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Microwaves Assisted Gabriel Synthesis of Phthalides

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Abstract: Cesium acetate was found to be the best catalyst for the synthesis of 3-benzylidenephthalide from phthalic anhydride and phenylacetic acid. Reasonable to good yields of different 3-arylmethylenephthalides were isolated from the microwave Gabriel synthesis, even when phenylthio- and 2-(3-)thienyl- acetic acids were used as the starting material.

INTRODUCTION

The synthesis of different types of 3-aryl- and 3-alkylmethylenephthalides has attracted a great deal of attention over the past several decades[1-4], as 3-alkylmethylenephthalides are known as essential oils from herbs[5], as cytotoxic materials[6], and as materials for cosmetics[7,8]. They are also essential intermediates for 2-aryl-1,3-indandione derivatives, which are well known as anticoagulants[9].

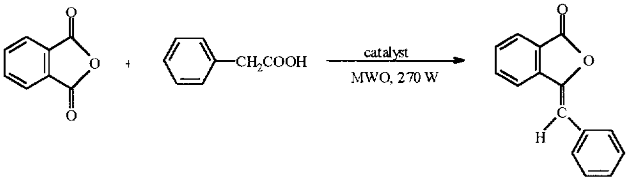
The classical synthesis[1-3,10] of 3-arylmethylenephthalides consists of prolonged (2 - 4 hours) heating of the phthalic anhydride, the appropriate acid and a catalyst to 240 - 260 °C. Yields achieved by this method are usually lower than 70 % and decrease when thermally labile acids are used. Even using higher temperatures (300 °C) the reaction times were long (2 -4 h), and yields of 60-79 % were achieved[11]. Modification of the procedure, using refluxing acetic anhydride as the reaction medium[12], resulted in lowering of the yield to 34%. Using potassium carbonate[13] or potassium carbonate in acetic anhydride[14] as the catalysts in the phthalide synthesis resulted in lowering of the yields of the products. It is well known, on the other hand, that microwave heating (reactions in microwave oven) shortens the exposure of the reaction mixture to high temperature, and higher yields and more pure products are often obtained[15-19]

The main goal of this work was to examine the catalyst effect on the Gabriel synthesis of 3-benzylidenephthalide. The next goal was to find convenient conditions for the synthesis of other 3-arylmethylene- as well as 3-aryloxy(thio)methylenephthalides. Our next aims were to find out if both possible Z/E isomers of phthalides are formed and to examine if 2-aryl-1,3-indandiones can be prepared in a microwave oven by one-pot procedure.

RESULTS AND DISCUSSION

Preliminary experiments on the Gabriel synthesis of 3-benzylidenephthalide (Scheme 1) proved that the course of the reaction is easy to follow by observing the colour of the reaction mixture. Microwave heating should be stopped when the colour became brown, as this was a sign of decomposition.

Scheme 1



1

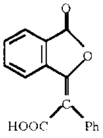
At the beginning of our study different catalysts were tested and the reactions were carried out under solvent free conditions. Using the molar ratio phthalic anhydride : phenylacetic acid : catalyst 1 : 1 : 0.2 the reaction was over after 5 - 10 min. The best yield (76 %) of 3-benzylidephthalide was achieved using cesium acetate as the catalyst (Table 1, column A). To our surprise, very low yields (35 %) of the product were achieved with the most common catalyst, sodium acetate, after 10 min in the microwave oven. Using potassium acetate an 82 % yield of the product was isolated after a reaction time of 10 min.

Our next step was to use the catalyst on alumina as an inorganic support as the reaction medium. This modification of the procedure resulted in raising yields of the product, which was most pronounced when sodium acetate or potassium carbonate were used as catalysts. The work up of the reaction mixture is more complicated in this case as the product had to be extracted from alumina into diethyl ether.

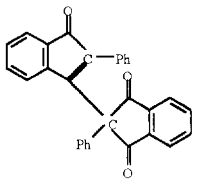
It was of interest to examine if the excess of phthalic anhydride would have a beneficial effect on the yields of the product. As can be seen from Table 1, column B, the 3-molar excess of phthalic anhydride did not have a dramatic effect on the yields, with the exception of sodium acetate or potassium carbonate as the catalyst.

