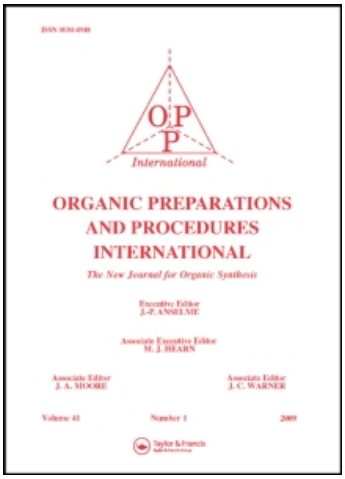

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USES OF THE FRIES REARRANGEMENT FOR THE PREPARATION OF HYDROXYARYLKETONES. A REVIEW

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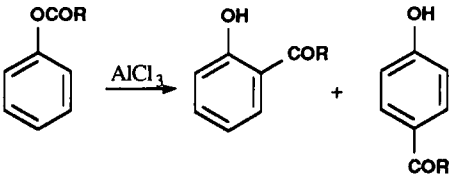
INTRODUCTION

The hydroxyarylketones have many industrial applications. Some of these compounds have properties which are useful in the pharmaceutical industry and in perfumery.[1] Hydroxybenzophenones find very important applications in paints and varnishes manufacturing, plastics, films, natural or synthetic rubbers by improving their stability.[2] Many hydroxyarylketones[3] and some of their derivatives[4] are used in the metallurgical industry, either for the extraction and separation of metals or for their selective estimation in ores and alloys. However, hydroxyarylketones are important, mainly as synthons in organic synthesis. Some hydroxyarylketones exist in the natural state.[5] Although several reactions allow the preparation of hydroxyarylketones (Friedel-Crafts reaction, Fries rearrangement, Hoesch and Nencki reactions, etc.), the Fries rearrangement is usually the most suitable process. It is easy to perform, isomer separation is easy and yields are good. The Fries rearrangement has been also made by photochemistry.[6] The last survey on Fries rearrangement dates back to 1964[7] and the purpose of our study is to review recent progress in this field.

I. PREPARATION OF *o*- AND *p*-HYDROXYARYLKETONES FROM MONOPHENOL ESTERS

The Fries reaction consists in the rearrangement of a phenolic ester to *o*- and/or *p*-phenolic ketones, by heating with aluminum chloride or other Lewis acid catalysts (Eq. 1).[8]



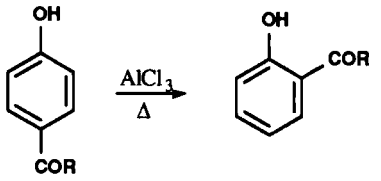
(1)

Some protic acids, namely hydrofluoric, perchloric, polyphosphoric and sulfonic acids also catalyze the Fries reaction, which is an intermolecular electrophilic substitution reaction.[9]

1. Phenyl Esters

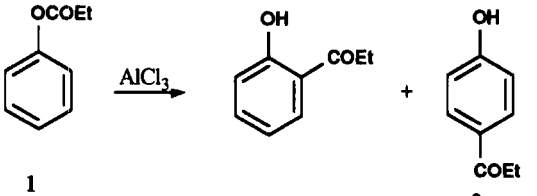
The phenyl esters of aliphatic acids, when treated with aluminum chloride at room temperature, give *p*-hydroxyarylketones, the *para* isomer being kinetically favored without any other substituent on the aromatic ring. High temperatures, on the other hand, promote the formation of *o*-

hydroxyarylketones, since the *p*-hydroxyarylketones rearrange to *o*-hydroxyarylketones with aluminum chloride (Eq. 2).[10]



(2)

The behavior of phenyl propionate **1** with aluminum chloride[11] is illustrative (Eq. 3). Treatment of ester **1** with $ZrCl_4$ at 120° also gives the ketone **2** (83%).[12]

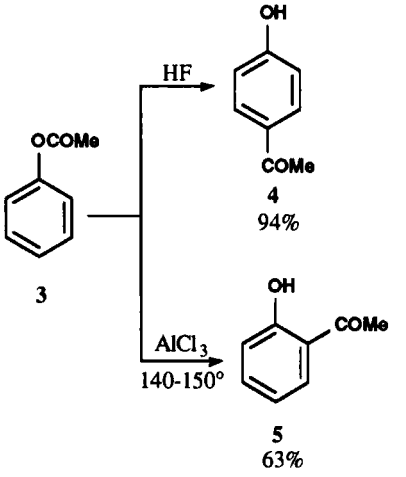


1 **2**

$MeNO_2$/20°	80%	20%
180-200°	–	78%

(3)

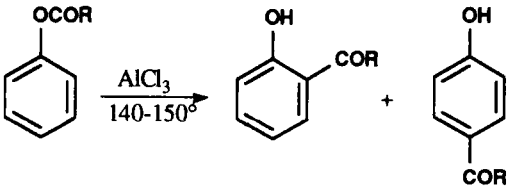
The Fries rearrangement of phenyl acetate **3** leads to *o*- and *p*-hydroxyketones **4** [13] and **5** [14] (Eq. 4)



(4)

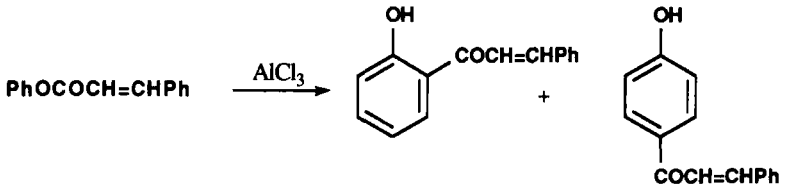
o-Hydroxyketone **5** has been reported to be formed in 80% yield by action of $AlCl_3$ on phenyl acetate **3** in petroleum ether solution,[15] but this result remains unreliable. Some specific catalysts have been used for rearrangement of ester **3** (zeolites,[16] sulfonated cation exchange resins[17]), but the yields obtained are not of preparative interest. The action of $AlCl_3$ on phenyl esters of greater molecular weight (from phenyl butanoate up to phenyl dodecanoate) in nitrobenzene gives *p*-hydroxyketones (60-80%).[18] Treatment of phenyl 2-methylpentanoate with $AlCl_3$ under mild conditions affords the expected optically active *p*-hydroxyketone (59%).[19] On the other hand, previous reports of the rearrangement of esters of greater molecular weight with $AlCl_3$ at 140-150° led to mixtures of isomers

(Eq. 5).[20] The phenyl esters, prepared from unsaturated aliphatic acids have been subjected to the Fries rearrangement. In the case of phenyl cinnamate, a mixture of isomers is obtained, and the solvent polarity influences the ratio of isomers (Eq. 6).[21]



(5)

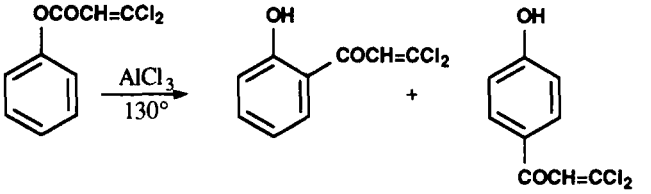
R = n-C_9H_{19}	46%	32%
n-$C_{11}H_{23}$	33%	42%



(6)

$PhNO_2$/130°	2%	36%
PhMe/110°	24%	10%

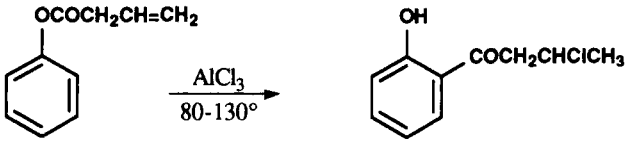
Phenyl dichloroacrylate, on treatment with $AlCl_3$ at 130° affords the expected isomeric ketones, without cyclization (Eq. 7).[22]



(7)

43% 38%

In the case of unsaturated phenyl esters of very high molecular weight, besides the isomeric ketones, much tar is formed. Phenyl erucate and stearolate, treated with $AlCl_3$ between 115-120° led to mixtures of the following o- and p-hydroxyketones: (27:7% and 43:4% respectively).[23] Action of $AlCl_3$ on phenyl 3-butenoate gave the o-hydroxyketone to which hydrogen chloride had added to the double bond (Eq. 8).[24]

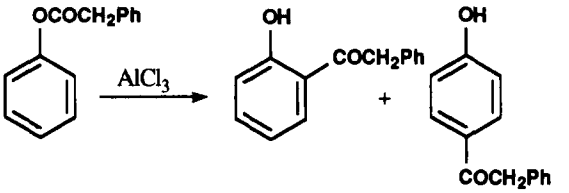


(8)

38%

The action of $AlCl_3$ on phenyl cyclohexanecarboxylate at 120° only affords the o-hydroxyketone (46%).[25] On the other hand, with phenyl phenylacetate, either of the expected isomers may be

obtained depending on the conditions (Eq. 9).[24,26]

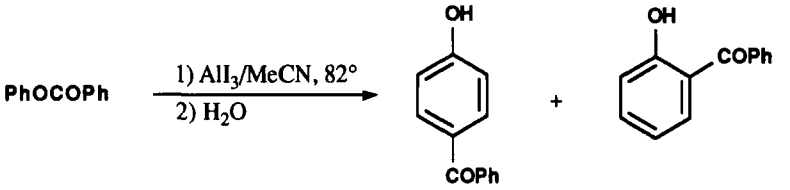


(9)

$EtNO_2$/120°	13%	70%
80-130°	72%	—

Phenyl diphenylacetate, treated with $AlCl_3/EtNO_2$ at 20°, gives exclusively the *p*-hydroxyketone (86%).[26] Phenyl 3-phenylpropanoate on the other hand, upon action of $AlCl_3$ between 80 and 130°, leads only to *o*-hydroxyketone (84%).[24] When treated with $AlCl_3$ at 100° in nitrobenzene, phenyl 3-cyclohexylpropanoate and phenyl 4-cyclohexylbutanoate, afford the corresponding *p*-hydroxyketones (70-75%).[27]

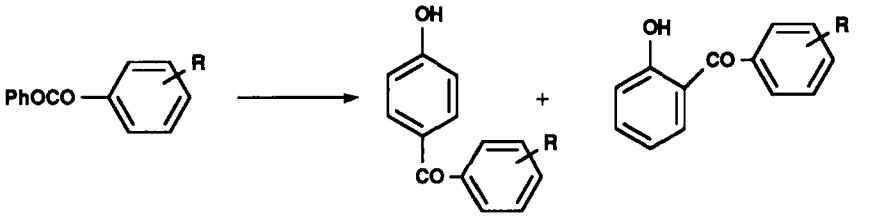
The Fries rearrangement of phenyl benzoate with HF at 55°[28] or $AlCl_3$ at 140°[29] yields *p*-hydroxybenzophenone (70%). On the other hand, when the reaction is carried out with $AlCl_3$ at 180-200°[29] or CF_3SO_3H at 170° in a sealed tube,[30] *o*-hydroxybenzophenone (38-39%) is formed. A rearrangement of phenyl benzoate with AlI_3, leads to both isomeric benzophenones (70%)(Eq. 10).[31]



(10)

47% 23%

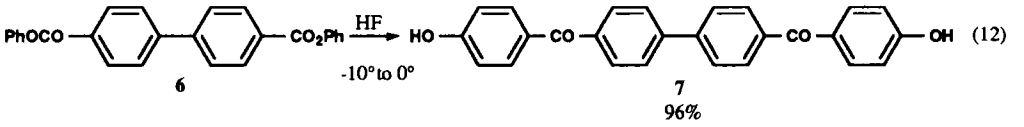
It is worth noting that treatment of phenyl benzoate with ion exchange resins (Nafion-H, Nafion-XR, Amberlite 200 C)[32] or with ion-exchanged stratified clay catalyst (synthetic mica treated with aluminum nitrate)[33] gives the expected hydroxybenzophenones. The Fries rearrangement of substituted phenyl benzoates carried out in different conditions in all cases favors the production of *p*-hydroxybenzophenone (Eq. 11).[34]



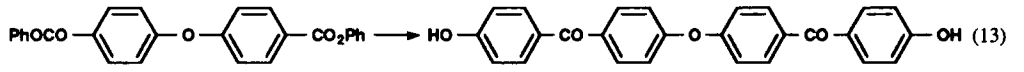
(11)

R	Conditions	%	%
4-MeO	$TiCl_4/MeNO_2$/20•	76	–
4-F	HF/20-40°	66	33
4-F	$AlCl_3/PhNO_2$/140-150°	65	35
3-NO_2	$AlCl_3$/160°	55	17

Specific phenyl esters have been rearranged with protic acids. Thus, ester **6**, treated with HF leads to ketone **7** (96%)(Eq. 12),whereas ester **8**, with $MeSO_3H$ or HF affords the ketone **9** (67-94%)(Eq. 13).[35]



6 **7** 96%



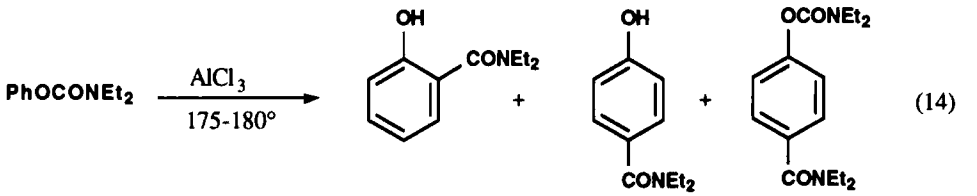
8 **9**

$MeSO_3H$/120° 67%

HF/-10° to 0° 94%

The phenyl 2-, 3- and 4-pyridinecarboxylates have been treated with $AlCl_3$ at 180°.[36] Phenyl picolinate lead to a mixture of *o*- and *p*-hydroxyketones (40:19%), whereas phenyl nicotinate and phenyl isonicotinate afford the *p*-hydroxyketones (60%), a small amount of the *o*-hydroxyketone (15%) being formed in the first case.

By action of $AlCl_3$ on phenyl 2-thiophenecarboxylate at 160°, one obtains a mixture of *o*- and *p*-hydroxyketones (16% and 5%).[37] Finally, phenyl N,N-diethylcarbamate when treated with $AlCl_3$ at 175-180° leads to a mixture of isomer ketones, in addition to the *p*-amide ester (Eq. 14).[38]



43% 26% 23%

2. Monosubstituted Phenyl Esters

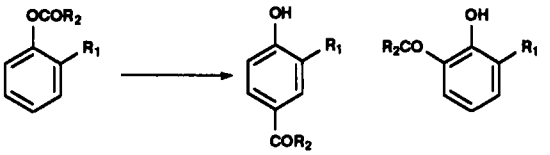
a) *o*-Substituted Phenyl Esters

During Fries transposition of monosubstituted phenyl esters, the position of substituent related to the ester group is of main importance on the course of reaction.[39] Thus, the presence of a substituent in the 2-position related to hydroxyl group of the original phenol favors rearrangement to the para position[9]; with halophenyl esters, the yields of *p*-hydroxyketones are in many case nearly quantitative (Table 1).

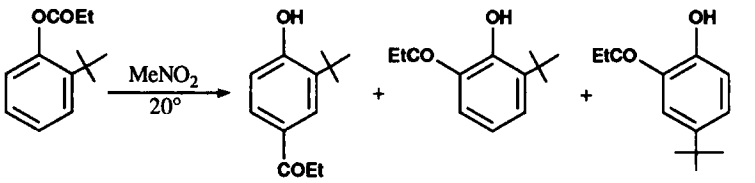
The parent *o*-hydroxyketones are easily preformed with the following processes (Scheme 1).

The 2-*t*-butylphenyl propionate **10**, under Fries conditions, follows an usual pathway. While the *p*-hydroxyketone **11** is formed, the *o*-hydroxyketone **12** is rarely obtained; but the unexpected

TABLE 1. Fries Rearrangement of 2-Substituted Phenol Esters



R_1	R_2	Conditions	Yield (%)	Yield	Ref.
Me	-Me	$AlC_3/PhNO_2/30°$	86	2	40
Me	-Me	$AlCl_3/165°$	61	24	40
Me	-Et	$AlCl_3/MeNO_2/20°$	58	18	41
Me	-Et	$AlCl_3/165°$	22	41	11
Me	$-CH_2Ph$	$AlCl_3/EtNO_2/20°$	74	—	26
Me	$-CH_2Ph$	$AlCl_3/140°$	30	45	42
Me	$-CH_2C_6H_4OMe(o)$	$AlCl_3/MeNO_2/20°$	60	12	43
Me	$-CH_2C_6H_4OMe(p)$	$AlCl_3/MeNO_2/20°$	71	11	43
Me	-Ph	$AlCl_3/PhNO_2/60°$	91	—	40
Me	-Ph	$AlCl_3/140°$	86	—	40
Me	-Ph	$TiCl_4/MeNO_2$/reflux	86	—	44
Me	-Ph	Nafion-XR/175°	45	—	32
Me	-Ph	$AlCl_3$/PhCl/reflux	46	6	45
Me	$-C_6H_4OMe(p)$	$TiCl_4/MeNO_2/20°$	84	—	34
Me	$-C_6H_4NO_2(m)$	$AlCl_3/160°$	56	4	34
Cl	-Me	$AlCl_3/140°$	81	9	46
Cl	-Et	$AlCl_3/165°$	98	—	41
Cl	-Ph	$AlCl_3/155°$	88	6	47
Br	-Me	$AlCl_3/140°$	80	13	46
Br	-Et	$AlCl_3/100°$	95	—	48
CO_2H	-Me	$AlCl_3/PhNO_2/O°$	82	—	49
CO_2H	-Me	$AlCl_3/PhNO_2/60°$	70	—	50



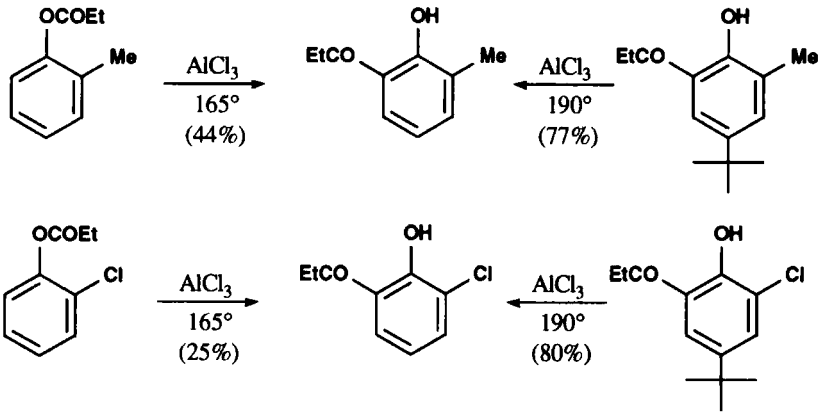
(15)

