33—ALIPHATIC COMPOUNDS

LAURENCE I. PETERSON AND HARRY L. YALE

Chlorocarbons and chlorohydrocarbons: chlorinated paraffins. D. W. F. Hardie. *Kirk-Othmer Encycl. Chem. Technol., 2nd Ed.* 5, 231–40(1964)(Eng). A review on chlorinated derivs. of natural or synthetic higher paraffins, without regard to whether the parent material is normally solid or liquid, including properties, manuf., economic aspects, handling, storage, and uses. 39 references. VNJZ

Automatic preparative gas chromatography apparatus. Ya. M. Kucherov and A. P. Lizogub. *Neftepererabotka i Neftekhim., Akad. Nauk Ukr. SSR, Resp. Mezhvedomstv. Sb.* 1965, 138–40(Russ). A 1:1:0.5 isooctane–octane–nonane mixt. was sepd. in a column of 6 m. length and 16 mm. diam., N carrier gas velocity 0.5 l./min., Wheatstone bridge current 170 ma., recorder sensitivity 50 mv. Samples (3.5 cc.) were injected at 112°, and the components were collected and frozen in glass tubes at 0°. The yield of the components was 55–60%, although by condensation of the vapors, the yield could be increased to 80%; the purity of the collected compds. was 99.9%. BNJR

Reactions of active nitrogen with organic substrates. IV. Isoprene. Terukiyo Hanafusa and Norman N. Lichtin (Boston Univ., Boston, Mass.). *Can. J. Chem.* 44(10), 1230–2(1966)(Eng); cf. *CA* 55, 17622*e*; 64, 11070*d*. The reaction of isoprene with active N at 60°/2 mm. was investigated. Products trapped at −196° were HCN, MeCH:CH_2, CH_2:CH_2, C_2H_4, HC:CH, propyne, EtMeC:CH_2, $(CH_2{:}CH)_2$, and propane. Monomeric products trapped at −78° but volatile at 60°/0.01 mm. were β-methylpyrrole, pyrrole, NH_3, 1-cyanoisoprene, and at least 12 other unidentified compds. The polymeric product was a complex mixt. which probably contained CN and amino groups. C. M. Buess

Study of heterogeneous oxidation of n-butenes to 1,3-butadiene in the presence of steam. I. I. Yukel'son and E. A. Boguslavskii. *Tr. Lab. Khim. Vysokomolekul. Soedin., Voronezhsk. Univ.* 1964(3), 63–6(Russ). The effect of steam concn. on oxidn. of n-butenes over newly developed catalysts (oxides of group VIII modified by elements of group IV) was studied. The raw material was an industrial fraction of butenes with the compn. H_2 0.1, C_2H_4 0.3, C_3H_6 0.6, C_4H_{10} 1.5, 1-C_4H_8 32.6, 2-C_4H_8 63.4, and C_4H_6 1.5 mole-%. Oxidn. was effected in a continuous flow app. at 650° and a 1:2.5 diln. of the butenes with air over 1 ml. catalyst (particle size 2–3 mm.) in a quartz tube (diam. 8 mm.). With an increase in butene–air–H_2O mole ratio from 1:1.6 to 1:15.8, the 1,3-butadiene (I) content of the contact gas increased from 13.8 to 20.8 mole-% (basis dry gas). Curves were obtained showing the dependence of total butene conversion and I yield per amt. of passed and decompd. butene on the steam concn. in the initial mixt. From *Ref. Zh., Khim.* 1966(4), Pt. II, Abstr. No. 4N7. MVRK

Chlorination reaction in the manufacture of hexachlorobenzene. Jerzy Jaworski and Tadeusz Mazonski (Katedra Technol. Chem. Org., Politech. Slaska, Poland). *Przemysl Chem.* 43 (2), 93–4(1964)(Pol). Continuous chlorination of o-dichlorobenzene in the gas phase (at 300–400°) and in the presence of a fixed bed catalyst was investigated. The catalyst used was inexpensive activated C, Carbopol Z, in the form of irregular granules, about 5 mm. in diam., with a density of 230 g./l. and a sp. surface area of 157.7 $m.^2/g$. A uniform temp. gradient was obtained when the upper part of the vertical pipe reactor was filled with less active catalyst from a previous charge. The use of a partly deactivated catalyst resulted in a total absence of catalyst baking, even when its load was increased by 40%. The reaction product contained more than 95% of hexachlorobenzene, besides some pentachlorobenzene. A schematic diagram of the equipment used is shown. Edward A. Ackermann