Using these solvent free conditions the product was very pure and crystallization from ethanol gave an analytical sample of the phthalide. Results of our experiments in acetic anhydride as the reaction medium are given in Table 2. The reaction was very vigorous in this case, and the b.p. of acetic anhydride was reached after several second; the reaction had to be interrupted several times to achieve the reaction time given in Table 2. It can be seen, that the yields of the product are lower than in the reactions without the solvent. From the aqueous solution, after acidification, 3-benzylidenephthalide carboxylic acid (**2**) was isolated together with yellow crystals of the 2-phenylindan-1,3-dione autocondensation product (**3**) (Chart 1). This is in accord with literature precedence[3-20,21], but in those cases triethylamine in acetic anhydride was used as the catalyst. This could be explained by the fact that the temperature of boiling acetic anhydride is not high enough to complete decarboxylation of **2**. Prolonging the reaction time led to polymer formation.

Chart 1



2

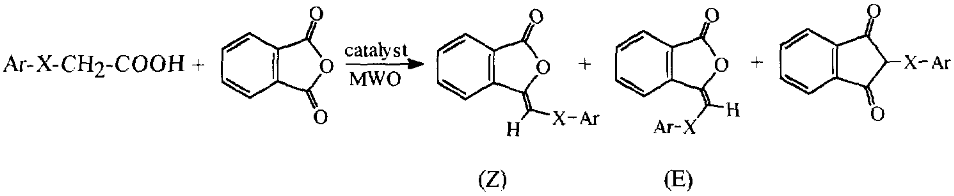


3

At the end of this part of our work we made an attempt to scale up the reaction. Using 0.05 mol of the reactants (appr. 14 g) a 57 % yield of 3-benzylidenphthalide was isolated using CH_3COOCs/Al_2O_3 as the catalyst or 52 % yield when $CH_3COOK/Al_2O_3$was used. Reaction time was 5 min with CH_3COOCs/Al_2O_3 and 6 min with CH_3COOK/Al_2O_3.

For our experiments with other arylacetic acids we used a ratio arylacetic acid : phthalic anhydride : catalyst of 1 : 2.3 : 0.02. The mixture of phthalic anhydride and the appropriate arylacetic acid was homogenized by melting, catalyst was then added, and the reaction was carried out in an Erlenmeyer flask fitted with condenser[22] in a microwave oven (Scheme 2).

Scheme 2



(For the results see Tables 3 - 5)

From the results shown in Table 3 it may be seen that good yields were achieved with 1-naphthylacetic acid, substituted phenylthioacetic acids and phenylsulfoxyacetic acid. Reasonable or poor yields were achieved with 2- or 3-thienylacetic acids, and substituted phenoxyacetic acids. It is of interest that in most cases both the **Z** and **E** isomers of 2-arylmethylenephthalides were isolated in ratios from 2 : 1 to 10 : 1. **Z**-Isomers, which are always predominant, are less soluble and therefore easy to isolate. Some of the **E**-isomers were described in the references given in Table 3. The photoisomerization of 2-alkylmethylenephthalides has been described[23] and it was of interest to find out if both **Z/E** isomers are formed during the reaction , or if they isomerize by heating in microwave oven.

We made unsuccessful attempts on such **Z**→**E** , as well as **E**→**Z** isomerizations with **Z**-3-phenoxymethylenephthalide, **Z**-3-phenylthiomethylenephthalide, and **Z**-3-(1-naphthyl)-methylenephthalide, and their **E**- isomers respectively. The unchanged **Z** (**E**) isomers were recovered also after prolonged (20 - 30 min) heating of 0.5g of the **Z** (**E**) phthalides in the microwave oven. These observations prove that both isomers are formed during the reaction of phthalic anhydride with the arylacetic acid.

From the data given in Table 3 it may be seen that poor yields of the corresponding phthalides were formed from both thienylacetic acids and substituted phenoxyacetic acids, which is in accord with the results of classical Gabriel syntheses[14,24,25]. Since cesium acetate proved to be the best catalyst at the synthesis of 3-benzylidenephthalide, we decided to test its efficacy in the case of thienylacetic and phenoxyacetic acids. The results given in Table 4 demonstrate that it is an efficient catalyst for the synthesis of 3-(2- or 3-thienylmethylene)phthalides, since yields of 40 - 66 % of the phthalides were isolated. On the other hand, the yields of 3-phenoxymethylenephthalides were still very low (8 - 13 %) even when CH_3COOCs / Al_2O_3 was used as the catalyst. This can be rationalized in terms of the thermal instability of phenoxyacetic acids.