10 **11** **12** **13**

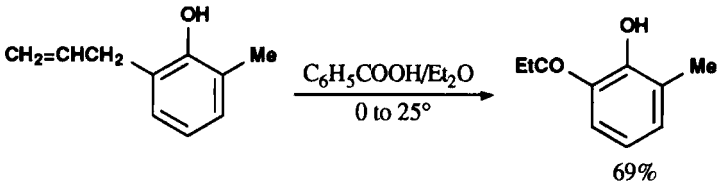
catalyst	%	%	%
$TiCl_4$	81	–	–
$SnCl_4$	49	–	–
$NbCl_4$	34	26	–
$ZrCl_4$	–	–	71
$GaCl_4$	15	–	73

Scheme 1

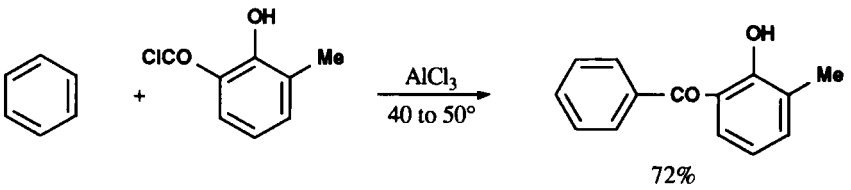
1. Dealkylation of 2,4-Disubstituted Hydroxyketones[51]



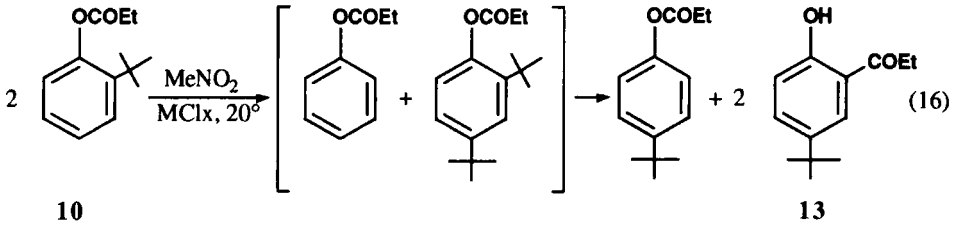
2. Oxidation of 2-Allylphenols by Perbenzoic Acid[52]



3. Acylation of Benzene According to Friedel-Crafts[53]



o-hydroxyketone **13** (Eq. 15)[54] is generated with some catalysts by migration of the *t*-butyl group prior to the Fries rearrangement (Eq. 16).[54]



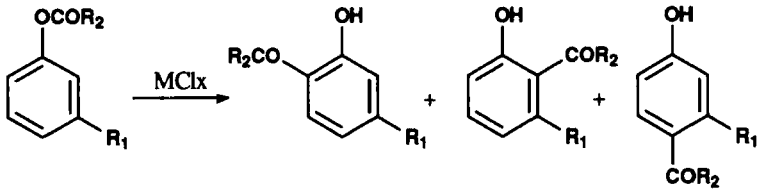
10 **13**

Yet the Fries rearrangement of *o*-cresyl esters (picolinate and isonicotinate,[36] cyclohexanecarboxylate,[25] 2-methoxybenzoate,[34] erucate and stearolate[23]), *o*-ethylphenyl chloroacetate,[55] *o*-isopropylphenyl propionate,[56] 2-*n*-propylphenyl propionate,[57] and 2-chlorophenyl esters (2-methylvalerate,[19] nicotinate and isonicotinate[36]) occurs normally.

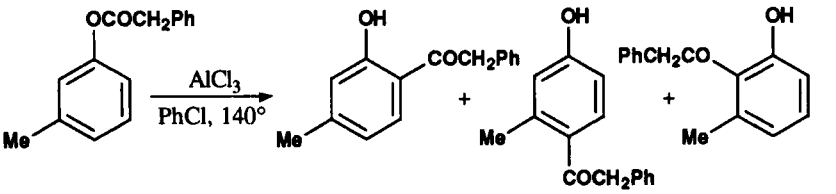
b) *m*-Substituted Phenyl Esters

The presence of a *meta*-substituent favors the formation of *o*-hydroxyketone, by a combination of electronic effects and steric hindrance at the *para*-position. Thus it should be more difficult to prepare the *p*-hydroxyketone (Table 2).

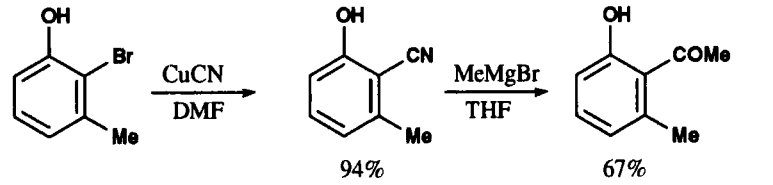
Theoretically, the Fries rearrangement of a phenyl ester carrying a *meta*-substituent to the ester function should provide two *o*-hydroxyketones. The carbonyl group may enter either at the 2-position and lead to vicinal *o*-hydroxyketone or at the 6-position. In this case, only *o*-hydroxyketone (6-position) is obtained in practice (Eq. 17).

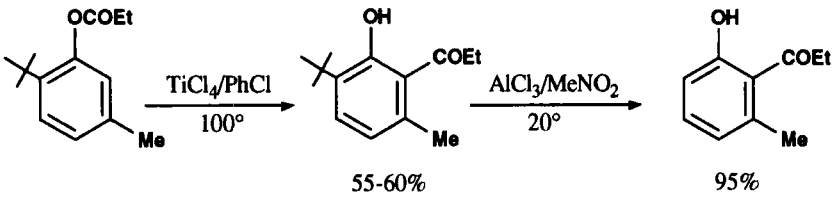


In only one case, after thirty-five years of experimentation, have we ever observed a vicinal *o*-hydroxyketone by Fries rearrangement of such a monosubstituted phenyl ester (Eq. 18).



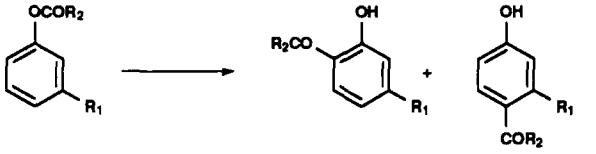
There are several ways to prepare vicinal *o*-hydroxyketones,[63-66] two of which are easy to carry out (Eq. 19)(Eq. 20).[65,66]





Finally one should also note the normal pattern of the Fries rearrangement of *meta*-cresyl esters (erucate and stearolate,[23] picolinate, nicotinate and isonicotinate[36]), 3-methoxyphenyl benzoate,[67] *o*-chlorophenyl picolinate, nicotinate and isonicotinate[36] and 3-(benzoyloxy)biphenyl.[68]

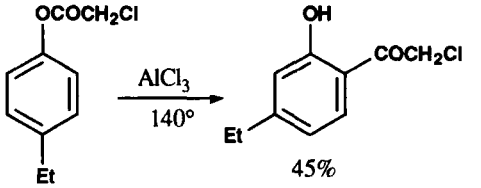
TABLE 2. Fries Rearrangement of 3-Substituted Phenol Esters



R_1	R_2	Conditions	Yield (%)	Yield	Ref.
Me	-Me	$AlCl_3$/65°	1	88	59
Me	-Me	$AlCl_3$/165°	95	—	59
Me	-Et	$AlCl_3/MeNO_2$/20°	81	3	58
Me	-Et	$TiCl_4$/100°	96	—	39
Me	$-C(Me)_3$	$HCl\text{-}SnCl_4/MeNO_2$/20°	60	—	41
Me	$-CH_2Ph$	$AlCl_3/MeNO_2$/reflux	49	3	45
Me	$-CH_2Ph$	$AlCl_3$/140°	50	10	42
Me	$-C_{11}H_{23}$(n)	$AlCl_3$/180°	70	—	60
Me	-Ph	Nafion-XR/150°	1	67	32
Me	-Ph	$AlCl_3$/175°	83	6	44
Me	$-C_6H_4NO_2$(m)	$AlCl_3$/160°	43	12	34
t-Bu	-Et	$TiCl_4/MeNO_2$/20°	91	—	54
t-Bu	-Ph	HF/25°	40	—	28
Br	-Et	$AlCl_3$/100°	87	—	41
Br	-Et	$AlCl_3$/165	97	—	48
Cl	-Et	$AlCl_3$/165°	82	—	41
Cl	-Et	$AlCl_3$/100°	92	—	11
Cl	-Ph	$AlCl_3$/175°	80	8	44
Cl	$-C_6H_4NO_2$(m)	$AlCl_3$/160°	40	11	34
I	-Me	$AlCl_3$/120°	65	—	61
NO_2	-Ph	$AlCl_3$/170°	11	—	62

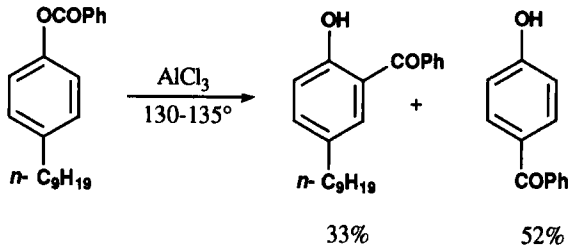
c) *p*-Substituted Phenyl Esters

The presence of substituent in 4-position to ester group almost always leads to *o*-hydroxyketone. The results of the Fries rearrangement obtained with usual esters are reported in Table 3. In some cases, one observes a migration (Eq. 21)[55] or the loss of an alkyl group (Eq. 22 and 23)[83,47], even



(21)

a peculiar acylation (Eq. 24).[43]



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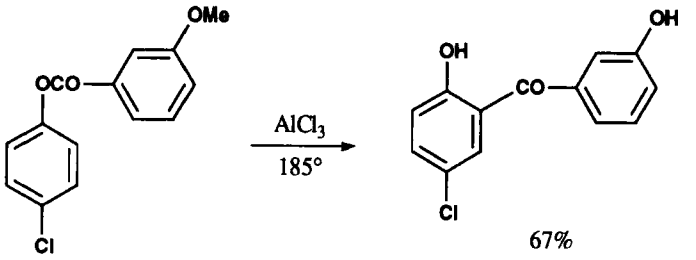
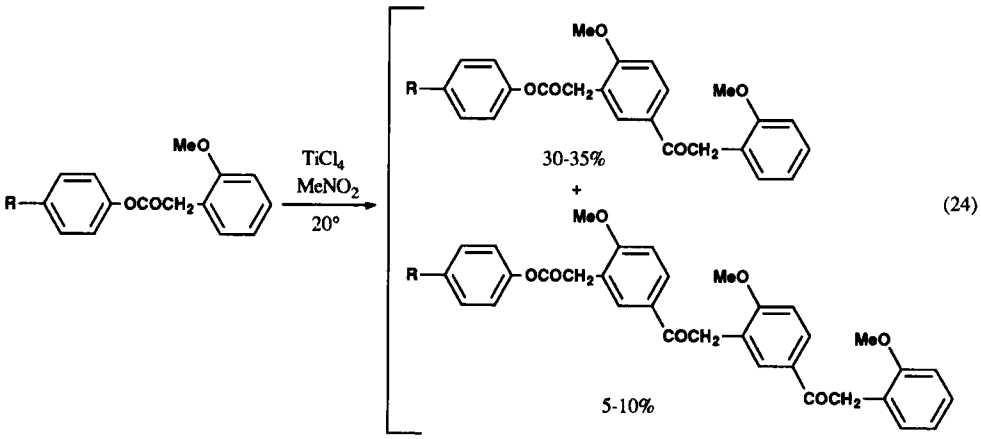


(23)



(24)

3. Disubstituted Phenyl Esters

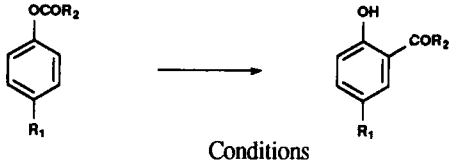
The Fries rearrangement of dimethylphenyl esters has already been the subject of many studies. There have been recent interesting progress in this area, namely:

a) 2,3-Dimethylphenyl Esters, see references 34, 39, 41, 58 and 88

b) 2,4-Dimethylphenyl Esters, see references 34, 39, 43, 58 and 89

The Fries rearrangement of 2,4-xylenyl succinate leads to the formation of four compounds (Scheme 2).[90]

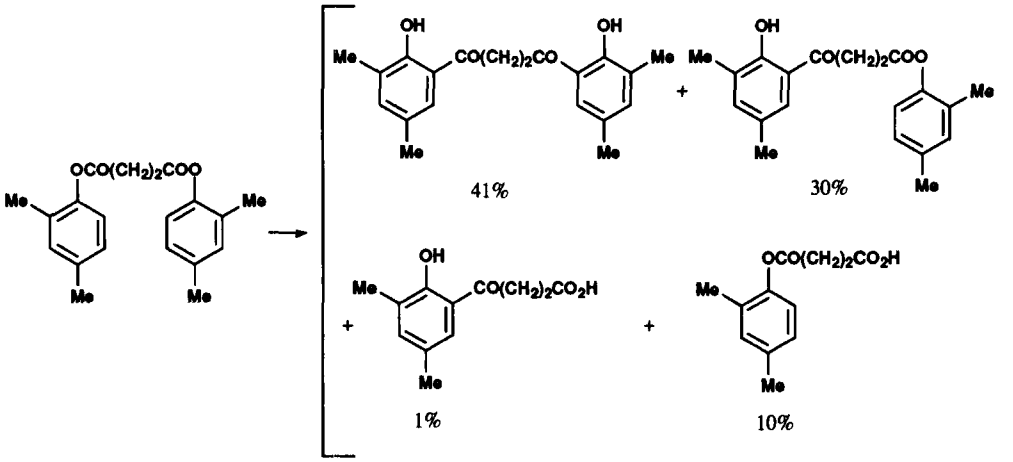
TABLE 3. Fries Rearrangement of 4-Substituted Phenol Esters



R_1	R_2	Conditions	Yield(%)	Ref.
Me	-Me	$AlCl_3$/120°	95	59
Me	-Et	$AlCl_3$/170°	96	69
Me	-n-Pr	$AlCl_3$/170°	90	69
Me	-i-Pr	$AlCl_3$/170°	92	69
Me	$-CH_2CH_2Br$	$AlCl_3$/115°	93	70
Me	$-CH{=}CCl_2$	$AlCl_3$/130°	78	22
Me	-CH=CHMe	$AlCl_3$/140-150°	61	71
Me	-CH=CHPh	$AlCl_3$/PhCl/130°	36	21
Me	$-CHBrC_6H_{13}$	$AlCl_3$/120-125°	82	70
Me	$-CH_2Ph$	$AlCl_3$/PhCl/reflux	87	72
Me	$-CH_2C_6H_3I(p)$	$AlCl_3/PhNO_2$/20°	70	42
Me	-Ph	$AlCl_3$/1,2-$C_6H_4Cl_2$/reflux	89	72
Me	$-C_6H_4Me(p)$	Nafion-H/$PhNO_2$/reflux	72	32
Me	$-C_6H_4Cl(m)$	Nafion-H/$PhNO_2$/reflux	71	32
Me	$-C_6H_4OMe(p)$	$TiCl_4$/120°	89	34
Me	$-C_6H_4NO_2$	$AlCl_3$/160°	70	34
Me	-α-naphthyl	$AlCl_3$/1,2-$C_6H_4Cl_2$/reflux	95	72
Et	-Et	$AlCl_3$/170°	82	69
Et	$-CHClCH_3$	$AlCl_3$/135-140°	48	55
t-Bu	-Et	$TiCl_4/PhNO_2$/50°	93	73
C_6H_{11}	-Me	$AlCl_3/PhNO_2$/85°	55	49
Ph	-Me	$AlCl_3/Cl_2CHCHCl_2$/140°	83	74
Ph	$-C_6H_4Cl(p)$	$AlCl_3$/1,2-$C_6H_4Cl_2$/120°	67	75
Ph	$-C_6H_4F(p)$	$AlCl_3$/1,2-$C_6H_4Cl_2$/120°	63	75
Br	-Me	$AlCl_3$/150°	90	76
Br	-Et	$AlCl_3$/165°	97	48
Cl	-Me	$AlCl_3$/120°	96	77
Cl	-Et	$AlCl_3$/165°	95	11
Cl	$-CH_2CH_2Br$	$AlCl_3$/95-105°	95	70
Cl	-Ph	$AlCl_3$/155°	90	47
Cl	$-C_6H_4F(p)$	$AlCl_3$/200°	88	78
Cl	$-C_6H_4NO_2(m)$	$AlCl_3$/160°	70	34
F	-Pr	$AlCl_3/ClCH_2CH_2Cl$/100°	83	79
F	$-C_5H_{11}$	$AlCl_3$/130°	88	80
F	$-C_7H_{13}$	$AlCl_3$/130°	95	80
F	-CH=CHPh	$AlCl_3$/130°	52	80
F	$-C_6H_4Cl(o)$	$AlCl_3$/130°	96	80
F	$-C_6H_4F(p)$	$AlCl_3$/130°	83	80
F	$-C_6H_4Me(m)$	$AlCl_3$/130°	93	80
NO_2	-Me	$AlCl_3$/140-150°	28	81
NO_2	-Ph	$AlCl_3$/130-160°	26	82
SMe	-Et	$TiCl_4$/150°	36	73

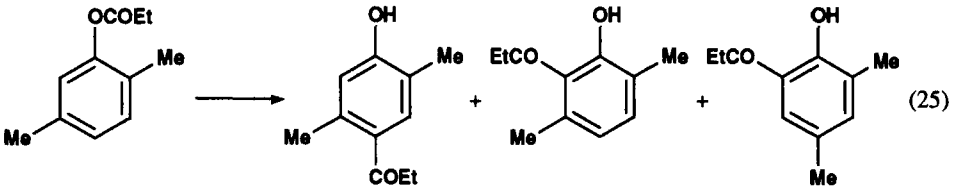
3. Disubstituted Phenyl Esters

Scheme 2



c) **2,5-Dimethylphenyl Esters**, see references 34, 57, 58 and 91

When 2,5-xylenyl propionate **14** is treated by $AlCl_3$ at high temperatures gives *o*-hydroxyketone **17** owing to migration of the methyl group on *o*-hydroxyketone **16** (Eq. 25).