Chlorination of isobutylene to methallyl chloride. E. M. Mokrii, Kh. Z. Kotovich, and D. K. Tolopko. *Khim. Prom., Inform. Nauk.-Tekhn. Zb.* 1965(4), 7–10(Ukrain). A 99.5% pure isobutylene (I) was prepd. by dehydration of *tert*-BuOH on Al_2O_3 at 350° with the 2 l./hr. rate of I formation. The catalyst was regenerated at 500–20° for 3 hrs. in a stream of hot air. Mixing 1.2 moles I with 1 mole Cl at 90–100° gave a mixt. of products, which on rectification at 70–2° gave methallyl chloride (II). The fraction collected at 72–5° consisted of a 95:4 ratio of II and dimethylvinyl chloride which were difficult to sep. A lower I–Cl molar ratio caused addnl. chlorination of the products and a higher ratio decreased the yield of II. At 90°, a 62–72.6% yield of II was obtained. BMJW

Chlorocarbons and chlorohydrocarbons: vinyl chloride. D. W. F. Hardie. *Kirk-Othmer Encycl. Chem. Technol., 2nd Ed.* 5, 171–8(1964)(Eng). A review on the phys. and chem. properties, manuf., economic aspects, standards, handling, toxicity, and uses. 38 references. VNJZ

Chlorocarbons and chlorohydrocarbons: methyl chloride. D. W. F. Hardie. *Kirk-Othmer Encycl. Chem. Technol., 2nd Ed.* 5, 100–11(1964)(Eng). A review on the phys. and chem. properties, manuf., economic aspects, standards, analysis, handling, toxicity, and uses. 43 references. VNJZ

Chlorocarbons and chlorohydrocarbons: allyl chloride. B. H. Pilori. *Kirk-Othmer Encycl. Chem. Technol., 2nd Ed.* 5, 205–15 (1964)(Eng). A review on the phys. and chem. properties (typical addns. to the double bond, simple replacements of Cl, formation of allyl esters and of N compds., and synthesis of complex mols.), manuf. (mechanism, reaction variables, com. practice, feed prepn., reaction system, and product recovery), safety and handling (toxicity, precautionary measures, and remedial treatment), and uses. 25 references. VNJZ

Chlorocarbons and chlorohydrocarbons: ethyl chloride. D. W. F. Hardie. *Kirk-Othmer Encycl. Chem. Technol., 2nd Ed.* 5, 140–7(1964)(Eng). A review on the phys. and chem. properties, manuf., economic aspects, standards, handling, toxicity, and uses. 39 references. VNJZ

Chlorocarbons and chlorohydrocarbons: dichloroethylenes. D. W. F. Hardie. *Kirk-Othmer Encycl. Chem. Technol., 2nd Ed.* 5, 178–83(1964)(Eng). A review on the phys. and chem. properties, manuf., and uses of 1,1- and 1,2-dichloroethylene. 10 references. VNJZ

Tri- and perchloroethylene. S. A. Miller. *Chem. Process Eng.* 47(6), 268–75(1966)(Eng). A review of processes for the manuf. of C_2HCl_3 and C_2Cl_4. The relative feasibilities depend on the availability of raw materials and the utilization of by-products. 18 references. Paul A. Haas

Chlorocarbons and chlorohydrocarbons: chloroacetylenes. D. W. F. Hardie. *Kirk-Othmer Encycl. Chem. Technol., 2nd Ed.* 5, 203–5(1964)(Eng). A review on the properties of mono- and dichloroacetylene. 5 references. VNJZ

Chlorocarbons and chlorohydrocarbons: chloroprene. P. S. Bauchwitz (E. I. du Pont de Nemours & Co., Inc., Wilmington, Del.). *Kirk-Othmer Encycl. Chem. Technol., 2nd Ed.* 5, 215–31 (1964)(Eng). A review on the phys. and chem. properties (including reactions with O, S, SO_2, N_2O_4, halogens, H, halides, and hypohalous acids and esters, Diels-Alder addns. and dimerizations, free-radical reactions, and polymerization), prepn. (from C_2H_2 via monovinylacetylene, butadiene, butanes and butenes, and 1,3-dichloro-2-butene), industrial manuf., health and safety factors, and isomers and homologs. 73 references. VNJZ

