Acknowledgment.—We are indebted to Dr. H. Agahigian for obtaining and interpreting the nuclear magnetic resonance spectra of 1,4-dichlorobutane-2-sulfonyl chloride and of N-benzenesulfonyl-1-butene-2,4-sultam, and to Dr. Sidney Siggia and the staff of the Olin Mathieson Central Analytical Department for microanalyses, infrared spectroscopy, vapor phase chromatography, and intrinsic viscosity determinations.

A Convenient, New Synthesis of *p*-Sexiphenyl from Biphenyl or *p*-Terphenyl in the Presence of Lewis Acid Catalyst–Oxidant[1]

PETER KOVACIC AND RICHARD M. LANGE[2]

The Department of Chemistry, Case Institute of Technology, Cleveland 6, Ohio

Received August 21, 1963

p-Sexiphenyl can be prepared in improved yield by a simple, one-step procedure involving treatment of biphenyl with aluminum chloride–cupric chloride, ferric chloride, or molybdenum pentachloride. Small amounts of *p*-quaterphenyl and higher molecular weight products were also formed. Under similar conditions, *p*-terphenyl yielded predominantly the dimer-type product, *p*-sexiphenyl. In attempted copolymerization of biphenyl and *p*-terphenyl, the main product obtained was *p*-sexiphenyl. Cuprous chloride proved to be a very effective inhibitor in the biphenyl–aluminum chloride–cupric chloride system. Studies were made of the relative rates of reaction for the monomers, benzene, biphenyl, and *p*-terphenyl, based on hydrogen chloride evolution. The theoretical aspects are discussed.

Aromatic hydrocarbons in the *p*-polyphenyl series have attracted considerable attention because of their good thermal stability, high melting points, insolubility, electronic configuration, and the interest in them as moderators in nuclear reactors. Previously, the individual, higher, isolable *p*-polyphenyls have usually been prepared by classical methods, such as the Ullmann coupling, Fittig reaction, or the Grignard synthesis. However, these routes suffer from one or more of the following limitations: very low yields, necessity of drastic conditions, tedious purifications, difficulties in reproducing results, multistep syntheses from the aromatic hydrocarbon precursor, and the formation of gross mixtures due to competing reactions.

Since our work is primarily concerned with *p*-sexiphenyl, discussion of the prior literature will be limited to this homolog. For example, in the Ullmann synthesis from 4-iodo-*p*-terphenyl and silver powder at 330°, Pummerer and Bittner[3] remarked on the difficulty of effecting condensation. Subsequently, this method was applied to a mixture of 4-iodobiphenyl, 4,4′-diiodobiphenyl, and copper powder, which provided a 25% yield based upon the iodo aromatics.[4a] In a modified version, Kuhn[4b] obtained *p*-sexiphenyl by zinc–acetic acid reduction of the product derived from 4,4′-diiodobiphenyl and copper. More recently,[5] Nozaki and co-workers[6] also investigated the Ullmann procedure with 4-iodo-*p*-terphenyl and reported a 10% yield based upon the *p*-terphenyl precursor in this multistep synthesis. In connection with their studies of *p*-polyphenyls and the corresponding methylated derivatives, Kern and Wirth[7] utilized the Ullmann and Grignard reactions for preparative purposes. In addition, the catalytic reduction of *p*-dibromobenzene in the presence of methanol afforded a gross mixture from which *p*-sexiphenyl was isolated in 0.7% yield.[8]

The objective of the present work was to effect the nuclear coupling of biphenyl and of *p*-terphenyl by treatment with a Lewis acid catalyst and oxidant, and to investigate the theoretical aspects.

Results and Discussion

We have succeeded in synthesizing *p*-sexiphenyl in good yield and high purity by a novel, one-step procedure involving biphenyl–Lewis acid catalyst–oxidant. Inexpensive, readily available starting materials are used. Under mild conditions, biphenyl was converted to the trimer-type product on treatment with aluminum chloride–cupric chloride, ferric chloride, or molybdenum pentachloride. Minor amounts of higher *p*-polyphenyls were formed, as well as small quantities of *p*-quaterphenyl. The isolated products were characterized by comparison with authentic materials (melting points and ultraviolet and infrared spectra). Apparently, the formation of *p*-sexiphenyl from biphenyl–aluminum chloride–cupric chloride proceeds as indicated below.

$$3\text{ biphenyl} + 4CuCl_2 \xrightarrow{AlCl_3} p\text{-sexiphenyl} + 4CuCl + 4HCl$$

This transformation resembles the synthesis of bimesityl from mesitylene and ferric chloride.[9] Furthermore, analogy may be drawn to the conversion of benzene to *p*-polyphenyl,[10-12] except that the product from biphenyl is of much lower molecular weight.

