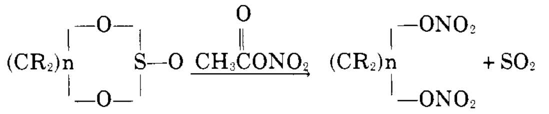
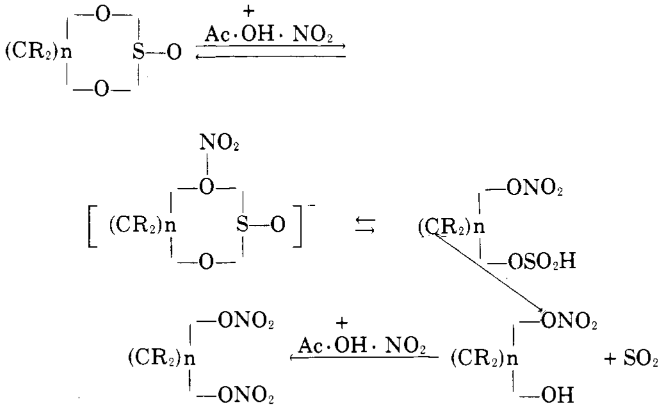
preparation of dinitrates under comparatively mild conditions.



Sulfites are known to hydrolyze under acidic conditions with the cyclic class reacting more slowly (*1, 3, 4*) in acid catalyzed hydrolysis. A possible mechanism based on this hypothesis is shown below.



Several of the dinitrates were new compounds; their properties are listed in Table I. The identity of these compounds was checked in each case by comparison with a sample obtained by nitration of the starting diol with nitric acid-sulfuric acid.

Treatment of the two sulfites containing benzenoid rings with nitrating agents gave only the corresponding nitrosulfites. The sulfite linkage in these compounds resisted cleavage even when a large excess of nitrating agent and longer reaction times were employed.

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Esters of Naphthalenedicarboxylic Acids

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The melting points or boiling points of a number of esters of four positional isomers of naphthalenedicarboxylic acid (1,6-; 2,3-; 2,6-; and 2,7-) are reported. For an ester of a given alcohol, the 2,6- isomer invariably has the higher melting point. With the exception of the dimethyl esters, the order of decreasing melting points for the esters of a given alcohol is 2,6> 2,7> 2,3> 1,6.

A NUMBER OF ESTERS of four positional isomers of naphthalenedicarboxylic acid (1,6-; 2,3-; 2,6-; and 2,7-) were investigated. Apparently, only a limited number of these esters have been previously reported in the literature (*1, 5, 6, 7*), perhaps because of the relative difficulty involved in obtaining the dicarboxylic acids (*1*). In the past few years, however, preparative methods have become available which make possible the oxidation of dimethylnaphthalenes directly to the corresponding dicarboxylic acids (*4, 7, 8*).

EXPERIMENTAL

The esters were prepared from the corresponding diacid chlorides (Method A), by the direct esterification of the dicarboxylic acids (Method B), or by the acid-catalyzed alcoholysis of the 2,3-dicarboxylic acid anhydride (Method C).

The acid chlorides listed in Table I were prepared by the action of an excess of thionyl chloride upon the solid dicarboxylic acids when a small amount of dimethylformamide was added to the reaction mixture (*2, 3*). Similar treatment of the 2,3-dicarboxylic acid, however, resulted in the isolation of the monomeric anhydride (*9*).

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Table I. Naphthalenedicarboxylic Acid Ester Intermediates

Positional Isomer	Compound	Formula	Melting Point Found	Melting Point Ref.
1,6	Diacid chloride	$C_{12}H_6O_2Cl_2$	124-125°	
2,6	Diacid chloride	$C_{12}H_6O_2Cl_2$	187.5-189°	186-187° (7)
2,7	Diacid chloride	$C_{12}H_6O_2Cl_2$	144.5-145.5°	130° (*6*)
2,3	Diacid anhydride	$C_{12}H_6O_3$	245-247°	245° (*9*)

All melting points were taken by the capillary method and are corrected. Where boiling points are given, they refer to the fraction for which the analytical data were obtained. Boiling points are uncorrected.