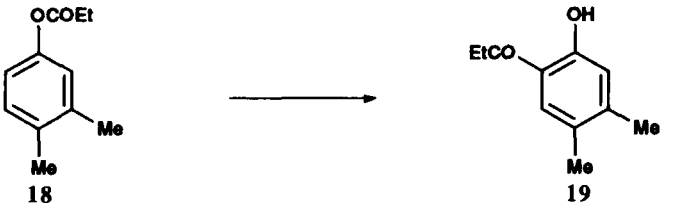


14	15	16	17
Conditions	%	%	%
$AlCl_3/PhNO_2/20°$	70	–	–
$TiCl_4/120°$	17	76	–
$AlCl_3/170°$	–	–	96

d) **2,6-Dimethylphenyl Esters**, see references 34, 41, 43, 58, 91 and 92

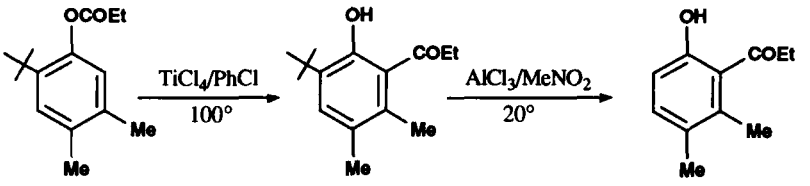
e) **3,4-Dimethylphenyl Esters**, see references 34, 41, 58, 91, 93, 94, and 95

The Fries rearrangement of 3,4-xylenyl propionate **18** provides only the *o*-hydroxyketone **19**. The vicinal *o*-hydroxyketone isomer **22** can be obtained by a two-step synthesis (Eq. 26). During the



Conditions	%
$AlCl_3/MeNO_2/20°$	89
$AlCl_3/165°$	92

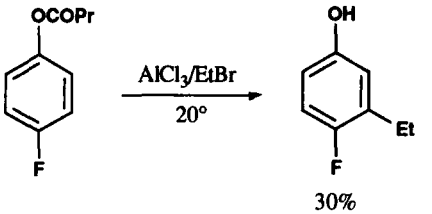
(26)



f) 3,5-Dimethylphenyl Esters, see references 34, 39, 58, 95 and 96

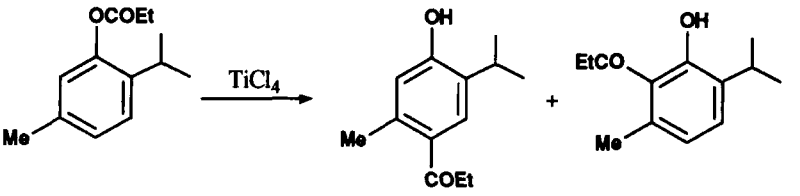
transposition of 3,5-xylenyl propionate, the *o*-hydroxyketone is the sole product, the *para* position being sterically hindered. *p*-Hydroxyketone may be obtained by an indirect way.[97] The Fries rearrangement of other disubstituted esters has been carried out and the results obtained are listed in Table 4.

Many esters of 2-bromo- and 2-chloro-4-fluorophenol have also been submitted to the Fries reaction.[102] Moreover, a disubstituted *o*-hydroxyketone has been obtained in an interesting way by action of $AlCl_3$ on 4-fluorophenyl *n*-butyrate (Eq. 27).[79]



(27)

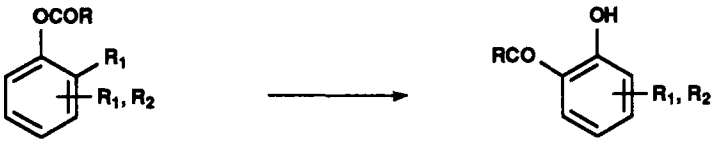
Thymyl propionate treated with $TiCl_4$ gives the *p*- or *o*-hydroxyketone depending on the experimental conditions (Eq. 28).



Conditions	%	%
$MeNO_2/20°$	61	10
120°	14	79

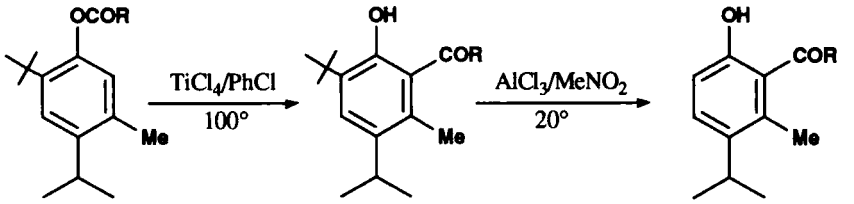
(28)

TABLE 4. Fries Rearrangement of Disubstituted Phenol Esters



R	R_1	R_2	Conditions	Yield(%)	Ref.
Me	2-Me	5-Me	$AlCl_3/PhNO_2/20°$	40	57
Et	2-*i*-Pr	3-Me	$AlCl_3/MeNO_2/20°$	98	98
Et	2-*i*-Pr	4-Me	$TiCl_4/100°$	95	98
Me	3-Me	4-*i*-Pr	$TiCl_4/MeNO_2/20°$	95	98
Et	3-Me	4-*i*-Pr	$TiCl_4/MeNO_2/20°$	99	95
n-C_6H_{13}	3-Me	4-*i*-Pr	$TiCl_4/MeNO_2/20°$	95	98
$C_6H_4OMe(p)$	3-Me	4-*i*-Pr	$TiCl_4/MeNO_2/20°$	66	98
Et	3-Me	5-*i*-Pr	$TiCl_4/120°$	98	95
Et	3-Me	6-*i*-Pr	$TiCl_4/120°$	76	95
Me	2-Et	4-Me	$AlCl_3/\Delta$	40	99
Me	2-Et	5-Me	$AlCl_3/\Delta$	30	99
Et	2-*n*-Pr	4-*n*-Pr	$AlCl_3/130\text{-}150°$	75	57
Et	2-Me	4-*t*-Bu	$AlCl_3/MeNO_2/20°$	83	51
Me	2-*t*-Bu	4-Me	$AlCl_3/105°$	47	100
Et	2-*t*-Bu	5-Me	$TiCl_4/PhCl/100°$	60	66
Me	2-CO_2H	4-Me	$AlCl_3/170°$	61	101
Et	2-CO_2H	4-Me	$AlCl_3/170°$	30	101
Me	2-CO_2H	4-Br	$AlCl_3/170°$	26	101
Me	2-CO_2H	4-Cl	$AlCl_3/170°$	18	101
Me	2-Et	4-Br	$AlCl_3/\Delta$	40	99
Me	2-Et	4-Cl	$AlCl_3/\Delta$	50	99
Me	2-Et	5-Cl	$AlCl_3/\Delta$	40	99
Et	2-Cl	4-*t*-Bu	$AlCl_3/140°$	28	51
Et 2-Br	4-Br	$AlCl_3/100°$	88	48	
n-C_6H_{13}	2-Br	4-F	$AlCl_3/130\text{-}140°$	90	102
n-C_7H_{15}	2-Br	4-F	$AlCl_3/130\text{-}140°$	85	102
CH=CHMe 2-Cl	4-F	$AlCl_3/130\text{-}140°$	86	102	
n-C_3H_7	2-Cl	4-F	$AlCl_3/130\text{-}140°$	94	102
n-C_6H_{13}	2-Cl	4-F	$AlCl_3/130\text{-}140°$	90	102

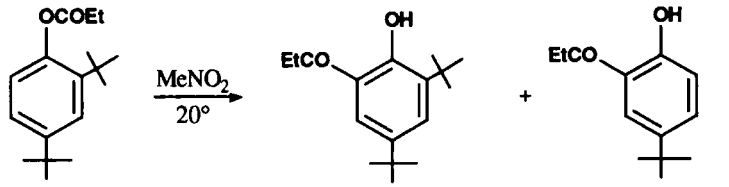
Vicinal *o*-hydroxyketones of *para*-thymol have been prepared by a two-step synthesis (Eq. 29).[95,98]



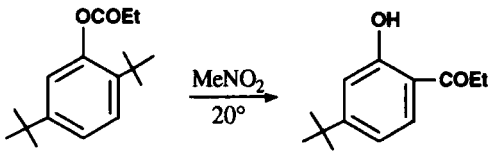
(29)

R	%	%
Me	23	84
Et	57	99
n-C_6H_{13}	67	82

One should recall the great mobility of the *t*-butyl group. One notes the elimination of the *t*-butyl group in the 2-position to the ester function, when the di-*t*-butylphenyl propionates are treated with $AlCl_3$, $SnCl_4$ and $ZrCl_4$ (Eq. 30).[103]

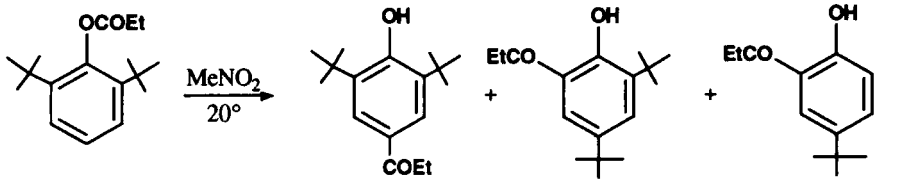


Catalyst	%	%
$TiCl_4$	69	–
$SnCl_4$	5	59



(30)

Catalyst	%
$ZrCl_4$	67

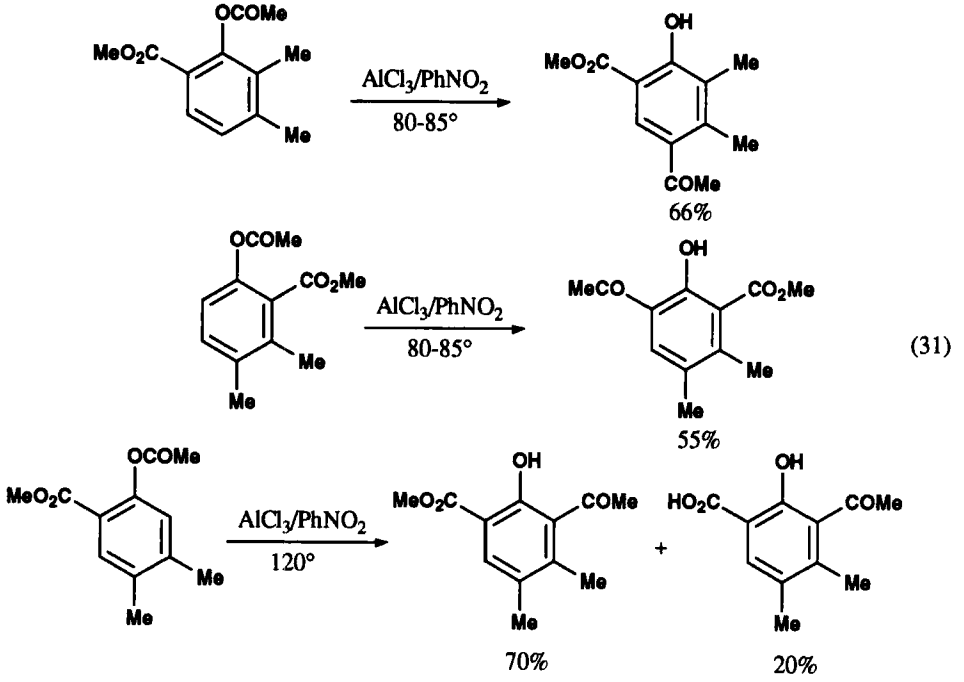


Catalyst	%	%	%
$TiCl_4$	66	17	–
$AlCl_4$	–	5	50

4. Trisubstituted Phenyl Esters

Some trisubstituted phenyl esters have also been treated with $AlCl_3$. Thus, the Fries rearrangement of 4-chloro-3,5-dimethylphenyl acetate[104] and 4-bromo-3,5-dimethylphenyl propionate[91] gives

the *o*-hydroxyketones (90% and 79%). The Fries rearrangement of miscellaneous methyl dimethylacetoxybenzoates[105] leads to *o*- and *p*-hydroxyketones (Eq. 31).



(31)

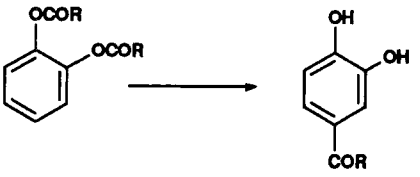
II. PREPARATION OF *o*- AND *p*-HYDROXYARYLKETONES FROM DIPHENOL AND POLYPHENOL ESTERS

The Fries rearrangement of diphenol and polyphenol esters has been subject of many studies. Recent results of interest in this area are discussed below.

1. Diphenol Esters

a) Pyrocatechol Esters

The Fries rearrangement of pyrocatechol dibenzoate,[32] diisobutyrate,[106] and dipropionate[107] only leads to 4-acyl derivatives (Eq. 32).



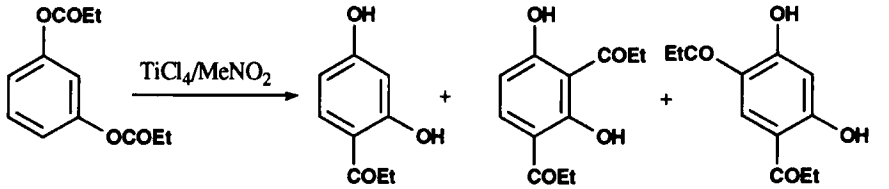
(32)

R	Conditions	%
Et	$AlCl_3$/130°	83
Et	$AlCl_3/MeNO_2$/20°	86
i-Pr	$AlCl_3$/PhCl/110-115°	41
Ph	Nafion-XR/175	38

Use of BF_3 at 160° on 2-methoxy-4-methylphenol in acetic acid solution gives the 2,3-dihydroxy-5-methylacetophenone (78%)[108] via acetic ester formation.

b) Resorcinol Esters

The Fries rearrangement of resorcinol monoesters, e.g. acetate,[109,110] benzoate,[32,111-113] 2,4-dihydroxybenzoate,[114] nicotinate and isonicotinate,[36] leads to 4-acylresorcinols (70-90%). The Fries rearrangement of resorcinol diesters, e.g. diacetate,[115,116] dinicotinate and diisonicotinate,[36] diphenylacetate[116] and dipropionate,[107] also provides the 4-acylresorcinols (15-65%). The Fries rearrangement of resorcinol dipropionate gives three compounds (Eq. 33).

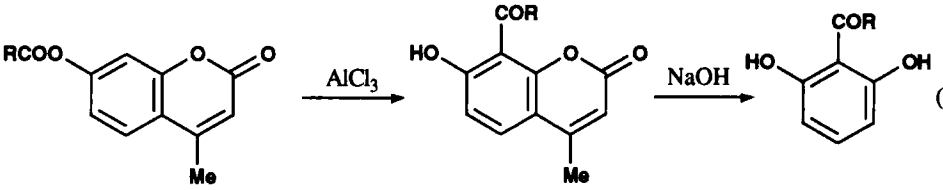


(33)

The 4-propionylresorcinol **23** (83%) is obtained by heating a mixture of resorcinol, propionic acid and $ZnCl_2$ at reflux.[107] The diketone **25** (63%) is obtained by heating a mixture of resorcinol, propionic anhydride and $SnCl_4$ at reflux.

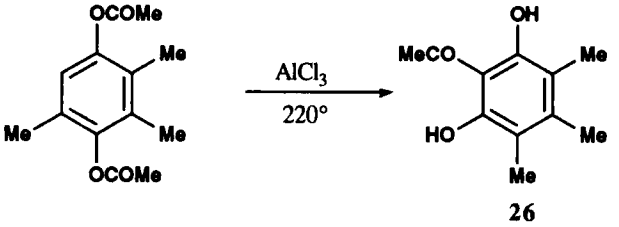
The resorcinol monomethylethers, such as nicotinate and isonicotinate,[36] treated with $AlCl_3$ at 180-190° also lead to 4-acylresorcinols (80-90%) owing to demethylation. One should note that there exist two other monoacylresorcinol isomers: namely 2-acyl and 5-acylresorcinols.

One prepares the vicinal 2-acylresorcinols[117] by saponification of 8-acyl-7-hydroxycoumarins, themselves being obtained by Fries rearrangement of corresponding 7-acyloxycoumarins (Eq. 34).



(34)

The vicinal trimethylated ketone **26** has been isolated from an unexpected Fries rearrangement of 2,3,5-trimethylhydroquinone diacetate ($AlCl_3$, 220°) to 2,6-dihydroxy-3,4,5-trimethylacetophenone; the expected 2,5-dihydroxy-3,4,6-trimethylacetophenone (Eq. 35) was not detected.

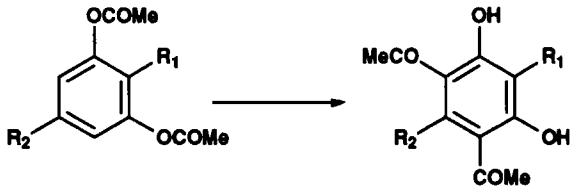


(35)

Resorcinol **26** arises via subsequent rearrangement of the normal products.[118] 5-Acylresorcinols are

prepared by means of organocadmium derivatives (45-65%).[119]

The Fries rearrangement of monosubstituted resorcinol diacetates, as for resorcinol dipropionate, easily yields diketones (Eq. 36).[120]

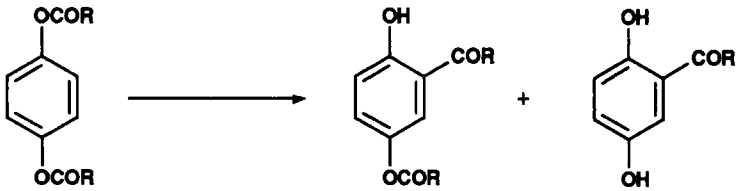


(36)

R_1	R_2	Conditions	%
Me	H	$AlCl_3/PhNO_2$/65-75°	63-77
H	OMe	BF_3/Et_2O/75°	66

c) Hydroquinone Esters

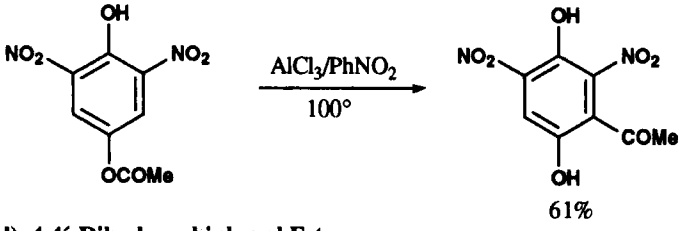
The Fries rearrangement of hydroquinone diesters leads either to ketoester or to monoketone or to a mixture of both compounds. No diketones are obtained (Eq. 37).[107,121,122]



(37)

R	Conditions	%	%
Me	$AlCl_3$/120°	31	>30
Me	BF_3/Et_2O/120°	90	–
Me	$AlCl_3/PhNO_2$/160-165°	–	89-90
Et	$AlCl_3/ClCH_2CH_2Cl$/20°	91	–
Et	$AlCl_3$/180°	3	89

The Fries rearrangement of substituted hydroquinone diacetates, such as 2-bromo,[123] 3-bromo and 3-chloro,[124] 2-methoxy,[125] 2,6-dimethoxy[126] and 2,6-dimethyl,[127] leads to corresponding monoketones (30-70%). One should point out that a dinitrohydroquinone monoacetate, treated by $AlCl_3$, leads to the corresponding monoketone (61%)(Eq. 38).[128]



(38)

61%

d) 4,4′-Dihydroxybiphenol Esters

Treatment of many 4,4′-dihydroxybiphenyl diesters[129] (from diacetate up to dihexadecanoate, and dibenzoate) with $AlCl_3$ gives the 3,3′-diacyl-4,4′-biphenols (30-100%).