The biphenyl reaction was investigated at some length with the aim, in part, of determining the optimum conditions for *p*-sexiphenyl formation (Table I). We found that the reaction, which proceeded with good rapidity, was quite sensitive to changes in the $AlCl_3$–$CuCl_2$ molar ratio. The yield of *p*-sexiphenyl attained a maximum

---

(1) Paper VII: "Polymerization of Aromatic Nuclei," from the Ph.D. Thesis, 1964, of R. M. Lange, Case Institute of Technology; presented at the 145th National Meeting of the American Chemical Society, New York, N. Y., Sept., 1963.

(2) Department of Chemistry Fellow, Case Institute of Technology, 1962–1963.

(3) R. Pummerer and K. Bittner, *Ber.*, **57**, 84 (1924).

(4) (a) R. Pummerer and L. Seligsberger, *ibid.*, **64**, 2477 (1931); (b) R. Kuhn, *Ann.*, **475**, 131 (1929).

(5) NOTE ADDED IN PROOF.—J. A. Cade and A. Pilbean [*J. Chem. Soc.*, 114 (1964)] report a 29% yield (crude) of *p*-sexiphenyl from *p*-terphenyl *via* treatment of 4-bromo-*p*-terphenyl with butyllithium.

(6) T. Nozaki, M. Tamura, Y. Harada, and K. Saito, *Bull. Chem. Soc. Japan*, **33**, 1329 (1960).

(7) W. Kern and O. H. Wirth, *Kunststoffe-Plastics*, **6**, 12 (1958).

(8) M. Busch, W. Weber, *et al.*, *J. prakt. Chem.*, **146**, 1 (1936).

(9) P. Kovacic and C. Wu, *J. Org. Chem.*, **26**, 759 (1961).

(10) P. Kovacic and A. Kyriakis, *J. Am. Chem. Soc.*, **85**, 454 (1963).

(11) P. Kovacic and R. M. Lange, *J. Org. Chem.*, **28**, 968 (1963).

(12) P. Kovacic and F. W. Koch, *ibid.*, **28**, 1864 (1963).

TABLE I

BIPHENYL AND METAL HALIDES[a]

Metal halide	Mole	Temp., °C.	Crude product, g.	Yield, %[b] p-Quaterphenyl	Yield, %[b] p-Sexiphenyl
$CuCl_2$–$AlCl_3$	0.25:0.25	80–85	17	2	40
$CuCl_2$–$AlCl_3$	0.25:0.5	80 ± 2	21.8	<1	67[c]
$CuCl_2$–$AlCl_3$	0.25:0.25	155–160	30[d]		
$CuCl_2$–$AlCl_3$[e]	0.25:0.25	50 ± 2	11.5	2	22
$CuCl_2$–$AlCl_3$[e]	0.25:0.25	80 ± 2	12	0	22
$CuCl_2$–$AlCl_3$[e]	0.25:0.25	100 ± 2	15	0	7
$CuCl_2$–$AlCl_3$[e,f]	0.125:0.25	80 ± 2	0.4		
$FeCl_3$[e,g]	0.25	80–83	8.5	3	17
$FeCl_3$[e]	0.25	80 ± 2	3.5	0.9	6.7
$FeCl_3$	0.25	80–83	5	1.3	7
$FeCl_3$–$AlCl_3$[e,h]	0.25:0.50	80 ± 2	2.8	1.0	4.1
$FeCl_3$–$AlCl_3$[e,g,h]	0.25:0.50	80 ± 2	7.6	3.6	12
$MoCl_5$	0.25	80–83	9.3	7	5
$MoCl_5$–$AlCl_3$[e,h]	0.25:0.50	80 ± 2	30	7.1	9.8
$CuCl_2$[i]	0.25	80 ± 2	0	0	0
$AlCl_3$[i]	0.25	80 ± 2	0.066[j]	0	0

[a] Biphenyl, 0.5 mole; 0.5 hr. [b] Sublimed material, based on the oxidant. [c] Yield 52% after recrystallization from 1,2,4-trichlorobenzene. [d] Black tar. [e] In *o*-dichlorobenzene (3 moles). [f] Biphenyl, 0.25 mole; CuCl, 0.25 mole. [g] Water, 0.25 mole, as cocatalyst. [h] Time, 2 hr. [i] Time, 1.5 hr. [j] Unidentified (not a *p*-polyphenyl).

