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Nucleophilic Addition of Phenylethynylcopper to 1,3,5-Trinitrobenzene

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Phenylethynylcopper reacts with 1,3,5-trinitrobenzene in pyridine at room temperature to form an intensely coloured solution. The visible spectrum shows absorptions typical for Meisenheimer anions, σ-complexes, from 1,3,5-trinitrobenzene. Decomposition with strong acid gives small amounts of 2,4,6-trinitrotolane and 4,6-dinitro-2-phenylisatogen together with unchanged trinitrobenzene.

On standing, the coloured solution forms a red precipitate. This, upon treatment with acid, is transformed into a red crystalline compound, probably 6-hydroxy-4-nitro-2-phenylisatogen.

The mechanism for the initial reaction is discussed and related to those for other organocopper reactions.

Copper acetylides react with iodoarenes to form new carbon-carbon bonds and copper(I) iodide [1,2] (reaction 1, R = alkynyl). Analogous reactions with alkyl-,[3] alkenyl-,[4] and arylcopper [3,5,6] compounds have been reported.

$$\mathrm{R-Cu+I-Ar} \longrightarrow \mathrm{R-Ar+CuI} \qquad (1)$$

With the exception of the reaction with copper acetylides, for which Castro and co-workers have reported second-order kinetics,[2] the mechanism(s) for these reactions have not been systematically studied. Certain *ortho* substituents in the iodoarene, such as a nitro, carboxyl or hydroxyl group, increase the reaction rate significantly. Similar *ortho* effects are known in other copper-promoted reactions.[5] These effects have been attributed to the co-ordination, in the transition state, between copper and the *ortho* substituent.[2,5]

Coupling of organocopper compounds with iodoarenes (reaction 1) can be regarded as nucleophilic aromatic substitution reactions, in which the organocopper compounds act as the source of the nucleophiles. This analogy is supported by the observation of a stable Meisenheimer compound from 2,6-dimethoxyphenylcopper and 1,3,5-trinitrobenzene (TNB).[7] The present work deals with the corresponding reaction between phenylethynylcopper and TNB.

RESULTS

Phenylethynylcopper reacts slowly at room temperature with 1,3,5-trinitrobenzene (TNB) in pyridine to form an intensely red solution. The visible spectrum of the solution is shown in Fig. 1. It is typical for Meisenheimer anions from TNB.[8] The conversion to the Meisenheimer anion can be estimated to about 70 % assuming $\varepsilon = 2.7 \times 10^4$ l mol^{-1} cm^{-1} at 442 nm for the pure compound.[8] The complex, which could not be isolated, was decomposed with strong acid. Separation of the products gave unchanged TNB (67 %) and two significant products: 2,4,6-trinitrotolane (*1*, 5 %) and 4,6-dinitro-2-phenylisatogen (*2*, 6 %) (Scheme 1). The stoicheiometry for the formation of these compounds is not clear. A nitro group or oxygen from air could act as the oxidising agent.

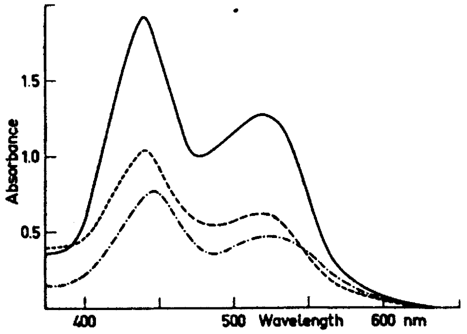


Fig. 1. Visible spectra of an equimolar solution (10^{-4} M) of 1,3,5-trinitrobenzene and phenylethynylcopper in pyridine at 0°. — · — ·, 1 min; ———, 20 min; and - - -, 300 min after mixing.

The deep red solution is rather stable at room temperature when stored under nitrogen in the dark. When exposed to air and daylight, the solution slowly deposits a red precipitate. This is insoluble in most solvents, but reacts with acids to form a red crystalline compound, believed to be 6-hydroxy-4-nitro-2-phenylisatogen on basis of elemental analysis as well as of mass, IR, NMR, and UV spectra.

