Letters to the Editor

2,6-Dioxo-4,8-diphenyl-1,5-dichlorotricyclo[5.1.0.0^{3,5}]octane as a product of the reaction of 3,3-dichloropentane-2,4-dione with benzaldehyde

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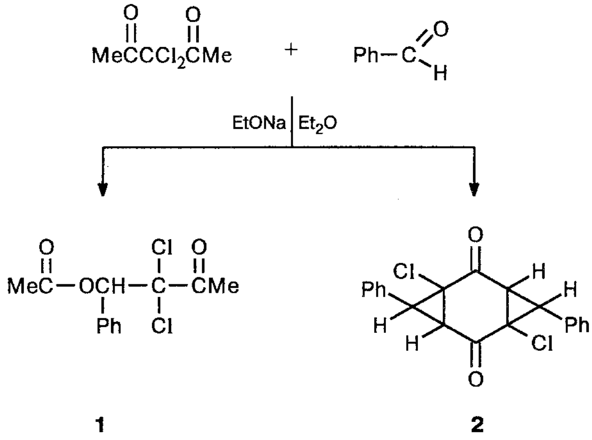
It has been previously demonstrated[1] that 1-acetoxy-1-phenyl-2,2-dichlorobutan-3-one (**1**) is the main product of condensation of 3,3-dichloropentan-2,4-dione with benzaldehyde in the presence of EtONa; **1** is formed due to the insertion of benzaldehyde into the C—C σ-bond of dichloropentane-2,4-dione.

A more detailed investigation of the reaction products by spectral methods (IR, ^{1}H and ^{13}C NMR) and X-ray analysis indicated the formation of 2,6-dioxo-4,8-diphenyl-1,5-dichlorotricyclo[5.1.0^{3,5}]octane (**2**) (m.p. 236—237 °C, from DMSO), as a result of the side process, along with compound **1** (Scheme 1).

^{1}H NMR (DMSO-d$_6$, δ, J/Hz): 7.55 (br.s, 10 H, 2 C_6H_5); 4.15 (d, 2 H, H(3) and H(7), $^3J_{H(7),H(3)} = {}^3J_{H(3),H4} = 7.26$); 3.59 (d, 2 H, H(4) and H(a)). ^{13}C NMR: 195.7 (s, C(2) and C(6)); 135.4 (s, C_i); 133.2 (d, C_o); 132.3 (d, C_m); 132.2 (d, C_p); 55.2 (s, C(1) and C(5)); 41.63 (d, C(3) and C(7)); 39.2 (d, C(4) and C(8)). Found (%): C, 67.31; H, 3.87; Cl, 19.77. $C_{20}H_{14}Cl_2O_2$. Calculated (%): C, 67.24; H, 3.95; Cl, 19.85.

Scheme 1



1066-5285/95/4404-0766 $12.50

References

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Received October 30, 1993;
in revised form January 12, 1995

Regioselective α-arylation of *N*-vinylpyrroles by the Heck reaction

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N-Vinylpyrroles which became available from ketoximes and acetylene[1,2] have been used by as substrates in the Heck reaction (Scheme 1).

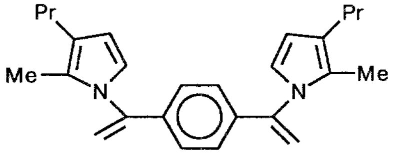
All of the experiments were carried out under conditions routinely used for Heck arylation (DMF as a solvent, NBu_3 as a base, $PdCl_2$ as a catalyst, 80 °C).

Unsubstituted *N*-vinylpyrrole was found to be the most reactive (Table 1, Entry *1*). As usual in the Heck reaction, β-*trans*-substitution (α/β = 30/70) dominates in this case. However, arylation of *N*-vinyl-2,3-dialkylpyrroles (see Table 1, Entries *2* to *7*) unexpectedly exhibits high regioselectivity toward the α-position of the vinyl group for different aryl iodides. This high percentage of α-arylation under the standard conditions of the Heck reaction has not been observed previously, and it was achieved in the arylation of vinyl ethers only when the halogen in the aryl halides was replaced by a triflate substituent.[3]

Table 1. *N*-Vinylpyrroles in the Heck reaction

Entry	R^1	R^2	Aryl halide	By-product	Rate, $w \cdot 10^{-3}$ /mol L^{-1} min^{-1}	α/β ratio*	Yield α+β (%)
1	H	H	PhI	Not found	9.4	30 : 70	100
2	Me	Me	PhI	Diphenyl	1.75	95 : 5	90
3	Me	Pr^i	PhI	Diphenyl	1.80	100 : 0	90
4	Me	Pr^n	PhI	Diphenyl	4.3	95 : 5	85.0
5	Me	Pr^n	p-C_6H_4IPh	Quaterphenyl	2.22	100 : 0	66.5
6	Me	Pr^n	p-$C_6H_4I_2$**	Not found	1.97	100 : 0	82
7	Ph	Pr^i	PhI	Diphenyl	1.23	100 : 0	83

* β-Products contained only the *trans*-isomer.

** 

This compound was obtained as the product.

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 4, pp. 786—787, April, 1995.