EFFECT OF GROUPS ON CYCLISATION REACTIONS

A Thesis
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"Self-condensation of Arylpropiolic Acids
and
Cyclisation of 1,4-Diaryl-but-1,3-diene-
2,3-dicarboxylic Anhydrides"

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CHAPTER I

CHAPTER II

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SUMMARY

m-Chloro(CXIa)-: *m*-bromo(CXIb)-, and *m*-iodo(CXIc)-phenylpropiolic acids are prepared and their self-condensation are studied. Thus, self-condensation of *m*-chlorophenylpropiolic acid gives 6-chloro(CIIa) and 8-chloro(CIIIa)-1-(*m*-chlorophenyl)naphthalene-2:3-dicarboxylic anhydride in the ratio of 3:1, respectively. When *m*-bromophenylpropiolic acid is similarly treated, it gives 6-bromo (CIIb) and 8-bromo(CIIIb)-1-(*m*-bromophenyl)naphthalene-2:3-dicarboxylic anhydrides in the ratio of 6:1, respectively. Self-condensation of *m*-iodophenylpropiolic acid (XCIc), gives only 6-iodo-1-(*m*-iodophenyl)naphthalene-2:3-dicarboxylic anhydride (CIIc). The structures of these anhydrides are established by analogy of their electronic spectra, with those of 6-methoxy(XXVI) and 8-methoxy(XXV)-1-(*m*-methoxyphenyl) naphthalene-2:3-dicarboxylic anhydrides.

Similarly, when 3-bromo-4-methylphenylpropiolic acid (XCVIa) is self-condensed, it gives only 6-bromo-7-methyl-1-(3-bromo-4-methylphenyl)naphthalene-2:3-dicarboxylic anhydride (CIVa). On the other hand, 3-iodo-4-methylphenylpropiolic acid (XCVIb) gives mainly 6-iodo-7-methyl (CIVb, predominant) and 8-iodo-7-methyl (CVb, trace)-1-(3-iodo-4-methylphenyl)naphthalene-2:3-dicarboxylic anhydrides.

Structures of these anhydrides are established by analogy of their electronic spectra with that of 6-halogeno (Cl, Br and I) phenylnaphthalene-2:3-dicarboxylic anhydrides.

When 3-fluoro-4-methoxyphenylpropiolic acid (CI) is similarly treated, it gives 6-fluoro-7-methoxy (CVI, predominant) and 8-fluoro-7-methoxy (CVII, trace)-1-(3-fluoro-4-methoxyphenyl)naphthalene-2:3-dicarboxylic anhydrides. The structure of the above anhydrides is established by analogy of their electronic spectra with those of 6-chloro-7-methoxy (XXXIII; x = Cl) and 8-chloro-7-methoxy (XXXIV, x = Cl)-1-(3-chloro-4-methoxyphenyl)naphthalene-2:3-dicarboxylic anhydrides[33].

Infrared data are also used to differentiate between the different isomers.

On the other hand, symmetrical 1:4-di-m-chloro(CXIIa)-, m-bromo(CXIIb)-, m-iodo(CXIIc)-, m-methoxy (CXVI)-, (3-bromo- and 3-chloro-4-methoxyphenyl)(CXXa and CXXb, respectively) - but-1:3-diene-2:3-dicarboxylic anhydrides are prepared and their cyclisations with sunlight are studied.

Thus, cyclisation of 1:4-di-(m-chloro-; m-bromo-, and m-iodophenyl)-but-1:3-diene-2:3-dicarboxylic anhydrides failed to give a crystalline product. The product was found to be a mixture of acids and anhydrides (I.R. spectrum).

When 1:4-di(*m*-methoxyphenyl)-but-1:3-diene-2;3-dicarboxylic anhydride (CXVI) is similarly treated, it gives 6-methoxy-1-(*m*-methoxyphenyl)-naphthalene-2:3-dicarboxylic anhydride (CXXVI), which is found to be identical with an authentic specimen obtained by the self-condensation of *m*-methoxyphenylpropiolic acid.[26]

On the other hand, cyclisation of 1:4-di(3-bromo(CXX*a*) and 3-chloro(CXX*b*)-4-methoxyphenyl)-naphthalene-2:3-dicarboxylic anhydrides gives in both cases after2-3 days exposure to sunlight, a red intermediate, the structure of which is inferred from the following :

1) Analytical data.
2) Ozonolysis of its diester (CXXXIV) which gives 3-chloro-4-methoxybenzaldehyde, indicating that it is a geometrical isomer of the initial anhydride.
3) Its electronic and infrared spectra.

By continuous exposure to direct sunlight, the red intermediate anhydride redissolves to give after 28 days exposure 6-bromo-7-methoxy-1-(3-bromo-4-methoxyphenyl) napthalene-2:3-dicarboxylic anhydride (CIV*a*) and 6-chloro-7-methoxy-1-(3-chloro-4-methoxyphenyl)naphthalene-2:3-dicarboxylic anhydride (CIV*b*).

Similarly, unsymmetrical-but-1:3-diene-2:3-dicarboxylic anhydrides are prepared and their cyclisation in sunlight are studied. When 1-(*o*-chlorophenyl)-4-(*p*-methoxyphenyl)-but-1:3-diene-2:3-dicarboxylic anhydride (CXXV) is similarly treated, it gives 6-chloro-1-(*p*-methoxyphenyl)naphthalene-2:3-dicarboxylic anhydride (CXXVII), the structure of which is verified by the infrared spectrum of the dechlorinated product, which shows no bands characteristic of the bending frequency of 5-adjacent hydrogen atoms, but shows a band at 740 cm^{-1}, characteristic for the out-of-plane bending frequency of 4-adjacent hydrogen atoms.

