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

The Retropinacolone Rearrangement. I

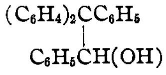
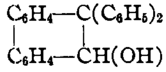
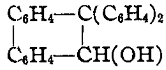
BY W. E. BACHMANN

Delacre[1] found that *as*-tetraphenylethyl alcohol is converted to tetraphenylethylene when it is heated with acetyl chloride at 200° in a sealed tube. We have now undertaken an investigation of the reaction in order to learn whether the reaction is general for the whole class of tetraarylethanols and also to discover if the rearrangement can be employed to determine the relative migration aptitudes of aryl groups.

An attempt was made to rearrange *as*-tetraphenylethyl alcohol by heating it with acetyl chloride at ordinary pressure; under these conditions tetraphenylethyl acetate was formed. We then tried the action of a solution of iodine in acetic acid, which is an excellent rearranging agent for pinacols;[2] it was found that tetraarylethanols are rapidly and completely rearranged when they are heated with iodine and acetic acid at ordinary pressure.

If a mixed tetraarylethanol of the type $R_1R_1R_2CCH(OH)R_2$ is subjected to rearrangement, two courses are open since either R_1 or R_2 can migrate. From the relative amounts of the two ethylenes that are formed it is possible to determine the extent to which each group migrated in the rearrangement. We have prepared and rearranged three tetraarylethanols of this type; namely, 1,2-diphenyl-2-biphenyleneëthanol (IV), 10,10-diphenylphenanthrol-9 (V) and 10-biphenylenephenanthrol-9 (VI). The results of the rearrangements are presented in Table I.

TABLE I

No.	Ethanol	Group migrated	Yield, %	Products
I	$(C_6H_5)_3CCH(OH)C_6H_5$		100	Tetraphenylethylene
II	$(CH_3C_6H_4)_3CCH(OH)C_6H_4CH_3$		100	Tetra-*p*-tolylethylene
III	$(CH_3OC_6H_4)_3CCH(OH)C_6H_4OCH_3$		100	Tetraanisylethylene
IV	 $\begin{array}{l}(C_6H_4)_2CC_6H_5\\ \quad\quad\;\;\vert\\ C_6H_5CH(OH)\end{array}$	Phenyl	0	Diphenylbiphenyleneethylene
		Biphenylene	100	9,10-Diphenylphenanthrene
V	 $\begin{array}{l}C_6H_4—C(C_6H_5)_2\\ \vert\quad\quad\;\vert\\ C_6H_4—CH(OH)\end{array}$	Phenyl	100	9,10-Diphenylphenanthrene
		Biphenylene	0	Diphenylbiphenyleneethylene
VI	 $\begin{array}{l}C_6H_4—C(C_6H_4)_2\\ \vert\quad\quad\;\vert\\ C_6H_4—CH(OH)\end{array}$		0	Dibiphenyleneëthylene
		Biphenylene	100	9,10-Biphenylenephenanthrene

It is noteworthy that only a single rearrangement product is obtained from the three mixed ethanols. It appears that the formation of the phenanthrene ring is favored, for the same product 9,10-diphenylphen-

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[1] Delacre, *Bull. acad. roy. Belg.*, [3] **20**, 109 (1890).

[2] Gomberg and Bachmann, THIS JOURNAL, **49**, 236 (1927).

anthrene is produced from two different ethanols, 1,2-diphenyl-2-biphenylene-ethanol (IV) and 10,10-diphenylphenanthrol-9 (V). Werner and Grob[3] obtained similar products by the interaction of hydrogen iodide and the pinacolones corresponding to the mixed ethanols; they postulated the intermediate formation of the ethanols in the reaction.

In a future communication will be reported the results obtained with a large number of aryl groups.

Experimental

Preparation of Tetraarylethanols.—We prepared the tetraarylethanols by reduction of pinacolones by isopropylmagnesium iodide[4] and bromide. To a solution of the Grignard reagent prepared from 5 cc. of isopropyl iodide in 20 cc. of ether was added 20 cc. of benzene and then 0.02 g. mole of solid pinacolone in portions; the reaction usually took place at once with evolution of gas. After being refluxed, the mixture was hydrolyzed; all of the compounds were obtained as colorless crystals. The essential data are given in Table II.

YIELDS AND PROPERTIES OF TETRAARYLETHANOLS

Abbreviations: alc, alcohol; ac, acetone; bz, benzene; ch, chloroform; h, hot; v, very; s, soluble; sls, slightly soluble; i, insoluble or very slightly soluble

Ethanol	Time, hrs.	Yield, %	Rec. solv.	Cryst. form	M. p., °C.	Solubility			Analyses, %	
						alc	ac	ch	Calcd.	Found
1,2,2,2-Tetraphenyl-	1.0	95	Ch + alc	Plates	150–151					
1,2,2,2-Tetra-*p*-tolyl-[a]	0.5	98	Ac + alc	Heavy needles	161–162	sls	vs		C, 88.7 H, 7.4	88.1 7.6
1,2,2,2-Tetraanisyl-	1.0	60	Ch + alc	Heavy needles	148–150	sls	vs	s	C, 76.6 H, 6.4	76.0 6.4
1,2-Diphenyl-2-biphenylene	0.2	72	Ac + alc	Cubes	159–160	sls	vs		C, 89.7 H, 5.8	89.7 5.9
10,10-Diphenylphenanthrol-9	0.8	93	Ch + alc	Prisms	205–206	i		s	C, 89.7 H, 5.8	89.2 6.0
10-Biphenylenephenanthrol-9	0.2	50	Ac + alc	Clusters needles	177–178	sls	vs (h)		C, 90.2 H, 5.2	90.1 5.3

[a] The ethanol crystallizes from alcohol with solvent of crystallization.