Potassium acetate in acetic anhydride[26] and potassium carbonate in acetic anhydride[14] have also been described as the catalysts for phthalide synthesis . We decided therefore to examine their efficacy when reactions were performed in the microwave oven. The described procedure[26] was modified (see Experimental) by pre-formation of the mixed arylacetic acetic anhydride or arylacetic anhydride (the structure of this intermediate was not proved). Most attention was paid to the reaction of phthalic anhydride with 1-naphthylacetic acid. The effect of reaction time (K_2CO_3) as well as the reactant : catalyst ratio (CH_3COOK) was also studied . From the results given in Table 5 it is clear that for both K_2CO_3 as well as CH_3COOK as catalyst the conversion of 1-naphthylacetic acid to products was lower than 50%, and a mixture of 3-(1-naphthylmethylene)phthalide and 2-(1-naphthyl)-1,3-indandione was formed. The ratio phthalide / indandione changed from 1 :1 after 1 min in the microwave oven to 1 : 3 after 3 min in the oven when potassium carbonate was used as the catalyst. Using CH_3COOK as the catalyst, we showed that this ratio depends on the amount of the catalyst also. The ratio changed from 1 : 4 using 0.5 equivalent of the catalyst to ca. 1 : 1 using 0.05 equivalent or less of the catalyst. (Formation of both phthalide and indandione was described[27,28] when the reaction was carried out using Et_3N/Ac_2O mixture.) We attempted to effect the 3-(1-naphthylmethylene)phthalide to 2-(1-naphthyl)-1,3-indandione rearrangement by heating the phthalide with CH_3COOK in acetic anhydride in the microwave oven. After 5.5 min heating the reaction mixture (1g of phthalide, 2 ml Ac_2O and 0.1g of CH_3COOK) was brownish, but only starting material was isolated. This is in agreement with[27] and constitutes an indirect proof that 2-aryl-1,3-indandione must be formed under the above conditions by a different mechanism, not via the 3-arylmethylenephthalide.

Preliminary attempts at phthalide synthesis from acetic anhydride and other arylacetic acids in CH_3COOK / Ac_2O mixtures gave complicated mixtures of products. The presence of 2-aryl-1,3-indandione was detected in the crude reaction product by a typical two coupled ν_{CO} vibration at 1580 - 1660 cm^{-1}.

EXPERIMENTAL SECTION

All reactions were carried out in a DAEWOO microwave oven at 270 W. Melting points were determined on a Kofler-hot-stage and are uncorrected. ^{1}H-NMR spectra were measured in $CDCl_3$ solution, tetramethylsilane being the internal standard (δ, ppm) on a TESLA BS 487A (80 MHz) instrument.

General procedure for preparation of the catalysts on Al_2O_3 : A solution of 0.03 mol of the catalyst (CH_3COOM or K_2CO_3) in 40 ml of distilled water was added to 10 g of Al_2O_3. Mixture was stirred for 5 - 10 min and water was then evaporated under reduced pressure. The catalyst was then dried for 5 hours at 110 - 140 °C/5 torr.

Synthesis of 3-benzilidenephthalide under solvent free conditions: A mixture of phthalic anhydride (0.74 g, 5 mmol), phenylacetic acid (0.68 g, 5 mmol) and the catalyst (1 mmol) in an Erlenmeyer flask with condenser[22] was heated in the microwave oven for the time given in Table 1. Reaction mixture was then poured into 100 ml of 5 % $NaHCO_3$ and left to stand overnight. The solid material was filtered off and crystallized from ethanol. 3-Benzilidenephthalide (1), white crystals, m. p. 99 - 102 °C (99 - 101 °C, ref[27]), ^{1}H-NMR (80 MHz, $CDCl_3$): 6.4, s, 1H (=CH), 7.25 - 7.96, m, 9H (aromatic) was isolated.

The same procedure was used when ratio 3 : 1 : 0.1 was used. The results are given in Table 1.

