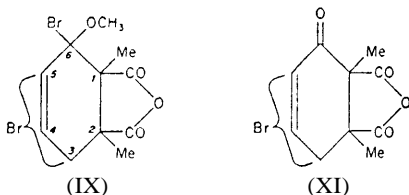


disappeared, and filtered hot; the filtrate yielded on cooling a *labile di-Br compd.* (IX), m. 95–100° (decompn.). Freshly prepd. IX (5 g.) and 70 cc. abs. MeOH refluxed 8–10 min. on a steam bath gave on cooling in a Dry Ice–Me₂CO bath 2.5 g. crystals of *6,6-dimethoxy- α -bromo-1,2,3,6-tetrahydro-*a*-phthalic anhydride* (X), m. 128° (decompn.). The Br in X is not removed by alc. AgNO₃, except after long heating; its position (3, 4, or 5) is not definitely known. X (1.5 g.) was refluxed 20 min. with 300 mg. NaOMe in 15 cc. MeOH, the NaBr filtered, and the soln. decompd. with 30 cc. H₂O and neutralized with 2 N H₂SO₄, yielding an oil and CO₂; the oil, extd. with Et₂O, gave 0.5 g. yellow crystals, m. 54°, of a *lactone*, C₈H₈O₂(OMe). Freshly prepd. IX was shaken 1.5 hrs. with 50 cc. CHCl₃ and 30 cc. H₂O; neutralization of the water layer with 0.1 N KOH showed loss of 1 mol. HBr/mol. dibromide, and evapn. of the CHCl₃ gave a *bromo ketone*, C₁₀H₈O₄Br (XI), m. 189°. The Br reactivity was similar to that of X. IX also slowly changes to XI upon standing in the air or over NaOH *in vacuo*. It is not believed that the MeOCH:CHCH:CH₂ route is of value for the synthesis of cantharidin.



M. Winicov

Molecular structure of 1,2,3,4,5,6-hexachlorocyclohexane and its related compounds. Toshihiko Oiwa, Ryoichi Yamada, Masayuki Hamada, Michiko Inoue, and Minoru Ohno (Kyoto Univ.). *Botyu Kagaku* No. 14, 42-3(1949) (English summary).—Chlorination of C₆H₆Cl₆ (I) isomers in CCl₄ produced the following compds.: from α -I, 7-C₆H₅Cl₇ (II), m. 85–6°, and *o*-C₆H₄Cl₈ (1,1,2,2,3,4,5,6-Cl₈C₆H₄) (III), m. 148–9°; from β -I, α -II, m. 153–4°, III, and β -*p*-C₆H₄Cl₈ (1,1,2,3,4,4,5,6-Cl₈C₆H₄) (IV), m. 262° (decompn.); from γ -I, γ -II; from δ -I, *a*-II, III, and IV; from α -II, III, and IV; also from γ -I, no III but a substance more stable than III, showing a half-wave potential –0.25 v. (*N* calomel electrode standard) on the polarograph, and likewise from γ -II, no III but a substance showing a half-wave potential of –0.15 v. In reference to the already known mol. structure of α -, β -, γ -, and δ -I (chair form) and a tetrahedral model of the C₆H₁₂ ring (where 3 consecutive positions are the apices of an equilateral triangle, 4 of which are in different planes) the structures of *a*- and 7-II, III, and IV were shown to be of the chair form and the positions of Cl were detd. definitely in *a*- and δ -I, *a*-II, III, and IV, and tentatively in γ -I and γ -II. The above structures agree with the röntgenogram of γ -I and assumptions and exptl. results by others except for δ -I, which is polar, as assumed from the dehydrochlorination velocity, contrary to a sym. form proposed by Daasch (*C.A.* 42, 62g) and also by Jatkar and Kulkarni (*C.A.* 43, 6877g).

