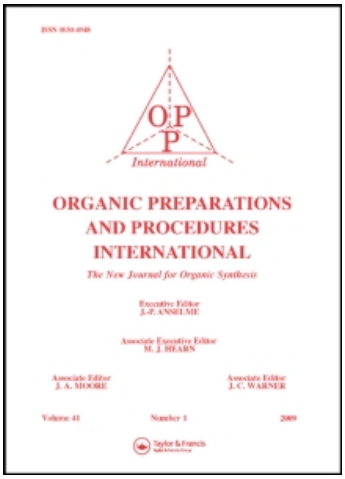

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o-DIACYLBENZENES IN ORGANIC SYNTHESIS. A REVIEW

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INTRODUCTION

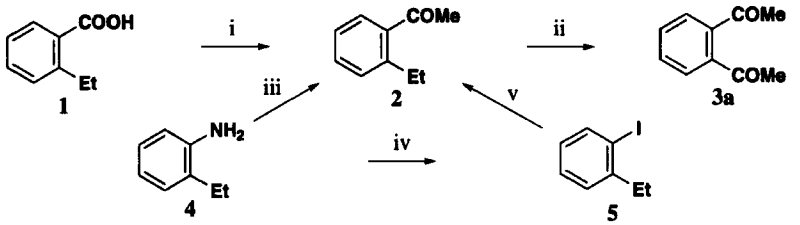
o-Diacylbenzenes are very interesting molecules because of their biological applications and their usefulness as synthons in organic synthesis. The presence of the two acyl groups *ortho* to each allows the formation of novel heterocycles as well as other non-heterocyclic aromatic compounds. A variety of products as quinones, isoindoles, indenes, indanes, benzoxazines have been prepared starting from *o*-diacylbenzenes. The products are usually obtained by using simple experimental conditions. Although there are several methods for the synthesis of *o*-diacylbenzenes in the literature,[1-17] most of them are not general; in addition, they involve too many steps with low yields. This is the reason that there are only a few of *o*-diacylbenzenes commercially available and at rather high prices, *e. g.* 100 mg of *o*-diacetylbenzene cost 71.90 DM. Several years ago, we prepared *o*-diacylbenzenes in high yields, *via* the reaction of *N*-monoacylhydrazones of *o*-hydroxyaryl ketones with lead tetraacetate (LTA).[16] The reaction is general and the unusual rearrangement was investigated further.[18] Moreover, it was applied to appropriate substrates to afford 1,2,3-triacylbenzenes as well as 1,2,4,5- and 1,2,3,4-tetraacylbenzenes.[19,20]

The purpose of this review is to present all the synthetic approaches for the preparation of *o*-diacylbenzenes as well as the progress made using them as starting materials in organic synthesis. We have attempted to cover the reported general synthetic methods, up to 2002, that afford products in high yields. The presentation will begin with the methods of synthesis of *o*-diacylbenzenes. Papers dealing with the reactivity of *o*-diacylbenzenes will be described next, starting with the synthesis of quinone derivatives. Photochemical reactions, bromination and

reactions with nitrogen compounds (*e. g.* amines, phenylhydrazine, amino acids, hydroxylamine) will follow. Finally, some of the applications of *o*-diacylbenzenes will be presented. It is hoped that this review will illustrate the synthetic usefulness of *o*-diacylbenzenes and generate some new ideas about their potentiality in this area.

I. SYNTHESIS OF *o*-DIACYLBENZENES

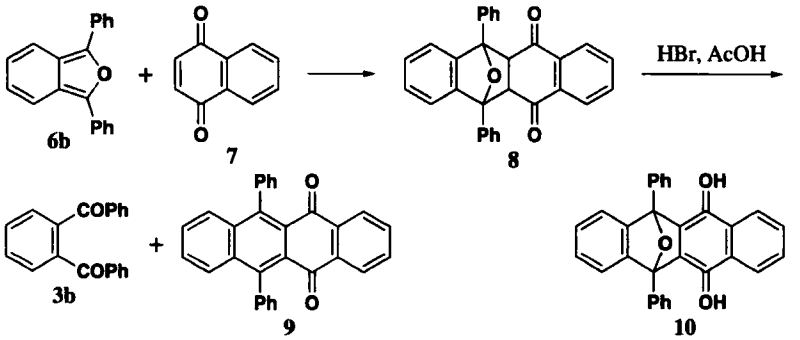
o-Disubstituted benzene derivatives cannot be synthezised by conventional methods and thus are difficult to prepare. Although several methods dealing with the synthesis of *o*-diacylbenzenes exist,[1-17] in most cases they are not general, leading to 1,2-diacetylbenzene or 1,2-dibenzoylbenzene specifically. The oxidation of *o*-ethylacetophenone **2** wih potasium permanganate was the first reported synthesis of *o*-diacetylbenzene (**3a**) in 32% yield.[1] *o*-Ethylacetophenone (**2**) has been alternatively prepared either starting from *o*-ethylbenzoic acid **1** or by *o*-ethylaniline (**4**).[1,2]



i) AcOH, ThO_2, 450°C 24 h, (42% yield); ii) $KMnO_4$, $MgNO_3$, H_2O, 65-70°C 2.5 h, (32% yield) iii) HNO_2, MeCH=NOH, HCl, (30% yield); iv) HNO_2, KJ, (75% yield); v) Mg, MeCHO, CrO_3, (50% yield)

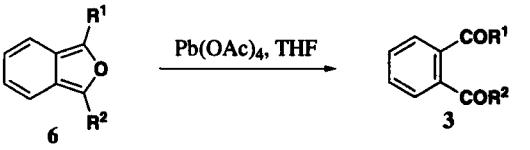
Scheme 1

In 1954, Badger *et al.* described the formation of 1,2-dibenzoylbenzene (**3b**) in addition to small amounts of **9** *via* an initial Diels-Alder reaction of 1,4-napthoquinone (**7**) with 1,3-diphenylisobenzofuran (**6b**) and subsequent treatment with hydrobromic and acetic acid. However, no experimental details or yields were reported.[3a] It is to be noted that initially the product was incorrectly thought to have the structure of **10** and finally identified as 1,2-dibenzoylbenzene (**3b**).[3b]



