COMMUNICATIONS TO THE EDITOR

Synthetic Studies on the Derivatives of Dibenzoylbenzenes

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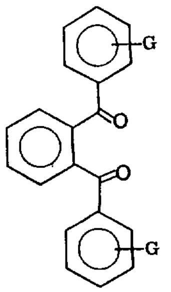
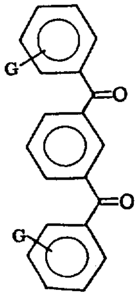
Three isomers of dibenzoylbenzene were prepared for the first time by some workers[1,2,3] around early 1900. From that time on, the synthetic studies of this field have been overlooked and longforgotten. Although dibenzoylbenzene themselves by no means have any utility, derivatives of them are of considerable utility in organic synthesis. Inasmuch as there has no systematic study to date, it is of synthetic interest to prepare functional derivatives of dibenzoylbenzenes. In this communication the authors wish to provide general synthetic routes for derivatives of dibenzoylbenzene in which various functional groups are introduced to every positions of benzoyl group, as shown in structures I, II, and III.



I



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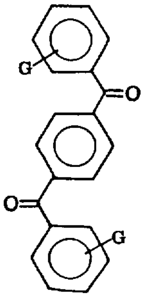
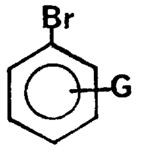


III

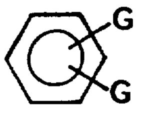
a. $G=2-OCH_3$ d. $G=2-CH_3$ g. $G=2-OH$
b. $G=3-OCH_3$ e. $G=3-CH_3$ h. $G=2-CO_2H$
c. $G=4-OCH_3$ f. $G=4-CH_3$ i. $G=2-CO_2R$

Many possible procedures were investigated in this work, which involves the condensation of arylmetallic reagents prepared from aryl bromide(**1,2**) with three isomers of benzenedicarboxylic chloride(**3**), dicyanobenzene(**4**), benzenedicarboxaldehyde(**5**), benzenedicarboxylic acid(**6**) and the ester(**7**), respectively



1,2

a: ortho
b: meta
c: para



3—7

1. $G=OCH_3$
2. $G=CH_3$

3. $G=COCl$
4. $G=CN$
5. $G=CHO$
6. $G=CO_2H$
7. $G=CO_2R$

Firstly, the reactions of arylmetallics with phthaloyl(**3a**), isophthaloyl(**3b**), and terephthaloyl chloride(**3c**) were thoroughly examined. In 1929, E. Clar *et al.*[4] accomplished analogous reaction in a mixed solvent of benzene and ether at -10 °C, but without indicating the yield. In this work, the authors carried out the reaction in tetrahydrofuran at -78 °C, following the procedure of F. Sato *et al.*,[5] to give much better yield. This reaction gave in general lower yield, which may be due to the successive attack of the arylmetallics on the resultant ketone to produce a tertiary alcohol(**8**) as a side product.

In some cases, the side product was obtained as a major product according to the reaction conditions. To minimize the side reaction, the arylmetallic reagent should be added at a low temperature(-78 °C) to a solution of the acyl chloride(**3**) rather than the reverse, and a large excess amount of arylmetallic reagent should be avoided. When aryllithium was used, it was necessary to quench the reaction mixture with acid at a low temperature (-78 °C). The reaction of the acyl chloride with arylmagnesium bromide gave better yield than with aryllithium, as shown in Table 1.

The reaction of arylmetallic reagent with dicyanobenzenes(**4**)[6], followed by hydrolysis of the resultant diketimine(**9**), also gave rise to aromatic diketones.

Terephthalonitrile(**4c**) afforded fairly good yield(60-80%) (Table 3), where as isophthalonitrile(**4b**) gave generally lower yield(20-30%) of expected aromatic diketones. Phthalonitrile(**4a**), however, by no means gave expected diketones (Table 1).