Note: When CH_3COOM/Al_2O_3 or K_2CO_3/Al_2O_3 were used as the catalyst, the amount of MK/Al_2O_3 containing 1 mmol of the MK was taken in reaction. Product was extracted into diethylether, solution was dried over anhydrous Na_2SO_4, solvent evaporated and residue crystallized from ethanol.

Synthesis of 3- benzilidenephthalide in acetic anhydride: Phthalic anhydride (0.74 g, 5 mmol), phenylacetic acid (0.68 g, 5 mmol) and the catalyst (1 mmol) were dissolved in 5 ml of acetic anhydride in an Erlenmeyer flask[22] and heated with several interruptions, for the time given in Table 2. The reaction mixture was then poured into 200 ml of 5 % $NaHCO_3$ and the mixture left to stand overnight. Oily organic fraction was extracted three times into 150 ml of diethyl ether. The solution was dried over anhydrous Na_2SO_4, solvent was evaporated and the residue was crystallized from ethanol. Slightly yellow crystals of 3-benzylidenephthalide (**1**), m. p. 99-102 °C were isolated. Phthalide carboxylic acid (**2**) m. p. 228°C (ref[20],m. p. 229-231°C), $M^{+\bullet}$ 266 was isolated from the acidified aqueous solution . A small amount of **3** (m. p. 177-178°C, ref[21] 181°C), was isolated as yellow crystals isolated by column chromatography of the crude **1**. Results are given in Table 2.

Table 1. Results of Gabriel Synthesis of 3-Benzylidenephthalide under Solvent Free Conditions

Catalyst	**Time (min)**	**Yields (%) A**	**Yields (%) B**
CH_3COOLi	14	17	—
CH_3COONa	10	35	63
CH_3COOK	10	82	79
CH_3COOCs	5	76	73

K_2CO_3	6	38	82
CH_3COONa/Al_2O_3	10	50	54
CH_3COOK/Al_2O_3	10	81	77
CH_3COOCs/Al_2O_3	5	83	71
K_2CO_3/Al_2O_3	10	55	7

A Molar ratio phthalic anhydride : phenylacetic acid : catalyst = 1 : 1 : 0.2

B Molar ratio phthalic anhydride : phenylacetic acid : catalyst = 3 : 1 : 0.2

Table 2. Results of Gabriel Synthesis of 3-Benzylidenephthalide (**1**) in Acetic Anhydride

Catalyst	**$(CH_3CO)_2O$ (ml)**	**Time (min)**	**Yield 1 (%)**	**Yield 2 (%)**
CH_3COOLi	5	10	0	0
CH_3COONa	5	2.5	38	19
CH_3COOK	5	3.5	45	21
CH_3COOCs	5	2.0	63	31
K_2CO_3	5	2.0	25	8

General procedures for Gabriel synthesis of 3-arylmethylenephthalides

A. In excess of phthalic anhydride. The mixture of the appropriate arylacetic acid (5 mmol) and phthalic anhydride (13.5 mmol) was fused on a hot plate, and stirred during cooling. Potassium acetate (0.1 mmol) was then added and the reaction mixture was heated in the microwave oven for the time given in Table 1 (till the change of colour was observed). The mixture was then poured into 50 ml of a saturated solution of $NaHCO_3$ and the resulted mixture stirred for 6 h at room temperature. The insoluble product was filtered off and dried. The dry crude product was added to 20 ml of ethanol and the mixture stirred for another 4 h at room temperature. The insoluble **Z**-isomer was separated and crystallized from ethanol. The ethanol solution, left after separation of **Z**-phthalide, was evaporated to dryness and the **E**-isomer of the phthalide was crystallized from diethyl ether. The results are given in Tables 3 and 4.

B. Synthesis via mixed anhydride with acetic anhydride. A solution of 5 mmol of arylacetic acid in 3 ml of acetic anhydride was heated under reflux for 10 min . The solution was then concentrated to 1 ml, phthalic anhydride (10 mmol) and the catalyst (0.1 mmol) were added and the reaction mixture was heated in the microwave oven for the time given in Table 5. The work up was as described in method **A.**.

Note: In the reaction with 1-naphthylacetic acid 2-(1-naphthyl)-1,3-indandione was isolated as an ethanol-insoluble material.

