

Products Laboratory, along with a detailed study of its toxicity to various wood-destroying fungi.

MADISON, WISCONSIN

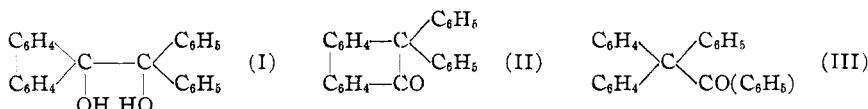
RECEIVED MAY 26, 1933
PUBLISHED SEPTEMBER 5, 1933

[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF THE UNIVERSITY OF MICHIGAN]

The Pinacol-Pinacolone Rearrangement. IV. The Rearrangement of Pinacols Containing the Biphenylene Group

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Meerwein² found that diphenylbiphenyleneglycol (I) on treatment with sulfuric acid gives 10,10-diphenylphenanthrone (II) but does not give any of the isomeric benzoylphenylfluorene (III) by migration of the phenyl



group. Recently, Bergmann and Schuchardt³ observed that dehydration by acetyl chloride gives benzoylphenylfluorene (III) and no diphenylphenanthrone. Furthermore, their discovery that benzoylphenylfluorene is isomerized into diphenylphenanthrone by sulfuric acid makes it appear probable that benzoylphenylfluorene is the true product of the rearrangement.

We find that diphenylbiphenyleneglycol (I) when treated with acetyl chloride actually gives a mixture of diphenylphenanthrone and benzoylphenylfluorene and not a single product as has been reported. Similarly,

TABLE I
REARRANGEMENT OF PINACOLS

Group Ar	Products	%	Group migrated
Phenyl	Benzoylphenylfluorene	78	Phenyl
	Diphenylphenanthrone	22	Biphenylene
<i>m</i> -Tolyl	<i>m</i> -Toluyyl- <i>m</i> -tolylfluorene	54	<i>m</i> -Tolyl
	Di- <i>m</i> -tolylphenanthrone	46	Biphenylene
<i>p</i> -Tolyl ⁴	<i>p</i> -Toluyyl- <i>p</i> -tolylfluorene	14	<i>p</i> -Tolyl
	Di- <i>p</i> -tolylphenanthrone	86	Biphenylene
Anisyl ⁴	Anisoylanisylfluorene	2	Anisyl
	Dianisylphenanthrone	98	Biphenylene
Phenetyl	<i>p</i> -Ethoxybenzoylphenetylfluorene	4	Phenetyl
	Diphenetylphenanthrone	96	Biphenylene

(1) Presented in partial fulfilment of the requirements for the Ph.D. degree.

(2) Meerwein, *Ann.*, **396**, 200 (1913).

(3) Bergmann and Schuchardt, *ibid.*, **487**, 225 (1931).

(4) Bergmann and Schuchardt obtained a single rearrangement product.

two rearrangement products, corresponding to (II) and (III), are obtained from four other pinacols. The results are presented in Table I.

Giving a value of unity to the migration aptitude of the phenyl group one has the following series representing the relative migration aptitudes of the groups in biphenylene pinacols: phenyl, 1.0; *m*-tolyl, 0.33; biphenylene, 0.31; *p*-tolyl, 0.046; phenetyl, 0.012; anisyl, 0.006. The migration aptitudes of five of these groups, phenyl, *m*-tolyl, *p*-tolyl, phenetyl and anisyl, have been determined when they are situated in symmetrical pinacols.⁵ In Table II is given a comparison of the relative migration aptitudes of these five groups in the two types of pinacols.

TABLE II
MIGRATION APTITUDES

Group	M_s (symmetrical pinacol)	M_b (biphenylene pinacol)	$1/M_b$
Phenyl	1.0	1.0	1.0
<i>m</i> -Tolyl	1.95	0.33	3.0
<i>p</i> -Tolyl	15.0	.046	22
Phenetyl	66	.112	83
Anisyl	70+	.006	170

It is observed that the order in the two series is exactly reversed; moreover, the reciprocals of the values for the migration aptitudes in the biphenylene pinacols are roughly of the same order as the values for the symmetrical pinacols. We are preparing and rearranging a large number of pinacols in order to determine whether the relation holds true for the whole class of biphenylene pinacols.

Experimental

Preparation of the Pinacols.—The pinacols were prepared by the action of a Grignard reagent on the methyl ester of biphenyleneglycolic acid.^{2,3} A solution of 15 g. of the methyl ester was added to the Grignard reagent which had been prepared from 0.25 gram mole of aryl halide (*m*-bromotoluene, *p*-bromophenetole, etc.). After being refluxed for twelve hours the mixture was hydrolyzed. In this manner, dianisylbiphenyleneglycol, prepared by Bergmann and Schuchardt in 37% yield, was obtained by us in 80% yield. The yields and properties of the two new pinacols, di-*m*-tolylbiphenyleneglycol and diphenetyl biphenyleneglycol, are given in Table III.

