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68. Iron Carbonyls in Organic Synthesis, I. Iron Pentacarbonyl Induced Decomposition and Transfer Hydrogenation of Aryl Azides to Substituted Ureas¹⁾

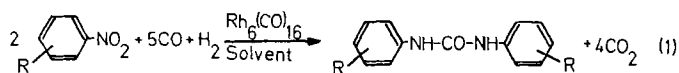
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(23. XII. 75)

Summary. Iron pentacarbonyl catalyzes smooth decomposition of aryl azides in the presence of acetic acid to afford good (70–90%) yields of the corresponding disubstituted ureas. Possible and alternative reaction mechanism pathways are discussed.

Introduction. – The homogeneous transition metal catalyzed deoxygenation of aromatic nitro compounds by carbon monoxide and hydrogen, under controlled conditions, affords high yields of 1,3-diarylureas [1] [2] (compare also [3]), according to equation 1 below. Such reductive carbonylation of nitrobenzenes to diphenylureas



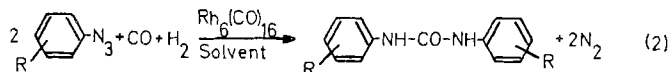
is regarded [1] [2] [4] as occurring through the agency of nitrenoid complexes of transition metals [5–7], the phenyl-nitrene moiety most likely being generated at the coordination sphere of the metal by two subsequent reductions by carbon monoxide groups and there remaining as stabilized ligand.

In quest of more compelling evidence for the foregoing hypothesis, we subsequently looked into a few analogous reactions of aryl nitrenes, independently generated by transition metal induced decomposition of the corresponding azides.

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Thus, we found that rhodium catalyzed pressure reaction of aryl azides with carbon monoxide and hydrogen [8] led to carbanilide derivatives (equ. 2).

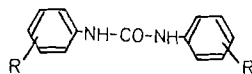


Continuing investigations now reveal that above formation of diarylureas can also be accomplished at ambient pressure, without rhodium carbonyl, by merely replacing carbon monoxide and hydrogen of reaction 2 by iron pentacarbonyl and a carboxylic acid, respectively. Pertinent results and observations, so far, are discussed in this paper.

Results and Discussion. – Upon heating (oil-bath 100°) under argon a mixture of phenyl azide and iron pentacarbonyl in glacial acetic acid, the initially clear solution turned turbid within a few minutes, and a white crystalline product started precipitating with simultaneous evolution of nitrogen and carbon monoxide. After heating under stirring for approximately 5–6 hours, water was introduced and the mixture stirred vigorously before being filtered. The residue was washed with water, dried and unambiguously identified as 1,3-diphenylurea. This, to our knowledge, represents the first example of smooth, selective formation of symmetrical 1,3-disubstituted ureas from corresponding azides *via* iron pentacarbonyl.

Results and relevant operating conditions for a few ring-substituted phenyl azides have been compiled in Table 1. Iron pentacarbonyl was used in one-molar excess of the azide. All experiments were performed in glacial acetic acid. Subsequent, cursory investigations have however shown that a variety of other carboxylic acids, such as formic, propionic, benzoic acids, *etc.* may also be conveniently employed as solvent.

Table 1. *Synthesis of symmetrical disubstituted ureas by the reaction of aryl azides and iron pentacarbonyl in the presence of acetic acid*



Expt. No.	Product R =	Yield ^{a)} [%]	Melting point ^{c)} [°C]	¹ H-NMR. chemical shift δ [ppm] ^{e)}		
				NH	aromatic	CH ₃
1	H	67	239	8.97	8.0–7.0	–
2	<i>m</i> -CH ₃	71	219–220	8.87	7.8–6.9	2.58
3	<i>p</i> -CH ₃	68	263–265	8.81	7.8–7.2	2.56
4	<i>m</i> -Cl	92	239–241	9.30	8.2–7.1	–
5 ^{a)}	<i>m</i> -Cl	15	240–241	9.30	8.2–7.1	–
6	<i>p</i> -Cl	72	284	9.16	8.1–7.2	–
7	<i>m</i> -OCH ₃	74	167–168	8.95	7.8–6.6	4.04
8	<i>p</i> -OCH ₃	70	236–238	8.70	7.9–7.0	4.03

Constant reaction conditions: Azide = 0.01 mol, Fe(CO)₅ = 0.02 mol, CH₃COOH = 5 ml, 100°/6 h, under argon.

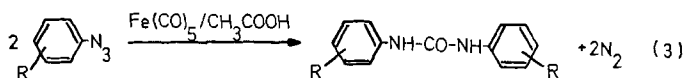
^{a)} Crude yield based on azide (*cf.* exper. section).

^{b)} Melting points are uncorrected, good agreement with literature values.

^{c)} Measured in dimethylsulfoxide.