The reaction of arylmetallic reagent with benzenedicarboxaldehyde(**5**), followed by oxidation of the resultant benzylic diol(**8**), gave corresponding dibenzoylbenzene derivatives. Though two steps this route was superior to other procedures we worked out, because it gave very high yield in each step with little side product.

By the action of 4 moles of aryllithium, benzenedicarboxylic acids(**6**) afforded dibenzoylbenzene derivative with very low yield, producing the same side product which was obtained from the action of arylmetallics on the acyl chlorides(**3**).

Reaction of arylmetallics with benzenedicarboxylate esters(**7**) also gave dibenzoylbenzene derivatives, but with lower yield and some side products.

In summary, the reaction of arylmetallics with benzenedicarboxylic chloride(**3**) gives generally lower yield of dibenzoylbenzene derivatives with some exceptions of isophthaloyl chloride (Table 2). Though it is generally applicable, this method is not recommendable. Of the reactions of arylmetallics with dicyanobenzenes, followed by hydrolysis of resultant diketimine, only terephthalonitrile(**4c**) gives higher yield of dibenzoylbenzene derivatives, and is recommendable.

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†This investigation was supported by a Grant (1986) from the Korean Research Foundation.

Table 1. Derivatives of 1,2-Dibenzoylbenzene

Entry	Products	Reactants	General Procedure	Yield[a] (%)	m.p[b] (°C)	MS m/e(M⁺)	IR[c] ν(cm⁻¹)	H-NMR(TMS)[d] δ(ppm)
1	Ia	1a, 3a	1	45	152-153	346	3010,2980 1650,1590 1495,1310	7.8-6.8(m, 12Harom.) 3.7(s, 6H, OCH_3)
2	Ia	anisole, 3a	2	10				
3	Ia	1a, 4a	3	0				
4	Ia	1a, 4a	4	0				
5	Ia	1a, 5a	5	75				
6	Ia	anisole, 5a	6	55				
7	Ia	anisole, 6a	7	20				
8	Ia	1a, 7a	8	40				
9	Ib	Ib, 3a	1	20	oil	346	1660,1600 1490,1440	7.8-6.8(m, 12Harom.) 3.7(s, 6H, OCH_3)
10	Ic	1c, 3a	1	57	165-166	346	1645,1600 1500,1440	7.8-6.74(m, 12Harom.) 3.8(s, 6H, OCH_3)
11	Id[e]	2a, 3a	1	65	145-146	314	1675,1660 1600,1490 1460	7.8-6.9(m, 12Harom.) 2.3(s, 6H, CH_3)
12	Id	2a, 4a	3	0				
13	Id	2a, 5a	5	80				
14	Ie	2b, 3a	1	35	oil	314	1660,1600 1470,1440	7.8-7.0(m, 12Harom.) 2.3(s, 6H, CH_3)
15	If	2c, 3a	1	44	190-191	314	1660,1600 1470,1440	7.8-7.0(m, 12Harom.) 2.3(s, 6H, CH_3)
16	Ig	1a	9	95	160-161	318	3400,1620 1600,1480	7.8-6.8(m, 12Harom.) 11.8(s, 2H, OH)
17	Ih[f]	1d	10	45	129-130	420	1720,1670	7.8-6.8(m, 12Harom.) 4.2(q, 4H, CH_2) 1.2(t, 6H, CH_3)

[a] Isolated and overall yield. [b] Melting points were not corrected. [c] IR spectra were recorded with Perkin-Elmer Model 782 spectrometer. [d] NMR spectra were recorded on a Varian EM 360A spectrometer. [e] Microanalysis: C(calcd 84.1%, Found 84.2%), H(calcd 5.7%, Found 5.7%), [f] Ethyl ester.