Scheme 2

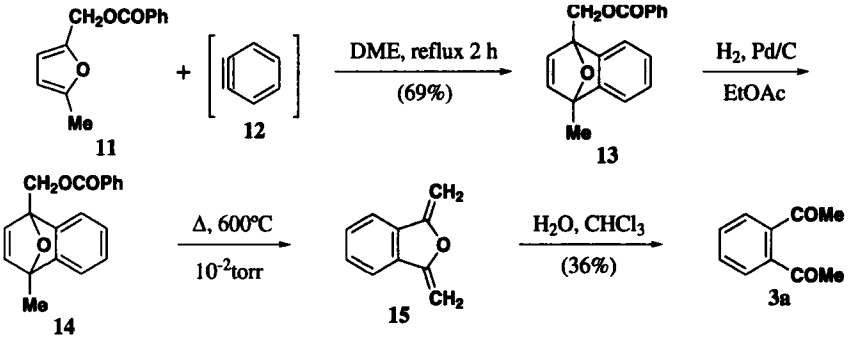
In 1961, it was reported that oxidation of 1,3-diarylisobenzofurans **6** with lead tetraacetate affords *o*-diaroylbenzenes in high yields, generally reported to be over 80%.[4]



b) $R^1 = R^2 = Ph$ c) $R^1 = Ph$, R^2 = mesityl d) $R^1 = R^2$ = mesityl

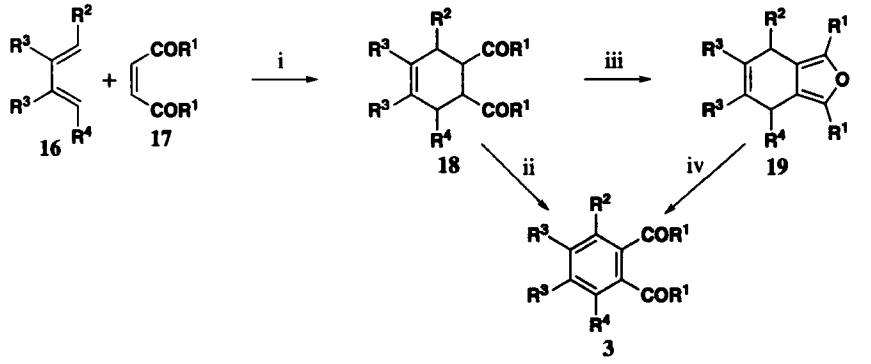
Scheme 3

1,2-Diacetylbenzene (**3a**) has been recently obtained in 36% yield from hydration of 1,3-dimethylene-1,3-dihydroisobenzofuran (**15**), synthesized in three steps; Diels-Alder reaction of benzoate **11** with benzyne **12a** (generated *in situ* by reaction of anthranilic acid with isoamyl nitrite) in refluxing 1,2-dimethoxyethane (DME) gave **13**,which was hydrogenated to **14**; subsequent pyrolysis of **14** gave **15**.[5]



Scheme 4

Furthermore, Diels-Alder reaction of butadiene **16a** with diacetylethylene (**17a**) led to the formation of 1,2-diacetyl-4-cyclohexene (**18a**) as shown in *Scheme 5*. Subsequent



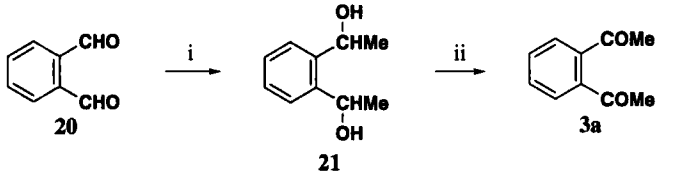
a) R^1 = Me, $R^2 = R^3 = R^4$ = H; e) R^1 = Ph, $R^2 = R^4$ = Ph, R^3 = H; f) R^1 = Ph, $R^2 = R^4$ = H, R^3 = Ph; g) R^1 = Ph, $R^2 = R^4$ = Me, R^3 = H; h) R^1 = Ph, $R^2 = R^4$ = H, R^3 = Me; i) R^1 = Ph, R^2 = Me, R^4 = CO_2Me, R^3 = H; j) R^1 = Ph, $R^2 = R^4$ = Ph, R^3 = Me

i) 130°C 10 h, (38% yield for **18i**); 180°C 0.5 h, (87% yield for **18j**) ii) Pd/C, (15% yield for **3a**)
iii) AcOH, H_3PO_4, 120 °C, (91% yield for **19j**) iv) AcO, /Br_2, 120°C, (70% yield for **3i** and 70% for **3j**)

Scheme 5

aromatization with Pd/C afforded *o*-diacetylbenzene (**3a**) in 15% yield.[6] There is also a reference in the Japanese literature about the formation of 1-acetyl-2-benzoylbenzene *via* the same procedure.[7] In 1973, the method was extended further to a variety of substrates giving rise to several *o*-diacylbenzenes **3e-3j**, as shown in *Scheme 5*.