2. Triphenol Esters

Pyrogallol Esters

The Fries rearrangement of pyrogallol monoesters, e.g. benzoate[32] and phenylacetate,[116] provides the expected monoketones.

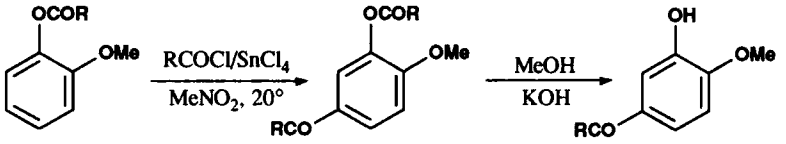
III. PREPARATION OF *m*-HYDROXYARYLKETONES

1. By Fries Rearrangement

The Fries rearrangement of phenyl esters generally leads to the formation of *o*- and *p*-hydroxyketones, formation of *m*-hydroxyketones in this reaction rarely occurs. It is related to the presence of a methoxy group on the ring in the 2-position to the ester function.[130] The -COR carbocations that appear during the heterolysis of those esters proceed to the *p*- (or *o*-) positions of oxygenated functions. The acylation of the phenoxy anions *p*- (or *o*-) positions is particularly favored.

a) Of Guaiacol Esters

The Fries rearrangement of guaiacol acetate[131] and propionate[130] affords 6-10% yield of *m*-hydroxyketone besides the *p*-hydroxyketone as the major product. 5-Acylguaiacols are readily prepared by acylation of ester, followed by saponification of the ketoesters obtained (Eq. 39).[130]

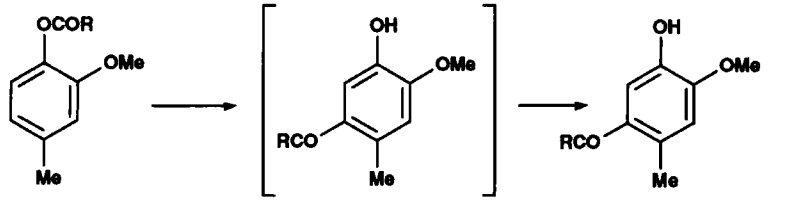


(39)

R	%	%
Me	79	90-100
Et	89	"
n-C_9H_{19}	61	"
CH_2Ph	76	"
Ph	82	"

b) Of Creosol and Isocreosol Esters

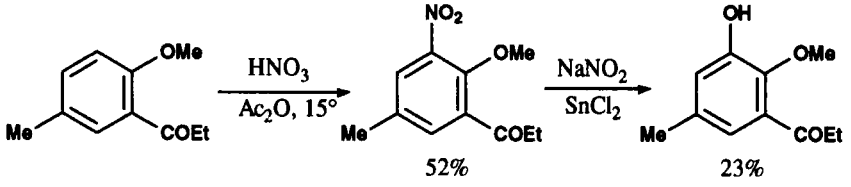
The Fries rearrangement of creosol acetate[108,132] and propionate[132] provides the *m*-hydroxyketones directly (Eq. 40), the intermediate ketoesters undergoing hydrolysis during the course of reaction.



(40)

R	Conditions	%
Me	BF_3/25°	90
Me	BF_3/CH_2Cl_2/120°	82
Et	$AlCl_3/CH_2Cl_2$/20°	59

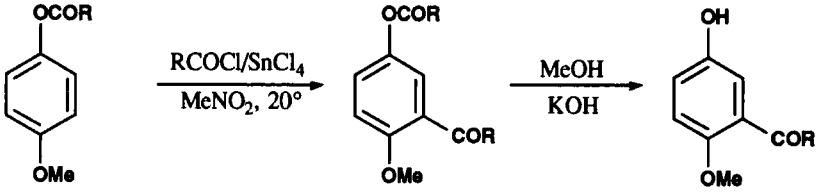
In the case of isocreosol, the 5-acyl derivative is prepared by a two-step synthesis (Eq. 41).[132]



(41)

c) Of 4-Methoxyphenol Esters

The Fries rearrangement of 4-methoxyphenol esters only provides *o*-hydroxyketones. One prepares the *m*-hydroxyketones by treatment of these esters in the same way as for those of guaiacol (Eq. 42).[133]



(42)

R	%	%
Et	56	90-100
n-C_9H_{19}	41	"
CH_2Ph	74	"
Ph	90	"
$C_6H_4NO_2$(p)	49	"
C_6H_4OMe(p)	73	"

2. By Other Methods

a) Diazotation of *m*-Aminoketones

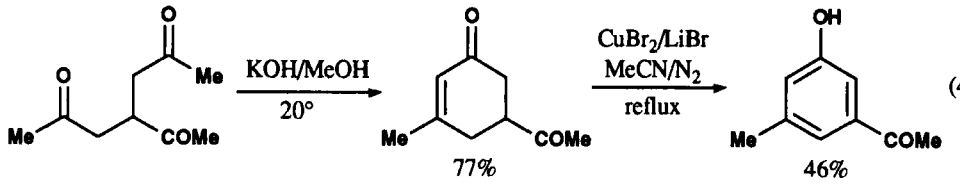
However, generally, the preparation of *m*-hydroxyketones may be carried out through two different methods. From the aromatic ketone, the sequence nitration, reduction and diazotation is achieved, which allows the introduction of an hydroxy group in the *meta*-position to carbonyl group.[134]

b) Action of an Organometallic Compound on *m*-Hydroxybenzoic Acids

In the other case, starting from *m*-hydroxybenzoic acid, one achieves a synthesis using either an organometallic compound with Mg[135] or Cd[136] (70-80%).

c) From 4-Acyl-2,6-heptadienone

The 3-hydroxy-5-methylacetophenone is obtained by an original synthesis from 4-acetyl-2,6-heptanedione (Eq. 43).[137]



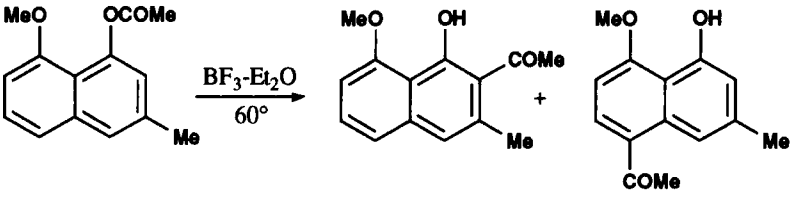
(43)

IV. FRIES REARRANGEMENT OF POLYCYCLIC AND HETEROCYCLIC ESTERS

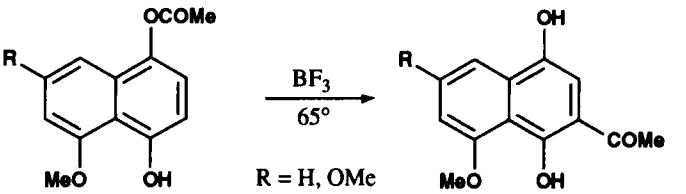
1. Polycyclic Esters

a) Acyloxynaphthalenes

The Fries rearrangement of 1-acyloxynaphthalenes leads to 2-acyl and 4-acyl-1-naphthols. The *o*-hydroxyketones are always the major compounds (50-90%).[138] Two disubstituted 1-naphthol acetates, treated by BF_3, lead to unusual compounds. The acylation is strongly influenced by the presence of other substituents (OH, OMe) on 1-naphthol esters (Eq. 44)(Eq. 45).[139]



(44)



(45)

One also obtains in some cases ketoesters. Thus, the 3-methoxy-2-methyl-1-naphthol acetate and benzoate provide the corresponding 7-acyl-3-methoxy-2-methyl-1-naphthol esters (35 and 22% respectively) with $AlCl_3$.[140]

The Fries rearrangement of 2-acyloxynaphthalenes leads to 1-acyl and 6-acyl-2-naphthols; $AlCl_3$ favors the formation of *o*-hydroxyketone (60%),[138] whereas HF gives mainly 6-acylnaphthols (60-70%).[141] The 1,3-dioxy-2-methylnaphthalene diacetate with $AlCl_3$ provides the 4-acetyl and 4,7-diacetyl-3-hydroxy-2-methyl-1-naphthyl acetate.[140]

In the series of 1,4-diacetoxynaphthalenes (with H or Me in 2-position), only one acyloxy group participates in the reaction. Thus one obtains the corresponding *o*-ketoesters (80-90%).[142] 2,3-Dioxynaphthalene dibenzoate and diacetate with $AlBr_3$ lead to 1-acyl-2,3-dioxynaphthalenes (75 and 80%).[143]

b) Acyloxyanthracenes

2-Acetoxyanthracene with $AlCl_3$ leads to 1-acetyl and 3-acetylanthracenes.[144] By action of Lewis acids on 9-acyloxyanthracenes, one obtains 10-acylanthrones.[145]

c) Acyloxyphenanthrenes

$AlBr_3$ transforms the 9-oxyphenanthrene benzoate in 9-benzoyl-10-hydroxyphenanthrene.[146] Fries rearrangement of 4H-cyclopenta[def] phenanthren-1-yl acetate gives 2- and 7-acetyl derivatives. The reaction of isomeric 2-acetoxy compounds afford 1- and 7-acetyl derivatives. The acetyl group of the 3- and 8-acetoxy compounds rearranges into the 2- and 9-position respectively.[147]

d) Acyloxyfluoranthenes

Fries rearrangement of mono, di and triacyloxyfluoranthenes with $AlCl_3$ was the subject of an important study. Various hydroxyketones are obtained, sometimes a ketoester but never diketones.[148]

2. Heterocyclic Esters

a) Acyloxybenzofurans

Fries rearrangement of 5-acetoxy-2-ethylbenzofuran leads to a mixture of three compounds, namely the 3-, 4- and 6-acyl derivatives.[149]

The Fries rearrangement of various esters of 2,3-disubstituted monohydroxybenzofuran has been investigated. In this series, the Fries rearrangement of 2,3-dimethyl-4-acetoxybenzofurans provides the *o*- and *p*-hydroxyketones, whereas the 2,3-disubstituted-5-acyloxybenzofurans give only the 6-acyl derivatives.[150]

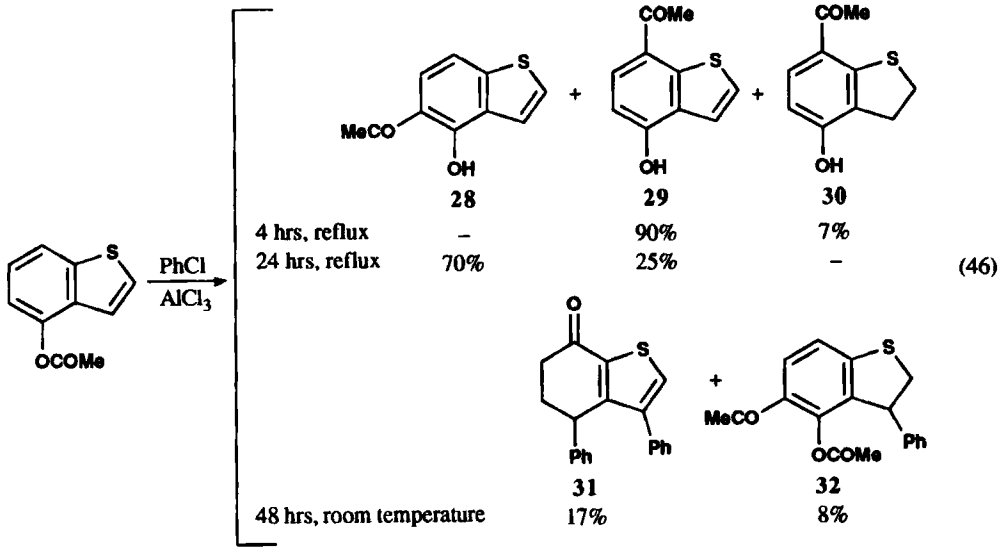
The Fries rearrangement of 2,3-disubstituted-6-acyloxybenzofurans leads to 5-acyl derivatives;[150] on the other hand, when the 5-position is occupied, the isomeric *o*-hydroxyketone, i.e. the 7-acyl derivatives is obtained.[151] The 7-acetoxy-2,3-dimethylbenzofuran when treated with $AlCl_3$, provides *o*- and *p*-hydroxyketones.[150]

b) Acyloxycoumarins

A number of substituted acyloxycoumarins have been submitted to Fries rearrangement. The substituted 7-alkyl-5-acyloxycoumarins lead to 6-acyl derivatives with $AlCl_3$.[152] The Fries rearrangement of 7-acyloxycoumarins provides mainly the 8-acyl derivative (50-70%),[152,153] with sometimes small quantities of the 6-acyl derivative (5-10%),[153] except when this position on the aromatic ring is occupied.[151] Yields are severely lowered in the case of substituted 7-oxycoumarin crotonates (20-40%).[154] The 4-substituted-5,7-diacetoxycoumarins lead to 5,7-diacetyl-4,6-dihydroxycoumarins when treated with $AlBr_3$ or $AlCl_3$.[152,155]

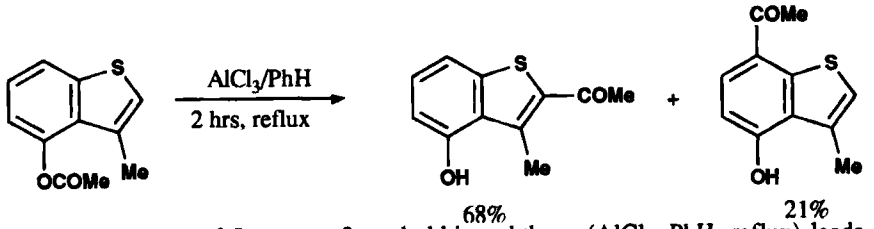
c) Acyloxythianaphthenes

The result of Fries rearrangement ($AlCl_3$/PhH) of 4-acetoxythianaphthene **27** is dependent upon experimental conditions. While the *o*- and *p*-hydroxyketones **28-29** are easily obtained, the formation of unusual compounds **30, 31** and **32** is also observed at room temperature.[156] However, under the normal in Fries rearrangement conditions (20 hours, reflux), **29** is almost quantitatively (95%) converted into compound **30** (Eq. 46).[156]



(46)

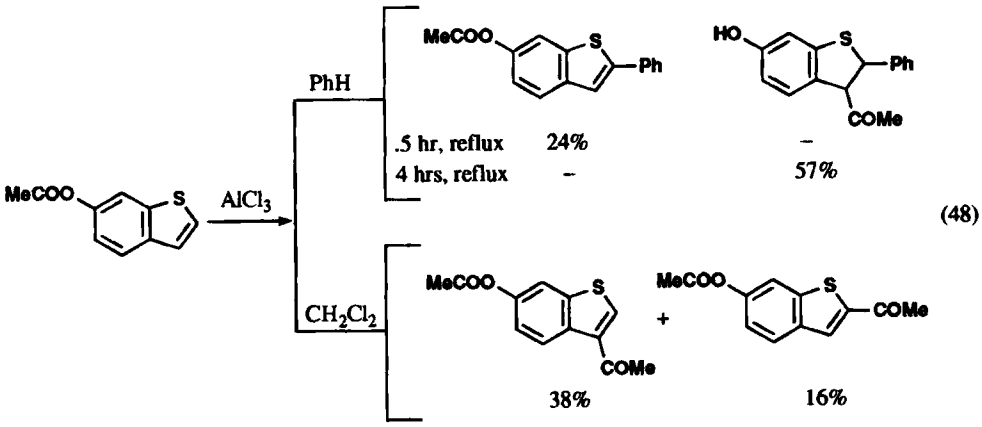
In the Fries rearrangement of 4-acetoxy-3-methylthianaphthene, the acetyl group migrates mostly to the 2-position (Eq. 47).[156]



(47)

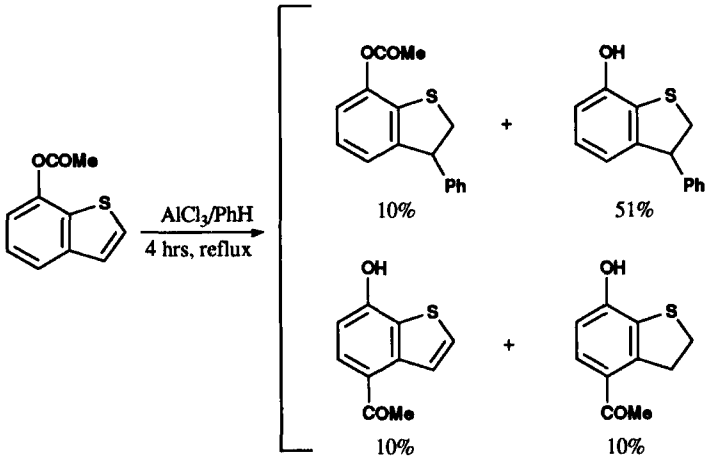
The treatment of 5-acetoxy-3-methylthianaphthene ($AlCl_3$, PhH, reflux) leads only to 2-acetyl-5-hydroxy-3-methylthianaphthene (90%).[157]

Fries rearrangement of 6-acetoxythianaphthene is specific (Eq. 48).[156]



(48)

The Fries rearrangement of 7-acetoxythianaphthene ($AlCl_3$, PhH, reflux) leads to a mixture of three compounds (Eq. 49).[156]



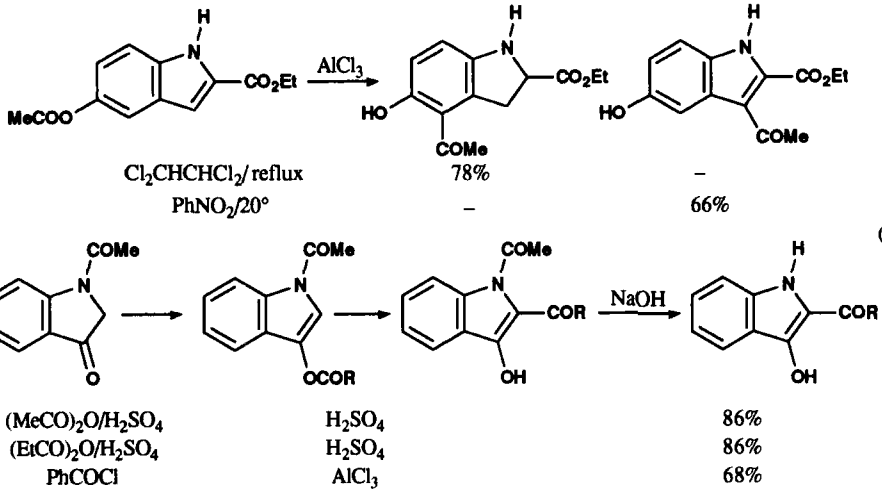
(49)

On the other hand, under the same conditions, the 7-acetoxy-3-methylthianaphthene only provides 2-acetyl -7-hydroxy-3-methylthianaphthene (78%).[158]