J. G. Yoshioka

The influence of temperature and catalysts on substitution in the aromatic nucleus. J. P. Wibaut (Univ. Amsterdam). *Experientia* 5, 337-47(1949) (in German).—At 300°, H in gaseous pyridine is substituted by Br mainly at the 3- or 3,5-positions whereas at 500° H in the 2- or 2,6-positions are substituted. Monobromination of gaseous PhBr with a pumice-FeBr₃ catalyst is an ortho-para type of substitution at 200–450°, the ratio of the isomeric C₆H₄Br₂ being detd. by the differences in activation energy required for substitution in the ortho, meta, or para position in the PhBr mol. With pumice or graphite below 410° the substitution is an ortho-para type whereas at 410–600° meta substitution is predominant. In non-catalytic bromination of liquid C₁₀H₈ at 85–215°, 1-C₁₀H₇Br and small amts. of 2-C₁₀H₇Br are formed, the ratio being detd. by the difference in activation energy required for substitution at 1- and 2-positions; the same is true for non-catalytic bromination of gaseous C₁₀H₈ at 250–300°. In noncatalytic bromination of C₁₀H₈ vapor at 500–650° equal amts. of 1- and 2-C₁₀H₇Br are formed; at these temps. the 1:2-ratio is not detd. by energies of activation but is exclusively dependent on the probability of collision of Br with a 1- or 2-position. With a FeBr₃ or FeCl₃ cata-

lyst at 150° in the bromination of liquid C₁₀H₈, up to 60% of 2-C₁₀H₇Br may be formed. The action is reversible with FeCl₃.

D. S. Farnar

Isomerization reactions. I. Isomerization of alkyl halides. Eiichi Ibuki. *J. Chem. Soc. Japan* 67, 103–4 (1946).—The isomerization of alkyl radicals introduced into an aromatic nucleus by the Friedel-Crafts reaction was studied. Isomerization depends on the water content of the catalyst. For PrCl, the effect of AlCl₃ is strongest at –50 to 0° when the water content is min. AlCl₃ with water of crystn. lacks this effect. With FeCl₃ –5° to 0° is the optimum range for the isomerization. It is assumed that the alkyl halide isomerized by the catalytic action of FeCl₃ is condensed catalytically with the aromatic nucleus.

Y. Majima

The activity of aluminum chloride prepared by the method of Radzivanovskii. I. Action of aluminum chloride prepared according to Radzivanovskii in the reaction of benzene with ethyl bromide. B. X. Dolgov and N. A. Kuchumova (A. A. Zhdanov State Univ., Leningrad). *Zhur. Obshchei Khim.* (J. Gen. Chem.) 20, 445–9(1950).—AlCl₃ prepd. according to Radzivanovskii [*Ber.* 28, 1135(1895)] from Al and HCl is an active Friedel-Crafts catalyst. In the C₆H₆–EtBr reaction with 2% catalyst a 73% yield of *EtPh* is attained at 10–12°. C₆H₆ (200 g.) and 4 g. Al shavings treated with dry HCl until a brown coating covered the catalyst, then with 100 g. EtBr, and let stand 48 hrs. at 10–12°, followed by refluxing 2 hrs., gave 73% *EtPh*, b. 132–4°, d₄²⁰ 0.8703, n_D²⁰ 1.4950, 16–18% *Et₂C₆H₄*, mostly the *m*-isomer with a trace of *p*-isomer [sepd. according to Voswinkel, *Ber.* 22, 315(1889)], and 2.5% *1,3,5-Et₃C₆H₃*, b. 212–14°. Nitration of *EtPh* (25 g.) by addn. in 4 hrs. to 20.5 g. HNO₃ (d. 1.5) and 27 g. H₂SO₄ (cl. 1.86) in the cold, followed by heating to 135°, gave mainly the *2-nitro deriv.*, b. 224–7°, d₄²⁰ 0.8605, n_D²⁰ 1.4892. Similarly *m-Et₂C₆H₄* gave the *2,4,6-trinitro deriv.*, m. 62–3°, while *Et₂C₆H₄* yielded the *2,4,6-trinitro deriv.*, rn. 108°. Some 2% of higher alkylate was obtained. Increase of the catalyst to 10% lowers the formation of *EtPh* to 40–5% with a decrease of the di-*Et* deriv. to 10% and a rise of the tri-*Et* deriv. to 8–10%. The yield was unchanged in 4.5–15.0 hr. reaction periods with dry HCl in the initial step, but the condensation reaction reached a const. yield in 48 hrs.; shorter periods cut the yield severely. G. M. Kosolapoff