E-3-(1-Naphthylmethylene)phthalide. For $C_{38}H_{22}O_6$ (M = 574) calculated 79.43 % C, 3.85 % H; found 80.1 % C, 3.92 % H. ^{1}H-NMR (DMSO): 7.54, m, 1H (naphthyl); 7.63, s, 1H (CH=); 7.70 - 8.0, m, 9H (arom CH); 8.07, d, 1H, J = 7 Hz (Ch$_{phth}$). IR: $\nu_{(CO)}$ 1778 cm^{-1} , $\nu_{(C=C)}$ 1680 cm^{-1} $\nu_{(C-O-C)}$ 1290 cm^{-1}.

E-3-(2-Thienylmethylene)phthalide. For $C_{13}H_8O_2S$ (m = 228) calculated 68.40 % C, 3.68 % H; found 68.54 % C, 3.68 % H. ^{1}H-NMR ($CDCl_3$): 6.68, s, 1H (CH=); 7.02 - 7.97, m, 7H (arom CH). IR : $\nu_{(CO)}$ 1760 cm^{-1}, $\nu_{(C=C)}$ 1660 cm^{-1} ,$\nu_{(C-O-C)}$ .1270 cm^{-1}.

Z-3-(3-Thienylmethylene)phthalide. For $C_{13}H_8O_2S$ (m = 228) calculated 68.40 % C, 3.68 % H; found 69.20 % C, 3.81 %H. ^{1}H-NMR ($CDCl_3$): 6.49, s, 1H (CH=); 7.29 - 7.96, m, 7H (arom CH). IR : $\nu_{(C=O)}$ 1760 cm^{-1}, $\nu_{(C=C)}$ 1660 cm^{-1}, $\nu_{(C-O-C)}$ 1270 cm $^{-1}$.

E-3-(3-Thienylmethylene)phthalide. For $C_{13}H_8O_2S$ (m = 228) calculated 68.40 % C, 3.68 % H; found 68.29 % C, 3.28 % H. ^{1}H-NMR ($CDCl_3$): 6.51, s, 1H (CH=); 7.29 - 7.96, m, 7H (arom CH). IR :$\nu_{(C=O)}$ 1780 cm^{-1} , $\nu_{(C=C)}$ 1700 cm^{-1} ,$\nu_{(C-O-C)}$ 1280 cm^{-1} .

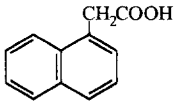
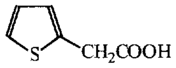
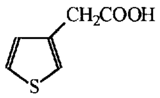
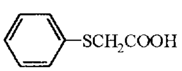
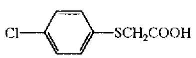
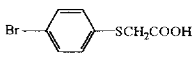
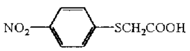
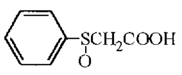
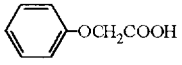
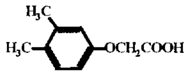
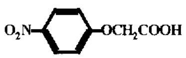
E-3-(4-Chlorphenylthiomethylene)phthalide. For $C_{15}H_9O_2ClS$ (M = 288) calculated 62.39 % C, 3.14 % H; found 62.59 % C, 3.29 % H. ^{1}H-NMR ($CDCl_3$): 6.24, s, 1H (CH=); 7.38 - 7.92, m, 8h (arom CH); (Z = 6.35). IR : $\nu_{(C=O)}$ 1778 cm^{-1}, $\nu_{(C=C)}$ 1710 cm^{-1} , ν(C-O-C) 1280 cm^{-1}.

E-3-(4-Nitrophenylthiomethylene)phthalide. For $C_{15}H_9O_4NS$ (M = 299) calculated 60.17 % C, 3.03% H; found 60.47 % C, 3.12 % H. ^{1}H-NMR (DMSO): 7.20, s, 1H (CH=); 7.37 - 7.75, m, 4H (CH$_{phth}$); 7.80, d, 2H, J = 8 Hz (CH$_{phen}$); 8.24, d, 2H, J = 8 Hz (Ch$_{phen}$). IR : $\nu_{(C=O)}$ 1780 cm^{-1}, $\nu_{(C=C)}$ 1708 cm^{-1}, $\nu_{(C-O-C)}$ 1280 cm^{-1}, $\nu_{(NO2)as}$ 1510 cm^{-1},$\nu_{(NO2)s}$ 1340 cm^{-1}.