3. Miscellaneous Esters

Several 3-acyloxythiophenes substituted at the 4- or/and 5-position have been treated by $AlCl_3$. They all lead to substituted 2-acyl-3-hydroxythiophene (30-80%).[159] The Fries rearrangement of 6-acetoxy-3-methylbenz[1,2]isoxazole ($AlCl_3$, 140°) leads to 7-acetyl-6-hydroxy-3-methyl-benz[1,2]isoxazole (75-85%).[160] The treatment of 2-phenyl-4 (4´-acetoxybenzylidene)-5(4H)-oxazolone ($AlCl_3$, $PhNO_2$, 100°) likewise provides the expected *o*-hydroxyketone (51%).[161]

8-Acetoxyquinoline-5-aldehyde,[162] 5-acyloxy-1,4-benzodioxanes,[163] 2- and 4-acetoxy-α–benzylidene-δ-butyrolactones[164] and 4- and 5-acetoxy-2,1,3-benzothiadiazoles[165] were converted by Fries rearrangement into the corresponding *o*- and *p*-hydroxyketones. Solutions of phenolphthalein and of bisphenol A dibenzoates in $PhNO_2$, treated with $AlCl_3$ at 170°, provide the expected di-*o*-hydroxyketones (57% and 45%).[166]



(50)

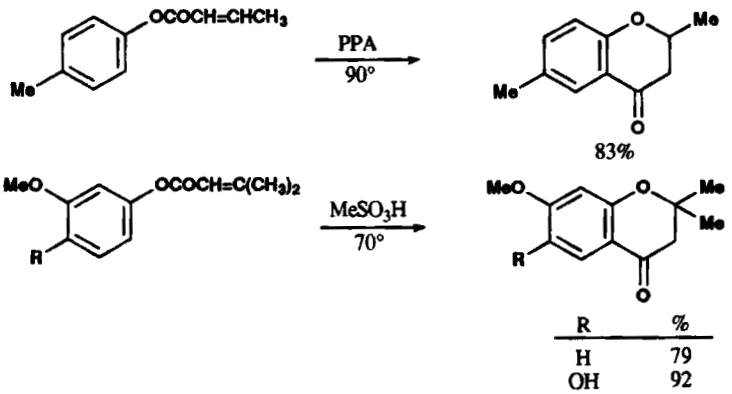
The Fries rearrangement of substituted 3- and 5-hydroxyindole esters leads to different hydroxyketones according to the experimental conditions (70-85%)(Eq. 50).[167]

V. CYCLIZATION REACTION IN THE COURSE OF THE FRIES REACTION

1. From Phenolic Esters of α,β-Ethylenic Acids

The phenolic esters prepared from α,β-ethylenic acids under Fries conditions lead to different cyclizations. The compounds obtained vary according to the experimental conditions. Thus, the Fries rearrangement of phenyl and naphthyl cinnamates is strongly influenced by the nature of solvent.[168]

Phenyl crotonate and 3-methyl-2-butenoate provide the chromanones (Eq. 51).[169]



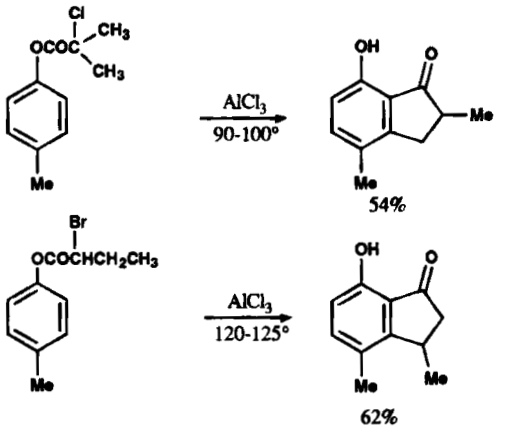
R	%
H	79
OH	92

(51)

The Fries rearrangement of 4-substituted phenyl furylacrylates ($AlCl_3$, PhCl, reflux) leads to 6-substituted coumarins (65-80%).[170]

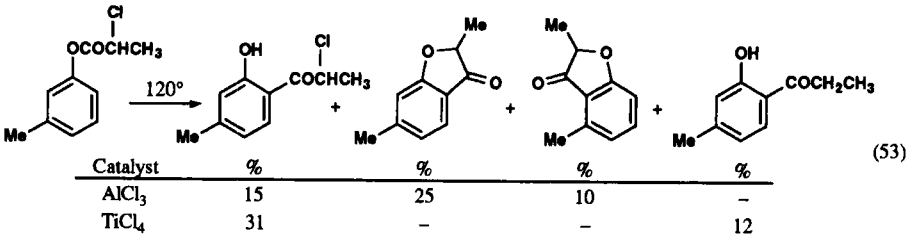
2. From Phenolic Esters of α-Halogenated Acids

The phenolic esters obtained from α-halogenated acids undergo cyclization under the action of $AlCl_3$ with formation of indanones (Eq. 52)[171] or coumaranones. Some *m*-cresol and tar are also



(52)

formed from *m*-cresyl α-chloropropionate (Eq. 53).[66] The action of $SnCl_4$ on *p*-tolyl acetate may lead

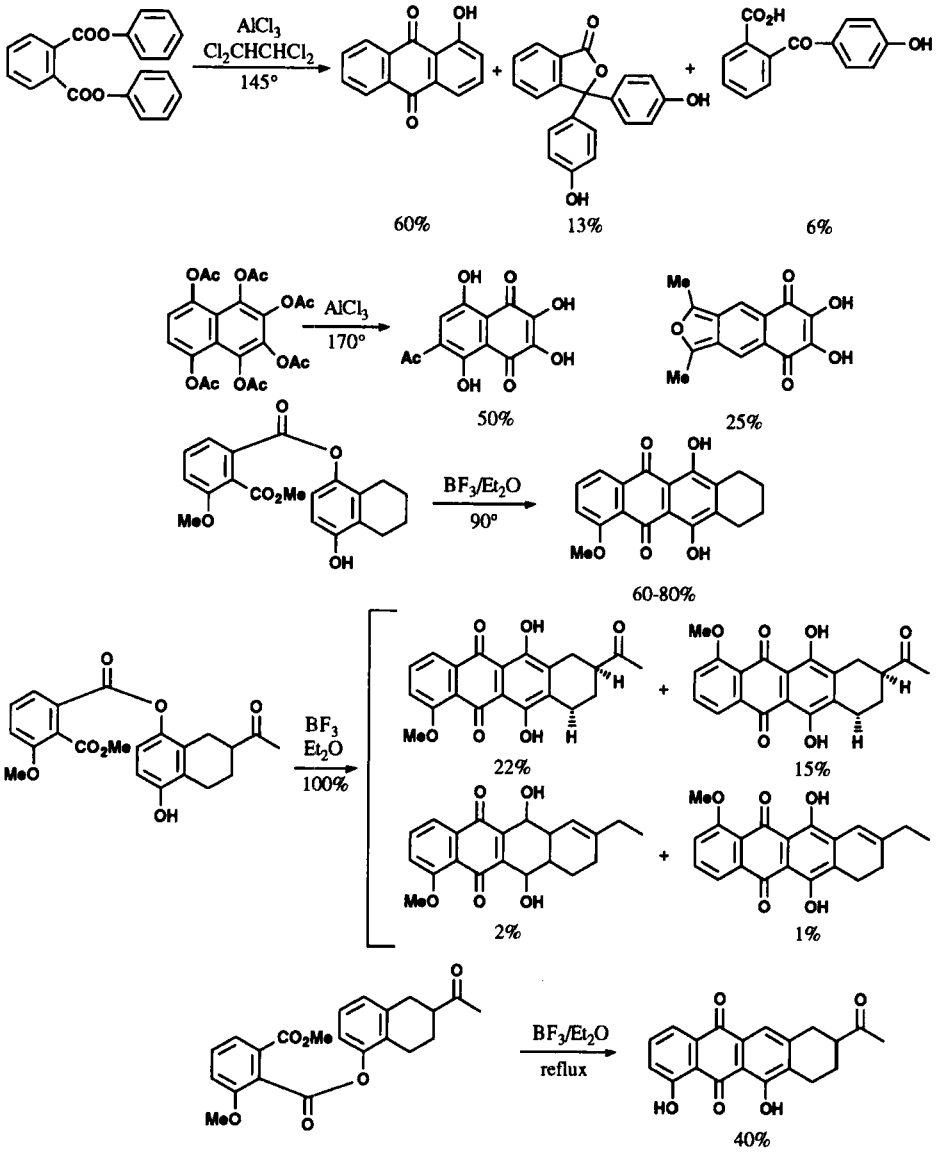


Catalyst	%	%	%	%
$AlCl_3$	15	25	10	–
$TiCl_4$	31	–	–	12

(53)

directly to anthocyanin compounds, *via* the formation of 2-hydroxy-5-methylacetophenone.[172] The Fries rearrangement of some specific esters gives complex polycyclic quinones (Scheme 3).[173]

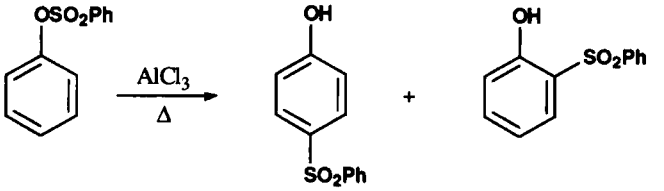
Scheme 3



VI. FORMATION OF HYDROXYARYLSULFONES FROM ARYLSULFONATES

1. Phenyl and Naphthyl Arylsulfonates

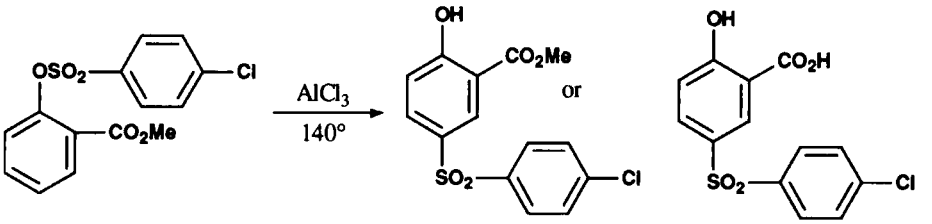
The action of $AlCl_3$ on arylsulfonates leads to *o*- and *p*-hydroxyarylsulfones. The reaction is carried out either in $PhNO_2$ at 100° or without solvent between 120 and 160° (Eq. 54).The phenyl and naphthyl benzenesulfonates provide the hydroxyarylsulfones in low yields (<20%).[174] The presence of halogens on the phenolic part of the ester, or the presence of a substituent in *para*-position (Me, halogen) of the arylsulfonic acid usually promotes the rearrangement (20-60%).



(54)

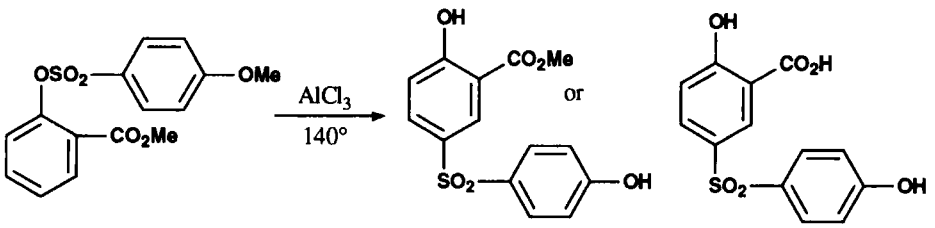
Many *p*-halo substituted phenyl phenylsulfonates,[175] *p*-methoxyphenylsulfonates,[175] α- and β-naphthylsulfonates[175,176] and *p*-toluenesulfonates[174,177] have been subjected to the action of $AlCl_3$. Cation-exchanged montmorillonite clays have been used as Lewis acid catalysts in the Fries rearrangement of phenyl *p*-toluenesulfonates to *o*-hydroxyarylsulfones (<5%).[178]

The action of $AlCl_3$ on arylsulfonates involving methoxy and carbomethoxy groups usually induces partial cleavage of methyl groups (Eq. 55).



with $PhNO_2$	62%	–
without $PhNO_2$	–	40%

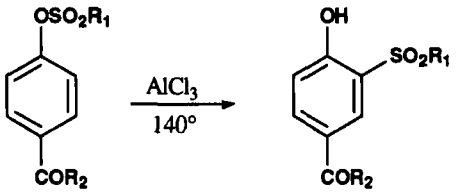
(55)



with $PhNO_2$	35%	–
without $PhNO_2$	–	85%

The presence of carbomethoxy, carboxy, cyano and nitro on the phenolic part of the ester does not seem to modify the course of reaction. The Fries rearrangement of resorcinol and hydroquinone di-*p*-bromophenylsulfonates does not provide the disulfones but only tars.[175]

The Fries rearrangement of 4-acylphenyl arylsulfonates leads to 2-hydroxy-5-ketoarylsulfones. However, the nature of acyl group influences the course of the reaction (Eq. 56).[179]



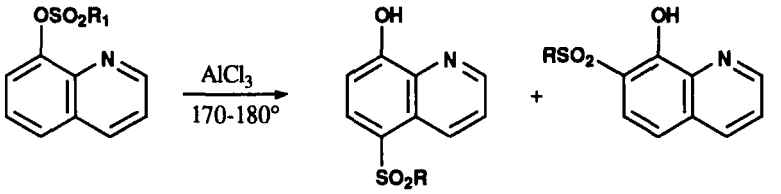
(56)

R_2	%
Me	20-60
Et	85-100

R_1 = Ph, C_6H_4Me(p), $C_6H_4Hal.$(p), $C_{10}H_7$(α) and (β)

2. 8-Hydroxyquinolinyl Arylsulfonates

The Fries rearrangement of eight 8-quinolinyl arylsulfonates leads to 5- or 7-arylsulfonyl-8-hydroxyquinolines (15-20%) (Eq. 57).[180]



(57)

R = Ph, C_6H_4Me(p), $C_6H_4Hal.$(p), C_6H_4OMe(p), $C_{10}H_7$(α) and (β)

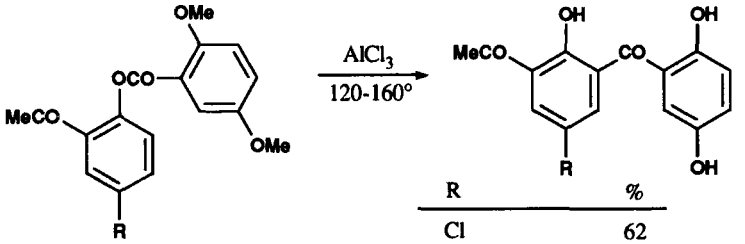
VII. MISCELLANEOUS REACTIONS

1. Preparation of Diketones

In some cases, the Fries rearrangement of a phenyl monoester provides, in addition to the expected compounds, small quantities of hydroxyaryldiketones (<20%). The most rational process to get these compounds is to treat ketoesters with $AlCl_3$ between 120° and 160°.

a) 2,6-Diacylphenols

The *o*-ketoesters having an halogen atom (Cl, F) or a methyl group in the para position to the ester function lead to 2,6-diacylphenols (60-80%).[102,181] The nature of the acyl groups is of no importance. Sometimes the reaction proceeds with demethylation when one of the rings carries a MeO group (Eq. 58).

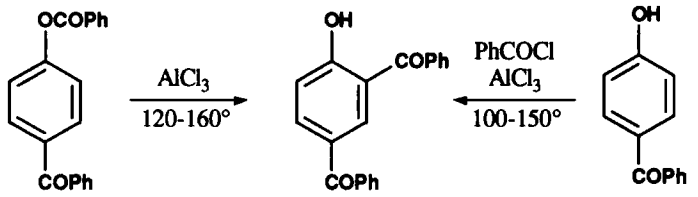


(58)

R	%
Cl	62
Me	65

b) 2,4-Diacylphenols

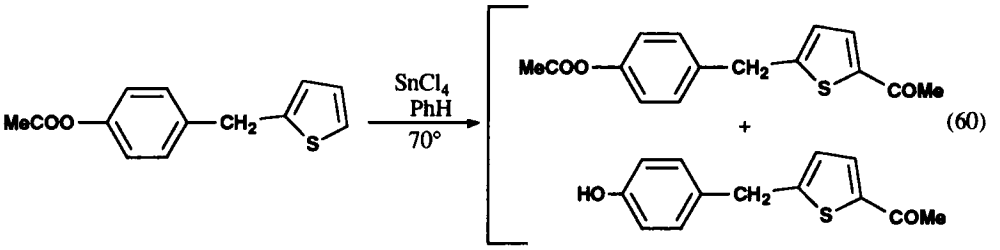
An acyl group is in the para position to ester function. The acyl groups may be of identical or different nature. The phenolic part of the ketoester may carry a substituent (halogen, methyl) in 2- or 3-position to the ester function.[66,182] One may also treat a *p*-acylphenol according to Friedel-Crafts (Eq. 59).[183] Yields may vary between 40 and 80%.