The analogous reaction was tried with hexynylcopper and TNB in pyridine. The visible spectrum of the solution at maximum absorption intensity is shown in Fig. 2. No stable product was, however, isolated from the solution.

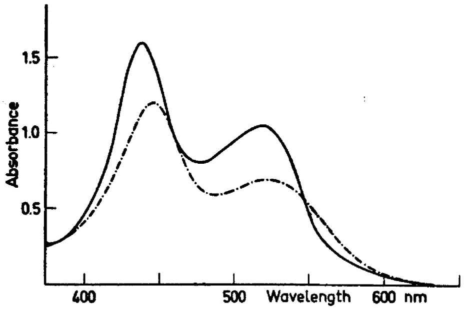
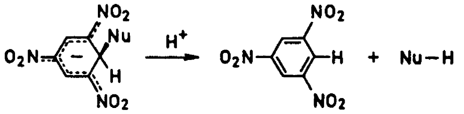


Fig. 2. Visible spectra of equimolar solutions (10^{-4} M) of 1,3,5-trinitrobenzene and hexynylcopper (——— 25 min after mixing) or phenylethynylsilver (— · — · 140 min after mixing) in pyridine at 25°.

Phenylethynylsilver also reacts with TNB in pyridine at room temperature. Except for the intensity, the visible spectrum of the solution at maximum absorption, shown in Fig. 2, is the same as that obtained from phenylethynylcopper. Decomposition of the initially formed Meisenheimer compound with strong acid gave unchanged TNB only.

DISCUSSION

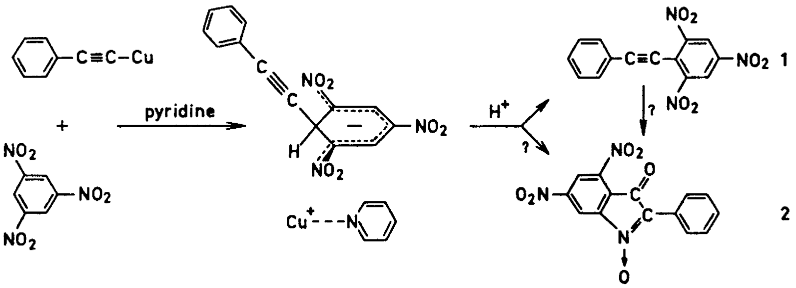
Meisenheimer anions can be regarded as nitronate anions (dissociated nitronic acids). They are usually unstable towards acids and decompose to the nitroarene and the protonated nucleophile (reaction 2).[9] Meisenheimer anions from arylcopper,[7] arylsilver,[10] alkynylcopper or alkynylsilver compounds are more stable towards acids, since the aryl- and alkynyl groups are poor leaving groups. The latter Meisenheimer anions can decompose, to a biphenyl or a tolane, when treated with acid. In these reactions a nitro group might act as the oxidising agent.



(2)

Nu = amine, alkoxide or enolate anion.

2-Nitrotolanes are known to cyclise to 2-phenylisatogens in pyridine by a light-induced reaction.[11] Several similar cyclisations of 2-substituted tolanes to heterocyclic systems have recently been reported to be catalysed by copper.[2] Pyridine is a good solvent for these reactions too. The 4,6-dinitro-2-phenylisatogen (*2*) found in the present study therefore could be formed from 2,4,6-trinitrotolane (*1*) or possibly from the Meisenheimer anion (Scheme 1).



Scheme 1

The formation of 6-hydroxy-4-nitro-2-phenylisatogen (Fig. 3) must be a rather complex reaction. No attempts have been made to investigate the mechanism. One reasonable path for its formation would be an initial formation of the heterocyclic ring by a cyclisation between the triple bond and a nitro group in the Meisenheimer anion. The next reaction would then be oxidation of the bicyclic nitronate anion to a dienone.[15] Finally, an acid-catalysed rearrangement to 6-hydroxy-4-nitro-2-phenylisatogen could occur.