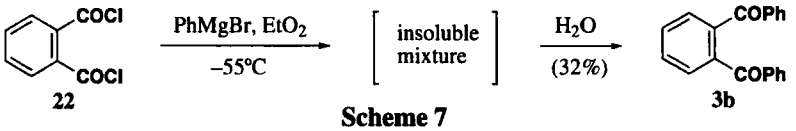
However, the experimental details and yields (38 and 87%) are only described for products **3i** and **3j**.[8] The same method has been used later in 1990, by Volz and Voβ, for the synthesis of *o*-diacylbenzenes **3c** and **3d**, shown in *Scheme 3*, in 74 and 88% yield respectively.[9] It has been also reported that treatment of *o*-phthalaldehyde (**20**) with methylmagnesium bromide gave 1,2-di-(α-hydroxyethyl)benzene (**21**) which upon oxidation with permanganate solution led to the formation of *o*-diacetylbenzene (**3a**) in 50% overall yield (*Scheme 6*).[6]



i) MeMgBr, Et_2O or THF; ii) $Mg(NO_3)_2{\cdot}6H_2O$, 3 h, $KMnO_4$, 1 h (50% yield)

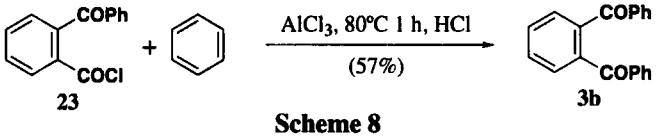
Scheme 6

The preparation of *o*-dibenzoylbenzene (**3b**) (32%) from phthaloyl chloride (**22**) and phenylmagnesium bromide was also successfully carried out.[10] Although the yield is poor, the procedure involves a simple reaction using inexpensive, readily available starting materials. The addition of phthaloyl chloride to phenylmagnesium bromide in ether at -55 °C led to an ether insoluble mixture. After the removal of the solvent, addition of water to the residue afforded *o*-dibenzoylbenzene (**3b**) in 32% .



Scheme 7

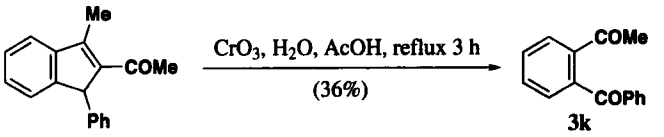
o-Dibenzoylbenzene (**3b**) was also obtained in 57% yield by the Friedel-Crafts reaction of *o*-benzoylbenzoyl chloride (**23**) with benzene and aluminum chloride.[11]



Scheme 8

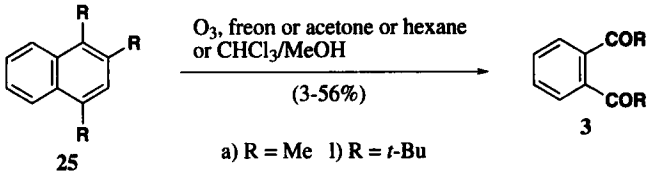
In 1974, it was reported that oxidation of indene **24** with chromic anhydride in the presence of acetic acid led to the formation of 1-acetyl-2-benzoylbenzene (**3k**) in 36% yield.[12] Later,

ozonolysis of napthalenes **25** was reported to afford 1,2-diacetylbenzene **3a** and 1,2-dipivaloylbenzene **3l** in yields ranging between 3-56% depending on the solvent. The ozonolysis of **25** was



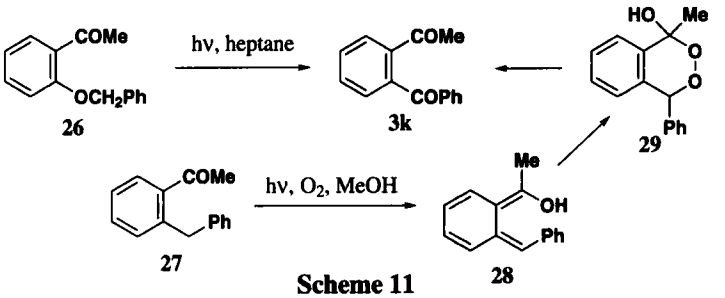
Scheme 9

performed in solvents such as freon-11, *n*-hexane, acetone, pyridine/freon-12, chloroform/methanol. The best yields were obtained in chloroform/methanol whereas the lowest yields occurred in pyridine/freon-12.[13]



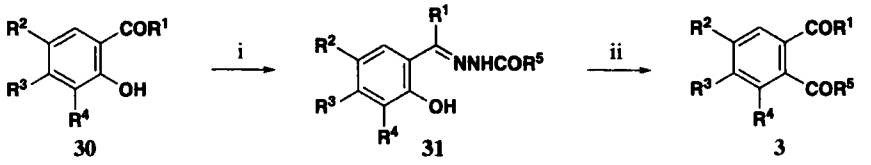
Scheme 10

There are also two publications on the photochemical formation of 1-acetyl-2-benzoylbenzene (**3k**). In 1990, 1-acetyl-2-benzoylbenzene (**3k**) was obtained as the major *photoproduct* of the irradiation of *o*-benzyloxyacetophenone (**26**) in heptane both in the presence and the absence of pyridine.[14] In 1998, Wagner *et al.* reported that irradiation of *o*-benzylacetophenone (**27**) in oxygen-saturated methanol led to a mixture of products with NMR spectra characteristic of cyclic peroxide **29**, presumably by addition of oxygen to the *o*-xylylenol **28**. Peroxide **29** was gradually converted to 1-acetyl-2-benzoylbenzene (**3k**) which is the expected homolysis product.[15] Although these reactions are interesting mechanistically, they are synthetically less useful.



Scheme 11

In 1987, we found that monoacylhydrazones of *o*-hydroxyarylketones (**31**) when treated with lead tetraacetate undergo an unusual rearrangement resulting in replacement of the phenolic hydroxyl with an acyl substituent to give 1,2-diacylbenzenes **3** in excellent yields 68-95%.[16] The same results were obtained when phenyliodoso diacetate (PID) was used instead of LTA.[17]