(59)

2. Migration of Acyl Group on Another Ring in the Fries Reaction

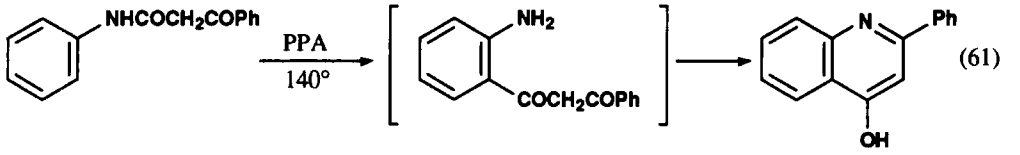
In benzene, $SnCl_4$ causes the migration of the acetyl group of 2-(4′-acetoxybenzyl)thiophene (Eq. 60).[184]



(60)

3. Behavior of Amides and Sulfamides in Relation to the Fries Reaction

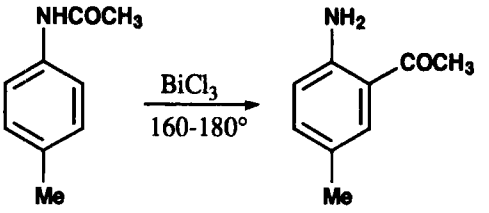
Aromatic amides when treated by PPA, $TiCl_4$, $ThCl_4$, $ZrOCl_2$ lead to *o*- and *p*-acylanilines.[185] Two specific cases will be pointed out. The Fries rearrangement of benzoylacetanilide with PPA does not stop at the *o*-amino-2-benzoylacetophenone step, but directly leads to 4-hydroxyquinoline (Eq. 61).[186]



(61)

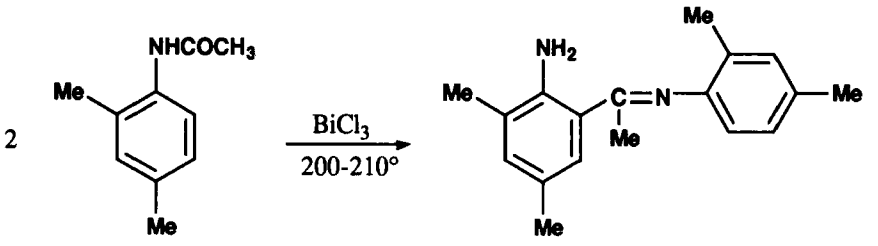
20%

In the same manner, the action of $BiCl_3$ (160-245°) on the amides does not always stop at the *o*- or *p*-acylaniline step, but may lead to a condensation product (Eq. 62).[187]



85%

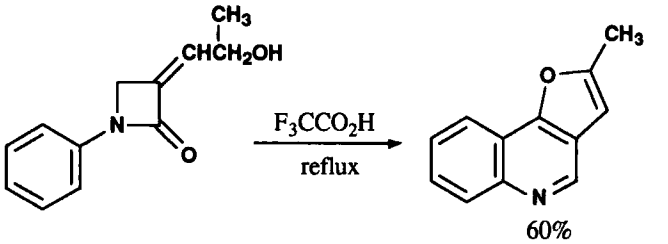
(62)



40%

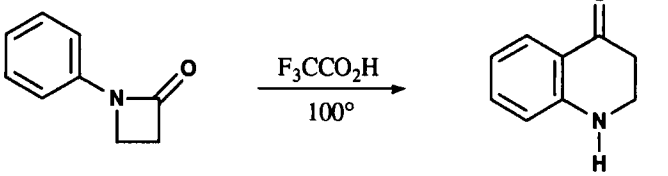
The Fries rearrangement of N-benzoylsulfonylanilines with $AlCl_3$ at 180-200° leads to 4-aminodiphenylsulfones.[188]

1-Arylazetidin-2-ones, at reflux in F_3CCO_2H give a reaction related to the Fries rearrangement. They provide the furo[3,2-c]quinolines or the 2,3-dihydro-4-(1H)-quinolones (Eq. 63).[189]



60%

(63)

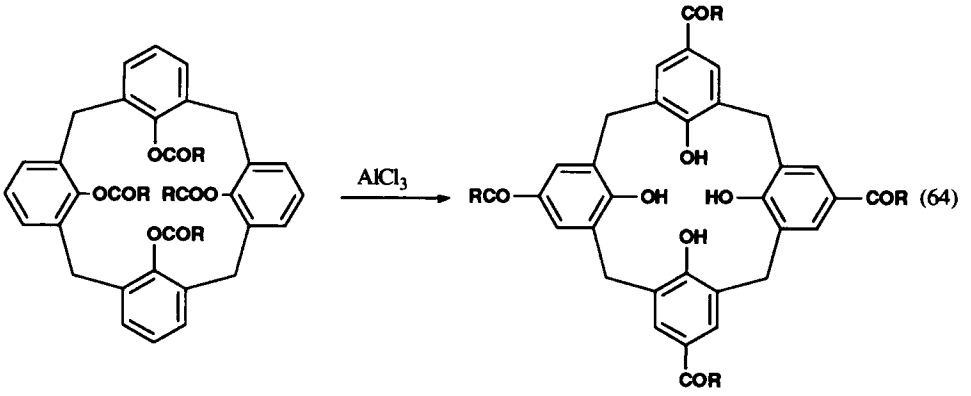


80%

4. Synthesis of Polymeric Hydroxyarylketones

a) Cyclic

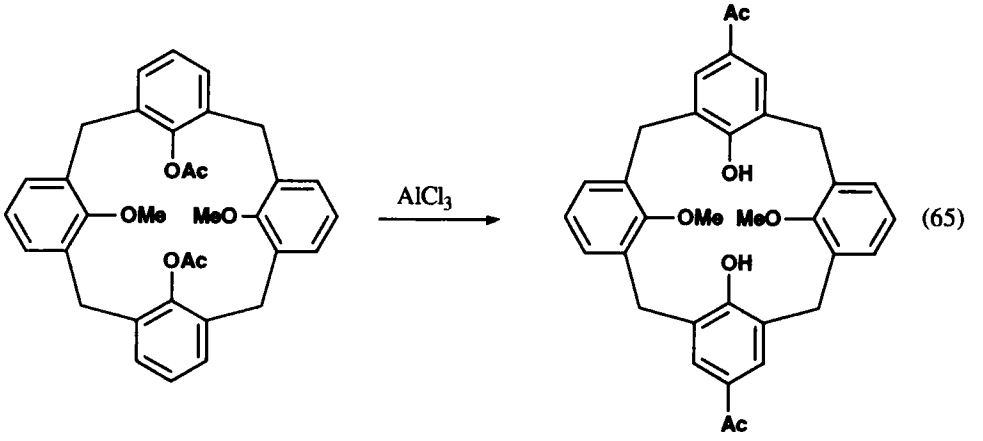
Calix[4]arene tetraalkanoates **33** undergo Fries rearrangement ($AlCl_3$, 150° or $AlCl_3$, $PhNO_2$, 20°) to yield *p*-acylcalix[4]arenes **34** (60-80%)(Eq. 64).[190]



33 R = Me, Et, *n*-Pr, *i*-Pr, Ph 34 (64)

60-80%

A method is described for the selective functionalization of calix[4]arene at the *para*-positions of the phenyl rings (70%)(Eq. 65).[191]



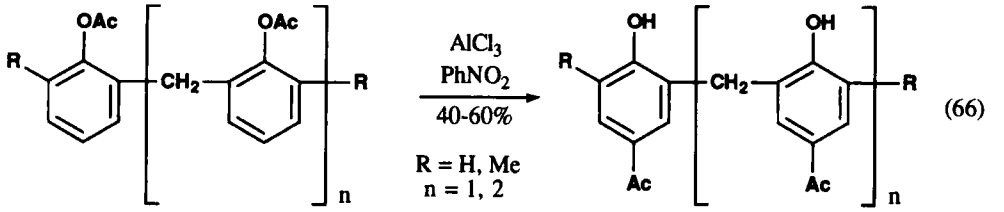
(65)

70%

The Fries rearrangement of hexakis (acyloxy) calix[6]arene ($AlCl_3$, PhCl, 45-50°) leads to hexaacyl-calix[6]arene (30-35%).[192]

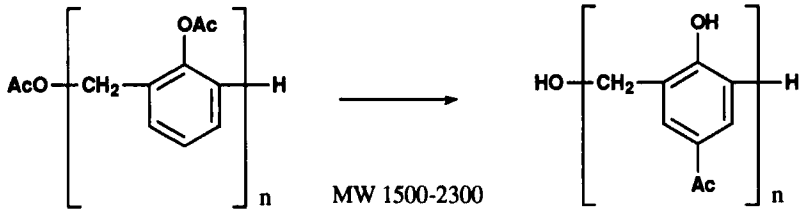
b) Acyclic

The Fries rearrangement has been used for the preparation of new polymers by action of $AlCl_3$ on polyesters (30-60%) (Eq. 66).[193]



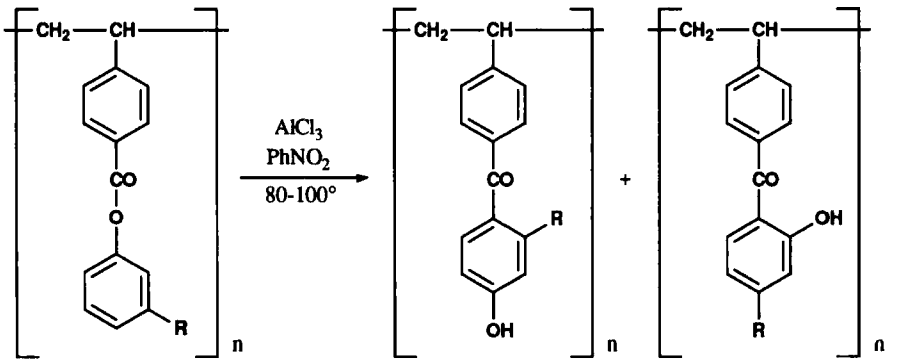
(66)

Oligomer-analogous Fries rearrangement of oligomeric-2-acetoxy-1,3-phenylenemethylenes leads to two poly(5-chloro-2-hydroxy-1,3-phenylenemethylenes (MW 1500-2300) (Eq. 67).[194]



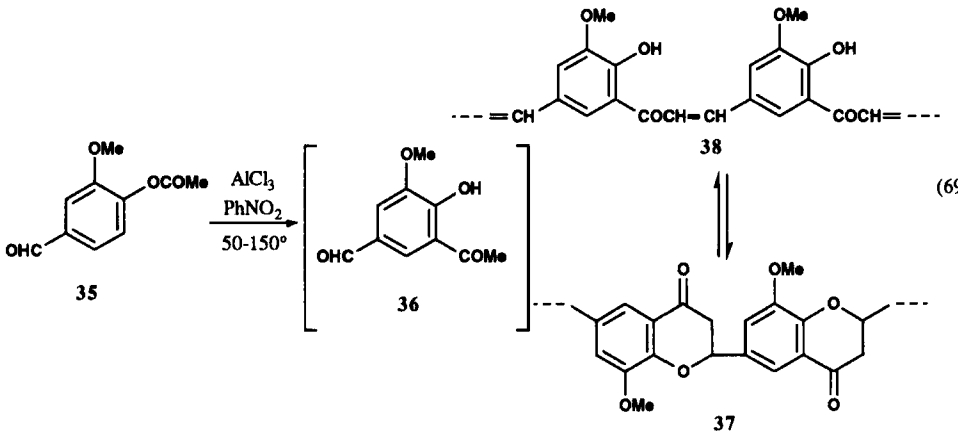
(67)

Fries rearrangement of phenyl 4-vinylbenzoate polymer (I) and 3-methoxy 4-vinylbenzoate polymer (II) resulted in formation of polymer containing hydroxybenzoylphenyl groups and a large number of the derivatives were *p*-substituted in the case of (I) and *o*-substituted in the case of (II) (Eq. 68).[195]



(68)

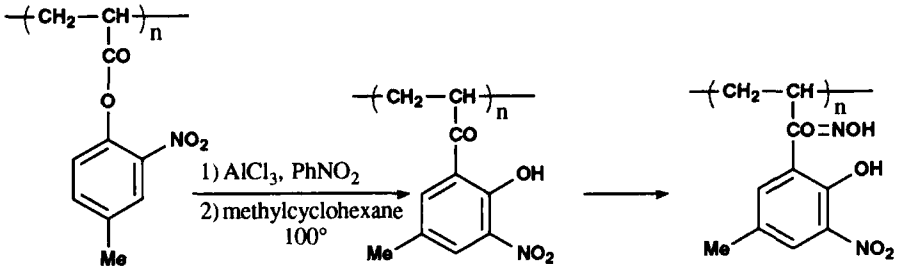
The Fries rearrangement of vanillin acetate **35** proceeds via the formation of 3-acetyl-4-hydroxy-5-methoxybenzaldehyde **36** and it spontaneously condenses to an equilibrium mixture of a polychalcone **37** and a poly(8-methoxydihydrobenzopyrone) **38** (Eq. 69).[196]



(69)

Specific ion-exchange resins containing hydroxy oxime groups were prepared from 4-methyl-

2-nitrophenyl or 4-chlorophenyl acrylate polymers *via* the Fries rearrangement (Eq. 70).[197]

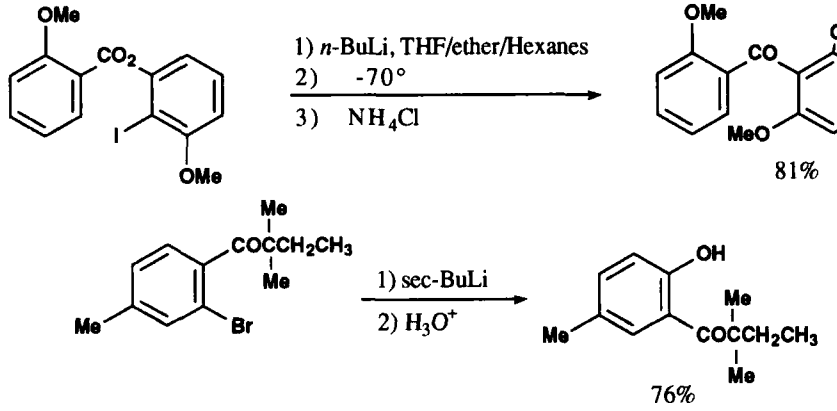


(70)

One can increase the photochemical and thermal stability of polymers by introduction of esters groups in chain. Thus one obtains self-protecting polyacrylates. After the Fries rearrangement, phenolphthalein terephthalate polymers and dimethylsiloxane-phenolphthalein terephthalate block copolymers contain carbonyl and hydroxyl groups ortho to each other.[198] Thus, by reaction on polyacrylates, polymers containing inhibiting groups in the chain were obtained.[198]

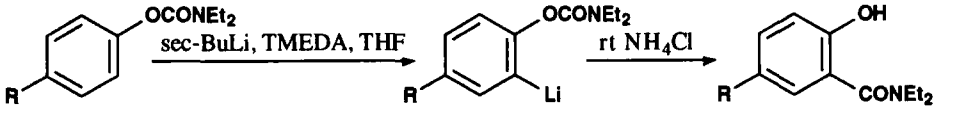
5. Anionic *ortho*-Fries Rearrangement

o-Halogenophenyl esters undergo an intramolecular acyl migration to produce, after hydrolysis, the corresponding *o*-hydroxyketone (50-90%) (Eq. 71).[199]



(71)

ortho-Lithiated *O*-arylcarbamates constitute new synthetic intermediates which provide salicylamides by rearrangement (Eq. 72).[200]

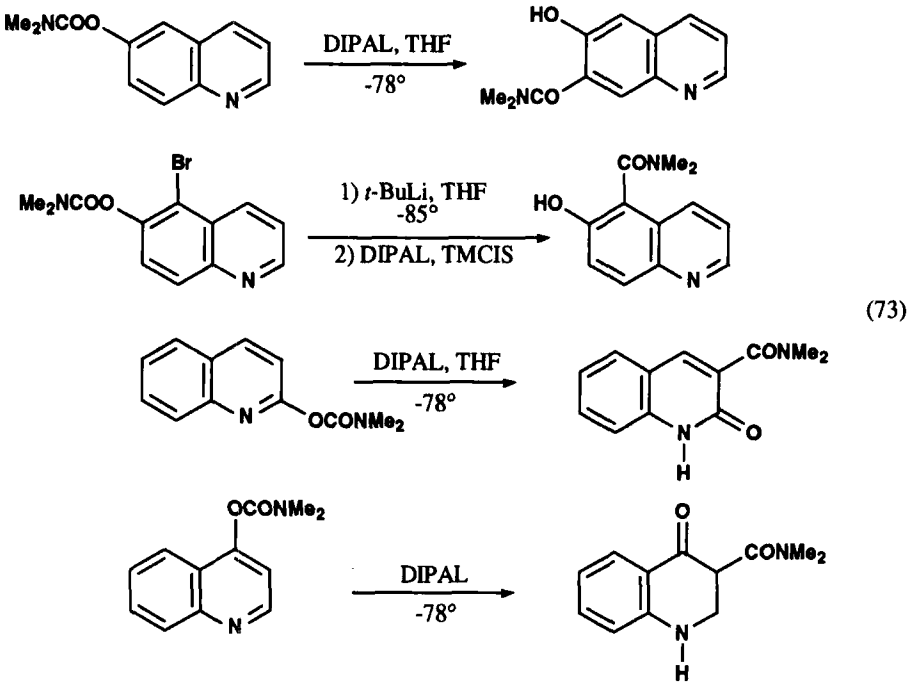


(72)

R	%
H	75
p-OMe	60
p-Cl	65

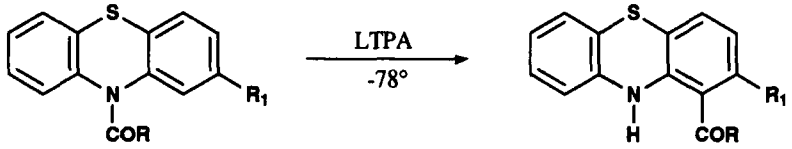
N,N-Dialkylcarbamoyloxyquinolines after metalation and normal work up lead to miscella-

neous compounds (substituted quinolines and quinolones depending on the position of substituent relative to nitrogen and to the work-up treatment) (Eq. 73).[201]



(73)

Some 2-substituted N-acylphenothiazines undergo a rapid intramolecular N→C migration of reaction with lithium N,N-dialkylamides at -78° to give rearrangement acylphenothiazines (Eq. 74).[202]



(74)

$R = CF_3$ $R_1 = H, Cl, CF_3$ 30-45%
R = 3-pyridyl $R_1 = Cl$

VIII. PHOTO-INDUCED FRIES REARRANGEMENT

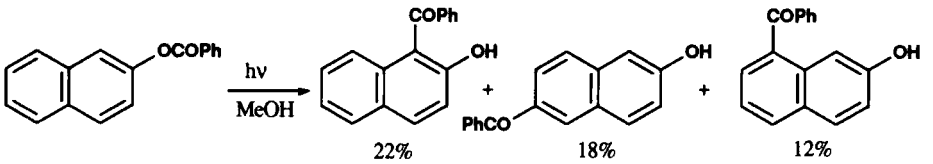
The photo-Fries reaction of phenolic esters proceeds by a radical mechanism.[6] The solvents used are mainly hydrocarbons and alcohols. Polar solvents favor rearrangement and the non-polar solvents to lead mostly the formation of phenol.[6] The photo-Fries reaction leads most often to the same compounds as the Fries reaction catalyzed by acids. However, one may observe decarbonylation and decarboxylation reactions in the course of rearrangement,[203] as well as cyclization sometimes with the formation of unusual compounds.