(67% good purity, 52% analytically pure) at an $AlCl_3$–$CuCl_2$ ratio of 2:1, and then fell as the ratio decreased. Evidence was obtained from studies on the benzene polymerization[13] that cuprous chloride inhibits reaction, apparently by placing the aluminum chloride catalyst in an inactive complex form, C_6H_6–CuCl–$AlCl_3$.[14] A similar situation prevailed in the case of biphenyl since only a negligible yield of product was obtained when cuprous chloride was added initially in large amount. The hypothesis concerning complex formation was supported by solubility data. Cuprous chloride was essentially insoluble in biphenyl–*o*-dichlorobenzene at 80°. When aluminum chloride was added in the ratio, $AlCl_3$: CuCl = 1, almost all of the solid dissolved indicating the presence of a soluble, ternary complex.

When the temperature was increased from 80 to 155–160°, a black, intractable tar was formed, presumably as a result of polymerization and isomerization under the more drastic conditions. With dichlorobenzene as solvent at 80°, the principal effect was a decrease in the yield of *p*-sexiphenyl. In a further examination of the temperature variable, experiments were carried out at 50, 80, and 100° in the solvent system. The yield was essentially the same at the lower temperatures, but decreased markedly at 100°. At the higher temperature, the product was highly colored and difficult to purify.

Ferric chloride and molybdenum pentachloride also produced nuclear coupling with formation of *p*-sexiphenyl. However, these metal halides generally proved to be less effective than aluminum chloride–cupric chloride. In *o*-dichlorobenzene, addition of water as cocatalyst resulted in a significant increase in the yield of *p*-sexiphenyl from the ferric chloride reaction. Several experiments were performed with aluminum chloride added as the catalyst. Surprisingly, not only was there little change in the yield of desired product, which was difficult to purify, but also the aluminum chloride acted as an inhibitor in the presence of ferric chloride or molybdenum pentachloride. In comparison with the other metal halides, aluminum chloride–cupric chloride gave higher ratios of *p*-sexiphenyl–*p*-quaterphenyl in the product mixture. This may be related to the high strength of aluminum chloride as a Lewis acid. Approximately the same amount of higher molecular weight residue, 15–20% of the crude product, was obtained from the sublimations in all cases.

Gas chromatography of chloroform extracts of the crude reaction products revealed the presence of only unchanged aromatic monomer. It is interesting that nuclear chlorination[15] of biphenyl by the metal halides does not compete effectively with the coupling reaction.

Similarly, reaction variables were investigated in the case of *p*-terphenyl with *o*-dichlorobenzene as solvent (Table II). The results paralleled those observed with biphenyl. In addition, an increase in the ratio of metal halides–*p*-terphenyl acted to enhance the *p*-sexiphenyl yield. At higher temperatures (120°), some isomerization occurred as evidenced by the presence of *m*-terphenyl.

Olah and Meyer, as well as Swisher, investigated the isomerization of terphenyls induced by aluminum chloride at about 140–220°.[16] Each of the isomers yielded an equilibrium mixture consisting of approximately 63% *m*- and 35% *p*-terphenyl.[16a]

Ferric chloride and molybdenum pentachloride were inferior to the combination of aluminum chloride–cupric chloride. In an investigation involving ferric chloride and water cocatalyst, the nature of the solvent appeared to play an important role. With 1,2,4-trichlorobenzene, the yield of *p*-sexiphenyl was substantially lower than with *o*-dichlorobenzene. This result brings to mind the recent work of Choi and Brown[17] concerning solvent effects in gallium bromide catalyzed alkylations.

Attempted copolymerization of biphenyl and *p*-terphenyl, in the presence of ferric chloride, molybdenum pentachloride, or aluminum chloride–cupric chloride with *o*-dichlorobenzene as solvent, yielded

---

(13) P. Kovacic and J. Oziomek, *J. Org. Chem.*, **29**, 100 (1964).

(14) R. W. Turner and E. L. Amma, *J. Am. Chem. Soc.*, **85**, 4046 (1963).

(15) P. Kovacic and N. O. Brace, *ibid.*, **76**, 5491 (1954); P. Kovacic, C. Wu, and R. W. Stewart, *ibid.*, **82**, 1917 (1960); P. Kovacic and R. M. Lange, unpublished work.

(16) (a) G. A. Olah and M. W. Meyer, *J. Org. Chem.*, **27**, 3682 (1962); (b) R. D. Swisher, U. S. Patent 2,363,209 (1944).

