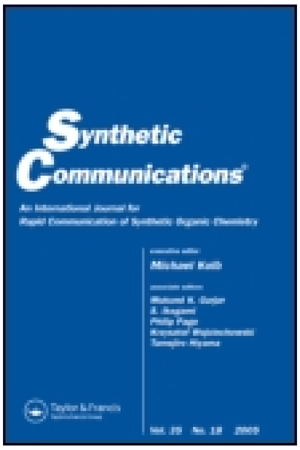

Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/lsyc20

THE NITROMETHANE INITIATOR OF THE FRIEDEL-CRAFTS NAPHTHALENE REACTION USING MICROWAVES

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To cite this article: G. Brãtulescu , Y. Le Bigot & M. Delmas (2001): THE NITROMETHANE INITIATOR OF THE FRIEDEL-CRAFTS NAPHTHALENE REACTION USING MICROWAVES, Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry, 31:21, 3309-3313

To link to this article: http://dx.doi.org/10.1081/SCC-100106041

SYNTHETIC COMMUNICATIONS, 31(21), 3309–3313 (2001)

THE NITROMETHANE INITIATOR OF THE FRIEDEL–CRAFTS NAPHTHALENE REACTION USING MICROWAVES

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ABSTRACT

The alkylation of naphthalene using halogen derivatives may be achieved under very simple conditions by the Friedel–Crafts reaction. The products are obtained by irradiation of the paste containing the reaction mixture and a small quantity of nitromethane to initiate the reaction.

The alkylation of naphthalene by the Friedel–Crafts reaction is, in general, difficult to achieve (1–3). It requires high temperatures, very long reaction times and the yields are nonetheless mediocre. Another method of obtaining alkyl derivatives of naphthalene relies on the reactivity of

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organometallic compounds (4), however, the operating conditions for this procedure can be very delicate. Furthermore, these reactions are not selective and the yields are again limited (less than 50%).

Use of microwaves can sometimes favour certain reaction rates but this technique often necessitates the use of absorbent supports. The separation of products from the absorbents, however, can at times reveal itself to be difficult. With this in mind we have previously described methods for the synthesis of ethers (5) and azoethers (6) with microwaves in the absence of a support.

During previous work (7), we presented a process in which the absorbent support is replaced by a small quantity of ethanol. This addition of ethanol initiates the chemical reaction by creating catalytic centres and has the advantage of being easily extracted from the reaction mixture. However, the alkylation of naphthalene reaction using microwaves was not initiated by ethanol due to its reactivity with the constituents of the reaction mixture in particular aluminium chloride and further cationic species.

The search for a ethanol substitute led us to choose nitromethane because:

- It is inert with regard to the other reactants.
- It has sufficient polar characteristics to enable it to absorb microwaves (Table 1).
- It has a relatively a low boiling point (101.2°C).

The alkylation of naphthalene is achieved with good yields (Table 2). At the experimental level the reaction is carried out in two steps:

- Preparation of the cation by the reaction of an halogen derivative with aluminium chloride.
- Addition of naphthalene with a few drops of nitromethane.

The obtained paste is irradiated in an open beaker for a very short time (see Table 2). The strong polarity of nitromethane permits it to absorb this radiation and to initiate the electrophilic substitution reaction.

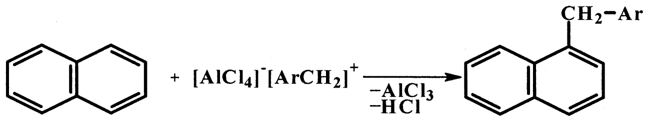
Table 1. Comparison of the Polarity of Ethanol to That of Nitromethane (8)

	ε	μ	E_T^N*
EtOH	24.55	5.8	51.9
CH_3NO_2	35.94	11.9	46.3

*-empirical parameters of solvent polarity.