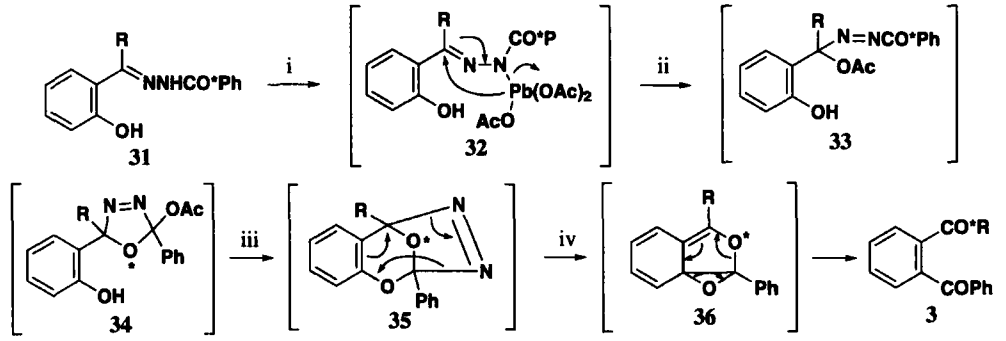


a) R^1 = Me, R^2 = R^3 = R^4 = H, R^5 = Me; b) R^1 = Me, R^2 = R^3 = R^4 = H, R^5 = Ph; m) R^1 = R^2 = Me, R^3 = R^4 = H, R^5 = Ph; n) R^1 = Me, R^2 = R^4 = H, R^3 = OMe, R^5 = Ph; o) R^1 = Me, R^2 = R^4 = Br, R^3 = H, R^5 = Ph; p) R^1 = Me, R^2 = R^3 = R^4 = H, R^5 = *p*-$NO_2C_6H_4$; q) R^1 = Me, R^2 = R^3 = R^4 = H, R^5 = *p*-pyridyl; r) R^1 = Ph, R^2 = R^3 = R^4 = H, R^5 = *p*-pyridyl

i) $R_3CONHNH_2$, propanol, reflux 24 h, (65-91% yield); ii) $Pb(OAc)_4$, THF, 25°C 2 h, (68-95% yield)

Scheme 12

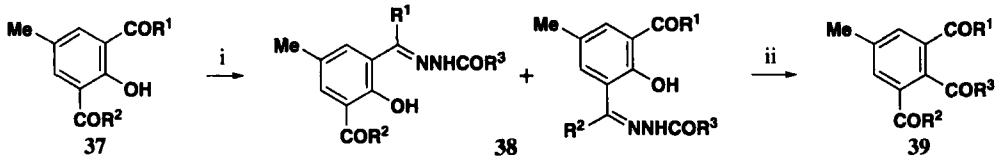
Since no analogous transformations had been previously reported, the mechanism of this novel reaction was investigated.[18] Cross-over experiments demonstrated that the reaction is intramolecular. Furthermore, based on oxygen-labeling evidence, we suggested that 1,3,4-oxadiazoline **34** is initially formed. At this stage, the *o*-hydroxyl group reacts with the oxadiazoline to give the 1,3-dioxane species **35**. Elimination of nitrogen leads to the formation of epoxide **36**, which can undergo electrocyclic rearrangement to give 1,2-diacylbenzene **3**.



i) $Pb(OAc)_4$, –AcOH; ii) $-Pb(OAc)_2$; iii) –AcOH; iv) $-N_2$

Scheme 13

The unusual transformation was also applied to ketones bearing two acyl groups *ortho* to a hydroxy group as starting compounds.[19] Thus, the starting ketones **37** were initially treated with the appropriate hydrazide, in 1:1 ratio to give monohydrazones **38** either as a single isomer (when $R^1 = R^2$) or as a mixture of two isomers (when $R^1 \neq R^2$), *Scheme 14*. It was not necessary

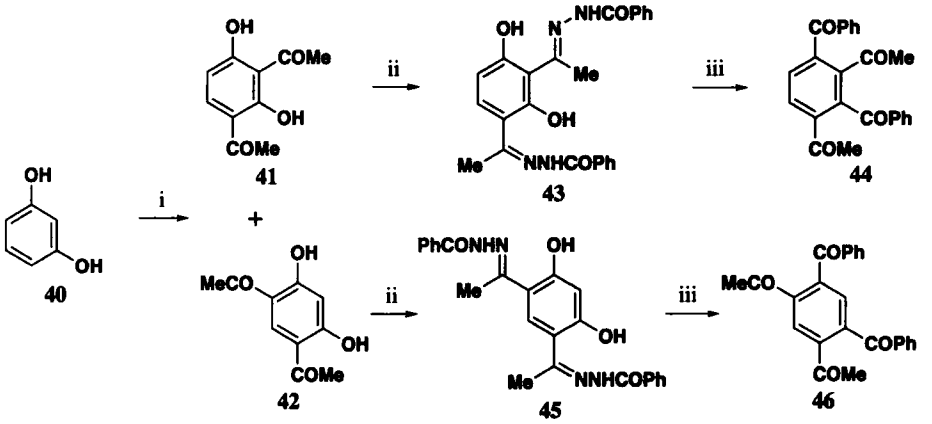


a) R^1 = Me, R^2 = Ph, R^3 = Me; b) R^1 = Me, R^2 = Me, R^2 = Ph, R^3 = *p*-pyridyl; c) R^1 = Me, R^2 = Ph, R^3 = *p*-$NO_2C_6H_4$; d) R^1 = Me, R^2 = R^3 = Ph; e) R^1 = R^2 = R^3 = Ph; f) R^1 = R^2 = Ph, R^3 = Me

i) $R^3CONHNH_2$, propanol, reflux 24 h, (68-90% yield); ii) $Pb(OAc)_4$, THF, 25°C 2 h, (63-92% yield)

Scheme 14

to separate the isomeric mixtures of **38** for the conversion to **39**. LTA oxidation of **38a** afforded triacylbenzenes **39** in good to excellent yields (63-92%). Later, the methodology was extended to the preparation of tetraacylbenzenes **44** and **46** in 73% and 55% yields respectively (*Scheme 15*).[20]



i) $AlCl_3$, MeCOCl, 120°C 2 h, (40% yield for **41** and 24% yield for **42**); ii) $PhCONHNH_2$, 2-propanol, reflux 24 h, (88% yield for **43** and 82% yield for **45**); iii) $Pb(OAc)_4$, THF, 25°C 2 h, (73% yield for **44** and 55% yield for **46**)