1. Irradiation of Aryl Esters in Solution

a) Monophenol Esters

Various phenol esters have been subjected to photo-Fries rearrangement, namely phenyl acetate,[6,204] phenyl benzoate,[6,205] phenyl *p*-chlorobenzoate (2-acyl: 49%, 4-acyl: 6%),[6] phenyl cinnamate,[206] phenyl *p*-methoxycinnamate,[206] phenyl ferrocenoate (4-acyl: 44%),[6] phenyl *o*-toluate[6] and phenyl nicotinate, isonicotinate and picolinate,[207] as well as simple or mixed diesters: diphenyl malonate,[208] ethyl phenyl carbonate[209] and methyl phenyl oxalate.[210]

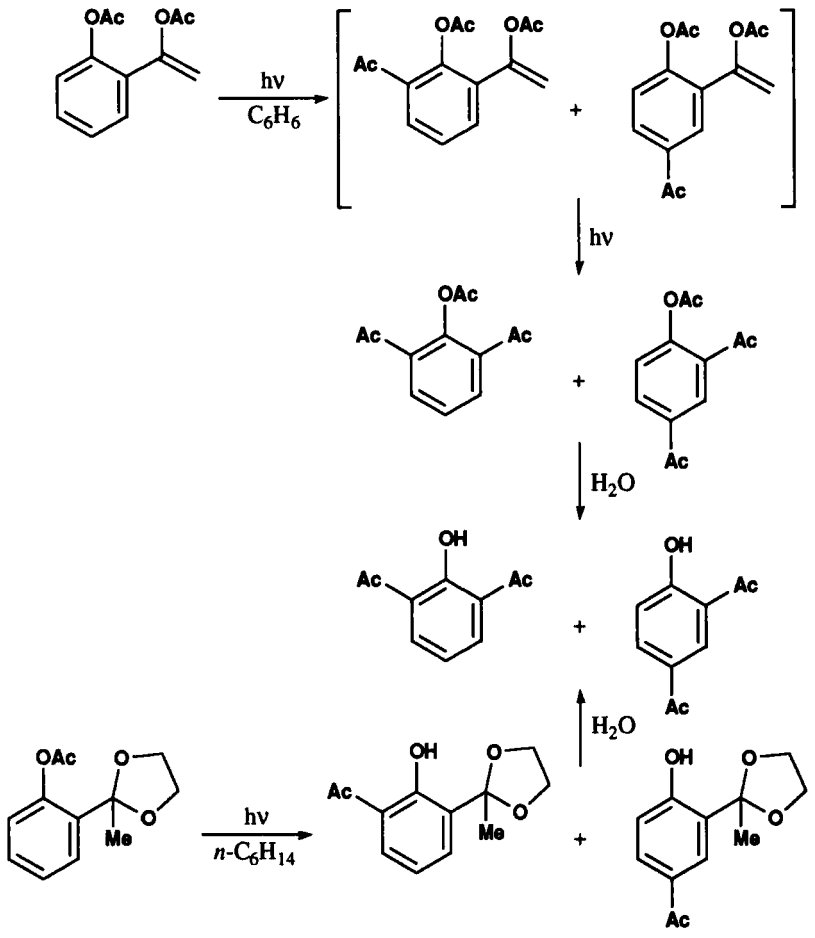
The photo-Fries reaction has been also applied to the following esters: 1-naphthyl acetate,[211] cinnamate[212] and 4-methylcinnamate (2-acyl: 35%),[212] as well as 2-naphthyl acetate[205] and benzoate.[213] The 2-naphthyl esters always provide a mixture of three isomeric hydroxyketones (Eq. 75).



(75)

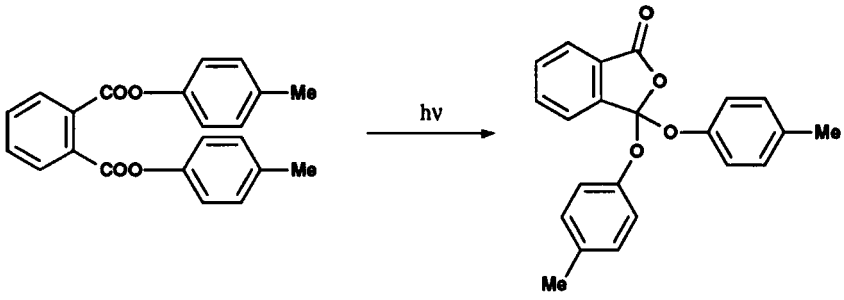
Various monosubstituted phenyl esters have been irradiated by UV-light in solution. Under these conditions, 2-*t*-butylphenyl pivalate yields, besides hydroxyketones (4-acyl: 3%, 6-acyl: 14%) and 2-*t*-butylphenol, a mixture of di-*t*-butylbenzene isomers,[214] whereas 2-phenylphenyl formate and acetate give only 2-phenylphenol by heterolysis.[215] The photo-Fries reaction has also been applied to *o*-tolyl nicotinate,[207] 2-chlorophenyl ethylcarbonate,[209] as well as 2-methoxyphenyl 2,3-dimethoxybenzoate and acetate.[216] In the last case, 52% of 2-methoxyphenyl acetate is recovered after photo-Fries reaction. However, 2-hydroxy-3-methoxyacetophenone obtained represents 48% of the total of the other compounds, which is of obvious preparative interest. Indeed, this ketone is obtained with a very low yield (1%) by action of $AlCl_3$ on the ester.[131] The acetate and benzoate of *o*-hydroxyacetophenone, whose ketone function has been protected, were irradiated. Thus, the enol-acetate of 2-benzoyloxyacetophenone afforded the hydroxydiketones as the major products (2,4-diacyl: 24%, 2,6-diacyl: 27%), by way of photo-Fries rearrangement of the acyl ester group, followed by intramolecular transacetylation of the resulting hydroxyketones and hydrolysis.[217] Similar results are obtained with the enol-acetate of 2-acetoxyacetophenone.[217] The cyclic ethylene acetals of *o*-acetoxyacetophenone give upon irradiation and hydrolysis the expected diacetylphenols (2,4-diacyl: 13%, 2,6-diacyl: 17%) (Eq. 76).[217] By contrast, *o*-acetoxyacetophenone does not undergo any appreciable change upon irradiation, showing the deactivating effect of the acetyl side-chain. Some *m*-substituted phenyl esters - benzoate,[205] ethylcarbonate[209] and nicotinate[207] - have been subjected to the photo-Fries.

On the other hand, the irradiation of several *p*-substituted phenyl esters has been performed and leads to the expected *o*-hydroxyketones or to the formation of heterocyclic compounds. So *p*-tolyl acetate,[218] benzoate,[6,218,219] 2-butynoate,[220] *p*-chlorobenzoate,[221] cinnamate,[206] dihydrocinnamate,[222] indole-2-carboxylate,[223] propynoate,[220] hemisuccinate and methylsuccinate,[224] have been treated similarly and all lead to *o*-hydroxyketones with various yields. In the case of *p*-tolyl acetate, a discordance



(76)

does appear; irradiation according to Pathak and Khanna[225] does not afford the expected product; instead 4-hydroxy-2-methylacetophenone is obtained (26%). 7-Methyl-4-azaxanthone (28%) was prepared by UV irradiation of *p*-tolyl 2-chloronicotinate by way of the photo-Fries product.[226] The photo-Fries reaction of di-*p*-tolyl malonate gave 4-hydroxy-6-methylcoumarin.[208] The *p*-tolyl phthalate also affords an heterocyclic compound (Eq. 77).[205]

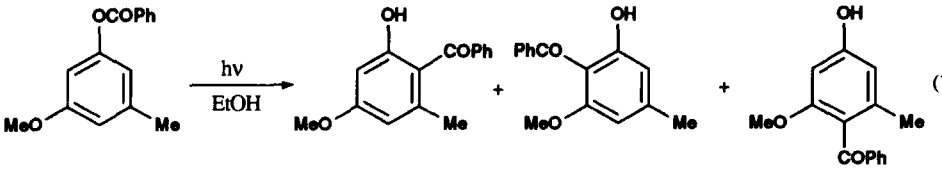


(77)

Similarly the irradiation has been carried out on 4-*t*-butylphenyl,[6,214] *p*-chlorophenyl,[6,205,209] and *p*-

methoxyphenyl esters.[205,216,220,222,224,227] The 5-methoxy-1-naphthyl esters gave the 2-acyl-5-methoxy-1-naphthols (50-70%) by irradiation.[228]

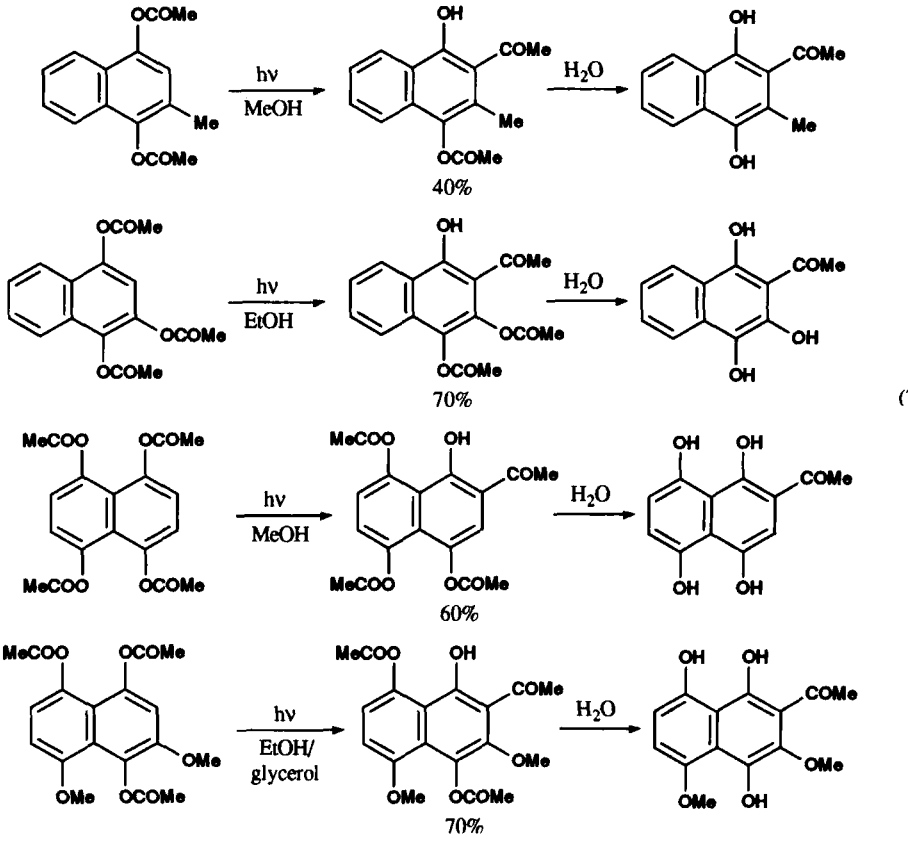
Miscellaneous disubstituted phenyl esters have been subjected to the photo-Fries reaction and led to the formation of α-hydroxyketones. These esters were 3,5-di-*t*-butylphenyl benzoate (2-acyl: 48%),[214] carvacryl nicotinate,[207] 2,4-dimethoxyphenyl acetate (6-acyl: 61%),[216] 2,4-dimethylphenyl acetate (6-acyl: 54%),[216] 2,4-dimethylphenyl hemisuccinate (6-acyl: 60%),[222,227] creosol acetate (6-acyl: 68%), benzoate (6-acyl: 63%) and isocreosol butyrate (4-acyl: 16%, 6-acyl: 24%),[216] orcinol esters (Eq. 78)[229] and various thymyl esters.[207,225]



21% 14% 8% (78)

b) Di and Polyphenol Esters

The normal acid-catalyzed Fries rearrangement of catechol acetate yields predominantly 3,4-dihydroxyacetophenone, whereas the photochemical rearrangement apparently favors the



(79)

2,3-dihydroxyacetophenone isomer.[230] The irradiation of various hydroquinone esters,[231,232] pyrogallol, hydroxyquinol and phloroglucinol esters has been effected.[232] The photo-Fries rearrangement of several polyacetoxynaphthalenes offers preparative possibilities (Eq. 79).[233]

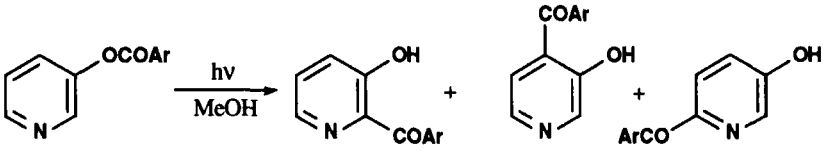
In all the cases, it was observed that the acetyl group migrates to an available β-position and only one acetyl group migrates.

2. Irradiation of Various Compounds in Solution

a) Heterocyclic Esters

The photo-Fries reaction of 7-furoyloxy-4-methylcoumarin gave 6-furoyl-7-hydroxy-4-methylcoumarin as major product (75%). The isomeric 8-furoyl-7-hydroxy-4-methylcoumarin on the other hand dominates in the normal Fries migration.[234]

The irradiation of 6-acetoxyindole leads to a mixture of 5-acetyl-6-hydroxyindole (7%) and 7-acetyl-6-hydroxyindole (66%).[235] 3-Benzoyloxypyridine also has been photolyzed under Fries condition (Eq. 80).[236]



(80)

Ar	%	%	%
C_6H_5	12	11	9
C_6H_4-Me(O)	16	14	14

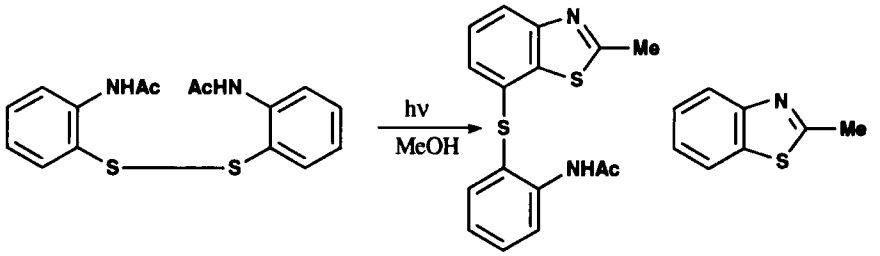
The photochemical reactions of N-acetyldiphenylamine and N-acetylcarbazole,[237] N-acetyl and N,N-diacetylbenzimidazolones[238] in solution have been studied. The reaction products consist of the ortho and *para*-acyl isomers.

b) Various Amides

The irradiation of acetanilide leads to *o*- and *p*-acetylanilines (36% and 32%),[239] whereas N,N-diacetylaniline gives *o*- and *p*-acetylanilides (30% and 25%).[240] 2,4-Dimethoxyacetanilide is irradiated in C_6H_6 to give three photo-Fries rearrangement products: 2-amino-3,5-dimethoxyacetophenone (63%), 2-amino-5-methoxyacetophenone (5%) and 4-amino-3-methoxyacetophenone (11%) from displaced ortho and para methoxy photo-Fries reaction.[241] The Fries rearrangement of 2-acetamidobenzoic acid gave *o*- and *p*-photoproducts expected when the reaction is carried out in CH_3CN or 2-methyl-4H-3,1-benzoxazin-4-one in benzene medium.[242]

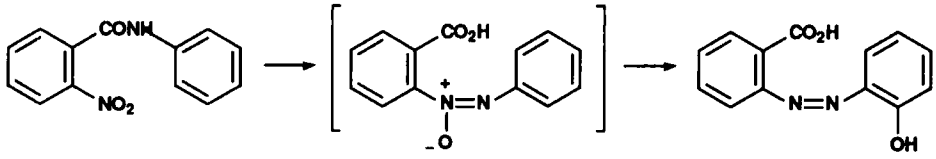
The irradiation of bis (2-acetylaminophenyl) disulfide leads to the formation of heterocycles (Eq. 81).[243]

While 2-chlorobenzanilides were photocyclized, benzanilide, 2- and 2′-methylbenzanilides, N,N-dibenzoylaniline and N,N-di-(2-chlorobenzoyl)aniline gave photo-Fries type reaction products efficiently.[244] *o*-Nitrobenzanilide rearranges to 2(-2-hydroxyphenylazo)benzoic acid, *via* an



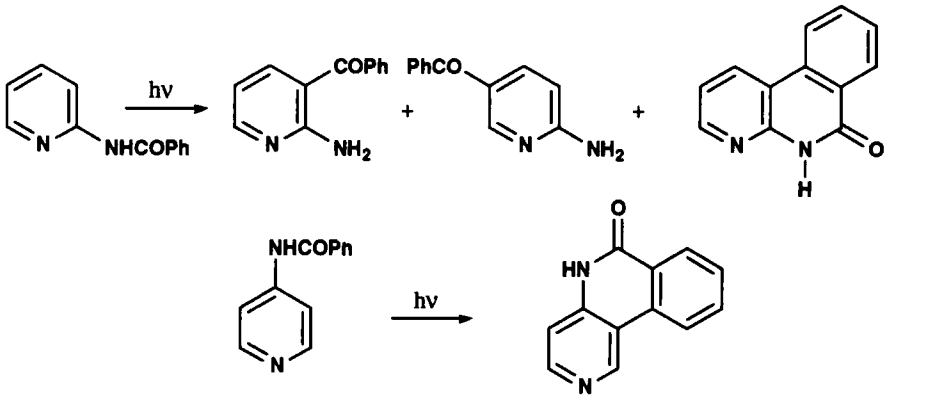
(81)

intermediate azoxybenzene derivative, under the influence of light (Eq. 82).[245]



(82)

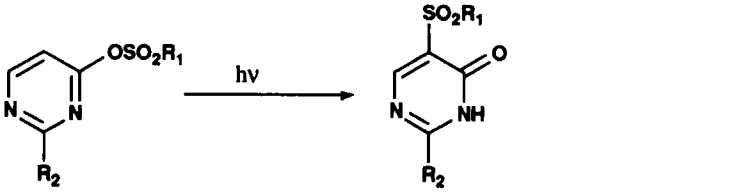
While 3-benzoylaminopyridine gave only normal rearrangement products, 2- and 4-benzoylaminopyridines, by photolytic rearrangement, gave heterocyclic compounds (Eq. 83).[246]



(83)

c) Aryl Sulfonates and Sulfamides

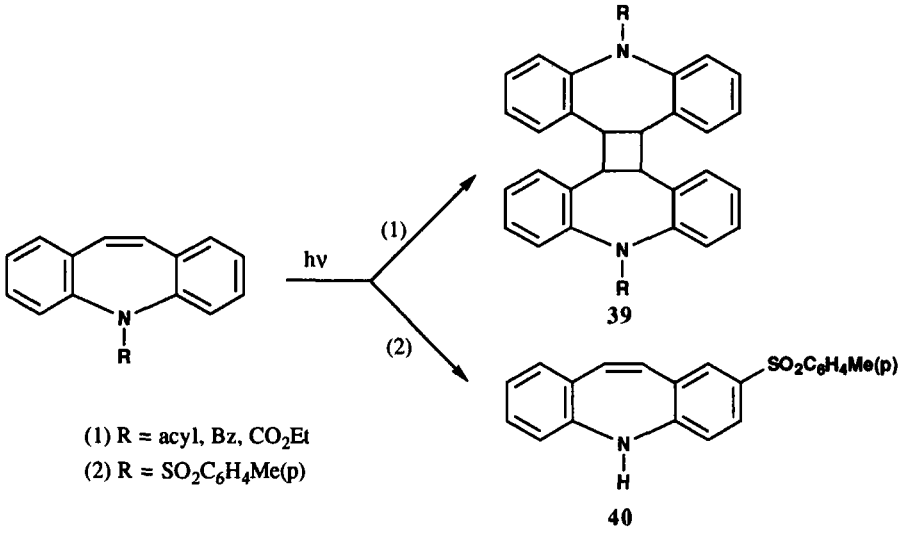
Phenyl *p*-toluenesulfonate rearranges to *o*- and *p*-hydroxyphenyl-*p*-tolylsulfones.[247] 2-Alkyl-4-[(arylsulfonyl)oxy]pyrimidines underwent photochemical Fries rearrangement to give the corresponding 2-Alkyl-5-(arylsulfonyl)pyrimidines.[248] The photo-Fries reaction of 2-dialkylamino-4-pyrimidinyl esters of alkyl and arylsulfonic acids, in which the pyrimidine 5-position is unsubstituted, affords the corresponding 5-alkylsulfonyl and 5-arylsulfonyl-2-dialkylamino-4-hydroxypyrimidines respectively, in yields of up to 60% (Eq. 84).[248]



