

Anal. Calcd. for $C_{12}H_{12}O_4$: C, 65.45; H, 5.46; neut. equiv., 220. Found: C, 67.44; H, 6.92; neut. equiv., 271.

In a similar run in which the ethereal solution of the cadmium alkenyl was added to the anhydride there was isolated a yellow semi-solid product of neutral equivalent 265. A similar run in which the ethereal solution of the cadmium alkenyl was added slowly to a warm (50–57°) solution of the anhydride yielded finally a small amount of product having a neutral equivalent of 244. All of these products were bicarbonate soluble and gave positive tests for olefinic unsaturation.

A Grignard reagent (prepared in ether in the usual way under nitrogen) from 6.05 g. (0.05 mole) of isopropenyl bromide and 1.3 g. (0.05 g. atom) of magnesium was carbonated by pouring onto finely crushed Dry Ice. After acidification with dilute hydrochloric acid and extraction several times with ether, the combined ether layers were extracted with saturated bicarbonate solution. The combined bicarbonate extracts were just acidified to congo red under ether with dil. sulfuric acid. The ether extracts were washed once with water, dried over anhydrous sodium sulfate and evaporated on a hot plate. After several evacuations while warm the liquid acids were titrated with standard base.

Anal. Calcd. for $C_3H_5CO_2H$: neut. equiv., 86; calcd. for $C_6H_{10}CO_2H$: neut. equiv., 127. Found: neut. equiv., 94.

Summary

Several benzene derivatives possessing the substituent groups of penicillic acid have been prepared and tested for bacteriostatic activity. The methacrylyl-methoxybenzoic acids appear to be superior to their saturated counterparts.

Methoxyphthalic anhydride has been condensed with diisopropylcadmium to yield a mixture of ketonic acids.

When pure isopropenyl bromide reacts with magnesium to produce a Grignard reagent it appears simultaneously to undergo a process which results in an enlargement of the alkenyl radical. The process appears to differ from the usual olefinic polymerization.

BETHLEHEM, PA.

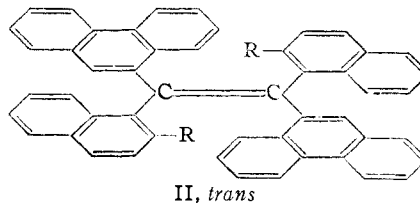
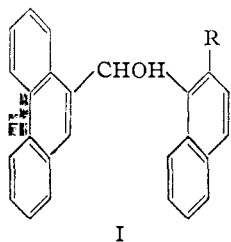
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[CONTRIBUTION FROM THE DANIEL SIEFF RESEARCH INSTITUTE]

The Formation of Tetraarylethylenes from Diarylcarbinols

BY FELIX BERGMANN AND SHALOM ISRAELASHVILI¹

Under the influence of electrophilic reagents, such as strong acids, diaryl carbinols may be converted into ethers,² fluorenes³ or tetraaryl ethylenes.⁴ Whereas the formation of the first two products appears now to be clearly understood,^{3,5} no reasonable mechanism has as yet been formulated for the "ethylenization." We have studied this "dehydration dimerization" reaction, especially in such cases, where di-ortho substitution of one of the aryl groups in the carbinol prevents cyclization to the five-membered ring system of fluorene. Thus, (9-phenanthryl)-(2-ethoxynaphthyl-1)-carbinol (I, R = OC_2H_5) and (9-phenanthryl)-(2-methyl-naphthyl-1)-carbinol (I, R = CH_3) were converted quantitatively into the corresponding ethylenes (II) by a boiling mixture of hydrobromic and acetic acids.



As recorded earlier,³ the carbinol (I, R = H) could not be isolated, but cyclized spontaneously to 1,2,3,4,7,8-tribenzfluorene, whereas di-(9-phenanthryl)-carbinol exclusively gave the tetraaryl ethylene.⁶ No ethylenization was observed in the case of (1-naphthyl)-(2-naphthyl)- or di-(2-naphthyl)-carbinol. It is thus evident, that, with the exception of di-(1-naphthyl)carbinol,⁴ ethylenization occurs, when cyclization is impossible.

It was postulated by Magidson, that the first transformation product of a diaryl carbinol with strong acids is an ether, which is cleaved into water and two diarylmethylene radicals. These may undergo either intramolecular cyclization or intermolecular dimerization. However, benzhydrol or its ether does not cyclize to fluorene, whereas it has been found⁷ that the diphenylmethylene radical undergoes ring closure. Magidson's scheme can, therefore, not be valid under the usual reaction conditions. The following alternative hypothesis is offered:

Electrophilic reagents convert the carbinols first into diarylcarbonium ions, which cyclize directly, or, if this reaction is prohibited or slow—

(1) Part of a thesis, submitted to the Hebrew University, Jerusalem, 1945.