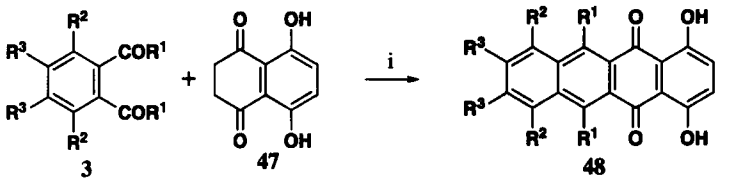
Scheme 15

1,3-Dibenzoyl-2,4-diacetyl- and 1,5-dibenzoyl-2,4-diacetylbenzenes (**44**) and (**46**) were also prepared in good yields 68 and 50% respectively, when PID was used instead of LTA.[20]

II. REACTIVITY OF *o*-DIACYLBENZENES

1. Condensation Reactions

In 1973, Peyrot and Lepage reported that the condensation of *o*-diacylbenzenes **3** with hydroquinones **47** in a mixture of acetic and sulfuric acid led to the formation of fused quinones **48** in yields 25-52%, (*Scheme 16*)[8] and in 1982, Lepage and Lepage performed the same reaction

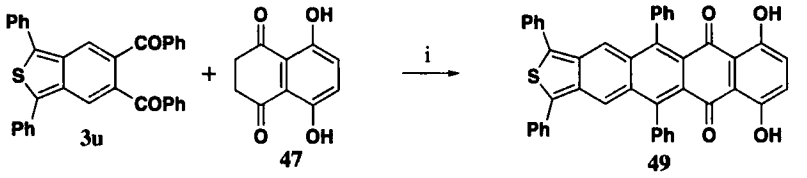


a) R^1 = Me, R^2 = R^3 = H; b) R^1 = Ph, R^2 = R^3 = H; e) R^1 = R^2 = Ph, R^3 = H; f) R^1 = R^3 = Ph, R^2 = H; g) R^1 = Ph, R^2 = Me, R^3 = H

i) AcOH, /H_2SO_4, 120°C 12-30 min, (25-52% yield)

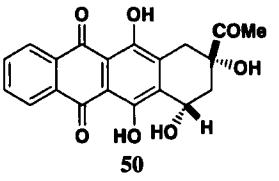
Scheme 16

in chloroform in the presence of *p*-toluenesulfonic acid.[21] They also synthesized the thieno-fused polycyclic quinone **49** (*Scheme 17*), as potential intermediates for the synthesis of (±)-4-demethoxydaunomycinone (**50**) (*Scheme 18*).[21]



i) $CHCl_3$, p-$CH_3C_6H_4SO_3H$, (25% yield)

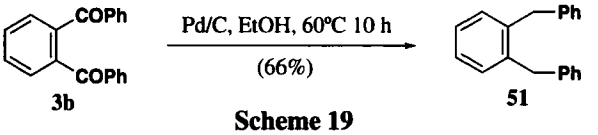
Scheme 17



Scheme 18

2. Reduction

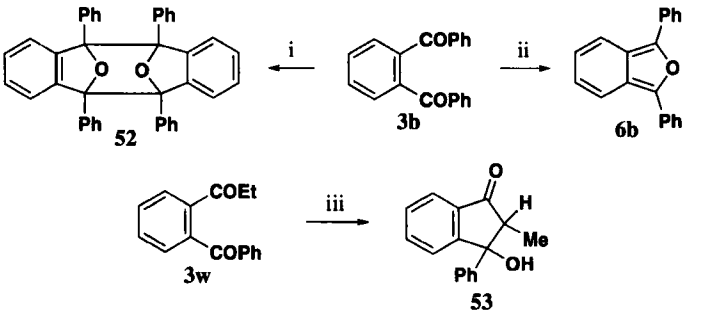
o-Dibenzoylbenzene **3b** has been reduced to *o*-dibenzylbenzene **51** by treatment with palladium on charcoal.[10]



Scheme 19

3. Photochemical Reactions

Irradiation of *o*-dibenzoylbenzene **3b** in isopropanol and hydrochloric acid has been claimed to lead to the photochemical reduction of **3b** to give **52** in 73% yield. In the absence of the catalytic amounts of acid, the photolysis afforded isobenzofuran **6b** as the main product in 60% yield.[22] Iirradiation of 1,2-diacylbenzene (**3w**) has been reported to lead to the formation of 3-hydroxy-3-phenylindanone **53** in 70% yield.[23]

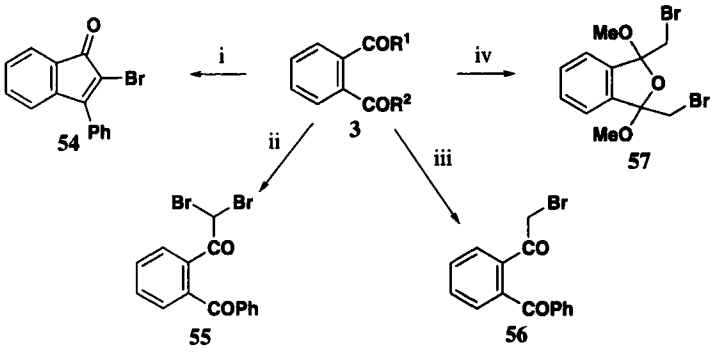


i) hv, *i*-PrOH, HCl, 5 h, (73% yield); ii) Hv, *i*-PrOH, 10 h (60% yield); iii) Hv, benzene, 48 h, (70% yield)