Table 2. Derivatives of 1,3-Dibenzoylbenzene

Entry	Product	Reactants	General Procedure	Yield (%)	m.p (°C)	MS m/e(M⁺)	IR ν(cm⁻¹)	H-NMR($CDCl_3$/TMS) δ(ppm)
1	IIa	1a, 3b	1	11	107.5-108.5	346	1660,1650 1590,1465	8.2-6.8(m, 12Harom.) 3.65(s, 6H, OCH_3)
2	IIa	1a, 4b	3	25				
3	IIb	1b, 3b	1	20	oil	346	1670,1600 1495,1260	8.2-7.0(m, 12Harom.) 3.8(s, 6H, OCH_3)
4	IIb	1b, 4b	3	28				
5	IIc	1c, 3b	1	32	144-145	346	1660,1590	8.1-6.9(m, 12Harom.) 3.8(s, 6H, OCH_3)
6	IIc	1c, 4b	3	67				
7	IId	2a, 3b	1	56	oil	314	1665,1600	8.2-7.2(m, 12Harom.) 2.3(s, 6H, CH_3)
8	IId	2a, 4b	3	27				
9	IIe	2b, 3b	1	42	93-94	314	1640,1590	8.2-7.2(m, 12Harom.) 2.3(s, 6H, CH_3)
10	IIe	2b, 4b	3	20				
11	IIf	2c, 3b	1	84	129-130	314	1650,1595	8.1-7.0(m, 12Harom.) 2.3(s, 6H, CH_3)
12	IIf	2c, 4b	3	25				

Phthalonitrile cannot be used for this purpose.

Reaction of arylmetallics with benzenedicarboxaldehyde (**5**), followed by oxidation of resultant diol, always gives high yield of expected diketone. Though two steps, this route is superior to other procedure for this purpose. Reactions of arylmetallics with benzenedicarboxylic(**6**) and the esters are not recommedable for this synthesis because of low yield and side product.

General procedure 1. Action of aryl Grignard reagent on benzenedicarboxylic chloride

In a 100 m*l* three-neck round-bottomed flask fitted with a reflux condenser and a dropping funnel, 1 g of magnesium turnings and 10 m*l* of dry THF were added. While stirring under nitrogen, a solution of 21 mmoles of aryl bromide(**1,2**) in 20 m*l* of THF was added dropwise through the dropping funnel during 30-40 min. The mixture was refluxed for more than 3 hr to complete the formation of the Grignard reagent. In a 300 m*l* two-neck round-bottomed flask was placed a solution of 2.0 g(10 mmoles) of benzenedicarboxylic chloride (**3**) in 50 m*l* of THF and cooled to −78 °C. To this solution

Table 3. Derivatives of 1,4-Dibenzoylbenzene

Entry	Product	Reactants	General Procedure	Yield (%)	m.p (°C)	MS m/e(M^+)	IR ν(cm^{-1})	H-NMR($CDCl_3$/TMS) δ(ppm)
1	IIIa	1a, 3c	1	11	192-193	346	1650,1595	8.3-6.8(m, 12Harom.)
2	IIIa	1a, 4c	3	68			1485	3.7(s, 6H, OCH_3)
3	IIIb	1b, 3c	1	10	160-161	346	1660,1595	7.8-7.0(m, 12Harom.)
4	IIIb	1b, 4c	3	52				3.8(s, 6H, OCH_3)
5	IIIc	1c, 3c	1	28	169-170	346	1640,1585	7.8-6.8(m, 12Harom.)
6	IIIc	1c, 4c	3	81				3.8(s, 6H, OCH_3)
7	IIId	1d, 3c	1	15	78-79	314	1660,1600	7.8-7.1(m, 12Harom.)
8	IIId	1d, 4c	3	72				2.3(s, 6H, CH_3)
9	IIIe	2b, 3c	1	14	139-140	314	1650,1580	8.3-7.0(m, 12Harom.)
10	IIIe	2b, 4c	3	78				2.3(s, 6H, CH_3)
11	IIIf	2c, 3c	1	22	188-189	314	1660,1640	7.8-7.1(m, 12Harom.)
12	IIIf	2c, 4c	3	78			1660	2.3(s, 6H, CH_3)

was added slowly the Grignard reagent by cannulation over a period of 30 min. Stirring with cooling was continued for 5 hr and the temperature of the reaction mixture was gradually raised to room temperature during 1-2 hr. Water(50 m*l*) was added followed by 2N HCl(20 m*l*). The solvent was removed by evaporation at a reduced pressure, and the mixture was extracted several times with dichloromethane. The combined organic layer was washed with water, aqueous $NaHCO_3$ and brine successively, and dried over anhydrous magnesium sulfate. Evaporation of the solvent yielded a crude product, which was chromatographed on silica gel.