(84)

R_1 = Aryl, R_2 = Alkyl or N-dialkyl

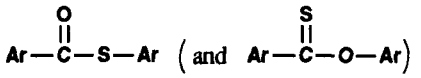
Irradiation of N-aryl, -aroyl and -ethoxycarbonyl derivatives of 5H-dibenz[b,f]azepine (iminostilbene) gives good yields of *trans*-cyclobutane dimers **39**, whereas the N-tosyl compound undergoes photo-Fries rearrangement to afford **40** (Eq. 85).[249]



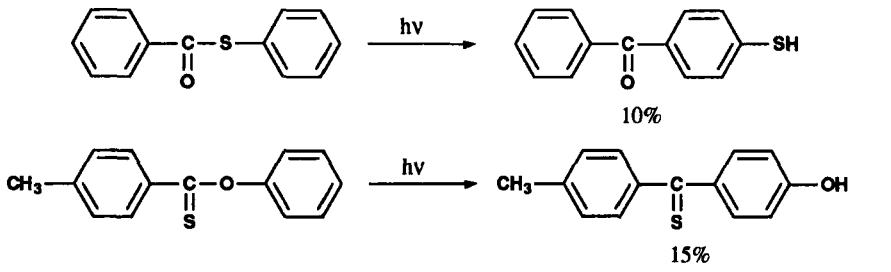
(85)

Photo-Fries rearrangement of N-sulfonylcarbazoles afforded the respectively 1- and 3-sulfonylcarbazoles in 29-55% yield.[250] The photolysis of 2-benzotriazol-2-yl-4-*t*-octylphenyl benzenesulfonate gave 66% 2-benzotriazol-2-yl-4-*t*-octyl-6-(phenylsulfonyl)phenol.[251]

d) Aryl Thioesters



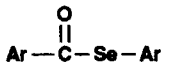
Irradiation of S-phenyl thiolacetate gave both *o*- and *p*-isomers, unlike S-phenyl thiolbenzoate which gave only the *p*-isomer (Eq. 86).[252]



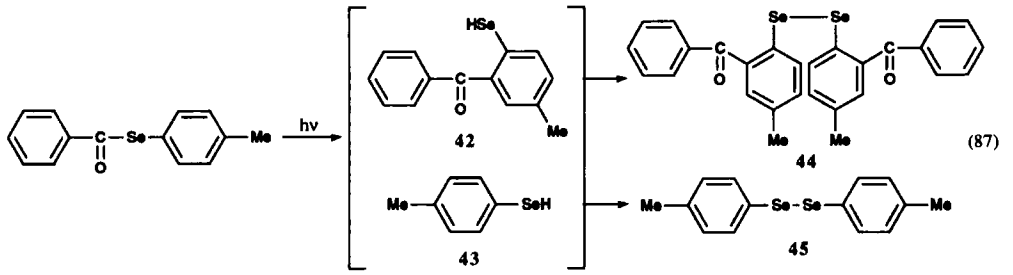
(86)

4′-Tolyl-2-methylsulfono-thio-benzoate undergoes a photo-rearrangement to give 2-methylthiaxanthone (34%). The isomeric 4′-tolyl-3-methyl-sulfono-thio-benzoate form bis-4′-tolyl disulfide (42%) and 3-methylsulfono-benzaldehyde (32%). No thiaphoto-Fries products are formed by the photolysis of these.[253] Irradiation of O-phenylthiobenzoate gave the ortho photo-Fries product (Eq. 86).[254]

e) Aryl Selenoesters



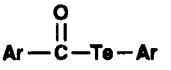
Se-*p*-tolyl selenobenzoate **41** upon irradiation gives the selenophoto-Fries product **42**, *p*-selenocresol **43** and benzaldehyde (12%). Immediate separation of the reaction products by chromatography yields the sensitive selenols **42** and **43**, which form the isolatable diselenide **44** and **45** in 33% and 46% yield, respectively, on air oxidation (Eq. 87).[255]



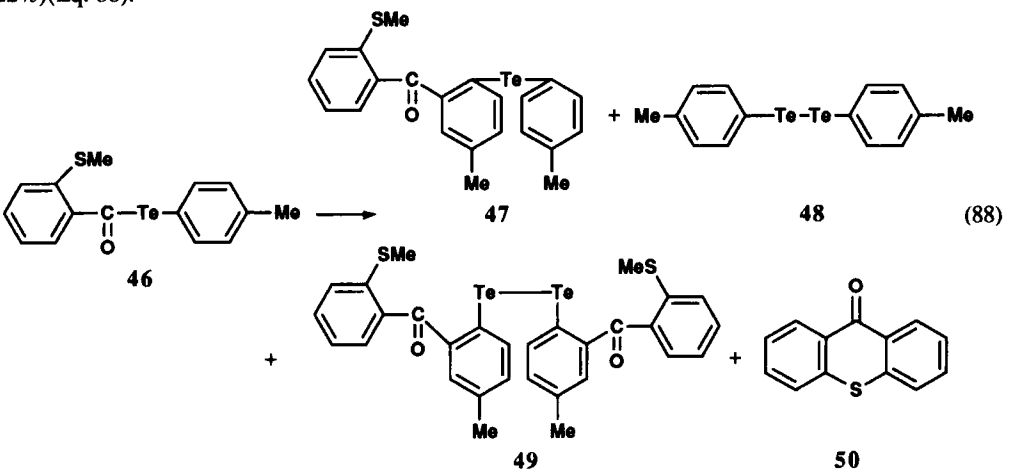
(87)

Irradiation of Se-phenyl-2-chloroselenobenzoate with UV light gives 19% selenoxanthone.

f) Aryl Telluroesters



Telluro ester **46** undergoes photo-induced α-cleavage and tellurophoto-Fries reactions with the formation of tellurides (**47**: 2%) or ditellurides (**48**: 33%, **49**: 11%) and 2-methylthioxanthone (**50**: 22%)(Eq. 88).[256]



(88)

3. Irradiation of Aryl Esters and Amides in particular conditions

a) In the Presence of β-Cyclodextrin

Photo-Fries rearrangement of phenyl acetate **51** [257] in aqueous β-cyclodextrin medium, where

less than one equivalent of β-cyclodextrin was present in the aqueous medium, per each equivalent of the substrate, takes place with predominant formation of *p*-hydroxyacetophenone (Table 5). However, in the presence of an excess of β-cyclodextrin, photo-Fries rearrangement of **51** shows a remarkable ortho-selectivity (Table 5).[258]

TABLE 5. Influence of β-cyclodextrin on the Course of the Photochemical Fries Rearrangement of Phenyl Acetate **52**

Reaction Mixture (molar ratio)	Conversion (%)	Relative Yields (%)			*p-/o-*
		o-Hydroxy-acetophenone	*p*-Hydroxy-acetophenone	Phenol	
52	12	25.7	25.7	48.6	1:1
β-cyclodextrin:**52**					
(0.45:1)	41	11.2	69.0	19.8	6.2:1
(10:1)	20	89.0	11.0	0	0.1:1

The irradiation of some phenyl and *m*-tolyl esters as well as diverse anilides in the presence of an excess of β-cyclodextrin confirms the previous observation.[258] Photolysis of benzenesulfoanilides upon cyclodextrin encapsulation in solid phase yields exclusively 2-aminodiphenylsulfone.[259]

b) In the Presence of Sodium Dodecylsulfate

Photo-Fries rearrangement of phenyl benzoate and phenyl cinnamate in micellar environment in aqueous sodium dodecylsulfate (SDS) results in an efficient and high yield synthesis of the corresponding 2´-hydroxyketones (Table 6).[260]

TABLE 6. Influence of Sodium Dedecylsulfate (SDS) on the Course of the Photochemical Fries Rearrangement of Phenyl Esters

Reaction Mixture	Conversion (%)	Relative Yields (%)	
		o-Hydroxyacetophenone	*p*-Hydroxyacetophenone
Phenyl Benzoate			
- in Ph		13	20
- in EtOH		20	28
- with SDS	100	74	23
Phenyl Cinnamate			
- in Ph		10	2
- in MeOH		23	<1
- with SDS	90	70	15

Photo-reaction of benzanilide in micellar environment of SDS gives selective formation of 2-aminobenzophenone as a major product (80%) and 4-aminobenzophenone (15%).[261]

c) In the Presence of Potassium Carbonate

When the irradiation is carried out in the presence of K_2CO_3, phenyl acetates are converted into the corresponding *o*-hydroxyacetophenones in very high yields.[262] The irradiation of the cyclic ethylene ketals of the acetoxyacetophenones in presence of potassium carbonate leads to the ortho-rearranged products with an average yield of 70%. Addition of K_2CO_3 inhibits the hydrolysis of the ketal group which inhibits the deactivating effect of the keto group. This method led to an improved procedure for the synthesis of diacylphenols.[263]

The photo-Fries rearrangement of esters of α,β-unsaturated carboxylic acids and *meta*-oxygenated phenol was studied as a key step in the synthesis of precocenes and related compounds. Photolysis in hexane did not give any observable transformation, but in the presence of K_2CO_3, the acyl group migrates to the two ortho positions.[264] Similarly, the acetoxy-2,2-dimethylchromans on irradiation with UV light in the presence of K_2CO_3 underwent photo-Fries rearrangement to afford acetyl hydroxy-2,2-dimethylchromans.[265]

d) in the presence of Sodium Hydroxide

The 4-chromanones were obtained in 91 and 82% yield respectively by photolysis of 4-methoxyphenyl crotonate and 3-methylcrotonate in C_6H_6-10% aqueous NaOH. When photolysis was carried out in homogeneous medium in C_6H_6, the Fries rearrangement products were obtained in only low yield.[266]

e) In the Presence of Silica Gel

The photo-Fries rearrangement of aryl benzoates was performed in pentane, in a SiO_2 gel-pentane slurry and on dry SiO_2 gel. All yields in pentane were low.[267]

The photo-Fries rearrangement of various anilides on the surface on dry silica gel leads to *o*- and *p*-acylanilines.[268]

4. Use of Photochemical Fries Rearrangement for Stabilization of Various Polymers and Copolymers

a) Grafting of Aromatic Esters on Polymers

p-Benzoyloxystyrene was grafted on cotton and nylon to impart improved UV stability. The grafted benzoyloxyphenyl moiety underwent the photo-Fries rearrangement to a hydroxybenzophenone moiety to give further improvement in UV stability.[269]

b) Addition of Aromatic Esters and Polyesters in Polymers

Poly (3-methoxyphenyl 4-vinylbenzoate) was an effective UV stabilizer for the copolymer of 4-vinylbenzaldehyde and malonic acid.[270]

Photodegradation of high-density polyethylene in air was delayed with nearly the same effectiveness by the aryl benzoate or decanoate as by the hydroxyketones. The effectiveness of aryl esters was ascribed to their light-induced rearrangement to hydroxyketones.[271] Sheets of aromatic polycar-

bonates and/or thermoplastic from UV by lamination with sheets of aromatic polyesters undergo photochemical rearrangement.[272]

Pendant phenol groups were introduced on polymer chains by photo-Fries rearrangement of the pendant Ph ester groups. Upon UV irradiation copolymers form from Ph methacrylate with Me methacrylate or styrene, 2- or 4-acylphenol groups were introduced as pendant groups.[273] The photochemical Fries rearrangement of 2-naphthyl acetate in glassy poly (methyl methacrylate) converted this compound into products that acted as long-range quenchers.[274]

c) Presence of Aromatic Esters in Polymer Chains

Poly (1-naphthyl acrylate), poly (2-naphthyl acrylate) and the corresponding methacrylate polymers undergo a photochemical Fries rearrangement, introducing quenching groups into the polymer chain. Because the photolysis products have high extinction coefficients throughout the near-ultraviolet region, the irradiation of copolymerized naphthyl esters constitutes a potentially useful method for *in situ* generation of photo-stabilizers.[275]

In general, retardation of light aging during UV photolysis of polymers and copolymers was due to formation of a *o*-hydroxyarylketones via the Fries photorearrangement producing a self-stabilizing effect. Thus, poly [9,9-bis-(4-hydroxyphenyl)fluorene terephthalate and isophthalate],[276] phenyl polyesters of mixed polyesters (from tere- and isophthalic acids and various phenol: phenol,[277] bisphenol A or resorcinol,[277] 2,2-bis-(4-hydroxyphenyl)propane),[277] various phenyl acrylate and methacrylate,[275,277,278] poly (*p*-acyloxystyrene)[278,279] and *p*-isopropenylphenyl acetate or benzoate - styrene copolymer[279] and bisphenol A polycarbonate[280] underwent Fries rearrangement in the presence of UV radiation to give *o*-hydroxyarylketone side groups which improved the light stability of the copolymers.

Polybenzoxazoles containing adamantane rings and their photochemical degradation was compared to that of monomer model compounds. Formation of Ni complexes increased the solar irradiation stability.[281]

Double-stranded P-containing homo- and copolyesters were prepared from 2,8-dihydroxy-5-phenyl-5H-dibenzophosphole-5-oxide, tere- or isophthaloyl chloride and optionally bisphenol A. The presence of dibenzophosphole ring in the polyester backbone improved the flame resistance and the stability to UV light.[277]

CONCLUSION

Aluminum chloride is the most used catalyst to carry out Fries reaction. In general, phenyl esters provide the *o*-hydroxyarylketones (>80%) at high temperature (180°). On the other hand, in carrying out the reaction in nitrobenzene or nitroalkane medium at room temperature, the formation of *p*-hydroxyarylketones isomers is preponderant. Under these mild conditions, optically active phenolic 2-methylvalerates when subjected to Fries migration gave optically active phenolic ketones (60%). Fries rearrangement of phenyl dichloroacrylate with aluminum chloride at 130° gave the ortho- and

para-hydroxyarylketones (80%), whereas phenyl crotonate treated by polyphosphoric acid or methanesulfonic acid leads to chromanones (80-90%).

4,4′-bis (*p*-Hydroxybenzoyl)diphenyl and 4,4′-bis (*p*-hydroxybenzoyl)diphenyl ether are prepared in good yields (95%) by treating 4,4′-bis (phenoxycarbonyl)diphenyl or 4,4′-bis (phenoxycarbonyl)diphenyl ether between -10° and 0° in the presence of liquid hydrofluoric acid. Fries rearrangement of 2-acyloxynaphthalenes with aluminum chloride leads to 1-acyl-2-naphthols (60%) or 6-acyl-2-naphthols in liquid hydrofluoric acid (60-70%). 2,4- and 4,6-Diacylphenols are obtained by treatment of corresponding ketoesters with aluminum chloride at 160° (60-80%).

The Fries rearrangement of monosubstituted phenyl esters in 2-position gave above all *p*-hydroxyarylketones, whereas those substituted in 3-position led to *o*-hydroxyarylketones. Quantitative yields of hydroxyarylketones are obtained by Fries rearrangement of monohalophenyl esters. Fries rearrangement of some 5′-alkyl- and 4′,5′-dialkyl-2′-*t*-butylphenyl alkanoates with titanium tetrachloride proves to be a convenient route to hindered 2′-alkyl- and 2′,3′-dialkyl-6′-hydroxyalkanophenones. The sequential use of "soft" titanium tetrachloride to perform the Fries rearrangement followed by "hard" aluminum chloride to achieve the elimination of a protecting *t*-butyl group allows the synthesis of some 2′-alkyl- and 2′,3′-dialkyl-6′-hydroxyalkanophenones (60%).

The Fries rearrangement of guaiacol esters gives above all *para*-acylguaiacols, whereas *para*-methoxyphenyl esters lead only to *ortho*-acylated phenol. The corresponding *meta*-acylated phenols were prepared in two steps. First, the ester is acylated with the corresponding acyl chloride and stannic chloride in nitromethane. In the second step, the resulting ketoesters are hydrolyzed (60-80%). The resorcinol esters upon Fries rearrangement give 4-acylresorcinols and 2,4- and 4,6-diacylresorcinols. The saponification of 8-acyl-7-hydroxycoumarins - obtained by Fries rearrangement of 7-acyloxycoumarins with aluminum chloride - leads to 2-acylresorcinols. Several diesters of 4,4′-dihydroxybiphenyl with aluminum chloride give 3,3′-diacyl-4,4′-biphenols (80%).

Calix[4]arene tetraalkanoates undergo Fries rearrangement with aluminum chloride to yield *p*-acylcalix[4]arenes (60-80%). The Fries rearrangement of aryl sulfonates leads to *o*- and *p*-hydroxyarylsulfones. Likewise, anilides by treatment with polyphosphoric acid gave *o*- and *p*-acylanilines.

Upon reaction with *sec*-butyllithium at low temperature *o*-bromophenyl esters undergo an intramolecular acyl migration to produce, after hydrolysis, the corresponding *o*-hydroxyarylketones (60-90%). This is metal-promoted Fries rearrangement. *ortho*-Lithiated O-aryl carbamates constitute new synthetic intermediates which by treatment with a variety of electrophiles lead to ortho-substituted carbamates and by rearrangement provide salicylamides.

Aryl esters of aliphatic and aromatic carboxylic acids undergo UV-light catalyzed Fries reaction in solution and provide *o*- and *p*-hydroxyarylketones. A predominantly intramolecular mechanism of rearrangement is favored. Irradiation of guaiacol acetate gives predominantly 2-hydroxy-3-methoxyacetophenone; this compound is not obtained by acid catalyzed Fries reaction. Likewise, the Fries rearrangement of catechol acetate yields predominantly 3,4-dihydroxyacetophenone, whereas the photochemical rearrangement apparently favors the 2,3-dihydroxyacetophenone isomer.

The photo-Fries rearrangement of aryl sulfonates leads to *o*- and *p*-hydroxyarylsulfones. Likewise, anilides gave *o*- and *p*-acylanilines by irradiation to UV-light. *o*-Nitrobenzanilide rearranges to 2-(2-hydroxyphenylazo)benzoic acid, via an intermediate azoxybenzene derivative under the influence of light.

The influence of β-cyclodextrin, sodium dodecylsulfate, potassium carbonate and sodium hydroxide on the course of the photochemical rearrangement of phenyl esters has been studied. These bring an improvement in this process. Likewise, photo-Fries rearrangement of aryl benzoates and various anilides was effected in the presence of silica gel. The introduction of aryl esters in polymer and copolymer chains increases the UV-stability. In general, retardation of light aging during UV-photolysis of polymers and copolymers was due to formation of a *o*-hydroxyarylketone *via* the photo-Fries rearrangement producing a self-stabilizing effect.

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