Scheme 20

4. Bromination Reactions

Treatment of 1-acetyl-2-benzoylbenzene (**3k**) with bromine in acetic acid afforded 2-bromo-3-phenylindene-1-one (**54**) in 98% yield.[24] Furthermore, treatment of **3k** with bromine in tetrachlomethane under ultraviolet irradiation led to the formation of dibromoacetylbenzophenone **55** in 68% yield.[24,25] Bromination of **3k** in dry ether with 5,5-dibromo-2,2-dimethyl-4,6-dioxo-1,3-dioxane (dibromo Meldrum acid) gave monobromoacetylbenzophenone **56**.[25-27] Finally, *o*-diacetylbenzene (**3a**) afforded isobenzofuran derivative **57** by treatment with bromine in methanol as shown in *Scheme 21*.[27]



a) $R^1 = R^2 = Me$; k) $R^1 = Me$, $R^2 = Ph$

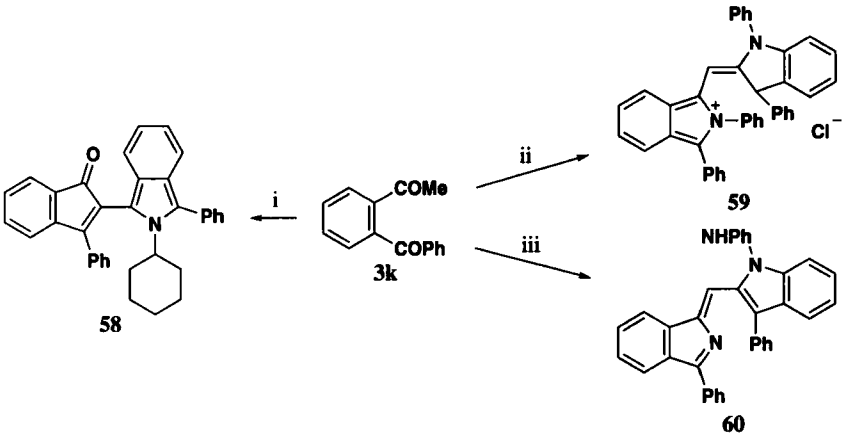
i) Br^2, HBr, AcOH, 0°C 2 h, (98% yield); ii) Br_2, CCl_4, hν, 25°C 0.5 h (68% yield); iii) Dibromomeldrum acid, Et_2O, reflux 4 days, (56% yield); iv) Br_2, MeOH, 0°C 13 h, H_2O, H_2SO_4, 15°C 20 h, (49% yield)

Scheme 21

5. Reactions With Nitrogen Compounds

a. Reactions with Amines and Phenylhydrazine

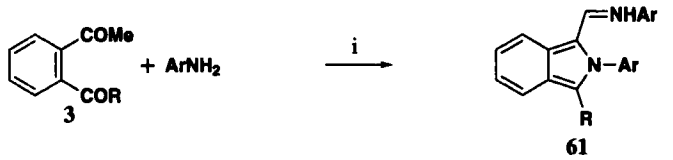
Treatment of 1-acetyl-2-benzoylbenzene (**3k**) with several primary amines and hydrazines in the presence of acid afforded one type of red and three types of deep blue pigments including isoindole moieties.[28-31] A typical example is given in *Scheme 22*. Reaction of **3k**



i) cyclohexylamine, benzene, AcOH; ii) $PhNH_2$, MeOH, HCl; iii) $PhNHNH_2$, EtOH, HCl

Scheme 22

with cyclohexylamine led to the formation of the stable blue pigment **58** whereas with aniline in methanol in the presence of hydrochloric acid, it gave the blue pigment **69**.[32] Reaction of 1-acetyl-2-benzoylbenzene (**3k**) with phenylhydrazine in ethanol in the presence of hydrochloric acid gave the blue pigment **60**.[33,34] Furthermore, 1-acetyl-2-acylbenzenes **3** produced the yellow 1,2-diaryl-3-(aryliminomethyl)isoindoles **61** *via* the reaction with aromatic amines in the absence of acid, as shown in *Scheme 23*.[35]



a) R = Me
k) R = Ph

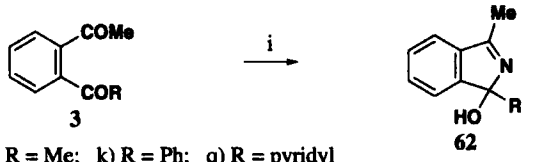
a) Ar = Ph
b) Ar = *p*-$MeOC_6H_4$

a) R = Me, Ar = Ph
b) R = Me, Ar = *p*-$MeOC_6H_4$
c) R = Ar = Ph
d) R = Ph, Ar = *p*-$MeOC_6H_4$

i) Et_2O or C_6H_6, 25°C 7-30 days, (20-24% yield)

Scheme 23

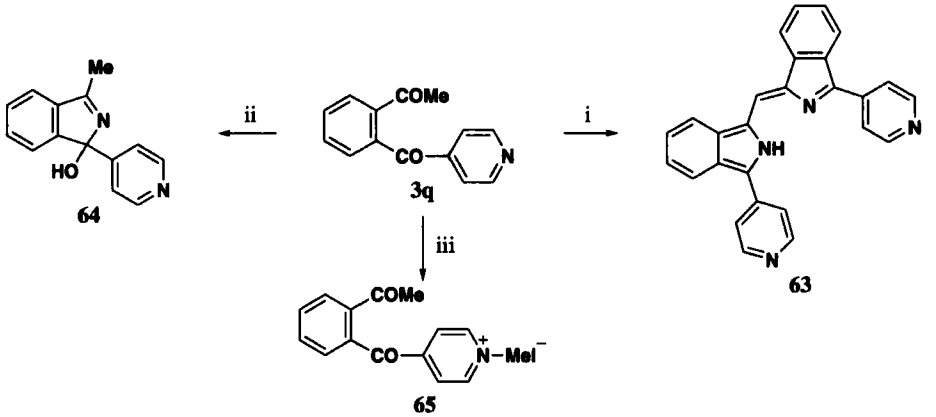
The reaction of *o*-diacylbenzenes **3** with ammonia afforded several isoindole derivatives in the presence or absence of acid.[36]



a) R = Me; k) R = Ph; q) R = pyridyl
i) NH_3, AcOH, MeOH, 25°C 0.5-70 h, (13% yield for pyridyl)