Chlorocarbons and chlorohydrocarbons: trichloroethylene. D. W. F. Hardie. *Kirk-Othmer Encycl. Chem. Technol., 2nd Ed.* 5, 183–95(1964)(Eng). A review on phys. and chem. properties, manuf., economic aspects, standards, handling, toxicity, and uses. 53 references. VNJZ

Chlorocarbons and chlorohydrocarbons: methylene chloride. D. W. F. Hardie. *Kirk-Othmer Encycl. Chem. Technol., 2nd Ed.* 5, 111–19(1964)(Eng). A review on the phys. and chem. properties, manuf., economic aspects, standards and analysis, handling, toxicity, and uses. 40 references. VNJZ

Chlorocarbons and chlorohydrocarbons: chloroform. D. W. F. Hardie. *Kirk-Othmer Encycl. Chem. Technol., 2nd Ed.* 5, 119–27(1964)(Eng). A review on phys. and chem. properties, manuf., economic aspects, standards, analysis, handling, toxicity, and uses. 25 references. VNJZ

Chlorocarbons and chlorohydrocarbons: tetrachloroethylene. D. W. F. Hardie. *Kirk-Othmer Encycl. Chem. Technol., 2nd Ed.* 5, 195–203(1964)(Eng). A review on the phys. and chem. properties, manuf., economic aspects, standards, handling, toxicity, and uses. 45 references. VNJZ

Chlorocarbons and chlorohydrocarbons: other chloroethanes. D. W. F. Hardie. *Kirk-Othmer Encycl. Chem. Technol., 2nd Ed.* 5, 148–70(1964)(Eng). A review on the phys. and chem. properties, manuf., economic aspects, standards, handling, toxicity, and uses of 1,1- and 1,2-dichloroethane, 1,1,1- and 1,1,2-trichloroethane, 1,1,1,2- and 1,1,2,2-tetrachloroethane, pentachloroethane, and hexachloroethane. 101 references. VNJZ

Chlorocarbons and chlorohydrocarbons: carbon tetrachloride. D. W. F. Hardie. *Kirk-Othmer Encycl. Chem. Technol., 2nd Ed.* 5, 128–39(1964)(Eng). A review on the phys. and chem. properties, manuf., economic aspects, standards and analysis, toxicity, and uses. 73 references. VNJZ

Synthesis of trialkylamine-type extraction agents by the Hofmann reaction. B. N. Laskorin, D. I. Skorovarov, and V. A. Semenov. *Zh. Prikl. Khim.* 39(5), 1049–55(1966)(Russ). Lab.- and bench-scale (~100 kg.) methods were described for prepn. of R_3N, where R is C_7–C_9. RBr was prepd. by heating a mixt. of ROH, HBr or NaBr, and H_2SO_4. The org. phase obtained, contg. 75–80% RBr and unreacted ROH, was treated with 8–34% NH_4OH at 100–180°/several atm. The yield of R_3N increased with decreasing NH_3–RBr ratio to 2–3:1 and with increasing temp. The yield was not affected by NH_4OH concn. or size or R. The yield of resin began to increase at ≥180°; the yield of solid product, probably R_4NBr, increased with decreasing temp. The starting conditions of ammonolysis became milder as the batch size increased, because the reaction is exothermic and a large batch provided a larger proportion of the required heat than a small batch under similar conditions. A typical final product of a C_7–C_9 mixt. contained R_3N 85–90,

(hemoglobin 70% satd. with CO) in 10 dogs respiring O under hyperbaric conditions. With 7% CO_2 present in the supplied O, the CO was eliminated nearly twice as fast as when pure O was respired. Of 22 patients with coal gas poisoning, the respiration of O at 2 atm. pressure led to recovery(no fatalities). All patients recovered consciousness 30–90 min. after inhalation of O under pressure began. Of 70 other severely coal-gassed patients, only 3 did not recover. The results demonstrated that hyperbaric O should be administered as soon as possible in CO poisoning. Data are given on 1 patient with barbiturate poisoning who recovered from respiratory and cardiovascular depression under hyperbaric O when other methods failed. Other reports indicate that there are no advantages in giving O at more than 2 atms. pressure. At higher pressures, toxic effects of O appear, perhaps resulting from the presence of CO in the blood.
W. C. Tobie