(17) S. U. Choi and H. C. Brown, *J. Am. Chem. Soc.*, **85**, 2596 (1963).

TABLE II

p-TERPHENYL AND METAL HALIDES[a]

Metal halide	Mole	Temp., °C.	Time, hr.	Crude product, g.	*p*-Sexiphenyl yield, %[b]
$CuCl_2$–$AlCl_3$	0.125:0.125	80 ± 2	0.5	6.4	19
$CuCl_2$–$AlCl_3$	0.125:0.25	80 ± 2	0.5	12.1	34
$CuCl_2$–$AlCl_3$	0.25:0.25	80 ± 2	0.5	22.2	30
$CuCl_2$–$AlCl_3$	0.50:0.25	80 ± 2	0.5	31.6	22
$CuCl_2$–$AlCl_3$	0.25:0.25	80 ± 2	1.5	26.1	35
$CuCl_2$–$AlCl_3$	0.25:0.25	120 ± 2	0.5	10.8	6
$MoCl_5$	0.25	80 ± 2	2	20.8	16
$MoCl_5$[c]	0.2	215 ± 7	0.5	21.6	13
$FeCl_3$[d]	0.125	80 ± 2	2	6.7	17
$FeCl_3$[d,e]	0.125	80 ± 2	4	3.8	9
$CuCl_2$	0.25	80 ± 2	1.5	0	0
$AlCl_3$	0.25	80 ± 2	1.5	0.7[f]	0.6

[a] *p*-Terphenyl, 0.25 mole; *o*-dichlorobenzene, 3 moles. [b] Sublimed material, based on the oxidant. [c] No solvent. [d] Water, 0.125 mole, as cocatalyst. [e] In 1,2,4-trichlorobenzene (3 moles). [f] M.p. (crude) 450–455°; infrared spectrum identical with that of *p*-sexiphenyl.

TABLE III

BIPHENYL–*p*-TERPHENYL WITH METAL HALIDES[a]

Metal halide	Mole	Time, hr.	Crude product, g.	Yield, %[b]		
				p-Quarterphenyl	*p*-Quinquephenyl	*p*-Sexiphenyl
$CuCl_2$–$AlCl_3$	0.125:0.125	0.5	8.2	3	0	20
$FeCl_3$[c]	0.125	2	4.2	<1	<1	12
$MoCl_5$	0.125	2	3.4	<1	0	4

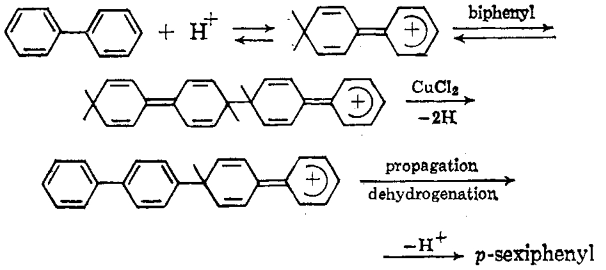
[a] Biphenyl, 0.125 mole; *p*-terphenyl, 0.125 mole; *o*-dichlorobenzene, 3 moles; 80 ± 2°. [b] Sublimed material, based on the oxidant. [c] Water, 0.125 mole, as cocatalyst.

predominantly *p*-sexiphenyl with only trace amounts of *p*-quaterphenyl and *p*-quinquephenyl (Table III).

Studies were made of the reaction rates for the aromatic monomers, benzene, biphenyl, and *p*-terphenyl, in the system, aluminum chloride–cupric chloride–*o*-dichlorobenzene. The reactions were followed by titration of the evolved hydrogen chloride, and the relative rates obtained by comparison of the rate curves for the first 3 min. of reaction. In all cases, linearity pertained in this region. At 80° the relative rates were found to be for benzene, 1.00; biphenyl, 0.83; and *p*-terphenyl, 0.57. Interestingly, at 40° the observed relative rates were, for benzene, 1.00; and biphenyl, 5.22.

Comparison of the present results with the polymerization of benzene to *p*-polyphenyl[10–12] reveals interesting similarities and differences. We propose that the reaction proceeds by an oxidative cationic mechanism similar to that advanced for the benzene polymerization.

$$H_2O + AlCl_3 \rightleftarrows H_2O\dashrightarrow AlCl_3 \rightleftarrows H^+AlCl_3(OH)^-$$



Aluminum chloride is designated the catalyst and cupric chloride the oxidant. In control experiments, no reaction occurred with either biphenyl or *p*-terphenyl when the aluminum chloride was omitted. In the absence of cupric chloride, biphenyl–aluminum chloride gave a negligible amount of unidentified solid, and, with *p*-terphenyl, less than 1% of *p*-sexiphenyl was formed.