Reactions with aluminum chloride obtained according to Radzivanovskii. Condensation of benzene with some aliphatic unsaturated halogen derivatives and polyhalogenated compounds. B. N. Dolgov and N. A. Larin (A. A. Zhdanov State Univ., Leningrad). *Zhur. Obshchei Khim.* (J. Gen. Chem.) 20, 450–7(1950).—The best results of the reaction of C₆H₆ with (CH₂Cl)₂ are obtained with 2% Al shavings, which gives 25.2% (PhCH₂)₂ with 10.1% tar. Higher amts. of Al lead to increased tar formation and decrease of definite products. A 24–48 hr. reaction period (room temp.) is best. A high ratio of C₆H₆ to (CH₂Cl)₂ (8:1) gives 30.6% (PhCH₂)₂; a 1:1 ratio yields but 6.5%; the tar formation is inversely affected by this change. In addn. to the sym. product, some Ph₂CHMe, b. 272–8°, n_D²⁰ 1.57428, d₄²⁰ 1.0049, is also obtained. (BrCH₂)₂ reacts analogously. A 1:4 mixt. of isobutylene dibromide and C₆H₆ with 2% Al in 25 hrs. at room temp. gave 6.5 g. crude C₆H₅Ph, contg. 89% *tert-BuPh*, and 28.82 g. of a mixt. b. 260–93°, from which was isolated 45% Me₂CPhCH₂Ph, b. 284–8°, d₄²⁰ 0.9815, n_D²⁰ 1.55632, n_D²² 1.54889, along with a *solid isomer*, m. 125° (from EtOH), identified by CrO₃ oxidation as (CHMePh)₂. The latter is obtained readily (50% yield) from the former on standing in C₆H₆ with the Radzivanovskii AlCl₃ catalyst (2%) 30 hrs. at room temp. In addn. a *low-melting isomer*, m. 8–10°, d₄²⁰ 0.9928, n_D²⁰ 1.56598, is also isolated. A 1:4 mixt. of ClCH₂CMe:CH₂ and C₆H₆ with the catalyst from 2% (by wt.) of Al in 23 hrs. at room temp. gave 7.2 g. crude C₆H₅Ph, contg. 80% *tert-BuPh*, 1 g. (CHPhMe)₂, m. 125°, 9 g. Me₂PhCCH₂Ph, b. 260–90°, d₄²⁰ 0.9808, n_D²⁰ 1.55635. Similarly CH₂:CH–CH₂Cl gave 1.9 g. *PrPh*, b. 148–50°, d₄²⁰ 0.8660, n_D²⁰ 1.49381, and 14.8 g. product, b. 266–90°, from which, apparently, some *diphenylpropane*, b. 279–81°, d₄²⁰ 0.9804, n_D²⁰ 1.55665, was isolated. A 1:6 mixt. of CHBr(CH₂Br)₂ and C₆H₆ with 2% Al catalyst gave in 20 hrs. 10% *diphenylpropane*, b. 295°, d₄²⁰ 1.0202, n_D²⁰ 1.57904; no triphenylpropane was found. MeCBr(CH₂Br)₂ gave in 20 hrs. 33.4% crude C₁₈H₁₈, from which was isolated 10 g. (CHPhMe)₂, m. 125°, along with 5 g. *liquid mixt.* of the 2 isomers.

$\text{BrCH}_2\text{CMeBrCH}_2\text{Cl}$ gave 8 g. (CHPhMe)₂, while $(\text{CHCl}_2)_2$ gave 0.5 g. anthracene, m. 208–9.5°. No reaction occurred when $(\text{CCl}_2)_2$ was tried, even with as much as 10% Al catalyst. G. M. Kosolapoff

