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AN UNUSUAL PHOTOCHEMICAL REACTION OF INDENE WITH FURAN AND THIOPHENE DERIVATIVES

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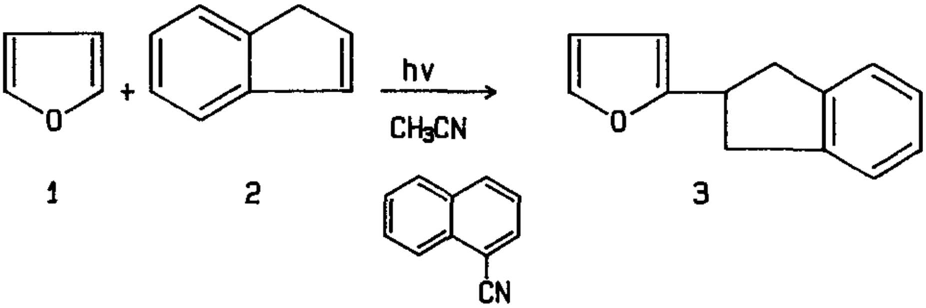
Abstract - 2-Indenylfuran and -thiophene derivatives are synthesized through a photochemical approach.

Furan 1 can undergo an addition reaction with various olefins such as indene 2 in the presence of cyanonaphthalenes with low yields (20%)[1].



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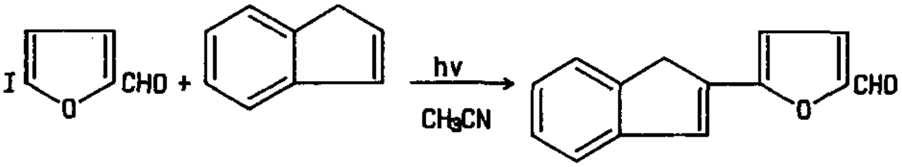
In the past years we have found that both halogenofurancarbaldehydes[2] and halogenothiophenecarbaldehydes[3] give the corresponding arylation products when irradiated in the presence of aromatic compounds.

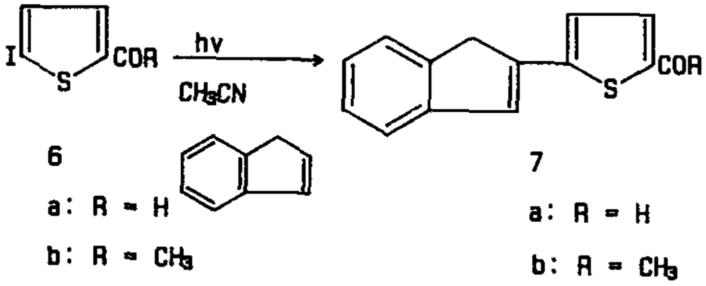
In this field we wanted to verifiy the reactivity of halogenofuran and -thiophene derivatives when they are irradiated in the presence of indene: we expected two possible products, one deriving from the arylation reaction, the other deriving from a photoaddition reaction.

Unexpectedly, the irradiation of 5-iodofuran-2-carbaldehyde[4,5] 4 in acetonitrile in the presence of indene led to the substitution product 5 in 53% yield.



4 2 5

The extension of this reaction to thiophene derivatives showed the same trend of reactivity. 5-Iodothiophene-2-carbaldehyde[5,6] 6a or methyl ketone 6b[5] gave the substitution products in 74 - 77% yield. Also, 3-iodothiophene-2-carbaldehyde[3,5] 8 furnished the substitution product in good yield (59%) in agreement with the results obtained in the photoarylation of thiophenes[3]. Finally, 3,5-diiodothiophene-2-carbaldehyde[3] 10 yielded the photoproduct in both iodinated positions (68%).



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a: R = H

b: R = CH_3

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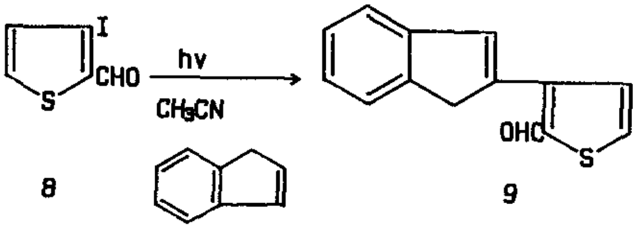
a: R = H

b: R = CH_3



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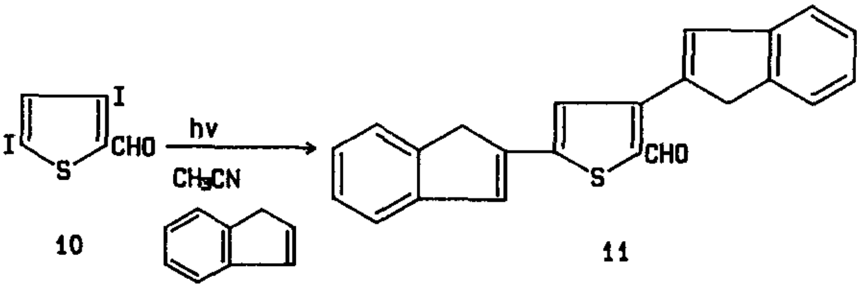

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In conclusion, this reaction seems to be a general synthetic method for furan and thiophene derivatives.