In previous related investigations,[18] it was found that biphenyl, when heated with aluminum chloride, yielded benzene, *p*-terphenyl, *p*-quaterphenyl, toluene, methylcyclopentane, cyclohexane, and resins. On treatment with aluminum chloride at elevated temperatures and for prolonged periods,[19] benzene was converted to biphenyl, phenylcyclohexane, phenylmethylcyclopentane, diphenylcyclohexane, and uncharacterized polymers. Apparently, in the absence of an added oxidant, the intermediates may undergo disproportionation and rearrangement under the proper conditions.

Ferric chloride[12] and molybdenum pentachloride[11] can presumably function in a dual capacity, both as catalyst and oxidant. Since the data for aluminum chloride–cupric chloride indicate the importance of a high catalyst–oxidant ratio, the generally inferior results with ferric chloride and molybdenum pentachloride might be attributed, in part, to destruction of the catalyst by reduction.

The data from the biphenyl reaction, in addition to earlier studies[20] involving benzene polymerization, suggest the operation of a cocatalytic effect with ferric chloride. Compounds of the Brønsted acid type, *e.g.*, water, functioned as cocatalysts. In the case of aluminum chloride and molybdenum pentachloride, the reasoning is by analogy to the benzene–ferric chloride reaction and the cationic polymerization of olefins.[21]

(18) C. Friedel and J. M. Crafts, *Compt. rend.*, **100**, 692 (1885); Yu. K. Yur'ev and R. Ya. Levina, *Sci. Rept. Moscow State Univ.*, **3**, 203 (1934); *Chem. Abstr.*, **30**, 8191 (1936); K. Shishido and I. Irie, *J. Soc. Chem. Ind. Japan*, **48**, 10 (1945); *Chem. Abstr.*, **42**, 6343 (1948).

(19) C. A. Thomas, "Anhydrous Aluminum Chloride in Organic Chemistry," Reinhold Publishing Corp., New York, N. Y., 1941, p. 716; M. G. Gonikberg and A. E. Gavrilova, *J. Gen. Chem. USSR*, **22**, 1429 (1952).

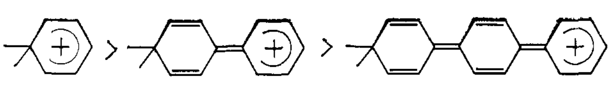
(20) P. Kovacic and C. Wu, *J. Polymer Sci.*, **47**, 45 (1960); P. Kovacic, F. W. Koch, and C. E. Stephan, *ibid.*, **2A**, 1193 (1964).

(21) D. C. Pepper, *Quart. Rev.* (London), **8**, 88 (1954); "Cationic Polymerization and Related Complexes," P. H. Plesch, Ed., Heffer, Cambridge, England, 1953.

There is evidence to support existence of the complexes, $H_2O-AlCl_3$[22] and $H_2O-AlBr_3$,[23] as well as the interaction of σ-complexes, $(ArH_2)^+(Al_2X_7)^-$, with additional molecules of aromatic substrate.[24] Proton-initiated intramolecular coupling of aromatic nuclei is apparently involved in the conversion of β,β-di(1-naphthyl)ethylene to 9-methyl-1,2,7,8-dibenzfluorene by treatment with stannic chloride.[25]

The hypothesis concerning the dehydrogenation of cyclohexadiene units to aromatic structures is supported by the facile transformation of 1,4-cyclohexadiene to benzene on treatment with ferric chloride[12] or molybdenum pentachloride.[11] Furthermore, Nonhebel[26] found that 9,10-dihydroanthracene is smoothly dehydrogenated by cupric halides under mild conditions. Admittedly, the exact stage at which dehydrogenation occurs during nuclear coupling, as well as the mechanism, is unknown.

It is significant that benzene yields p-polyphenyl; whereas, under similar conditions, biphenyl produces mainly a trimer-type product, and p-terphenyl affords a dimer-type. In searching for a rationalization, one must realize that the situation is quite complicated. Various factors should be considered, *e.g.*, the relative susceptibility of the aromatic monomers to attack, and possible catalysis or inhibition by the reduced metal halide. Furthermore, one cannot afford to overlook the possible influence of the solvent or excess aromatic monomer. Ease of termination would be enhanced by coordination of the growing carbonium ion with an aromatic molecule. This interpretation has been used previously to explain the effect of aromatic additives on molecular weight in the cationic polymerization of styrene.[27] In addition, the increasing ease of termination in the order, p-terphenyl > biphenyl >> benzene, suggests that the relative stabilities of the postulated σ-complex intermediates may be an important factor. Based on the degree of resonance stabilization, the order of reactivity would be



It is reasonable to correlate the increasing ease of termination with increasing degree of delocalization.