Rearrangement of the Pinacols.—The pinacols were rearranged by a twenty-four hour treatment with acetyl chloride in benzene and acetic acid.⁶ This agent does not isomerize benzoylphenylfluorene.

Analysis of Pinacolone Mixtures.—The mixture of benzoylphenylfluorene and diphenylphenanthrone from 3.64 g. (0.01 mole) of diphenylbiphenyleneglycol was heated with a solution of 6 g. of potassium hydroxide in 100 cc. of absolute alcohol for six hours. This process cleaved the benzoylphenylfluorene into benzoic acid and phenylfluorene but left the diphenylphenanthrone unchanged. Five separate runs gave an average of 0.0070 gram mole of benzoic acid. This represents a 78% migration of the phenyl group since a 95% yield of total products was obtained and a 95% yield of benzoic acid resulted by scission of pure benzoylphenylfluorene.

(5) Bachmann and Moser, *THIS JOURNAL*, **54**, 1124 (1932), and unpublished results.

Practically the same results were obtained when both the benzoylphenylfluorene and the diphenylphenanthrone were cleaved, the latter being converted to 2-benzhydryl-2'-carboxylbiphenyl. The mixture of pinacolones was heated with a solution of 25 g. of potassium hydroxide in 100 cc. of methanol for three days. After removal of the solvent the product was treated with a mixture of water and benzene; potassium benzoate dissolved in the water while the potassium salt of the 2-benzhydryl-2'-carboxylbiphenyl was contained in the benzene layer along with phenylfluorene. Treatment with hydrochloric acid converted the salt to the free acid; when the mixture of phenylfluorene and acid was dissolved in hot *n*-propyl alcohol and the solution was allowed to cool, the phenylfluorene deposited first. The 2-benzhydryl-2'-carboxylbiphenyl was obtained in large colorless prisms; m. p. 175° with previous softening.⁶ The potassium salt of the acid is little soluble in dry benzene but dissolves readily in wet benzene or in wet ether; it can be obtained as colorless leaflets by recrystallization from methanol.

The mixtures of pinacolones obtained from the other pinacols were analyzed in a similar manner; the values given in Table I represent the averages of several runs which checked each other closely. Di-*p*-tolylphenanthrone and dianisylphenanthrone are cleaved into the biphenyl acids by six hours of heating with 6% potassium hydroxide in ethanol; the properties of the acids and of other compounds are given in Table III. The yields are based on recrystallized product.

TABLE III
YIELDS AND PROPERTIES OF NEW COMPOUNDS

Compound	Yield, %	M. p., °C.	Recryst. solvents	Cryst. form	Analyses, % Calcd. Found	
Di- <i>m</i> -tolylbiphenyleneglycol	55	143.5–144.5	Acetone + alc.	Needles	C, 85.7 H, 6.2	85.2 6.2
Diphenetylbiphenyleneglycol	51	147–150	Acetone + alc.	Cubes	C, 79.6 H, 6.2	79.2 6.1
Di- <i>m</i> -tolylphenanthrone	62	198.0–198.5	Acetic acid	Diamond plates	C, 89.8 H, 5.9	89.6 6.0
Diphenetylphenanthrone	77	135.0–135.5	<i>n</i> -Propyl alc.	Fine needles	C, 82.9 H, 6.0	83.2 6.4
2-(Di- <i>p</i> -methylbenzhydryl)-2'-carboxybiphenyl ^a	76	193–194	<i>n</i> -Propyl alc.	Diamond plates	C, 85.7 H, 6.2	85.5 6.2
2-(Di- <i>p</i> -methoxybenzhydryl)-2'-carboxybiphenyl	75	136–137	<i>n</i> -Propyl alc.	Heavy needles	C, 79.2 H, 5.7	78.9 6.2

^a Bergmann and Schuchardt obtained an amorphous solid which they considered to be this acid from the reaction between ditolylphenanthrone and alkali.

Summary

Five pinacols containing the biphenylene group have been rearranged by acetyl chloride to mixtures of pinacolones. The order and extent of migration of the groups is the reverse of the migration aptitudes of the groups in symmetrical pinacols.

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RECEIVED MAY 27, 1933
PUBLISHED SEPTEMBER 5, 1933

(6) Compare Acree, *Am. Chem. J.*, **33**, 180 (1905).