Rearrangement of Tetraarylethanols.—A solution of 1.0 g. of tetraarylethanol and 0.05 g. of iodine in 10 cc. of acetic acid was refluxed for one hour. In several cases a large proportion of the rearrangement product precipitated from the solution after a few minutes; if the mixture bumped badly more solvent was added. The mixture was cooled slightly and treated with 5 cc. of alcohol saturated with sulfur dioxide. On being chilled the solution deposited the rearrangement product in the form of colorless crystals. The yields of the products were quantitative, showing that no side reactions occurred. The properties of the products with the exception of tetra-*p*-tolylethylene agreed with those described in the literature. Our tetra-*p*-tolylethylene crystallized in colorless needles and melted at 142°; Staudinger and Goldstein[5] reported a melting point of 151°.

Anal. Calcd. for $C_{30}H_{28}$: C, 92.8; H, 7.2. Found: C, 93.3; H, 7.5.

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[3] Werner and Grob, *Ber.*, **37**, 2895 (1904).

[4] Gorski, *J. Russ. Phys.-Chem. Soc.*, **45**, 163 (1913).

[5] Staudinger and Goldstein, *Ber.*, **49**, 1925 (1916).

A portion of our tetra-*p*-tolylethylene was reduced to the corresponding ethane by treating a boiling solution of 0.35 g. of the ethylene in 10 cc. of amyl alcohol with 0.5 g. of sodium cut in small pieces. After ten minutes water was added and the product was taken up in benzene; concentration of the solution deposited the *s*-tetra-*p*-tolylethane in colorless prisms; m. p. 278–279°; yield, 95%. The ethane is little soluble in hot alcohol or in cold benzene; it is soluble in hot benzene.

Anal. Calcd. for $C_{30}H_{30}$: C, 92.3; H, 7.7. Found: C, 92.1; H, 7.8.

s-Tetra-*p*-tolylethane was synthesized by heating a mixture of 1.1 g. of di-*p*-tolylbromomethane and 0.05 g. of magnesium ribbon in 5 cc. of ether and 5 cc. of benzene for twenty hours; yield, 50%; m. p. 278–279°; the product so obtained was identical in all respects with the product produced by reduction of the ethylene.

Tetraphenylethyl Acetate, $(C_6H_5)_3CCH(OCOCH_3)C_6H_5$.—A mixture of 1.0 g. of *as*-tetraphenylethyl alcohol, 10 cc. of acetyl chloride and 5 cc. of benzene was refluxed for ten hours. The product obtained by evaporation of the solvents was recrystallized from a mixture of benzene and alcohol; colorless needles; m. p. 151°; yield, 1.11 g. (99%); Delacre[1] reported a m. p. of 131°. Tetraphenylethyl acetate is little soluble in cold alcohol or acetic acid; it is readily soluble in hot benzene and in hot acetic acid.

Anal. Calcd. for $C_{28}H_{24}O_2$: C, 85.7; H, 6.1. Found: C, 85.7; H, 6.3.

A 0.1-g. portion of tetraphenylethyl acetate was warmed for a few minutes with a mixture of 1 cc. of 40% potassium hydroxide and 2 cc. of alcohol; this treatment hydrolyzed the ester to acetic acid and tetraphenylethyl alcohol; the latter was then cleaved into triphenylmethane[1] and benzaldehyde. When the ester was heated with acetic acid and iodine for a few minutes, rearrangement to tetraphenylethylene took place.

Summary

as-Tetraphenylethyl alcohol is dehydrated and rearranged to tetraphenylethylene when it is heated with a solution of iodine in acetic acid. Five new tetraarylethanols have been synthesized and subjected to the retropinacolone rearrangement.

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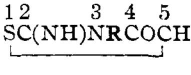
The Alkyl Derivatives of the Mono Substituted Thiazolidones. I

BY F. B. DAINS AND FLOYD EBERLY

Some years ago Beckurts and Frerich[1] published a paper on the ethylation of the monoarylthiazolidones which were prepared by the action of potassium thiocyanate upon the chloracet derivatives of various monoarylamines. Several intermediate products were described, but the ones used in their investigation were regarded as 2-imino-3-aryl-4-thiazolidones. The reason given for this structure was that on hydrolysis 3-aryl-2,4-thiazolediones were formed.



$$\overset{1}{S}\overset{2}{C}(NH)\overset{3}{N}R\overset{4}{C}O\overset{5}{C}H_2$$

Wheeler and Johnson[2] have shown in an exhaustive study that this

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(1) Beckurts and Frerich, *Arch. Pharm.*, **253**, 233–65 (1915).

(2) Wheeler and Johnson, *Am. Chem. J.*, **28**, 121–128 (1902).