General procedure 2. Action of aryllithium on benzenedicarboxylic chloride

In a 100 m*l* three-neck round-bottomed flask fitted with a reflux condenser, was placed 20 m*l* of dry ether, 3.24 g(30 mmoles) of anisole and 50 m*l* of tetramethylethylenediamine (TMEDA). While heating the solution at reflux under nitrogen, 3.0 m*l* 10N n-butyllithium was added dropwise with constant stirring. The mixture was refluxed for one day to insure the formation of 2-lithioanisole[7]. After cooling, the lithio compound was added by cannulation under nitrogen to a solution, at -78 °C, of 2.0 g (10 mmoles) of benzenedicarboxylic chloride(**3**) in 50 m*l* of THF. Stirring was continued for 5 hr and the reaction mixture was carefully quenched at -78 °C with aqueous NH_4Cl. A normal work-up and chromatography afforded a product.

The other aryllithium, other than 2-lithioanisole, was prepared by slow addition, at near 0 °C under argon, of an etherial solution of aryl bromide(**1,2**) to lithium shavings suspended in dry ether, followed by stirring for 5 hr.

General procedure 3. Action of aryl Grignard reagent on dicyanobenzene.

A Grignard reagent, prepared from 21 mmoles of aryl bromide(**1,2**) as described in general procedure 1, was added by cannulation with constant stirring under nitrogen to a solution of 1.0 g(8 mmoles) of dicyanobenzene(**4**) in 10 m*l* of THF for a period of 30 min. The mixture was heated under reflux for 10 hr to give a dark brown Grignard complex, to which 10 m*l* of 6N HCl was added, followed by refluxing for 4 hr. A normal work-up and chromatography gave a product.

General procedure 4. Action of aryllithium on dicyanobenzene.

About 18 mmoles of aryllithium, prepared by the reaction of metallic lithium on aryl bromide as described in general procedure 2, was added by cannulation under argon to an etherial solution (or suspension) of 1.0 g(8 mmoles) of dicyanobenzene(**4**) at -78 °C. After stirring for 2 hr, the red reaction mixture was allowed to warm to room temperature and hydrolysed by adding 6N HCl, followed by refluxing for 3 hr. A normal work-up and chromatography gave a product.

General procedure 5. Action of aryl Grignard reagent on benzenedicarboxaldehyde.

A Grignard reagent, prepared from 25 mmoles of aryl bromide (**1,2**), was added dropwise at 0 °C under nitrogen to a solution of 1.34 g(10 mmoles) of benzenedicarboxaldehyde (**5**) in 60 m*l* of THF. The reaction mixture was allowed to warm to room temperature and stirred for 3 hr. The normal hydrolytic work-up gave a corresponding benzylic diol, which was oxidized in acetone with Jone's reagent(CrO_3-H_2SO_4)[8] to give an aromatic diketone.

General procedure 6. Action of aryllithium on benzenedicarboxaldehyde.

About 25 mmoles of aryllithium, prepared as described in general procedure 2, was added at 0 °C to an etherial solution of 1.34 g(10 mmoles) of benzenedicarboxaldehyde(**5**) under nitrogen. Stirring with cooling was continued for 3 hr, and the mixture was allowed to warm to room temperature. The normal hydrolytic work-up afforded a benzylic diol, which was oxidized with Jone's reagent to give an aromatic diketone.

General procedure 7. Action of aryllithium on benzenedicarboxylic acid.

About 25 mmoles of aryllithium, prepared as described in general procedure 2, was added by cannulation under nitrogen to a solution of 0.83 g(5 mmoles) of benzenedicarboxylic acid in 50 m*l* of THF, and the mixture was refluxed for 24 hr. The normal hydrolytic work-up and chromatography afforded a product.

