 5 g of stannic chloride was heated in a test tube under N_2. The initially formed homogeneous melt deposited a solid. The solid was cooled to room temperature, slurried with CH_3OH, and filtered. Chromatography over neutral SilicAR and elution with 1:1 benzene–pentane gave 1 g of imidazolinone, which was recrystallized from CH_3CN, mp 166–168°. *Anal.* Found: C, 72.95; H, 4.60; N, 12.64. Nmr δ 10.6 (s, NH), 8.20 (m, 1 H), 7.62–7.51 (m, 7 H), 7.36 (t, J = 8 Hz, 2 H), 7.26–7.18 (m, 2 H), 7.13 (t, J = 7 Hz, 1 H), 6.99 (m, 1 H); ir 3.11, 3.16, 3.22, 5.75, 5.86, 6.22, 6.37, 6.64, 6.75, 13.20, 14.17 μ.

Reaction of Pentadeuterionitrobenzene with CO.—A solution of 0.7 ml of $C_6D_5NO_2$, 5 mg of $PdCl_2$, and 1 ml of CH_3CN was pressured with 100 atm of CO and heated at 275° for 2 hr. Volatile products were removed by distillation and the residue was sublimed using a Dowtherm bath at 0.05 Torr. The ir spectrum showed significant absorptions at 2495, 2455, and 2390 cm^{-1} (N–D stretch).

Registry No.—**1b**, 38456-60-9; **2a**, 38456-61-0; **2b**, 14813-85-5; **3a**, 38456-63-2; **3b**, 38456-64-3; 4-fluorophenyl azide, 3296-02-4; carbon monoxide, 630-08-0; 4-fluorophenyl isocyanate, 1195-45-5; 4-fluoronitrobenzene, 350-46-9; 1,3,5-tris(4-fluorophenyl)biuret, 38456-65-4; 4-chloronitrobenzene, 100-00-5; 4-chlorophenyl isocyanate, 104-12-1; phenyl isocyanate, 103-71-9.

Acknowledgment.—The author thanks Professor B. L. Trost for valuable discussions.

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[11] M. L. Oftedahl, R. W. Rädue, and M. W. Dietrich, *J. Org. Chem.*, **28**, 578 (1963).

[12] M. C. Kloetzel, S. J. Davis, U. Pandit, C. R. Smith, and H. Nishihara, *J. Med. Pharm. Chem.*, **1**, 197 (1959).

Reactions of Isocyanides with Activated Acetylenes in Protic Solvents[1]

THOMAS R. OAKES* AND DANIEL J. DONOVAN

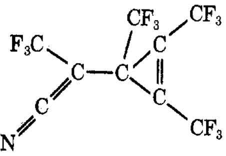
Department of Chemistry, Cleveland State University, Cleveland, Ohio 44115

Received October 24, 1972

The reaction of isocyanides with activated acetylenes in alcoholic solvents has been shown to produce a mixture of two different 1:1:1 adducts (isocyanide:acetylene:alcohol), an unsaturated imino ester, and a ketenimine. The configurations of the imino esters have been determined and the initial product is always that which results from trans addition. In some cases (methyl propiolate) the initial product is easily isomerized to the more stable isomer. The relative amounts of ketenimine and imino ester that form are dependent on the structures of the acetylene and the isocyanide and to some extent on the nature of the alcohol. In one case, the reaction of *p*-nitrophenyl isocyanide with dimethyl acetylenedicarboxylate in methanol, an ortho ester is obtained. In all cases the results are best interpreted by assuming the initial formation of a 1:1 intermediate (isocyanide:acetylene) with net trans addition to the acetylenic bond.

Previously we demonstrated that isocyanides would react with hexafluorobutyne-2 in aprotic solvents to produce 1:2 adducts of structure **1**.[2]

A few years prior to this work, Meinwald and Aue[3] had produced a similar type of product from the reaction of a nitrene with a normal acetylene. They postulated that their 1:2 product might be produced from an initially formed 1:1 intermediate that could possibly possess predominate carbene or carbonium ion character.



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[1] Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research. Presented in part at the 161st National Meeting of the American Chemical Society, Los Angeles, Calif., March 1971, Abstract ORGN-106.

[2] T. R. Oakes, H. G. David, and F. J. Nagel, *J. Amer. Chem. Soc.*, **91**, 4761 (1969).

[3] J. Meinwald and D. H. Aue, *ibid.*, **88**, 2849 (1966).