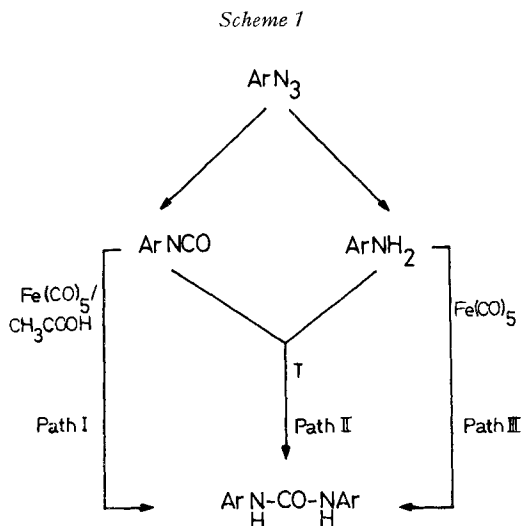
^{d)} Glacial acetic acid was replaced by benzene in this experiment.

As set forth by Table 1, the corresponding symmetrical diarylureas are formed in mostly good yields. The reaction (equ. 3) may be interpreted as reductive carbonylation of intermediate nitrene by iron pentacarbonyl (CO-source) and acetic acid (H-source).



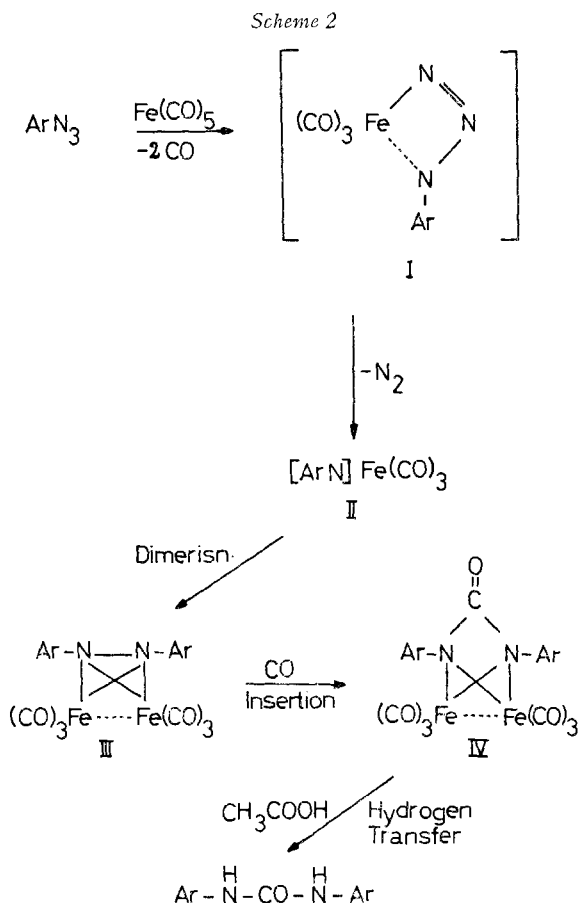
Replacement of acetic acid by an aprotic solvent like benzene, or a non-coordinating acid, such as *p*-toluenesulfonic, methanesulfonic acids, *etc.* afforded but low (<35%) yields of urea. Conversion of azides with iron pentacarbonyl in the absence of any solvent yielded intractable, dark red tars. No reaction took place in the absence of iron pentacarbonyl catalyst, as evidenced by recovery of the major portion of the starting azide. A carboxylic acid and iron pentacarbonyl are hence mutually essential for the present synthesis, the concomitance of coordinating and hydrogen donating capabilities of the coordinated solvent apparently playing a significant role.

Reaction Mechanism. - Certain transition metals [8-12], under specific conditions, catalyze decomposition of azides to amines and isocyanates, or derivatives thereof. Literature evidence for urea formation *via* reductive conversion of isocyanates [7], or dehydrogenative carbonylation of amines [13] [14] therefore suggests following paths (*Scheme 1*) for reaction 2. However, partial or total replacement of acetic acid by methanol, say, in appropriate control experiments with phenyl azide and iron pentacarbonyl failed to yield any isolatable amounts of aniline or methyl ester of carbanilic acid. Further, no formation of mixed disubstituted ureas of the type ArNH-CO-NHAr' was observed during the joint reaction of an azide, ArN₃, and an isocyanate, Ar'NCO, under conditions of the present synthesis. In view of these results, amine and/or isocyanate intermediacy and, hence, operation of reaction paths I to III (*Scheme 1*) are considered unlikely.



In our opinion, the mechanistic *Scheme 2*, reminiscent of earlier proposals [1] [2] [4] for analogous reactions, represents a rational alternative. The moiety square brackets should be looked upon as being coordinatively bound to the iron catalyst.

Assuming aryl azides to react as electrophilic 1,3-dipoles [11], the first step is envisaged as leading to an oxidative adduct such as I, from which nitrogen is rapidly extruded. The ensuing nitrene species II, transiently stabilized *via* coordination to tricarbonyl iron, subsequently dimerizes to the bisphenylnitrene complex III [5], which formally is the result of trapping by iron carbonyl the diradical of dehydro diphenylhydrazine. The N–N bond of the bisphenylnitrene complex is not totally ruptured, but each N atom is assumed to act as a three-electron donor [15]. Carbon monoxide insertion into the labile N–N bond of III leads to the urea-based complex IV



[5–7], which now abstracts hydrogen from the coordinated solvent (acetic acid) to give diphenylurea.