Table 2. Synthesis of 1-Alkylnaphthalene

$$AlCl_3 + XCH_2{-}Ar \longrightarrow [AlCl_4]^-[ArCH_2]^+$$



Nr.	Ar	Compound	Elementary analysis calculated found		Time [s]	T_f [°C]	Yield [%]	T[°C] T_l[°C]	Bands IR [cm^{-1}]
			%C	%H					
1	Ph	$C_{17}H_{14}$	93.57 93.55	6.42 6.41	90	64	68	60^f 59-60^9	$\nu_{C=C}$: 1628vs 1507m 1452M
2	(o-Cl)Ph	$C_{17}H_{13}Cl$	80.79 80.75	5.14 5.11	110	51	70	191^e 189-192^{10}	$\nu_{C=C}$: 1593s 1472vs 1429vs ν_{CCl}: 746vs
3	(p-Cl)Ph	$C_{17}H_{13}Cl$	80.79 80.76	5.14 5.11	120	46	76	135^f -	$\nu_{C=C}$: 1595f 1489vs 1430f ν_{CCl}: 753vs
4	(p-Br)Ph*	$C_{17}H_{13}Br$	68.68 68.63	4.37 4.36	50	36	45	61^f -	$\nu_{C=C}$: 1596m 1493vs 1445f ν_{CBr}: 558vs
5	(p-F)Ph	$C_{17}H_{13}F$	86.64 86.60	5.50 5.48	100	51	82	290^f_d -	$\nu_{C=C}$: 1600vs 1508vs 1435vs ν_{CF}: 1156f
6	(2-Me)Ph	$C_{18}H_{16}$	93.10 93.07	6.89 6.84	115	65	57	63^f 63^{11}	$\nu_{C=C}$: 1618m 1592vs 1439vs
7	(m-Me)Ph	$C_{18}H_{16}$	93.10 93.06	6.89 6.85	112	67	62	141^e 140-145^{12}/ 0.15mmHg	$\nu_{C=C}$: 1621m 1603vs 1445vs
8	(p-Me)Ph	$C_{18}H_{16}$	93.10 93.08	6.89 6.82	65	40	51	53^f 53^{13}	$\nu_{C=C}$: 1629m 1599vs 1435vs
9	N-phtalimide	$C_{19}H_{13}NO_2$	79.44 79.39	4.52 4.50	377	48	69	140^f -	$\nu_{C=O}$: 1772vs 1704vs $\nu_{C=C}$: 1518m : 1467f ν_{C-N}: 1106f 1192f

* from the corresponding bromides ;
f- melting temperatures
e- boiling temperatures

T_f : temperature after irradiation
T_l : reference temperature

The separation of the absorbing support from the reaction medium is easily achieved.

EXPERIMENTAL

All reagents were purchased from Aldrich.

Fusion points were measured using a Mettler Toledo apparatus.

Elemental analyses were performed with a Carlo Erba model 1106 apparatus.

IR/FT spectra were recorded on KBr pellets using a Perkin-Elmer 1600 spectrometer.

A Optiquick Y71 microwave oven was used: emission power $= 620\,W$, $\lambda = 12.2\,cm$.

Temperatures after irradiation were measured used a Hanna model HI 8757 thermocouple thermometer.

EXPERIMENTAL PROCEDURE

Five mmol of the halogen derivative is added with vigorous mixing to 5 mmol of anhydrous aluminium chloride. The mixture obtained is then added to an open beaker containing 5 mmol of finely grounded naphthalene. After mixing and addition of 2 drops of nitromethane the resulting paste is irradiated in a microwave oven for the required time (Table 2). Twenty mL of water is then added and the paste vigorously mixed after which 20 mL of chloroform is added, again with mixing. After phase separation and the drying of the organic phase the chloroform is evaporated under vacuum and the residue purified by recrystallisation in a mixture of ethanol : chloroform (1/1 vol.) or by distillation.

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Received in the USA December 26, 2000

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