Scheme 24

Furthermore, the deep blue isoindole **63** was obtained in only 13% yield on treatment of



i) NH_3 aq, AcOH, MeOH, 25°C 70 h, (13% yield); ii) NH_3 aq, MeOD, 25°C 2 h or dry NH_3, Et_2O, 25°C 5 h, (82% yield); iii) MeI, $CHCl_3$, 25°C 3 days, (99% yield)

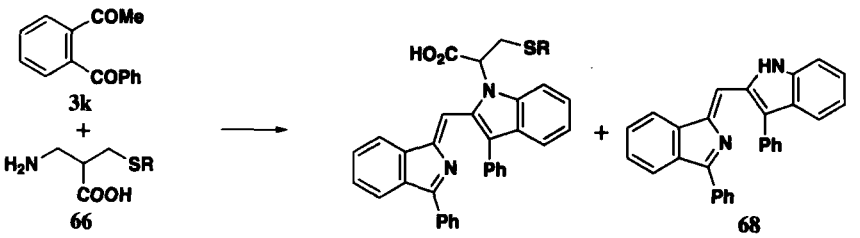
Scheme 25

3q with aqueous ammonia in methanol in the presence of acetic acid. Reaction of 1-acetyl-2-isonicotinoylbenzene (**3q**) with either aqueous ammonia or with dry ammonia in the absence of acid led to the formation of isoindole **64**. In the latter case, the yield was 82%. Reaction of **3q** with methyl iodide in chloroform resulted in methylation of pyridine nitrogen and compound **65** was obtained in 99% yield.[37]

b. Reactions with Amino Acids

In 1943, *o*-diacetylbenzene **3a** was described by Hillmann as a fluorogenic reagent for proteins.[38] Since then, several papers dealing with the specificity of *o*-diacetylbenzene as a reagent for free amino groups of proteins and amino acids have appeared.[39-42] In 1965, Goslar published a review about the possibilities of quantitative color reactions for proteins. The most promising reagent was found to be *o*-diacetylbenzene.[43] In 1971, Roth developed a sensitive technique for the detection of amino acids which involves use of *o*-diacetylbenzene **3a** or *o*-phthalaldehyde.[33] At that time, the most widely used reagent for α-amino acids was ninhydrin. Although the sensitivity of the ninhydrin reaction was quite adequate for many purposes, there were cases where a more sensitive test for amino acids was required. *o*-Diacetylbenzene (**3a**) was found to have a sensitivity of color reaction equal to that of ninhydrin. In addition to the color reaction of proteins, it was also found to show a blue fluorescence which permits their determination in cases where other reagents such as ninhydrin failed.[38,40,44]

Reaction of 1-acetyl-2-benzoylbenzene (**3k**) with S-methyl-l-cysteine and l-cysteine **66** gave deep blue pigments **67** and **68** (*Scheme 26*).[46]

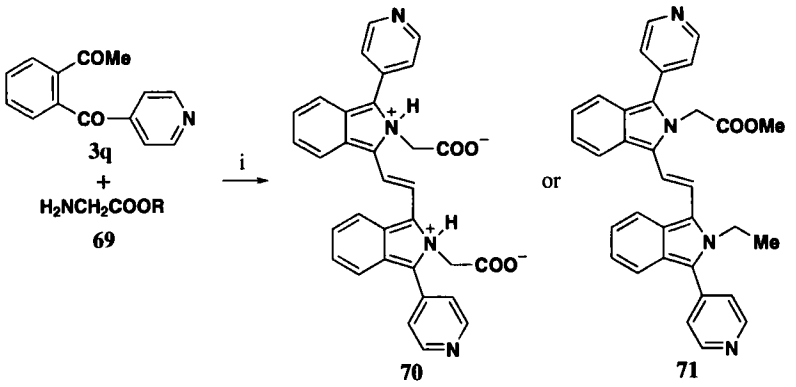


R = Me or H

Scheme 26

In methanol, treatment of 1-acetyl-2-isonicotinoylbenzene (**3q**) with glycine (**69a**) in the presence of acetic acid gave the red pigment **70**, whereas with glycine methyl ester (**69b**), it gave a deep blue pigment **71**, as shown in *Scheme 27*.[46]

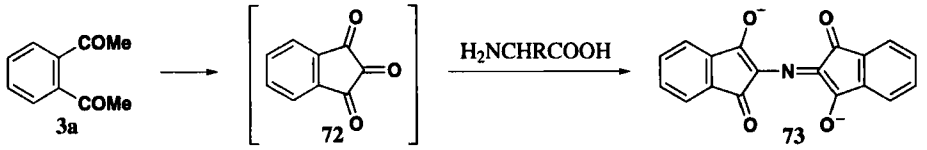
Color reactions of 1-acetyl-2-benzoylbenzene (**3k**) and *o*-diacetylbenzene (**3a**) with amino acids and human skin have also been studied. L-Cysteine was the only amino acid that gave a coloration (bluish green with **3k** and dark violet with **3a**) similar to that with human



a) R = H; b) R = Me
i) AcOH, 25°C 15-30 h, (57-86% yield)

Scheme 27

skin.[47] Recently, it was reported that aromatic nuclei bearing 1,2-diacetyl moiety display similar chromogenic properties.[48] *o*-Diacetylbenzene, which is the oxidation metabolite of the neurotoxic *o*-diethylbenzene, was found to form blue pigments on contact with proteins, skin and other tissues.[49,50] Rodents treated systemically with it developed blue discoloration of skin, eyes, and internal organs including the brain.[51,52,53] It is believed that the chromogenic and neurotoxic properties of **3a** are directly related through its reaction with amino acids. On the basis of computational calculations, it has been suggested that the chromogenic effects of **3a** are associated with the formation of ninhydrin-like reactions as shown in *Scheme 28*.[48] Although ninhydrin (**72**) has