Alkylation of aromatic compounds in the presence of zinc chloride. IV. Condensation of halides and alcohols with aromatic compounds under pressure. A. B. Kuchkarov and I. P. Tsukervanik (Middle-Asiatic State Univ.). *Zhur. Obshchei Khim.* (J. Gen. Chem.) 20, 458–61(1950); cf. *C.A.* 42, 4541h.—The following autoclave reactions were performed with freshly fused ZnCl_2 and a trace of added HCl. C_6H_6 (18 ml.), 9.2 g. BuCl, and 2.5 g. ZnCl_2 in 10 hrs. at 225–30° gave 70% crude $\text{C}_6\text{H}_5\text{Ph}$ (contg. *sec*-BuPh, b_{722} 171–3°, d_{20}^{25} 0.8628, n_D^{20} 1.4920) and 8% crude (C_6H_5)₂ C_6H_4 . Iso-AmCl (4 g.) gave 64% *mono*amylbenzenes (some *tert*-AmPh, b_{725} 185–90°, was identified), and 1.2 g. polyalkylbenzenes. PhMe (20 ml.) and 9.2 g. BuCl with 1.5 g. ZnCl_2 gave in 8 hrs. at 210–20° 71% *sec*-butyltoluenes and 2.5 g. polyalkylbenzenes. C_{10}H_8 (12.8 g.), 9.2 g. BuCl, and 4 g. ZnCl_2 in 12 hrs. at 160–70° gave 65% *butyl*naphthalenes, b_{722} 278–83°, d_{20}^{25} 0.9798, n_D^{20} 1.5700, and 9% *dibutyl*naphthalenes, b_{15} 170–80°, n_D^{20} 1.5807, d_{20}^{25} 0.9682. PhOH (19 g.), 14 g. BuCl, and 4 g. ZnCl_2 in 7 hrs. at 170–80° gave 72% *butyl*phenols (resolved into *sec*-butylphenol, b_{720} 230–5°, d_{20}^{25} 0.9890, n_D^{20} 1.5178, probably *ortho*, and the *para* isomer, b_{725} 242–6°, d_{20}^{25} 0.9860, n_D^{20} 1.5185). MePh (15 ml.), 11.0 g. EtBr, and 7 g. ZnCl_2 in 14 hrs. at 230–40° gave 30% *ethyl*toluenes, b. 156–65°, and 2 g. polyalkylates, b. 190–8°. C_6H_6 (20 ml.), 7.4 g. BuOH, and 3.4 g. ZnCl_2 , satd. with dry HCl at 0°, gave in 12 hrs. at 235–40° 67% butylbenzenes (some *sec*-BuPh isolated) and 10% dibutylbenzenes. MePh (20 ml.), 7.4 g. BuOH (satd. with HCl), and 13.6 g. ZnCl_2 similarly gave 74% *butyl*toluenes and 5% *dibutyl*toluenes; 3.4 g. ZnCl_2 gave 71.5% mono-Bu deriv., while 1.5 g. gave a 51% yield. C_6H_6 (10 ml.), 4.6 g. EtOH (satd. with HCl), and 3.4 g. ZnCl_2 in 12 hrs. at 330–40° gave 36% *EtPh* and 4 g. *polyethyl*benzenes; the results were similar with 13.6 g. ZnCl_2 at 280–90°. C_6H_6 (20 ml.), iso-PrOH (satd. with HCl), and 6.8 g. ZnCl_2 similarly gave in 10 hrs. at 210–20° 75% *iso*-PrPh, b_{720} 150–3°, d_{20}^{25} 0.8751, n_D^{20} 1.4895, and 15% *diisopropyl*benzenes. G. M. Kosolapoff