(2) Klinger and Lonnes, *Ber.*, **29**, 2158 (1896); Adams and Weeks, *THIS JOURNAL*, **38**, 2514 (1916).

(3) For a review of the literature, see Bergmann and Israelashvili, *ibid.*, **68**, 1 (1946).

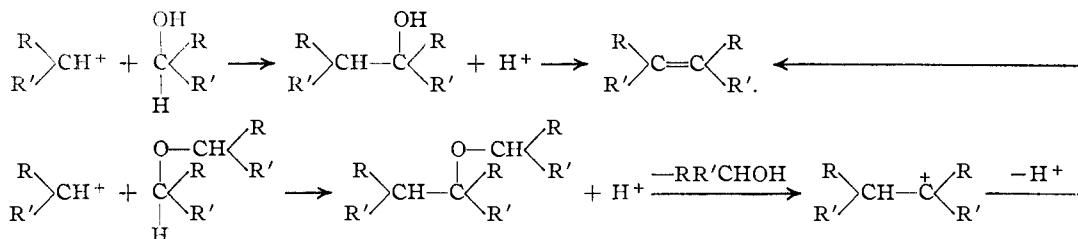
(4) Magidson, *Ber.*, **58**, 433 (1925).

(5) Hammett, "Physical Organic Chemistry," 1940, p. 300.

(6) Bergmann and Israelashvili, *THIS JOURNAL*, **67**, 1951 (1945).

(7) Staudinger and Endle, *Ber.*, **46**, 1437 (1913).

as is the case with di-(1-naphthyl) carbinol⁴—"dimerize" to ethylenes. The carbonium ions can react either with a molecule of the diaryl carbinol or with a molecule of the corresponding ether, formed independently.

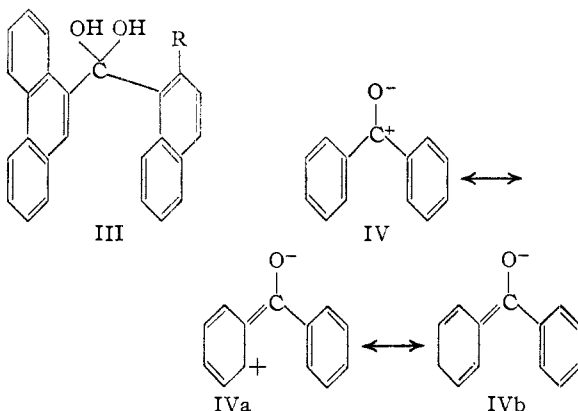


If this hypothesis is right, then diaryl carbinols should exchange their α -hydrogen against deuterium in acid medium and, under comparable conditions, the rate of exchange should correspond to the rate of ethylenization.

Reaction of the carbonium ion with the ether molecule may appear preferable, because the large bulk of the two substituents of the oxygen renders more difficult the approach of the positive ion to the oxygen and directs it toward the carbon atom, which constitutes the fundamental step in the reaction.⁸

In the course of the experiments here described, some peculiar observations were made, which are worth recording: The carbinol (I, R = OC₂H₅) was easily acetylated by boiling acetic anhydride, whereas I, R = CH₃, could not be acetylated, even in the presence of sodium acetate or pyridine. This different behavior shows the greater shielding effect of the methyl group as compared with the alkoxy group.⁹

Both carbinols, upon oxidation with chromic acid, gave ketone hydrates (III). This appears to be a steric effect occurring when at least three of the four ortho positions with regard to the carbonyl group are substituted; it deserves



(8) The above representation almost amounts to the statement that the carbonium ion first adds to the ether oxygen to form a trialkyloxonium ion and then migrates to the α -carbon atom, whilst the α -hydrogen shifts to the oxygen.