These transformations of biphenyl and p-terphenyl can be classified as an extension of the Scholl reaction. Our mechanistic interpretation is analogous to that proposed for the Scholl reaction by Nenitzescu and Balaban.[28]

Experimental[29]

Materials.—Anhydrous cupric chloride was dried at 130°; anhydrous molybdenum pentachloride was weighed under dry nitrogen; o-dichlorobenzene and 1,2,4-trichlorobenzene were distilled from calcium hydride.

Instrumental Procedure.—Ultraviolet spectra were taken in chloroform solution and infrared spectra in potassium bromide pellets; gas chromatography was done using a 9-ft. column, 20% silicone rubber on Chromosorb P, 100–350° at 11°/min., helium at 50 ml./min.

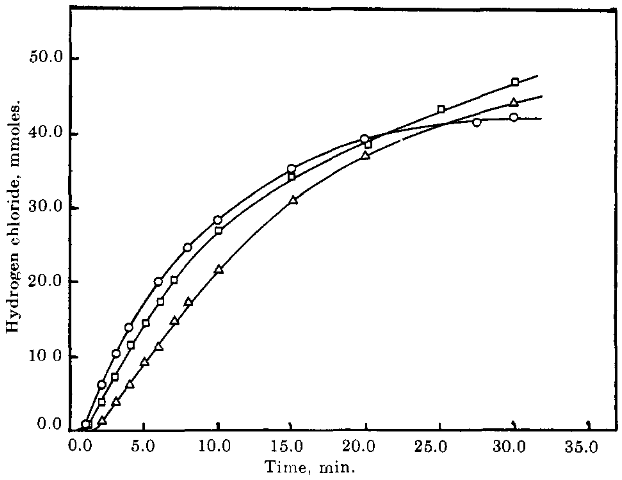


Fig. 1.—Rates of hydrogen chloride evolution in the reaction of (○) benzene, (□) biphenyl, and (△) p-terphenyl with cupric chloride–aluminum chloride in o-dichlorobenzene at 80–81°.

Biphenyl–Aluminum Chloride–Cupric Chloride. General Procedure.—Anhydrous aluminum chloride (66.6 g., 0.5 mole) was added to biphenyl (77 g., 0.5 mole) with stirring under dry nitrogen at 75°. After anhydrous cupric chloride (33.6 g., 0.25 mole) was introduced in the closed system by a suitable addition device, the reaction mixture was stirred efficiently under nitrogen at 80 ± 2° for 30 min. The evolved acid gas was titrated with standard base. Then, the molten mixture was quickly poured into 500 ml. of 18% hydrochloric acid and steam distilled. After the residue was pulverized with water in a blender, it was treated with hydrochloric acid, triturated repeatedly with ethanol, and sucked dry. Trituration with concentrated hydrochloric acid was continued until the filtrate became colorless, followed by washing with boiling water until a negative test (silver nitrate) for chloride ion was obtained. The crude product, a light brown powder, was dried at 130°; yield 21.8 g.

A portion (0.58 g.) on fractional sublimation at 290–310° (0.015 mm.) gave p-quaterphenyl, 3 mg., m.p. 308–310°, lit.[30] m.p. 310°; authentic material, m.p. 306–308°, m.m.p. 306–308°. The infrared and ultraviolet spectra were identical with those of the authentic material.

Continued sublimation at 400–440° (0.015 mm.) yielded p-sexiphenyl, 0.506 g., m.p. 452–456°. Recrystallization from 1,2,4-trichlorobenzene produced pure product, 0.387 g., m.p. 465–467°, mixture melting point with authentic material was not depressed; ultraviolet spectrum λ_{max} 316 mμ, lit.[30] λ_{max} 317 mμ; infrared spectrum, absorption maximum, 811 cm.$^{-1}$.

Anal. Calcd. for $C_{36}H_{26}$: C, 94.28; H, 5.72. Found: C, 94.14; H, 5.70.