RESULTS AND DISUCSSION

Tables II and III show that, for a given diester, the 2,6- isomer invariably has the higher melting point. Except for the dimethyl esters, the order of melting points for a given ester is 2,6 > 2,7 > 2,3 > 1,6. This order was definitely established by noting the melting points of those

Table II. Esters of Acid

Ester	Formula	Preparation Method	Melting Point	Boiling Point, Mm.	Analysis Calcd. C	Analysis Calcd. H	Analysis Found C	Analysis Found H
			1,6-Naphthalenedicarboxylic					
Dimethyl	$C_{14}H_{12}O_4$	A	98.0-98.5°[a]	...	68.82	4.92	68.91	4.91
Diethyl	$C_{16}H_{16}O_4$	A	...	140°/0.05	70.55	5.92	70.42	6.12
Dibutyl	$C_{20}H_{24}O_4$	B	...	172°/0.07	73.13	7.30	73.29	7.44
Dipentyl	$C_{22}H_{28}O_4$	B	...	185°/0.07	74.13	7.92	74.23	7.79
Dihexyl	$C_{24}H_{32}O_4$	B	...	197°/0.07	74.96	8.39	75.06	8.43
Dioctyl	$C_{28}H_{40}O_4$	B	...	213°/0.07	76.32	9.15	76.49	9.11
			2,3-Naphthalenedicarboxylic					
Dimethyl	$C_{14}H_{12}O_4$	C	50.0-51.0°[b]	...	68.82	4.92	68.99	4.98
Diethyl	$C_{16}H_{16}O_4$	C	56.5-57.0°	...	70.55	5.92	70.42	6.11
Dibutyl	$C_{20}H_{24}O_4$	C	37.0-37.5°	...	73.13	7.30	73.09	7.38
Dipentyl	$C_{22}H_{28}O_4$	C	...	183°/0.075	74.13	7.92	74.17	7.71
Dihexyl	$C_{24}H_{32}O_4$	C	...	203°/0.070	74.96	8.39	74.99	8.43
Dioctyl	$C_{28}H_{40}O_4$	C	...	224°/0.075	76.32	9.15	76.54	9.11

[a] Literature (*1*) m.p. 98°. [b] Literature (*1*) m.p. 47°.

Table III. Esters of Acid

Ester	Formula	Preparation Method	Melting Point	Analysis Calcd. C	Analysis Calcd. H	Analysis Found C	Analysis Found H
			2,6-Naphthalenedicarboxylic				
Dimethyl	$C_{14}H_{12}O_4$	A	189.5-190.0[a]	68.82	4.95	68.98	4.99
Diethyl	$C_{16}H_{16}O_4$	A	126.5-127.0	70.55	5.92	70.66	5.90
Dipropyl	$C_{18}H_{20}O_4$	A	83.5-85.0	71.98	6.71	72.25	6.64
Dibutyl	$C_{20}H_{24}O_4$	B	79.5-80.0	73.13	7.35	73.19	7.28
Dipentyl	$C_{22}H_{28}O_4$	B	76.0-77.0	74.13	7.92	73.92	8.06
Dihexyl	$C_{24}H_{32}O_4$	A	88.5-89.0	74.96	8.39	75.11	8.40
Diheptyl	$C_{26}H_{36}O_4$	B	81.0-82.0	75.74	8.78	75.81	8.92
Dioctyl	$C_{28}H_{40}O_4$	A	80.0-81.0	76.32	9.15	76.34	9.16
Dinonyl	$C_{30}H_{44}O_4$	A	68.5-69.5	76.87	9.47	76.59	9.46
Didecyl	$C_{32}H_{48}O_4$	A	80.5-81.0	77.37	9.74	77.63	9.78
Diundecyl	$C_{34}H_{50}O_4$	A	74.0-74.5	77.80	10.00	77.49	9.99
Didodecyl	$C_{36}H_{54}O_4$	B	52.0-53.0	78.20	10.21	78.08	10.32
Ditetradecyl	$C_{38}H_{58}O_4$	A	87.0-88.0	78.88	10.60	78.96	10.49
Dipentadecyl	$C_{40}H_{62}O_4$	A	82.0-83.0	79.18	10.76	79.34	10.59
Dihexadecyl	$C_{42}H_{66}O_4$	A	79.5-80.0	79.45	10.92	79.64	10.82
Diisopentyl	$C_{22}H_{28}O_4$	B	62.0-63.0	74.13	7.92	74.29	7.82
			2,7-Naphthalenedicarboxylic				
Dimethyl	$C_{14}H_{12}O_4$	A	135.5-136.0[a]	68.82	4.95	68.94	4.94
Diethyl	$C_{16}H_{16}O_4$	A	69.5-70.0	70.55	5.92	70.69	5.92
Dibutyl	$C_{20}H_{24}O_4$	B	44.5-45.0	73.13	7.30	73.13	7.36
Dipentyl	$C_{22}H_{28}O_4$	B	23.0-23.5	74.13	7.92	74.27	8.01
Dihexyl	$C_{24}H_{32}O_4$	A	38.5-39.0	74.96	8.39	74.88	8.18
Dioctyl	$C_{28}H_{40}O_4$	A	38.5-40.0	76.32	91.5	76.46	9.13