(9) For similar observations, see *e. g.* Adams and Mecorney, *THIS JOURNAL*, **67**, 798 (1945).

further study. Such substitution prevents the planar arrangement, which is a prerequisite of the normal resonance forms such as IVa and IVb and increases the positive charge on the carbonyl carbon (as in IV). Similar observa-

tions have been made in the oxidation of tetra-(9-phenanthryl)-ethylene⁶ and of (1-naphthyl)-9-phenanthryl-methane.³

Experimental¹⁰

(9-Phenanthryl)-(2-ethoxy-naphthyl-1)-carbinol (I, R = OC₂H₅)

To a Grignard solution from 9-bromophenanthrene (25 g.) and magnesium (3 g.) was added at 0° 2-ethoxy-1-naphthaldehyde¹¹ (20 g.) in absolute toluene (100 cc.). A yellow precipitate appeared during the addition. The ether was distilled off and the toluene solution refluxed for three hours. Decomposition with ammonium chloride gave a solid mass, which was recrystallized from petroleum ether (130°) with addition of a little xylene; m. p. 157–158° (I, R = OC₂H₅); yield 22 g., 58%. Cold concentrated sulfuric acid gives a green-blue color.

Anal. Calcd. for C₂₇H₂₂O₂: C, 85.7; H, 5.8. Found: C, 85.9; H, 5.6.

Acetylation.—The carbinol (1 g.) was refluxed for three hours with acetic anhydride (5 cc.). Decomposition with ethanol gave a gray precipitate, which was recrystallized from butyl acetate-ethanol, m. p. 190–191°.

Anal. Calcd. for C₂₉H₂₄O₃: C, 82.9; H, 5.7. Found: C, 82.6; H, 6.0.

Oxidation.—To the carbinol (1 g.) in acetic acid (5 cc.) was added a solution of chromic acid (0.25 g.). When the exothermic reaction had subsided, the mixture was heated on the water-bath for four hours. Water precipitated a yellow oil, which crystallized upon trituration with acetic acid; from petroleum ether (130°) and xylene yellow prisms, m. p. 177° (III, R = OC₂H₅).

Anal. Calcd. for C₂₇H₂₀O₃: C, 82.2; H, 5.6. Found: C, 82.2; H, 5.7.

Ethylenization.—The carbinol (0.7 g.), 48% hydrobromic acid (15 cc.) and acetic acid (15 cc.) were refluxed for forty-eight hours. The precipitate was filtered off and recrystallized from xylene as short, brown, prismatic rods; m. p. 280° (II, R = OC₂H₅).

Anal. Calcd. for C₃₄H₄₀O₂: C, 90.0; H, 5.6. Found: C, 90.4; H, 5.9.

(9-Phenanthryl)-(2-methyl-naphthyl-1)-carbinol (I, R = CH₃)

To a Grignard solution from 2-methyl-1-bromonaphthalene (11 g.) and magnesium (1.5 g.) was added a solution of 9-phenanthrene-aldehyde (11 g.) in benzene, and the mixture refluxed for four hours. The oily residue, which was left after decomposition with ammonium chloride and evaporation of the solvent, was treated with petroleum ether (80°). From propanol and a few drops of butyl acetate colorless prisms, m. p. 187° (I, R = CH₃). The substance gives a deep-blue color reaction with cold concentrated sulfuric acid.

(10) All melting points are uncorrected.

(11) "Organic Syntheses," **20**, 11 (1940).

Anal. Calcd. for $C_{26}H_{20}O$: C, 89.7; H, 5.7. Found: C, 89.4; H, 5.9.

Oxidation.—The carbinol (0.7 g.) was oxidized with chromic acid (0.66 g.) as described above. The yellow product crystallized spontaneously on cooling; from acetic acid orange prisms, m. p. 194° (III, R = CH_3).

Anal. Calcd. for $C_{26}H_{20}O_2$: C, 85.7; H, 5.5. Found: C, 86.0; H, 5.8.

Ethylenization.—The carbinol (1.5 g.) was refluxed for seventy-five hours with a mixture of acetic acid (155 cc.) and 48% hydrobromic acid (15 cc.). The ethylene (II, R = CH_3) formed brown, square plates, m. p. 236–237° (from xylene).

Anal. Calcd. for $C_{52}H_{36}$: C, 94.5; H, 5.5. Found: C, 94.9; H, 5.2.

Summary

1. Diarylcarbinols with two ortho substituents

in one aryl group such as (9'-phenanthryl)-(2-ethoxy-naphthyl-1)-carbinol or (9'-phenanthryl)-(2-methyl-naphthyl-1)-carbinol are converted quantitatively into ethylenes by strong mineral acids.

2. The mechanism of the formation of tetra-arylethylenes is represented as involving electrophilic substitution, by a diarylcarbonium ion, of the α -hydrogen of the diarylcarbinol or its ether.