Synthesis of *m*-iodostyrene. S. N. Ushakov and E. N. Freidberg (Polymer. Plastics Inst., Leningrad). *Izvest. Akad. Nauk S.S.S.R. Otdel. Khim. Nauk* 1950, 268–75.—Addn. of 106 g. BzH to 110 g. KNO_3 in 325 g. coned. H_2SO_4 at 5° over 4.5 hrs. and diln. with H_2O gives 46–61% *m*- $\text{O}_2\text{NC}_6\text{H}_4\text{CHO}$, m. 54°, along with some 25% *o*-isomer which remains in the mother liquor. At 25–35° the yield of *m*-isomer is raised to 75–8%. Addn. of the product with stirring to SnCl_2 in HCl with cooling (spontaneous rise of temp. to 60–80° occurs in spite of cooling), followed by diazotization at 2° with NaNO_2 , addn. of KI soln. at 5°, letting stand 12 hrs., and heating 1 hr. to 80–90° gave *m*- $\text{IC}_6\text{H}_4\text{CHO}$. The use of a very high proportion of HCl (40 mols.) gives poorer results (15–20% yield) than 8 moles HCl (theoretical amt.), which gave 28%, or 10–11 moles HCl (39–41% yield); the product, isolated by steam distn., m. 56–7°. The reaction of this with MeMgI conducted as usual in Et_2O gave 70% *m*- $\text{IC}_6\text{H}_4\text{CH}(\text{OH})\text{Me}$, b_3 119–20°, d_{20}^{25} 1.767, n_D^{20} 1.6215. Dehydration of this by passage over Al_2O_3 at 300° proceeds well for 15–20 min. with formation of 98% pure product, after which period decompn. begins and iodine is evolved; the same occurs at 260–70°. Distn. of the carbinol with KHSO_4 in the presence of hydroquinone (0.1–0.2%) at 190–200° and 50–60 mm. in a CO_2 atm. gave a 71.4% yield with 13–14% (by wt.) of KHSO_4 ; a smaller ratio of KHSO_4 gave lower yields. The pure *m*- $\text{IC}_6\text{H}_4\text{CH}:\text{CH}_2$, b. 69–71°, b_3 71–3°, d_{20}^{25} 1.674, n_D^{20} 1.6390, polymerizes with 0.1% Bz_2O_2 in 1–2 hrs. at 80–100° to a clear solid polymer, d_{20}^{25} 1.86, n_D^{20} 1.6850 (highest among org. polymers). G. M. Kosolapoff

Studies of chlorination, principally to obtain tetrachlorophthalic anhydride, pentachlorobenzoic acid, and a new (tetrachlorophenyl)trichloromethane, m. 121–122°. Manuel Ballester. *Mem. real acad. cienc. y artes Barcelona* 29, No. 7, 3–19(1948).—A 2-l., 1-neck flask was fitted with a stopper carrying an inlet tube passing to the bottom of the flask and a gas outlet tube. Another opening connected to the inlet tube allowed introduction of solid to the reaction mixt. o - $\text{C}_6\text{H}_4(\text{CO})_2\text{O}$ (200 g.), 800 g. 60% H_2SO_4 , and 5 g. iodine were added, the flask placed in an oil bath at 100°, Cl passed through the soln., with the temp. main-

tained at 100° until the mass began to solidify, an addnl. 5 g. iodine added during the course of the reaction, and the temp. elevated gradually until only a small amt. of solid remained. When no more Cl could pass through, at 230°, the operation was finished. The crystals were sepd. on a porous plate, treated with ice, filtered, and washed with H_2O ; after boiling with H_2O , filtering, washing, and drying, 300 g. (78%) tetrachlorophthalic anhydride was obtained. No new satisfactory prepn. for $\text{C}_6\text{Cl}_5\text{CO}_2\text{H}$ was found. Several attempts at prepn. are described. The new (tetrachlorophenyl)trichloromethane (I) was prepd. as follows: To 4.9 g. PhCCl_3 were added 20.3 g. Silberrad chlorinating agent (*C.A.* 16, 2851) and 0.5 g. pulverized AlCl_3 , the temp. maintained at 60° for 2 hrs., and the residue was treated with H_2O and left for 24 hrs., at the end of which 2 layers remained. The yellow layer gave an oil of the same color and a cryst. substance contaminated by oil. I, colorless needles from ligroin, m. 121–2°, very sol. in PhMe, slightly sol. in EtOH. Marjorie Mueller

Dehalogenation-condensation with sulfuric acid catalyzer. II. Dehalogenation-condensation of benzene with various aralkyl halides. Katsuhiko Ichikawa and Haruo Shingu. *J. Soc. Chem. Ind. Japan* 50, 126–8(1947).—Sixteen aralkyl halides (PhCH_2X and similar compds.) were subjected to dehalogenation-condensation with H_2SO_4 as a catalyst. The order of decreasing reactivity was: PhOH, C_{10}H_8 , PhMe, PhCH_2Cl , PhCl, BzOH, and PhNO_2 . M. Kubo