Z-3-(Phenylsulfoxymethylene)phthalide. For $C_{15}H_{10}O_3S$ (M = 270) calculated 66.64 % C, 3.72 % H; found 66.72 % C, 3.84 % H. ^{1}H-NMR ($CDCl_3$): 7.13 - 7.94, m, 8H (CH=, arom CH); 8.65, d, 1H, J= 6 Hz. IR : $\nu_{(C=O)}$ 1780 cm^{-1}, $\nu_{(C=C)}$ 1690 cm^{-1}, $\nu_{(C-O-C)}$ 1260 cm^{-1}, $\nu_{(S-O)}$ 1018 cm^{-1}.

E-Isomer has identical ^{1}H-NMR spectrum on 80 MHz instrument. IR :$\nu_{(C=O)}$ 1778 cm^{-1}, $\nu_{(C=C)}$ 1675 cm-1, $\nu_{(C-O-C)}$ 1260 cm^{-1}, $\nu_{(S-O)}$ 1010 cm^{-1}.

Table 3. Results of Gabriel Synthesis of 3-Arylmethylenephthalides in Microwave Oven Using CH_3COOK as Catalyst [a,b]

Acid	Time (min)	Yield (%)	Z / E ratio	M. p. (°C), ref.
	9	75	10 : 1	179 - 82 (**Z**) 181 - 81.5[29] 148 - 51 (**E**) -
	5	31	4 : 1	117 - 18 (**Z**) 117 - 18[14] 114 - 15 (**E**) -
	8.5	25	3 : 1	80 - 82 (**Z**) - 69 - 71 (**E**) -
	4.5	66	4 : 1	148 - 49 (**Z**) 148 - 49[30] 118 - 20 (**E**) 120 - 22[30]
	6.5	83	5 : 1	173 - 75 (**Z**) 173 - 75[30] 105 - 10 (**E**) -
	6.5	89	5 : 1	194 - 96, (**Z**) 194 - 96[21]
	6.5	64	5 : 4	228 - 30 (**Z**) 228 - 30[30] 128 - 34 (**E**) -
	3	31	8 :1	120 - 21 (**Z**) - 110 - 14 (**E**) -
	7	9.6	2 : 1	147 (**Z**) 153[24]
	10	16	4 : 1	103 - 4 (**E**) 103 - 4[24]
	15	9.6	2 : 1	
	10	20	2 : 1	188 - 91 (**Z**) 193[30] 162 - 64 (**E**) 164[30]
	10	21		228 - 29 (**Z**) 288 - 89[30]

[a] In all experiments 13.5 mmol of phthalic anhydride, 5 mmol of arylacetic acid and 0.1 mmol of CH_3COOK was used.

[b] Microanalysis , ^{1}H-NMR and IR spectra of new compounds only are given in Experimental.

Table 4. Results of Gabriel Synthesis of 3-Arylmethylenephthalides in Microwave Oven Using CH_3COOCs as Catalyst

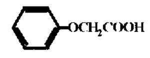
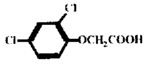
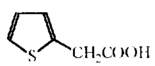
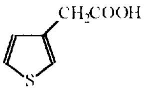
Acid	Catalyst	Time (min)	Yield (%)	M.p. (°C), ref.	
	CH_3COOCs CH_3COOCs/Al_2O_3	1.5 7	4.2 8.3	134 - 35	134 -35[30]
	CH_3COOCs CH_3COOCs/Al_2O_3	2 6	13 13	224	224[30]
	CH_3COOCs CH_3COOCs/Al_2O_3	0.75 2	39 32	117	117[30]
	CH_3COOCs	10	66	79 - 80	

Table 5. Results of Gabriel Synthesis of 3-(1-Naphthylmethylene)phthalide in Microwave Oven Using CH_3COOK/Ac_2O or K_2CO_3 as Catalyst[a]

Catalyst (mmol)		Time (min)	Yield (%)	Phthalide - indandione ratio
K_2CO_3	0.1	1	27	1 : 1
K_2CO_3	0.1	2	54	3 : 5
K_2CO_3	0.1	3	27	1 : 3
CH_3COOK	0.1	2	27	1 : 1
CH_3COOK	0.5	2	30	2 : 1
CH_3COOK	1	2	37	4 : 7
CH_3COOK	5	2	39	1 : 4

[a] In all reactions 5.4 mmol of 1-naphthylacetic acid and 6.7 mmol of phthalic anhydride was used.