Diagnosis of salt poisoning in animals. M. Bohosiewicz (Wyższa Szkoła Rolnicza, Wrocław, Poland). *Zeszyty Nauk. Wyższej Szkoły Rolniczej Wrocławiu, Weterynaria* 11(42), 3–43 (1962)(Pol). Administration of high NaCl doses (3–4 g./kg.) caused acute intoxication in mice and pigs. NaCl poisoning was noted when Na^+ values in the brain and liver exceeded 150 mg. % and those of Cl^- 180 mg. % in brain, 70 mg. % in muscles, and 250 mg. % in liver. The loss of water in brain, muscles, and liver amounted in mice to 3.8, 7.5, and 9.2%, resp. In pigs this decrease in brain, muscles, and in liver amounted to 4.5, 9.2, and 8.7%. K. Belzecka

Toxicity of the oleander leaves. Symptoms, pathological anatomical damages, and methods of glucoside identification. C. E. Eliakis, E. C. Eliakis, and A. S. Coutselinis. *Ann. Med. Legale Criminol., Police Sci. Toxicol.* 41(July-Aug.), 367–88(1961)(Fr). Decoctions (10:150) of oleander leaves, contg. 3×10^{-4} g. of neriin and 4.5×10^{-4} g. of oleandrin, were used. R_f values of 0.65–0.70 for neriin and 0.96 for deendrin were found by means of paper chromatography (Whatman No. 1, ascending, undimensional, 3:1:3 EtOAc–HOAc–H_2O). With the same method, very similar values were found for digitoxin, lanatoside, and other glucosides. No abortive effect could be detected on pregnant rats. Twenty ml. of decoction (concd. to 1/4) resulted in the appearance of toxic symptoms in rats after 20–60 min. The oleander components seem to affect the central nervous system, esp. parts related to the telencephalon and cerebellum, the symptoms resembling those of decerebration paralysis, according to Sherrington, also displaying tendency to total or partial disintegration of cerebellum. In rats, which received 3 ml. of decoction intraperitoneally 9 times every other day, congestion of the parenchymatosic organs took place. Damage to kidneys, liver, heart, and peribronchial inflammatory congestion and atelectasis of the lungs was detd. microscopically. From *CZ* 1963(24), 10175. MWCR

Use of the chicken embryo in the assay of aflatoxin toxicity. M. Jacqueline Verrett, Jean Pierre Marliac, and Joseph McLaughlin Jr. (Food & Drug Admin., Washington, D.C.). *J. Assoc. Offic. Agr. Chemists* 47(6), 1003–6(1964). Preliminary results of an investigation of the general systemic toxicity of aflatoxin (I) in chicken embryos are reported. The studies are not complete enough to verify if any I produces any specific pathol. lesion in the embryo. Injections of test solns., in propylene glycol vehicle, were made, before incubation, in fertile White Leghorn eggs either by way of the yolk or air cell. Development of the embryo was observed for the full 21-day incubation. Injection of solns. of pure I B_1 and G_1, and of exts. of I-producing mold cultures indicated that the chicken embryo was sensitive to these compds. The relation of toxicity of the samples to mortality at time of hatching, exhibited a dose response. Exts. of I-free peanut products were nontoxic to the embryo. Addn. of I B_1 to such uncontaminated exts. produced the expected toxicity. Injection of exts. from contaminated peanut products resulted in a toxic response that correlated well with that obtained by injection of pure I B_1 solns. at same dose levels, and in most instances the chem. analysis was confirmed. The presence of I G_1, B_2, and G_2 had no apparent effect on the toxicity due to I B_1 at the levels at which they occurred in the particular samples tested. Sepn. of I B_1 from contaminated exts. by thin-layer chromatography, and its subsequent elution from the plates and injection into the eggs, confirmed that the toxicity of these exts. was due primarily to their I B_1 content.
H. A. Lepper

Electrophoretic and chemical studies on serums of swine following the feeding of toxic peanut meal. E. Annau, A. H. Corner, E. E. Magwood, and K. Jericho (Animal Diseases Res. Inst., Hull). *Can. J. Comp. Med. Vet. Sci.* 28(11), 264–8(1964)(Eng). The consumption of toxic peanut meal by swine leads to marked alterations in their electrophoretic serum patterns. Expts. carried out by chem. assays, moving boundary electrophoresis, and starch-gel electrophoresis showed a relative decrease in the albumin, α_1-, α_2-, and β-globulins, while γ-globulin appeared to be considerably increased. Rudolph Seiden