In agreement with our previous results[3], this reactivity was able to give some informations about the reaction mechanism: probably, the reaction occurs via the formation of a triplet exciplex between 4 (the acceptor) and 2 (the donor). A subsequent radical coupling leads to the final product.

In our knowledge, this is the first reported photochemical substitution reaction on indene.

EXPERIMENTAL

5-Iodofuran-2-carbaldehyde 4 (1 g, 4.2 mmoles) and indene (3 ml, 26 mmoles) were dissolved in acetonitrile (300 ml) and the solution was outgassed with N_2 for 1 h. The mixture was then irradiated in an immersion apparatus with a 500 W high-pressure mercury arc (Helios-Italquartz) surrounded by a Pyrex water-jacket. After 1 h the mixture was dissolved in $CHCl_3$ and washed successively with 0.1 M $Na_2S_2O_3$ and then with brine. The organic phase was dried (Na_2SO_4). Removal of the solvent yielded a crude product which was chromatographed on SiO_2. Elution with benzene gave pure 5 (500 mg, 74%).

5-(1H-Inden-2-yl)-furan-2-carbaldehyde 5

^{1}H-Nmr ($CDCl_3$, δ): 9.60 (s, 1 H), 7.20(m, 6 H), 6.58 (d, 1 H, J = 4 Hz), 3.73 (s, 2 H); ir ($CHCl_3$, ν_{max} cm^{-1}): 1662, 1600, 1547, 1490, 1455, 1390, 1345, 1319, 1285, 1023, 968; ms (*m/z*): 210, 209.

5-(1H-Inden-2-yl)-thiophene-2-carbaldehyde 7a

^{1}H-Nmr ($CDCl_3$, δ): 9.84 (s, 1 H), 7.63 (d, 1 H, J = 4 Hz), 7.39 (m, 2 H), 7.24 (m, 2 H), 7.19 (d, 1 H, J = 4 Hz), 3.74 (s, 2 H); ir ($CHCl_3$, ν_{max} cm^{-1}): 1655, 1555, 1455, 1433, 1302; ms (*m/z*): 226, 225.

5-(1H-Inden-2-yl)-2-acetyl-thiophene 7b

^{1}H-Nmr ($CDCl_3$, δ): 7.57 (d, 1 H, J = 4 Hz), 7.45 (m, 2 H), 7.27 (m, 2 H), 7.20 (s, 1 H), 7.14 (d, 1 H, J = 4 Hz), 3.75 (s, 2 H), 2.51 (s, 3 H); ir ($CHCl_3$, ν_{max} cm^{-1}): 1660, 1460, 1440, 1360, 1317, 1270, 910; ms (*m/z*): 240.

3-(1H-Inden-2-yl)-thiophene-2-carbaldehyde 9

^{1}H-Nmr ($CDCl_3$, δ): 10.19 (d, 1 H, J = 1.4 Hz), 7.68 (dd, 1 H, J_1 = 5.0 Hz, J_2 = 1.4 Hz), 7.47 (m, 2 H), 7.32 (m, 2 H), 7.26 (d, 1 H, J = 5.0 Hz), 7.18 (m, 1 H), 3.83 (s, 2 H); ir ($CHCl_3$, ν_{max} cm^{-1}): 1655, 1460, 1420, 1395, 1378, 1343, 1105, 1005, 910; ms (*m/z*): 226, 225.

3,5-[Di-(1H-inden-2-yl)]-thiophene-2-carbaldehyde 11

^{1}H-Nmr ($CDCl_3$, δ): 9.72 (s, 1 H), 7.43 (m, 4 H), 7.28 (m, 5 H), 7.24 (s, 2 H), 3.74 (s, 4 H); ir ($CHCl_3$, ν_{max} cm^{-1}): 1650, 1560, 1455, 1428, 1355, 1340, 1305, 1135; ms (*m/z*): 340, 339.

REFERENCES AND NOTES

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3. R. Antonioletti, M. D'Auria, F. D'Onofrio, G. Piancatelli, and A. Scettri, J. Chem. Soc., Perkin Trans 1, 1986, 1755.
4. Z. N. Nazarova, Zh. Obshch. Khim., 1955, 25, 539 (Chem. Abstr., 1956, 50, 33831).
5. 4: uv, λ_{max} 294 nm (ε = 13900); 6a: uv, λ_{max} 306 nm (ε = 12100); 6b: uv, λ_{max} 306 nm (ε = 15400); 8: uv, λ_{max} 289 nm (ε = 11400).
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