Tetrahedron Letters No. 29, pp. 2713-2716, 1971. Pergamon Press. Printed in Great Britain.

MEISENHEIMER COMPOUNDS AND ARYL-2,4,6-TRINITROBENZENES FROM 2-FURYLCOPPER OR 2-THIENYLCOPPER AND 1,3,5-TRINITROBENZENE

Martin Nilsson, Christina Ullenius and Olof Wennerström
Department of Organic Chemistry, Royal Institute of Technology,
S-100 44 Stockholm 70, Sweden

(Received in UK 19 May 1971; accepted in UK for publication 16 June 1971)

Arylcopper compounds react with iodoarenes to form biaryls (reaction 1).[1-3] This is sometimes a convenient method to prepare unsymmetric biaryls. Alkynyl-[4], alkenyl-[5] and cyclopentadienylcopper[6] compounds react similarly.

$$\text{Ar-Cu} + \text{I-Ar'} \xrightarrow{\text{pyridine}} \text{Ar-Ar'} + \text{CuI} \qquad (1)$$

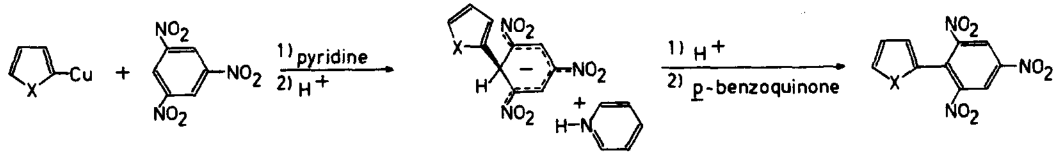
The influence of substituents in the iodoarenes on the reactivity towards organocopper compounds has been investigated in some cases.[2-4] Strongly electron-attracting substituents, such as nitro or methoxycarbonyl groups, especially in the ortho position, increase the rate of reaction, whereas methoxy groups seem to slow it down. The formation of Meisenheimer complexes, σ-complexes, from some organocopper compounds and 1,3,5-trinitrobenzene[7,8] shows further connection between the copper-promoted reactions and aromatic nucleophilic substitution.

Meisenheimer compounds have now been prepared by reaction of 1,3,5-trinitrobenzene with 2-furylcopper or 2-thienylcopper in pyridine (Scheme 1). The Meisenheimer compounds were treated with strong acid to give the corresponding nitronic acids which were oxidised in solution with p-benzoquinone to 2(2,4,6-trinitrophenyl)furan and 2(2,4,6-trinitrophenyl)thiophene, respectively, in analogy with reactions of Meisenheimer compounds from 1,3,5-trinitrobenzene and 2,6-dimethoxyphenylsilver,[8] cyclopentadiene or indene.[9]

2,6-Dimethoxyphenylcopper,[7] phenylethynylcopper,[8] 2-furylcopper and 2-thienylcopper all give Meisenheimer compounds with 1,3,5-trinitrobenzene. Some other arylcopper compounds, e.g. phenylcopper[7] and 3,4,5-trichloro-2-thienylcopper,[10] may be oxidised instead to biaryls by trinitrobenzene. Nitrobenzene has been used as an oxidising agent for other ether-soluble organocopper compounds or complexes.[11]

Pyridine has been reported to add to 1,3,5-trinitrobenzene to form a Meisenheimer compound. This compound probably is an intermediate in some reactions between organocopper or organosilver compounds and 1,3,5-trinitrobenzene.[7-9] However, in the present investigation no evidence was obtained for the formation of this compound.

Copper-carbon bonds can be cleaved homolytically or heterolytically in organocopper reactions. In the case of additions of organocopper compounds to 1,3,5-trinitrobenzene, homolysis seems less likely. Heterolysis of the copper-carbon bond, followed by nucleophilic attack, should give the observed products. However, a concerted reaction after primary co-ordination between copper and a nitro group seems even more likely. Co-ordination between the ortho substituent and copper has been suggested to explain the high reactivity of some ortho substituted arenes in copper-promoted reactions.[4,12] A similar mechanism has been suggested for the reaction between arylcopper compounds and iodoarenes in pyridine.[2,3]



X = O, S

1

2

Scheme 1

2-Furylcopper was prepared at -20° in the same manner as 2-thienylcopper.[2] 2-Furylcopper (15 mmol) and 1,3,5-trinitrobenzene (15 mmol) were stirred in pyridine (50 ml) for five hours at -10° to 0° with careful exclusion of air and moisture. The solution instantly turned dark red. The reaction was followed by visible spectroscopy, which showed the reaction to be complete within 1 min. The yield was 56 % according to spectra. Methylene chloride (150 ml) and an excess of cold sulphuric acid (2 M) were added. The mixture was shaken vigorously for five min. Beautiful dark red crystals separated from the organic phase on cooling and were collected and identified as the Meisenheimer salt 1, X = O; 22 %, m.p. 136-137° decomp. The mass spectrum showed the largest fragment at m/e = 279 (the mass of trinitrophenylfuran).