The infrared spectrum of the sublimation residue exhibited a major band at 807 cm.$^{-1}$.

p-Terphenyl–Aluminum Chloride–Cupric Chloride.—The general procedure was followed for the most part with o-dichlorobenzene as solvent. In the work-up procedure, steam distillation was omitted and the residue, after ethanol treatment, was triturated repeatedly with chloroform. The dry solid was then triturated with concentrated hydrochloric acid.

Sublimation yielded p-sexiphenyl and residual material (infrared absorption maximum, 807 cm.$^{-1}$).

Solubility of Metal Halides in Biphenyl–o-Dichlorobenzene.—A mixture of cupric chloride (8.4 g., 0.063 mole), biphenyl (19.2 g., 0.125 mole), and o-dichlorobenzene (100 g.) was stirred for 30 min. at 80°. After filtration of the hot mixture, the residue was washed with ligroin (25 ml., b.p. 30–60°) and sucked dry for several minutes; weight of cupric chloride residue, 8.25 g. The solubility of other metal halides was determined in a

---

[22] C. D. Nenitzescu, M. Avram, and E. Sliam, *Bull. soc. chim. France*, 1266 (1955).

[23] F. Fairbrother and W. C. Frith, *J. Chem. Soc.*, 2975 (1953).

[24] H. C. Brown and W. J. Wallace, *J. Am. Chem. Soc.*, **75**, 6268 (1953).

[25] G. Wolf, *ibid.*, **75**, 2673 (1953).

[26] D. C. Nonhebel, *J. Chem. Soc.*, 1216 (1963).

[27] N. Tokura, M. Matsuda, and Y. Watanabe, *J. Polymer Sci.*, **62**, 135 (1962).

[28] C. D. Nenitzescu and A. Balaban, *Ber.*, **91**, 2109 (1958).

[29] Melting points (block) are uncorrected. Elemental analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, N. Y.

[30] E. H. Smith, "Polyphenyls," Literature Search, U. S. Atomic Energy Commission, ER-8098, 1956.

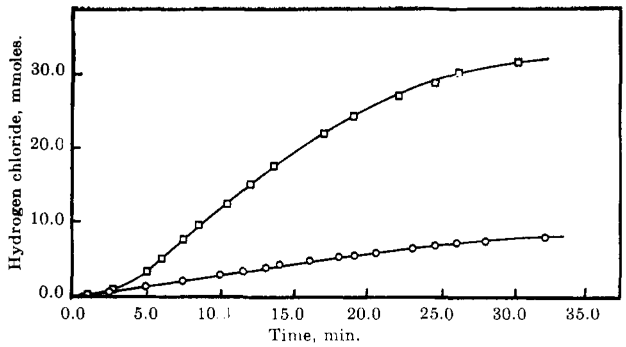


Fig. 2.—Rates of hydrogen chloride evolution in the reaction of (O) benzene and (□) biphenyl with aluminum chloride–cupric chloride in *o*-dichlorobenzene at 40°.

similar manner [metal halide, g. (mole), undissolved halide, g.]: cuprous chloride, 6.24 (0.063), 6.23; aluminum chloride, 8.40 (0.063), 0.92; aluminum chloride–cuprous chloride, 8.30:6.24 (0.063:0.063), 1.0.

Relative Rates. A. Benzene, Biphenyl, and *p*-Terphenyl at 80°.—The reactions were carried out according to the general procedure with the aromatic reactant (0.125 mole) in *o*-dichlorobenzene (1.5 moles). After the introduction of anhydrous aluminum chloride (0.063 mole), the mixture was heated to 79° with vigorous stirring under dry nitrogen (flow rate, 140 ml./min.). Anhydrous cupric chloride (0.063 mole) was added in a single portion and the reaction was followed at 80–81° by titration of the evolved acid gas with standard base. The rate data (average of two runs; deviation, ±7%) are summarized in Fig. 1.

B. Benzene and Biphenyl at 40°.—Rate data (average of two runs; deviation, ±2%) obtained at 40–41° in a similar manner are plotted in Fig. 2.

Authentic *p*-Sexiphenyl.—Synthesis of this compound was accomplished according to the procedure of Nozaki and coworkers,[6] m.p. 460–462° (sublimation and crystallization from 1,2,4-trichlorobenzene), lit.[30] m.p. 465°; infrared spectrum, absorption maximum, 811 cm.$^{-1}$; ultraviolet spectrum, λ_{max} 317 mμ.

Acknowledgment.—The authors wish to express their thanks to the National Science Foundation for partial support of this work.