In the context of the present reaction, it is noteworthy that also *Campbell & Rees* [12] investigated a similar reaction of *ortho*-substituted phenyl and *peri*-substituted

α -naphthyl azides to see if nitrenes really were intermediates and if this catalytic decomposition was a useful synthetic alternative to pyrolysis. The authors however carried out all reactions in benzene at 20° under nitrogen in the dark, with slightly more than 1 mol of diiron nonacarbonyl per azide group. The yield of the corresponding cyclic urea derivatives was rather low and accompanied by side-reactions. Hydrogen for urea formation evidently originated in benzene solvent. In a majority of experiments, the corresponding bisphenylnitrene complex III was also isolated from the reaction mixture.

In contrast, the significantly improved, selective yield of diarylurea in our hands, is ascribed to two major advantages deriving from the use of acetic acid as solvent: not only is the latter a more efficient hydrogen donor than benzene, but also a good coordinating ligand for iron. Iron carbonyl conceivably stabilizes the intermediate nitrene-derived moieties depicted in *Scheme 2*. Consequently retarded kinetic lability, superimposed with relative inertness of the hydrogen donor, might be one explanation for reduced formation of urea by way of transfer hydrogenation of IV by an aprotic, non-coordinating solvent, such as benzene (*cf.* Exper. 5, Table 1). In contrast, particularly hydrogen transfer with resultant cleavage of urea from complex IV is perhaps facilitated through prior coordination of acetic acid to iron. This view finds substantiation in actual formation of iron acetate derivatives during the reaction. It is however interesting to note that, neat reaction of acetic acid with iron pentacarbonyl afforded no iron acetate derivatives, at all. As soon as an aryl azide was added, copious formation of a white precipitate was immediately observed. One part of the precipitate (insoluble in water, soluble in dimethyl sulfoxide) was identified (m.p., IR., NMR.) as the corresponding diarylurea, while the rest consisted of an inorganic compound (highly water-soluble solid, turning reddish-brown on standing in air), which according to preliminary spectroscopic and qualitative analyses appeared to be an iron (II)-acetate derivative, slowly being oxidized by air to iron (III)-acetate. In other words, aryl azides, probably *via* prior oxidative addition to iron and ultimate conversion to nitrenoid complexes of tricarbonyliron (*vide supra*), catalyze formation of iron acetate derivatives from iron pentacarbonyl and acetic acid. Since nitro compounds are also known to be deoxygenated by iron carbonyls [5] [16] [17], a similar mechanism is held to be operative in the thermal reaction of iron pentacarbonyl with nitrobenzene and acetic acid leading to brick-red crystals of iron (III)-acetate – most likely an oxidation product of initially formed iron(II)-acetate.

Studies with complexes of type IV (*Scheme 2*), say, and various hydrogen donors should be helpful in more clearly defining the course of the present reaction and, in particular, the precise nature of various iron acetate derivatives thus far isolated.

Experimental Part. – Phenyl azide was prepared by nitrosation of phenylhydrazine [18]. Further azides employed in the present study were prepared by interaction of the corresponding aryldiazonium salts and sodium azide³⁾. As solvent were employed glacial acetic acid (*Fluka* puriss.) and dry benzene. Iron pentacarbonyl (*purum*) was purchased from *Fluka* AG, Buchs/Switzerland. NMR. spectra were run in dimethylsulfoxide with a *Varian* HA 60 IL instrument. Melting points are uncorrected.

³⁾ *Cf.*, for example, [19].

The reaction of aryl azides with iron pentacarbonyl and acetic acid. The general procedure employed is exemplified in the following by the conversion of *m*-chlorophenyl azide: 0.01 mol of *m*-chlorophenyl azide, 0.02 mol of iron pentacarbonyl and 5 ml of acetic acid are introduced in a 50 ml flask fitted with a reflux condenser. The reaction vessel is next purged with argon and maintained under the inert gas for the duration of reaction. The flask with the reactants is then lowered into a pre-heated (100°) oil-bath, and the contents stirred vigorously by means of a magnetic stirrer for ca. 6 h. The initially clear, orange-red solution turns turbid after about 5 min, which is followed by copious formation of a white precipitate. At the end of the reaction period, 25 ml of distilled water are added and the whole stirred vigorously for another 10 min without heating. After further dilution with 10 ml of water, the residue is suction-filtered off, washed several times with water, rinsed with a little alcohol to remove water, and dried under vacuum. The crude yield of 1,3-di(*m*-chlorophenyl)-urea, thus obtained, is approximately 92%, based on starting azide. The product is sufficiently pure for practical purposes and melts on recrystallization from methanol/chloroform 1:1 at 240–241°.

Crude yields and specific physico-chemical properties of symmetrical disubstituted ureas prepared by the foregoing procedure have been compiled in Table 1. All products have been unequivocally identified by micro analysis, mixed melting point and spectroscopic comparison (IR., NMR.) with authentic specimens.

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