The Meisenheimer compound 1, X = O, (1.3 mmol) was suspended in methylene chloride (100 ml) and shaken vigorously with sulphuric acid (3 M, 50 ml) to protonate the anion to the corresponding nitronic acid; p-benzoquinone (2.6 mmol) was added to the organic phase, which changed from red to bright yellow after 10 min. at 30°. The reaction mixture was chromatographed on silica gel with methylene chloride as mobile phase. 2(2,4,6-Trinitrophenyl)furan was isolated, 45 %, m.p. 160-162°, recrystallised from ethanol. (Found: C 43.1; H 1.8; N 15.1. Calc. for $C_{10}H_5N_3O_7$: C 43.0; H 1.8; M 15.1.) The mass spectrum showed the largest fragment at m/e 279 (base peak).

2-Thienylcopper[2] (13 mmol) and 1,3,5-trinitrobenzene (13 mmol) were stirred in pyridine (130 ml) at -10°. The reaction was followed by visible spectroscopy, which showed the formation of the Meisenheimer compound 1, X = S, to be slower than that for X = O, being completed within 10 min. The yield was 75 % according to spectra. The reaction mixture was treated as above and the Meisenheimer compound 1, X = S, was isolated in 44 % yield, m.p. 148-149°, decomp. (Found: C 47.8; H 3.1; N 14.7. Calc. for $C_{15}H_{12}N_4O_6S$: C 47.9; H 3.2; N 14.9.) The mass spectrum showed the largest fragment at m/e 295 (the mass of trinitrophenylthiophene).

The Meisenheimer compound 1, X = S, (1 mmol) was reacted as above with sulphuric acid and p-benzoquinone to give 2(2,4,6-trinitrophenyl)thiophene, 40 %, m.p. 199-200°, recrystallised from ethanol. (Found: C 40.8; H 1.7; N 14.4. Calc. for $C_{10}H_5N_3S$: C 40.7; H 1.7; N 14.2.) The mass spectrum showed the largest fragments at m/e 295 (the mass of trinitrophenylthiophene) and m/e 278 (base peak).

The infrared spectra (KBr) of the Meisenheimer compounds showed the strongest absorptions at 1492s, 1246vs, 1150vs (X = O) and 1490s, 1235vs, 1135vs (1, X = S). The infrared spectra (KBr) of the oxidation products showed N-O stretching at 1552s (broad), 1354s (2, X = O) and 1540s, 1555s, 1350s (2, X = S).

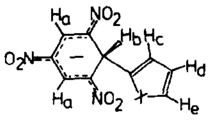
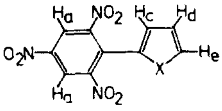
The visible spectra of the Meisenheimer compounds in acetone were identical, λ_1 = 454 nm, $\varepsilon_1 = 3.0\times10^4$, λ_2 = 558 nm, $\varepsilon_2 = 1.5\times10^4$.

The UV spectra of the oxidation products were recorded in ethanol, λ = 353 nm, $\varepsilon = 0.8\times10^4$ (2, X = O) and λ = 337 nm, $\varepsilon = 0.45\times10^4$ (2, X = S).

The assignment of NMR data for the Meisenheimer anions and the biaryls is shown in Table 1.

TABLE 1

Assignment of NMR data for the Meisenheimer anions and the biaryls.
Solvent dimethylsulphoxide-d_6.

		Chemical shifts, τ-values					Coupling constants, Hz			
		H_a	H_b	H_c	H_d	H_e	$J_{H_a-H_b}$	$J_{H_c-H_d}$	$J_{H_c-H_e}$	$J_{H_d-H_e}$
	X = O	1.67	4.14	3.88	3.68	2.57	<0.3	3.4	0.8	1.8
	X = S	1.67	4.00	3.17	3.14	2.70	<0.3	3.6	1.1	5.3
	X = O	0.86		3.07	3.27	1.99		3.6	0.8	1.8
	X = S	0.82		2.75	2.80	2.09		3.6	1.4	5.0

Acknowledgements. This work has been supported by the *Swedish Board of Technical Development* and by the *Swedish Natural Science Research Council*.

REFERENCES

1. A. Cairncross and W.A. Sheppard, *J. Am. Chem. Soc.*, **90**, 2186 (1968).
2. M. Nilsson and C. Ullenius, *Acta Chem. Scand.*, **24**, 2379 (1970).
3. M. Nilsson and O. Wennerström, *Acta Chem. Scand.*, **24**, 482 (1970).
4. C.E. Castro, R. Havlin, V.K. Honwad, A. Malte, and S. Mojé, *J. Am. Chem. Soc.*, **91**, 6464 (1969).
5. M. Nilsson and R. Wahren, *J. Organometal. Chem.*, **16**, 515 (1969).
6. M. Nilsson, R. Wahren, and O. Wennerström, *Tetrahedron Letters*, 4583 (1970).
7. C. Björklund, M. Nilsson, O. Wennerström, *Acta Chem. Scand.*, **24**, 3599 (1970).
8. O. Wennerström, *Acta Chem. Scand.*, in press.
9. C. Moberg and O. Wennerström, *Acta Chem. Scand.*, in press.
10. M. Nilsson and C. Ullenius, *Acta Chem. Scand.*, in press.
11. G.M. Whitesides, W.F. Fischer Jr., J. San Filippo Jr., R.W. Bashe, and H.O. House, *J. Am. Chem. Soc.*, **91**, 4871 (1969).
12. B. Liedholm, *Acta Chem. Scand.*, **23**, 3175 (1969).