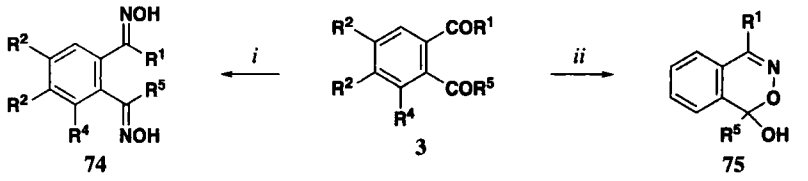


Scheme 28

not been isolated in these reactions, it has been suggested that ninhydrin might have been generated from 1,2-diacetylbenzene (**3a**), by an intramolecular aldol condensation followed by oxidation, loss of water and further oxidation. Since the authors did not specify the conditions of the reactions, it is difficult to speculate on a possible mechanism for the formation of **72**.[48]

c. Reactions with Hydroxylamine

Reaction of *o*-diacylbenzenes **3** with hydroxylamine hydrochloride and potassium carbonate under reflux afforded the corresponding dioximes **74** in 40-62% yield.[54] When stirred at room temperature in the presence of triethylamine instead of potassium carbonate, reaction gave 1*H*-2,3-benzoxazine derivatives **75** in 51-67% yield, as shown in *Scheme 29*.[36]



74 3 75

k) R^1 = Me, R^2 = R^3 = R^4 = H, R^5 = Ph
n) R^1 = Me, R^2 = R^4 = H, R^3 = OMe, R^5 = Ph
o) R^1 = Me, R^2 = R^4 = Br, R^3 = H, R^5 = Ph
q) R^1 = Me, R^2 = R^3 = R^4 = H, R^5 = *p*-pyridyl
r) R^1 = Ph, R^2 = R^3 = R^4 = H, R^5 = *p*-pyridyl
t) R^1 = R^5 = Me, R^2 = R^4 = Br, R^3 = H

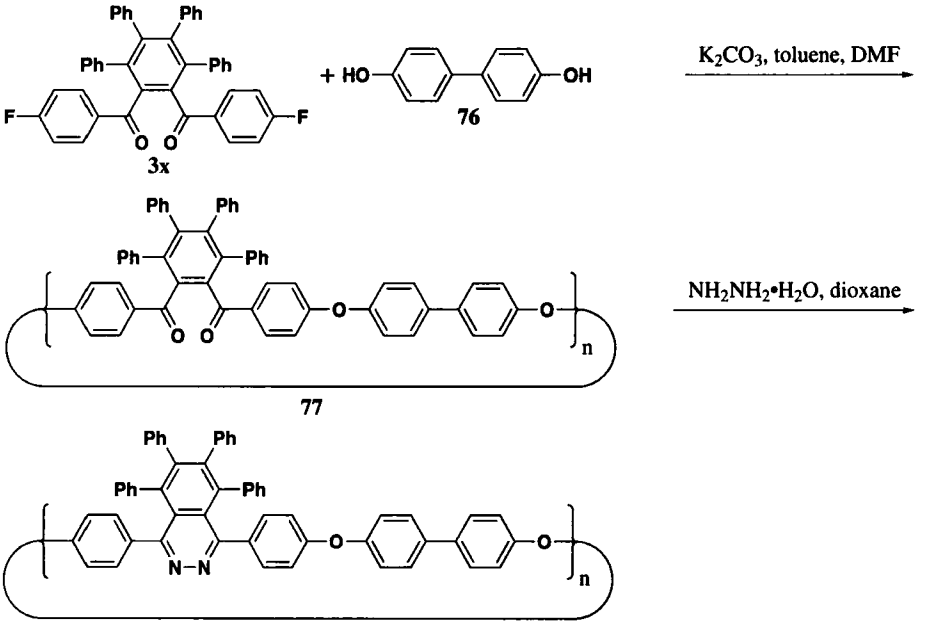
a) R^2 = R^5 = Me
k) R^1 = Me, R^5 = Ph

i) NH_2OH•HCl, EtOH, K_2CO_3, reflux 24 h, (40-62% yield); ii) NH_2OH•HCl, EtOH, Et_3N, 25°C 24 h, (51-67% yield)

Scheme 29

d. Reactions with Hydrazine

Condensation of *o*-diacylbenzenes with hydrazine is known to lead to phthalazines.[55] Reaction of 1,2-*bis*(4-fluorobenzoyl)-3,4,5,6-tetraphenylbenzene (**3x**)[56] with various bisphenols in dimethyl formamide in the presence of potassium carbonate led to the formation of cyclic aryl ether ketone oligomers containing the 1,2-dibenzoyl-3,4,5,6-tetraphenylbenzene moiety. The cyclic ether ketone oligomers were transformed into cyclic phthalazines by reaction with hydrazine,[56-58] as illustrated in *Scheme 30.*



Scheme 30

III. CONCLUSION

o-Diacylbenzenes have been of interest primarily as fluorescence reagents for both qualitative and quantitative high-sensitivity analyses of amines and amino acids. *o*-Diacetylbenzene in particular, has been used in a fluorometric assay for biotinase using biocytin because of its ability to react selectively with lysine.[59] *o*-Diacylbenzenes have proven to be useful precursors to quinone derivatives,[8] *o*-alkylbenzenes,[10] isobenzofurans,[22,27] indenes,[24] hydroxyphenylindanones[23] and isoindoles.[35,36] Thermoplastic or thermosetting resinous condensation products, varying from soft pliable to hard brittle masses, were obtained by the reaction of *o*-diacetylbenzene with either aliphatic or heterocyclic polysulfonamide.[60] These resins have been used in varnish and paint compounds for the preparation of glossy surfaces resistant to chemicals, water and abrasive agents, as rubber plasticizers and for molded articles.[60] Finally, polyetherketones containing the *o*-dibenzoylbenzene group are a class of soluble, amorphous, high-performance polymers with excellent mechanical properties.[56]

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