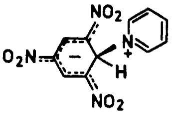
The formation of Meisenheimer anions from phenylethynylcopper or phenylethynylsilver and TNB is analogous to the reaction between 2,6-dimethoxyphenylcopper [7] or 2,6-dimethoxyphenylsilver [10] and TNB. The organocopper compounds react faster with TNB than do the corresponding organosilver compounds. However, the Meisenheimer compounds formed are more stable in the presence of silver than in that of copper, as shown by visible spectroscopy (Figs. 1 and 2).

It may be relevant to consider three effects in these reactions between organocopper or organosilver compounds and TNB.

1. The nucleophilicity of the aryl- or alkynyl groups in the organometallic compounds. This can be related to the polarisation of the metal-carbon bond, which can be changed by co-ordination of ligands to the metal atom.[12] Co-ordination of solvent molecules to the latter changes the equilibrium between monomer, dimer, and oligomer of the organometallic compound in solution. This also can affect the nucleophilicity.[13]

2. The "catalytic activity" of metals. This can depend on the co-ordination of the metal to a nitro group or to a delocalised π-electron system in the transition state. The metal can also catalyse the consecutive reactions which lead to stable products. The copper-catalysed cyclisation mentioned above exemplifies this.

3. The influence of the solvent. Pyridine has a strong influence on the reaction rates. This also has been reported for other copper promoted reactions.[5] The effect could be due to the solvating power of the organometallic compounds as mentioned above or, alternatively as previously suggested,[7] to the metal-catalysed formation of a Meisenheimer compound (3) from pyridine and 1,3,5-trinitrobenzene.



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EXPERIMENTAL

Melting points were determined on a micro hot stage. Infrared spectra were recorded on a Perkin Elmer No. 421, ultraviolet and visible spectra on a Beckman DK 2, nuclear magnetic resonance spectra on a Varian A-60 A, and mass spectra on an LKB 9000 spectrometer.

Pyridine (Mallinckrodt A.R.) and 1,3,5-trinitrobenzene (Eastman, recrystallised from ethanol) were used.

Phenylethynylcopper and 1,3,5-trinitrobenzene. Phenylethynylcopper [1] (0.25 mmol) was added to 1,3,5-trinitrobenzene (0.25 mmol), dissolved in pyridine (50 ml), and the mixture was kept at 0°. Small samples (0.2 ml), taken at intervals, were diluted with pyridine (to 10 ml) and their visible spectra recorded (Fig. 1). The absorption intensity increased to a maximum after approximately 20 min, and then slowly decreased. The position of the strongest absorption changed slowly with time indicating that two different Meisenheimer compounds might be present.

Phenylethynylcopper (1.65 g, 10 mmol) and 1,3,5-trinitrobenzene (2.13 g, 10 mmol) were reacted in pyridine (50 ml) at 25° for 15 min. The deep red solution was diluted with chloroform (200 ml) and the pyridine removed by extraction with cold sulfuric acid (2 M, 500 ml) in two portions. The colour changed to yellow-brown. The solvent was evaporated, and the residue was chromatographed on silica gel. Mixtures of light petroleum (b.p. 40 – 60°) and toluene were used as the mobile phase. Four substances were collected. The first was a white solid (m.p. 83 – 85°, 0.06 g, 6 %), probably 1,4-diphenylbutadiene (m.p. 87°). The second was 1,3,5-trinitrobenzene (1.42 g, 67 %), identified by comparison of its IR spectrum with that from authentic material. The third was a yellow substance (m.p. after sublimation 204 – 205°, 0.15 g, 5 %, believed to be 2,4,6-trinitrotolane (m.p. 205.5 – 206.5°).[1] The IR spectrum in KBr showed a strong absorption at 2207 cm^{-1} and the characteristics of an aromatic nitro compound. The mass spectrum showed the parent ion at *m/e* 313 (rel. intensity 0.4) and some important fragments at 284 (0.8), 283 (0.6), 267 (0.5), 239 (0.7), 174 (6), 105 (100), 77 (61), and 74 (5). The base peak at *m/e* 105 ($C_7H_5O^+$), which also is large in the mass spectrum of 4,6-dinitro-2-phenylisatogen described below, must be the result of a complex rearrangement, involving an internal oxidation of the triple bond.