[a] Literature (7) m.p. 184°. [b] Literature (*1*) m.p. 135°.

esters which were liquid at room temperature; for instance, the melting point of the dipentyl ester of the 1,6-dicarboxylic acid is −29° to −26°, while the melting point of the corresponding 2,3-diacid ester is −14° to −12°. The same relationship holds true for the other normally liquid 1,6- and 2,3-diacid esters. The melting points of these liquid esters were not considered accurate enough to record in the tables.

The fact that the 2,6-dicarboxylic acid derivatives are always the highest melting may be attributable to the higher degree of symmetry of the molecule. This isomer is the only one of the three di-β-isomers which possesses a point of symmetry.

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m-Dibenzylbenzene

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SOME CONFUSION exists in the literature with respect to physical properties of the isomeric dibenzylbenzenes and also with respect to their identification as products of acid catalyzed condensations with benzene.

We have repeated the reaction of benzene with:

A. Benzyl chloride and $TiCl_4$ according to Stadnikow (*6*).
B. Benzyl alcohol and *p*-toluenesulfonic acid according to Pratt (*4, 5*).

The reaction products were easily analyzed by gas chromatography. Table I compares present results with those previously reported.

Chromatographic separations were made on an Aerograph Model A-100-C instrument equipped with a 0.25-inch inner diameter asphalt-on-fire-brick column, 10 feet long, temperature = 285° C., flow rate = 30 cc./minute of helium. Under these conditions, retention times for the pure compounds were as follows: diphenylmethane, 5 minutes; *o*-dibenzylbenzene, 35.5 minutes; *m*-dibenzylbenzene, 38 minutes; *p*-dibenzylbenzene, 51 minutes:

Both Stadnikow and Pratt have reported a melting point of 58° C. for *m*-dibenzylbenzene, while a recent report (*1*) indicated that it was a liquid. Accordingly, all three isomeric dibenzoylbenzenes were synthesized unequivocally and subsequently converted to the corresponding dibenzylbenzenes by the previously unreported copper chromite catalyzed hydrogenation technique at 2000 p.s.i. and 200° C. The data are summarized in Table II.

Table I. Product Ratios of Dibenzylbenzenes from Alkylation of Benzene

Reaction Type	Stadnikow (*6*)	Pratt (*4, 5*)	Present Results	
A	mainly meta-	. . .	40 ortho- 10 meta- 50 para-	Total = 20%
B	. . .	17% meta-exclusively	35 ortho- 20 meta- 45 para-	Total = 17%

Table II. Properties of Dibenzoyl-and Dibenzylbenzenes

	Yield, %		Melting Point	
Product	Found	Lit. Ref.	Found	Lit. Ref.
		Dibenzoylbenzene		
o-	47^a	32	147	148
m-	66		100	99.5–100
p-	70^d		160	158–159
		Dibenzylbenzene		
o-	73^e	66	78–79	78.7–79.4
m-^{b}	81^c		16.9–17.0	58
p-	73		86	86

^{a} Method Preparation, Jensen (*2*). ^{b} b.p. 175°/1 mm. (223° C./13 mm.); N_D^{20} = 1.6037 (Lit. = 1.6038). ^{c} Method of preparation, Buu-Hoi (*1*). ^{d} Method of Preparation, Munchmeyer (*3*). ^{e} Method of preparation, Cat. hydrogenation of dibenzoylbenzene.

CONCLUSION

The acid catalyzed alkylation of benzene with benzylchloride and benzyl alcohol is not an exception to the general pattern; secondary alkylation occurs 80 to 90%, *ortho and para*.

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