General procedure 8. Action of aryl Grignard reagent on benzenedicarboxylate ester.

About 21 mmoles of aryl Grignard reagent was added by cannulation to a solution, at 0 °C, of 1.94 g(10 mmoles) of dimethyl benzenedicarboxylate in 50 m*l* of THF, and the mixture was stirred for 5 hr at room temperature. The normal hydrolytic work-up and chromatography gave an aromatic diketone.

General procedure 9. Bis(hydroxybenzoyl)benzenes.

In a round-bottomed flask, was placed 3.6 g(9 mmoles) of a bis(methoxybenzoyl)benzene and 20 m*l* of 47% HBr, and the mixture was heated under reflux for more than 5 hr. The normal work-up and chromatography afforded the corresponding phenolic derivative.

General procedure 10. Bis(carboxybenzoyl)benzenes.

In a 300 m*l* round-bottomed flask, 1.7 g(5 mmoles) of bis-(methylbenzoyl)benzene was dissolved in a mixture of 150 m*l*-glacial acetic acid and 50 m*l*-acetic anhydride. To this solution, 6 m*l* of conc. H_2SO_4 followed by 20 g(0.2 mole) of chromium trioxide in three portions was added. After stirring for 1 hr at room temperature, the dark green mixture was poured rapidly onto crushed ice, followed by stirring several minutes. About 300 m*l* of water was added and the resulting white solid was collected by filtration followed by washing it with water.

The crystalline products were in general hardly soluble in any organic solvents, and so in some cases recrystallization was impossible. The structure could then be determined by converting it into an ester.

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Synthesis of Soluble Poly(propargyl bromide) and Poly(propargyl chloride) by Transition Metal Chlorides and Ethylaluminum Dichloride

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The polymerization of acetylene and its derivatives is one of the fundamental methods for the synthesis of polymers with a conjugated polyene system, which are beginning to be used at present time as organic semiconductors and metals.[1-2] To date, the polymerization of propargyl bromide (PB) and propargyl chloride(PC) was attempted by the following catalysts: $PdCl_2$,[3] γ-rays[4], $NiI_2(Ph_3P)_2$[5], $NiBr_2(Ph_3P)_2$[5], $W(CO)_6$-CCl_4-$h\nu$[6], $MoCl_5$[7], and $MoCl_5$-polymer[8]. However, these catalysts generally give only insoluble and intractable polymers.

Recently, we have found that transition metal chlorides and organoaluminum compounds are very effective for the polymerization of some acetylene derivatives such as 1-chloro-2-thienylacetylene,[9] 2-ethynylpyridine,[10] and dipropargyl derivatives.[11-13]

The present communication reports that PB and PC could be effectively polymerized by the binary catalyst systems composed by transition metal chlorides (WCl_6, $MoCl_5$, and $TiCl_4$) and $EtAlCl_2$ to give polymers in high conversions. In some cases the polymers obtained were soluble in solvents and high molecular weight materials.

All the preparative procedures of catalysts and polymerization were carried out under dry nitrogen atmosphere.

As shown in Table 1, WCl_6 alone gave only moderate yield of polymers. However, $TiCl_4$ failed to give any polymeric product. $EtAlCl_2$ was found to be very effective cocatalyst in the polymerization of PB and PC when used with transition metal chlorides. The ratios of the portion of soluble polymeric product to insoluble product portion varied depending on the catalyst system used. $TiCl_4$-$EtAlCl_2$ gave completely soluble polymer, even though the polymer yield was low. The number-average molecular weight($\overline{M}n$)s of the resulting soluble polymers were in the range of 8,700 to 19,500.

The ^{13}C-NMR spectrum of poly(propargyl bromide) (PPB) showed the presence of the olefinic carbons at about 129 and 135 ppm and the methylene carbon at 40 ppm. In the UV-visible spectra of PPB and poly(propargyl chloride)