The fourth was a red compound (m.p. 254 – 257° from acetic acid, 0.2 g, 6 %). The UV spectrum was the same as that reported for 4,6-dinitro-2-phenylisatogen.[14] The mass spectrum showed the parent ion at *m/e* 313 (rel. intensity 83) and fragments at *m/e* 297 (17), 296 (17), 267 (9), 239 (10), 223 (34), 204 (18), 177 (24), 164 (12), 131 (9), 130 (9), 105 (100), 90 (18), 77 (45), 75 (24), and 74 (92).

Phenylethynylcopper (0.82 g, 5 mmol) and 1,3,5-trinitrobenzene (1.07 g, 5 mmol), were stirred in pyridine (50 ml) for 24 h at room temperature in an open flask. A fine precipitate was slowly formed. Filtration gave a microcrystalline red compound (0.26 g), insoluble in all solvents tried. It decomposed slowly at temperatures above 220° without any distinct melting point. The IR spectrum of the crude product showed the presence of a nitro group (1545 and 1345 cm^{-1}) and a carbonyl group (1665 cm^{-1} with shoulders). The mass spectrum showed a possible parent ion at *m/e* 284. The fragmentation pattern was very similar to that described below. The compound also contained pyridine according to the mass and IR spectra. The unidentified compound was soluble in warm acetic acid. A new red crystalline compound precipitated on the addition of water (0.16 g, 11 %). The compound after purification by sublimation had the following characteristics: M.p. 249 – 251° decomp. (Found: C 59.3; H 2.6; N 9.5. Calc. for $C_{14}H_8N_2O_5$: C 59.2; H 2.8; N 9.8.) The IR spectrum in KBr showed a broad band at 3400 – 3100 cm^{-1} (intermolecular hydrogen bonded H – O stretching), 3115 m (C – H stretch in nitroarenes), 1710 s (C = O stretch), and 1535 vs (asymmetric NO_2 stretch). The visible spectra in ethanol and in

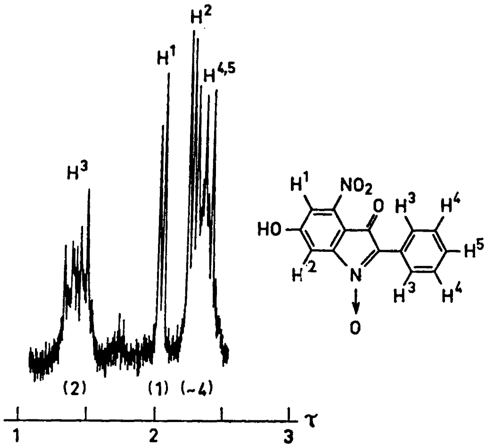

Fig. 3. NMR spectrum of 6-hydroxy-4-nitro-2-phenylisatogen in dimethylsulfoxide-d_6. The peak areas are shown within brackets. The coupling constant $J_{H^1-H^2} = 1.8$ Hz.

alkaline ethanol (2 mM NaOH) were different. The absorption minimum at 366 nm $\varepsilon = 0.37 \times 10^4$ l mol^{-1} cm^{-1} and maximum at 390 nm $\varepsilon = 0.42 \times 10^4$ in ethanol are shifted to 384 nm $\varepsilon = 0.28 \times 10^4$ and to 465 nm $\varepsilon = 0.46 \times 10^4$, respectively, in alkaline solution.