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REFERENCES

1. Gabriel, S. *Ber. Deutch.Chem.Gessel.* **1881**, *14*,921.
2. Weiss, R. *Organic Synthesis*; J. Wiley: New York, Vol 2, **1943**; p. 61.
3. Oschkaya, V. P. *Angidridnaya kondensacija*; Zinatue: Riga, **1973**; pp.202.
4. Hrnčiar, P. *Chem. Zvesti* **1963**, *17*, 666.
5. Gijbels, J. M.; Scheffer, J. J. C.; Svendson, A. *Planta Med.* **1980**, (suppl) 41; *Chem. Abstr.* **1981**, *94*, 127132.
6. Fuska, J.; Fusková, A.; Proksa, B. *Neoplasma* **1985**, *32*, 407.
7. Vaugham, C. D. *J. Soc. Cosmet. Chem.* **1985**, *33*, 319; *Chem. Abstr.* **1986**, *104*, 95253.
8. Conner, D. E. *Ger. Offen* 3,002,304; *Chem. Abstr.* **1981**, *94*, 36119.
9. Soulier, J. P.; Gueguen, J. *Rev. Hemat.* **1948**, *3*, 180.
10. Muller, E. *Ber.Deutch.Chem.Gessel.* **1909**, 42, 423.
11. Sam., J.,; Lopez, A.V.; Shafik, R.M. *J.Pharm. Sci.* 1968, 57, 1755.
12. Rein, M.; Hanack, M. *Chem.Ber.* 1989, 121, 1601.
13. Hrnciar, P. *Chem. Zvesti* **1962**, 16, 96.
14. Lacova, M.; Hrnciar, P. *Chem. Papers* **1985**, 39, 135.
15. Mingos, D. M. P.; Baghurst, D. R. *Chem. Soc. Rev.* **1991**, *20*,1.
16. Toma, Š. *Chem. Listy* **1993**, *87*, 627.
17. Bose, A.K.; Manhas, M. S.; Banik, B. K.; Robb, E.W. *Res. Chem. Interm.* **1994**, *20*, 1.
18. Strauss, C. R.; Trainer, R. W. *Austr. J. Chem.* **1995**, *48*, 1665.
19. Caddick, S. *Tetrahedron* **1995**, *51*, 10403.
20. Oschkaya, V.P.; Vanag, G.Ya. *Izv. AN Latv.SSR* **1961** , 67.
21. Oschkaya, V.P.; Vanag, G.Ya. *Izv.AN Latv.SSR* **1961**, 225.
22. Puciová, M.; Toma, Š. *Coll. Czech. Chem. Commun.* **1992**, *57*, 2407.
23. Lui, L. C.; Wang, C. B.; Woh, V. C.; Ko, W. C. *Bull. Inst. Chem. Acad. Sci.* **1984**, *31*, 9; *Chem. Abstr.* **1985**, *120*,78658.
24. Furdík, M.; Lácová, M.; Livař, M. *Acta Fac. Rer. Natur. Univ. Comen. (Chimia)* **1968**, *12*, 265; *Chem. Abstr.* **1969**, *71*, 38615.
25. Furdík, M.; Lácová, M.; Livař, M.; Hrivňák, J. *Chem. Zvesti* **1966**, *20*, 834.
26. Hrnčiar, P. *Acta Fac. Rer. Natur. Univ. Comen. (Chimia)* **1961**, *6*, 601; *Chem. Abstr.* **1963**, *59*, 2730.
27. Hrnčiar, P. *Acta Fac. Rer. Natur. Univ. Comen. (Chimia)* **1966**, *10*, 527.

28. Godfrey, J. C.; Barness, R.A.; *J. Am. Chem. Soc.* **1958**, *80*, 3904.
29. Hrnčiar, P.; Krasnec, Ľ.; Furdík, M. *Chem. Zvesti* **1956**, *10*, 12.
30. Lácová, M. *Chem. Zvesti* **1973**, *27*, 525.

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