3. Oxidation in acetic acid solution of diarylcarbinols with at least three of the four ortho positions substituted, yields hydrated ketones or their acetylation products.

REHOVOTH, PALESTINE

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[CONTRIBUTION FROM THE RESEARCH LABORATORY, GENERAL ELECTRIC CO.]

Thermal Rearrangement of Branched-Chain Methylpolysiloxanes¹

BY DONALD W. SCOTT

The higher molecular weight dimethylsilicone polymers obtained by hydrolysis of dimethyldichlorosilane have been found by Patnode² to undergo thermal rearrangement readily to give lower molecular weight cyclic structures, $[(CH_3)_2SiO]_n$. In the present work it has been found that branched-chain methylpolysiloxanes obtained by co-hydrolysis of dimethyldichlorosilane with methyltrichlorosilane and with silicon tetrachloride likewise undergo thermal rearrangement to yield lower molecular weight methylpolysiloxanes. From the products of such thermal rearrangements a total of ten new methylpolysiloxane compounds have been isolated.

Experimental

Thermal Rearrangement of the Co-hydrolysis Product of Dimethyldichlorosilane and Methyltrichlorosilane.—To a vigorously stirred, two-phase mixture of six liters of water, 1200 g. of butanol, and 600 g. of toluene was slowly added a mixture of 830 g. (6.4 moles) of dimethyldichlorosilane, 970 g. (6.4 moles) of methyltrichlorosilane and 600 g. of toluene. (Such a co-hydrolysis in the presence of a butanol-toluene mixture eliminates or greatly reduces the formation of insoluble gel.³) The organic layer was separated from the aqueous phase and washed free of acid, after which the toluene and butanol were removed by distillation under reduced pressure. The product so obtained was a viscous, translucent liquid. This material was heated in a Claisen flask, through which was passed a slow stream of nitrogen. Below 350° no distillate was obtained, indicating that little or no low molecular weight, volatile material was present. Above 350° thermal rearrangement commenced and distillate came over steadily as the temperature was raised slowly. At about 450°

the contents of the flask formed a gel which, however, continued to undergo thermal rearrangement as the temperature was raised slowly to a final value of 600°. In this manner approximately two-thirds of the original co-hydrolysis product was converted to volatile material, the remainder having been left in the bulb of the Claisen flask as a brittle solid.

The distillate collected was a mixture of amber colored liquid and a very small amount of a white crystalline solid. This crystalline material was found to be practically insoluble in hydrocarbon solvents and to sublime above 200°. Purification was accomplished by extraction with toluene followed by sublimation under reduced pressure. This compound is listed in Table I, which follows, as compound F. The remainder of the volatile product was distilled in a fractionating column, taking over all material boiling below 260°. In the boiling point range below 200° the only compounds found were $[(CH_3)_2SiO]_3$ and $[(CH_3)_2SiO]_4$.² Most of the distillation cuts in the boiling point range 200–260° deposited crystalline material when allowed to stand in a refrigerator for several days. By fractional crystallization, usually using toluene as solvent, five pure crystalline compounds were isolated from these distillation cuts. These five compounds are listed in Table I, compounds A to E inclusive.

The six compounds isolated from the thermally rearranged material were analyzed, and cryoscopic molecular weight determinations were made for all except compound F. Included in Table I are the empirical formulas found for these six compounds, their melting and boiling points, and the analytical and molecular weight data on which their identification is based.

The yield of each of these compounds was low—in all cases less than one per cent. of the original polymeric material subjected to thermal rearrangement. This is a consequence of the large number of possible compounds which can be formed by such a thermal rearrangement, so that the amount of any one particular compound is a small part of the total product. Separation by fractional crystallization, as was done in this case, tends to isolate preferentially compounds with higher melting points; the material in the boiling point range 200–260° no doubt contained a number of other compounds with lower melting points which were not isolated.

Thermal Rearrangement of the Co-hydrolysis Product of Dimethyldichlorosilane and Silicon Tetrachloride.—To a vigorously stirred, two-phase mixture of six liters of water, 1200 g. of butanol and 600 g. of toluene was added slowly

(1) The nomenclature used in this article is based on the system of organosilicon nomenclature discussed by Sauer [*J. Chem. Ed.*, **21**, 303 (1944)]. The numbering of the more complex siloxane ring structures follows that accepted for carbon ring compounds (Patterson and Capell, "The Ring Index," Reinhold Publishing Co., New York, N. Y., 1940).

(2) W. I. Patnode, private communication.

(3) R. O. Sauer, private communication.