Also, 1-phenyl-4-(*o*-methoxyphenyl)-but-1:3-diene-2:3-dicarboxylic anhydride (CXXII) gives 1-(*o*-methoxyphenyl)-naphthalene-2:3-dicarboxylic anhydride (XLVIII, R=H).

Electronic and infrared spectra of the above compounds are determined and discussed.

CHAPTER I

PREFACE

The review included in the historical part covers the following topics :

i) Preparation of arylpopiolic acids

ii) Self-condensation of β-arylpropiolic acids.

iii) The orienting influence of substituents in position 3- and 4- on the self-condensation of arylpropiolic acids.

iv) Condensation of dissimilarly substituted arylpropiolic acids.

v) Preparation of diarylidenesuccinic anhydrides.

vi) Cyclisation of diarylidenesuccinic anhydrides to 1-phenylnaphthalene-2:3-dicarboxylic anhydrides.

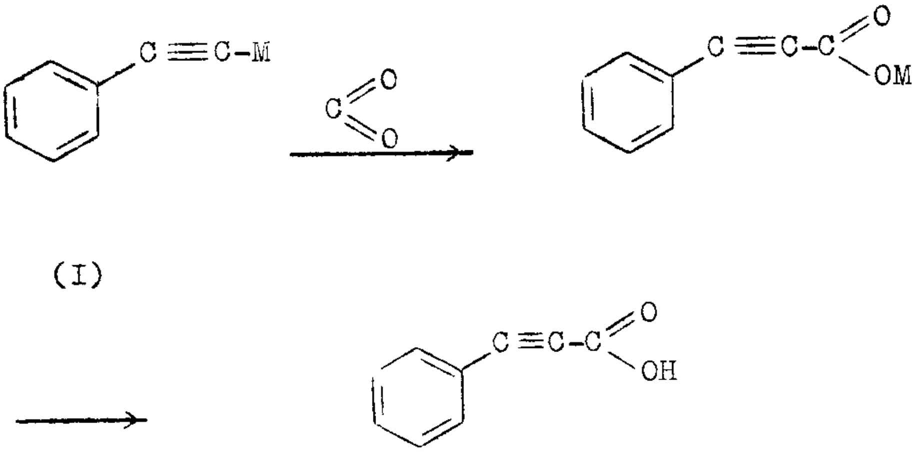
vii) Electronic spectra of 1-phenylnaphthalene-2:3-dicarboxylic anhydrides.

I- PREPARATION OF ARYLPROPIOLIC ACID

The methods encountered in the literature for the preparation of phenylpropiolic acids can be grouped into two distinct types :-

A) Methods depending upon the action of carbon dioxide on organo-metallic derivatives of phenylacetylenes.

The sodium derivatives of phenylacetylenes[1] (1, M=Na) or phenylacetylene magnesium bromide[2] (1, M=MgBr) were used for this purpose.



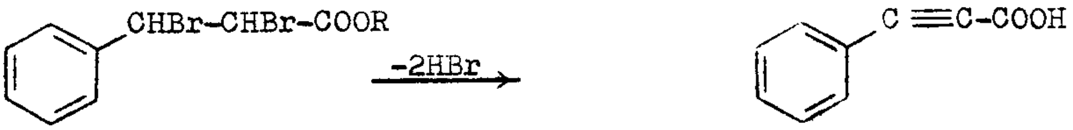
(I)

(M = Na or -MgBr)

[illegible] Methods depending upon the dehydrohalogenation of β-aryl-α:β-dihalogenopropionic acids or their esters.

The dehydrohalogenation was carried out either in one step or in two steps :

1) One step method .- A β-aryl-α:β-dibromopropionic acid or the ester is dehydrohalogenated by refluxing with basic reagents to give the corresponding arylpropiolic acid.



(II) (III)

To effect the dehydrohalogenation a variety of reagents were used including, alcoholic potassium hydroxide,[3-10] sodium ethoxide, sodium hydroxide,[11] or sodium hydroxide in liquid ammonia,[12] sodium ethoxide in benzene and ethyl alcohol,[6] and sodium hydroxide in benzene.[6]

The different β-aryl derivatives of α:β-dibromopropionic acid or its ester as well as the various reagents used are listed in Table 1, together with the products and the yields obtained.

Table I

Reagent	Substitution in benzene ring of II	R	% yield of III	Ref.
1- Alcoholic KOH	----	C_2H_5	--	4
	o-methoxy	H	--	3
	m-chloro	H	52	6
	2-methoxy-5-methyl	C_2H_5	68	7
	2-methoxy-4-methyl	H	21	7
	3:4:5-trimethoxy	CH_3	37	8
	3:4:5-trimethoxy	H	45	9
★ Alcoholic KOH with rapid method	----	H	80	5
	p-methyl	H	95	10
	o-methyl	H	95	10
	o-chloro	H	93	10
2- Aqueous NaOH	2-nitro-5-chloro	H	--	11
3- Excess of sodium ethoxide or NaOH in liquid ammonia	-----	H	86	12
4- C_2H_5ONa in C_6H_6 and C_2H_5OH	*o*-nitro	C_2H_5	--	6
	p-nitro	C_2H_5	12,54 as ester	6
5- NaOH in C_6H_6	----	C_6H_5	7, 60 as ester	6
Few mls. of C_2H_5OH	*o*-chloro	C_2H_5	10, 89 as ester	6
	p-chloro	C_2H_5	--	6

★ Reimer's[5] modification (rapid method), the aryldibromopropionic acid was treated with methanolic potassium hydroxide in a dish and the solvent repeatedly evaporated.