Silicic Acid Chromatographic Study of the Catalytic Hydrogenation Products of 9,10-Epoxystearates[1]

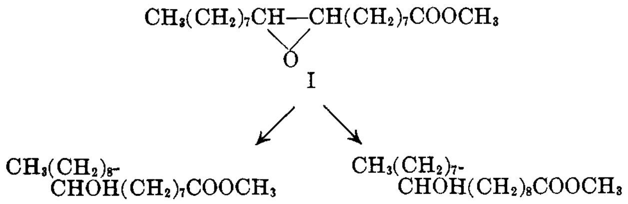
DAVID R. HOWTON AND RICHARD W. KAISER, JR.

The Laboratory of Nuclear Medicine and Radiation Biology, Department of Biophysics and Nuclear Medicine, University of California, Los Angeles, California

Received March 26, 1964

Hydrogenation of methyl *cis*-9,10-epoxystearate over palladium on charcoal in glacial acetic acid yields a mixture shown by silicic acid column chromatography to consist mainly of hydroxystearates, together with smaller amounts of stearate and ketostearates. Contrary to conclusions reached in earlier studies, degradation of the principal product (purification of the intermediate ketostearates, oximinostearates, and Beckmann-rearranged isomeric amido esters solely by adsorption chromatography assuring no discrimination between positional isomers) demonstrates that the 9- and 10-hydroxystearates are in fact formed in equal amounts.

Catalytic hydrogenolytic opening of the oxide ring of methyl 9,10-epoxystearates (I), (or of the free acids, readily obtained[2] by action of peracids on oleic and elaidic acids, would be expected *a priori* to yield equal amounts of DL-9- and -10-hydroxystearates (II), since the methyl and carboxyl termini of the oxide ring substituents are far too remote to impress any appreciable asymmetric reactivity on the site of reaction by inductive effects conducted along the long intervening polymethylene chains. Zook and Knight,[3] for example, have shown that a carboxyl group only two methylene groups away has very little influence on the randomness with which HBr adds to an olefinic center. Even more directly pertinent is the recent report[4] that catalytic hydrogenation of *cis*-6,7-epoxystearic acid yields equal amounts of DL-6- and -7-hydroxystearic acids.



I

9-II

10-II

$CH_3(CH_2)_8CHOH(CH_2)_7COOCH_3$ (9-II); $CH_3(CH_2)_7CHOH(CH_2)_8COOCH_3$ (10-II)

It is therefore difficult to rationalize the claims of a number of investigators[5–8] who have, without exception, indicated the predominant formation of 10-II[9] by hydrogenation of I. The patent improbability of such conclusions recommends careful examination of the evidence upon which they were based. In every case, samples of the product of interest were isolated by crystallization and identified solely (with a single exception[6]) on the basis of the melting behavior of the hydroxy acids, of the keto acids obtained from them by chromic acid oxidation, or of the corresponding semicarbazones. Following careful study of the phase properties of the 9- and 10-keto- and -DL-hydroxystearic acids, Cochrane and Harwood[10] have recently called attention to the strong possibility that these findings (together with a number of others bearing on the course of related reactions) were misinterpreted.

---

[1] This paper is based on work performed under Contract AT(04-1)-GEN-12 between the Atomic Energy Commission and the University of California at Los Angeles.

[2] T. W. Findley, D. Swern, and J. T. Scanlan, *J. Am. Chem. Soc.*, **67**, 412 (1945).

[3] H. D. Zook and J. A. Knight, *ibid.*, **76**, 2302 (1954).

[4] S. P. Fore and W. G. Bickford, *J. Org. Chem.*, **26**, 2104 (1961).

[5] I. G. V. Pigulevskii and Z. Y. Rubashko, *J. Gen. Chem. USSR*, **9**, 829 (1939); *Chem. Abstr.*, **34**, 378^2 (1940).

[6] J. Ross, A. I. Gebhart, and J. F. Gerecht, *J. Am. Chem. Soc.*, **71**, 284 (1949).

[7] C. H. Mack and W. G. Bickford, *J. Org. Chem.*, **18**, 686 (1953).

[8] F. J. Julietti, J. F. McGhie, B. L. Rao, W. A. Ross, and W. A. Cramp, *J. Chem. Soc.*, 4517 (1960).

[9] Even, in one case,[7] to the exclusion of 9-II; cursory perusal of the literature has revealed occurrence of at least two instances in which this claim has led to preparation of "authentic" samples of 10-hydroxystearic acid by this procedure.

[10] C. C. Cochrane and H. J. Harwood, *J. Org. Chem.*, **26**, 1278 (1961).