Molecular polarization and molecular interaction. III. The use of dielectric polarization measurements in studying the extent of molecular interaction in solution. The system aniline-dioxane-benzene. A. V. Few and J. W. Smith (Battersea Polytech., London). *J. Chem. Soc.* 1949, 2781–4; cf. *C.A.* 45, 13c.—For the mol. assocn. $\text{A} + \text{B} \rightarrow \text{AB}$ (complex), an equation is derived relating the equil. const. (K) and the mol. polarization of the complex (P_{AB}) with the apparent increase in the mol. polarization of A at infinite diln., on the assumption that activities can be represented by molar concns. K and PAB can then be calcd. from measurements of mol. polarization of A in mixts. of B with an inert solvent. Calcns. from measurements on dil. solns. of aniline in dioxane- C_6H_6 mixts. give about 188 debyes as the dipole moment of the aniline-dioxane complex; from the calcd. K , about 65% of the aniline is complexed. R. L. Wolke

Azomethines. II. Absorption curves and the constitution of bisazomethines. G. Sevens and G. Smets (Louvain Univ., Belg.). *Bull. soc. chim. Beiges* 57, 32–49(1948); cf. *C.A.* 41, 6469e; following abstr.—Condensation in concd. alc. soln. of the calcd. quantities of the appropriate aromatic aldehydes and aromatic amines gave 23 new diarylmono-(I) and triaryl bisazomethines (II), generally in excellent yields. The following *N*-benzylideneanilines were prepd. (color, % yield, and m.p., resp., given): *p*-nitro-*o*-amino, red, 72, 134°; *p*-nitro-*p*'-amino, violet, 72, 163–4°; *p*-hydroxy-*p*'-amino, orange-yellow, 87, 183–4°; *o*-hydroxy-*p*'-amino, orange, 72, 100°. Also prepd. were compds. of the general formula $\text{RC}_6\text{H}_4:\text{CHNR}^1:\text{NCH}:\text{C}_6\text{H}_4\text{R}^2$ (R^1, R^2 , color, % yield, and m.p., resp., given): *o*-OH, *o*- C_6H_4 , *o*-OH, yellow, 63, 162°; *o*-OH, *m*- C_6H_4 , *o*-OH, yellow, 79, 107°; *o*-OH, *p*- C_6H_4 , *o*-OH, orange, 64, 213°; *o*-OH, *p*- C_6H_4 , *m*- NO_2 , golden yellow, 89, 192–3°; *o*-OH, *p*- C_6H_4 , *p*- NO_2 , golden yellow, 62, 215–16°; *o*-OH, *p*- C_6H_4 , *p*- NMe_2 , golden yellow, 90, 193–4°; *m*-NO, *m*- C_6H_4 , *m*- NO_2 , yellow, 72, 185–6°; *m*-NO, *p*- C_6H_4 , *m*- NO_2 , yellow, 83, 249°; *p*- NO_2 , *m*- C_6H_4 , *p*- NO_2 , yellow, 73, 207°; *p*- NO_2 , *p*- C_6H_4 , *p*- NO_2 , yellow, 100, 242–4°; *m*- NO_2 , *p*- C_6H_4 , *p*- NO_2 , orange, 93, 205–6°; *p*- NMe_2 , *m*- C_6H_4 , *p*- NMe_2 , yellowish, 57, 168°; *p*- NMe_2 , *p*- C_6H_4 , *p*- NMe_2 , yellow, 50, 267°; *p*-MeO, *p*- C_6H_4 , *p*-MeO, gold, 100, 199–200°; *m*- NO_2 , *p*- C_6H_4 , *p*- NMe_2 , light orange, 36, 224–6°; *p*- NO_2 , *p*- C_6H_4 , *p*- NMe_2 , red, 74, 230–2°; *p*-MeO, *p*- C_6H_4 , *p*- NO_2 , golden yellow, 82, 172–3°. 1-*p*-Methoxybenzyl-2-(*p*-methoxyphenyl)benzimidazole, colorless, m. 129–30°, and 1-(*p*-hydroxybenzyl)-2-(*p*-hydroxyphenyl)benzimidazole, colorless, m. 226–8°, were prepd. in 72 and 63% yield, resp. An extensive compilation of their ultraviolet optical properties in acid, basic, and neutral soln. showed that the values of λ_{max} for the II depend markedly on their structures. Relative to the corresponding I, the II never show an appreciable displacement of λ_{max} toward the greater wave lengths, as would be predicted by their large no. of possible double bonds. In the II the existence of 3 conjugated aromatic nuclei minimizes somewhat the contribution of an