The mass spectrum of the compound showed the parent ion at *m/e* 284 (rel. intensity 41), fragments at *m/e* 268 (20), 256 (2.8), 254 (5.2), 240 (34), 238 (8), 194 (6), 135 (10), 122 (16), 107 (11), 105 (46), 104 (18), 103 (51), 91 (16), 77 (31), 76 (19), 63 (8), 51 (10), 44 (100), 39 (5), 30 (23), 28 (32), 18 (12) and metastable peaks corresponding to the fragmentations 284→268, 284→256, 268→240 and 223→194. The most important features thus are the successive losses of O and CO or *vice versa* to 240, followed by the loss of a nitro group in two steps to 194. The fragment at *m/e* 77 shows that a phenyl group is present.

The NMR spectrum of the red crystalline compound is shown in Fig. 3 together with a suggested interpretation. The relative peak areas are shown in brackets. No resonance peak from a hydroxylic hydrogen was observed.

The crystalline red compound thus is believed to be 6-hydroxy-4-nitro-2-phenylisatogen.

Hexynylcopper and 1,3,5-trinitrobenzene. Hexynylcopper[1] (0.25 mmol) and TNB (0.25 mmol) were stirred in pyridine (50 ml) at room temperature. Small samples (0.2 ml), taken at intervals, were diluted with pyridine (to 10 ml), and their visible spectra recorded. The spectrum at maximum intensity (after 30 min) is shown in Fig. 2.

Phenylethynylsilver and 1,3,5-trinitrobenzene. Phenylethynylsilver[1] (0.25 mmol) and TNB (0.25 mmol) were stirred in pyridine (50 ml) at room temperature. Small samples (0.2 ml), taken at intervals, were diluted with pyridine (to 10 ml), and their visible spectra recorded. The spectrum at maximum intensity (after 140 min) is shown in Fig. 2.

Phenylethynylsilver (10 mmol) and TNB (10 mmol) were stirred in pyridine (50 ml) for 2 h. The solution was diluted with chloroform (200 ml), The pyridine was removed by extractions with cold sulfuric acid (2M, 500 ml) in two portions. The deep red colour initially formed changed to brown-yellow. The solvent was evaporated and the residue chromatographed on silica gel, using mixtures of light petroleum (b.p. 40 – 60°) as mobile phase. TNB (8 mmol, 80 %) was the only isolated compound.

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REFERENCES

1. Castro, C. E., Gaughan, E. J. and Owsley, D. C. *J. Org. Chem.* **31** (1966) 4071.
2. Castro, C. E., Havlin, R., Honwad, V. K., Malte, A. and Mojé, S. *J. Am. Chem. Soc.* **91** (1969) 6464.
3. Whitesides, G. M., Fischer, W. J., Jr., Filippo, J. S., Jr., Bashe, R. W. and House, H. O. *J. Am. Chem. Soc.* **91** (1969) 4871.
4. Nilsson, M. and Wahren, R. *J. Organometal. Chem.* **16** (1969) 515.
5. Nilsson, M. and Wennerström, O. *Acta Chem. Scand.* **24** (1970) 482.
6. Jukes, A. E., Dua, S. S. and Gilman, H. *J. Organometal. Chem.* **21** (1970) 241.
7. Björklund, C., Nilsson, M. and Wennerström, O. *Acta Chem. Scand.* **24** (1970) 3599.
8. Foster, R. and Fyfe, C. A. *Rev. Pure and Appl. Chem.* **16** (1966) 61.
9. Feuer, H. *The Chemistry of the Nitro and Nitroso Groups*, Wiley, London 1969, Part 1, p. 377.
10. Wennerström, O. *Acta Chem. Scand. In press.*
11. Ruggli, P., Caspar, E. and Hegedus, B. *Helv. Chim. Acta* **20** (1937) 250.
12. Coates, G. E., Green, M. L. H. and Wade, K. *Organometallic Compounds*, Methuen, London 1967, Vol. 1, p. 18.
13. Brown, T. M. *Advan. Organometal. Chem.* **3** (1965) 392.
14. Splitter, J. and Calvin, M. *J. Org. Chem.* **20** (1955) 1086.
15. Russell, G. A. *J. Am. Chem. Soc.* **76** (1954) 1595.

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