Goitrogenic activity of allyl isothiocyanate. A widespread natural mustard oil. Pavel Langer and Viktor Stole (Czechoslov. Akad. Ved., Bratislava). *Endocrinology* 76(1), 151–5(1965)(Eng). Allyl isothiocyanate, administered in single doses of 2 to 4 mg. depressed significantly the radioiodine uptake by rat thyroids. The administration of allyl isothiocyanate to rats for 60 days, in doses corresponding approx. to the total content of mustard oils in cabbage, caused changes in the thyroid similar to those following cabbage feeding. RCFN

The physiological properties of aerosol propellants. Hans Kuebler (Spraytechnik G.m.b.H., Remscheid, Ger.). *Aerosol Age* 9(4), 44, 47–8, 50, 90–1(1964)(Eng). A discussion of the physiol. limits for many aerosol propellants was presented. Rats, mice, and guinea pigs were exposed for 2 hrs. daily for 100 days to 0.5, 1.5, and 5.0% vol. of the propellants, vinyl chloride (I), and mixts. of trichlorofluoromethane (II) and dichlorodifluoromethane (III) (50:50 and 10:90). The animals showed no reactions to the mixts. at any concn. or with pure I to 1.5%. With 5% I the animals first showed increased mobility which was then gradually reduced. Upon autopsy no histol. damage was seen. Mice under a plastic cover were sprayed with a shellac-based hairspray with I, II, and III propellants for 30 sec. daily for 5 weeks at a distance of 20–25 cm. There were no histol. changes in the lungs. The thermal decompn. was detd. at 1000°. One g. I yielded 39.5 mg. CO, 11 mg. $COCl_2$, and 102 mg. HCl; 1 g. II (1.5, 7.0, and 94); 1 g. III (1.5, 2.4, 79); 1 g. sym. dichlorotetrafluoroethane (0.8, 12.0, 59); and 1 g. methylene chloride (15.2, 18.0, 81). BKJN

Concentration on molecular sieves as preliminary determination of trace components of mine air. Jerzy Mazyczuk (Glowny Inst. Gornictwa, Katowice, Poland). *Chem. Anal.* (Warsaw) 9(4), 671–82(1964). Trace components of mine air, such as C_3H_8, C_2H_6, and n-C_4H_{10}, were concd. on a mol. sieve of 5 A. type at 0° and 30° and retention times were measured. Products of desorption at 300° were analyzed in a gas chromatograph with a conductometric detector. In some cases addnl. concn. was used. The method makes it possible to increase the sensitivity of the detn. of C_3H_8, C_2H_6, and C_3H_8 10–100 times. The results of the detn. of traces of gases in a sample of mine air are given. The effect of concn. can be estd. from the retention vols.
Z. Kurtyka

Permeability of newborn rat skin to a volatile hydrocarbon, ^{14}C-labeled p-cymene. Guillaume Valette, Yves Cohen, and Jacques Wepierre (Fac. Pharm., Paris). *Compt. Rend. Soc. Biol.* 158(5), 950–4(1964)(Fr). The compd. readily diffused through the hairless skin and was detected in various organs. A special app. was used to prevent any inhalation of the vapor which might invalidate the findings. Since the hair follicles had not yet been formed, they are not indispensible for penetration of a volatile hydrocarbon. L. E. Gilson

Flue gas from plants manufacturing synthetic fatty acids and alcohols. F. I. Dubrovskaya (F. F. Erisman Sci.-Res. Inst. Hyg., Moscow). *Gigiena i Sanit.* 26(1), 7–10(1901)(Russ). Results are reported on the investigation of 1252 air samples (580 in March/April and 672 in June/July) collected 250–5000 m. from factories manufg. fatty acids and fatty alcs. In all samples in the spring, hydrocarbons (max. 56 mg./m.^{3}) were detected; fatty acids, in 54% of the samples (same max.); and unsatd. hydrocarbons, in half the samples (max. 13 mg./m.^{3}). In the summer, 70% of the samples contained hydrocarbons (max. 63–90 mg./m.^{3}), 52% contained fatty acids, and 56% contained unsatd. hydrocarbons. Acetone and formaldehyde were found in only a few samples. From *CZ* 1962(47), 17163. MRCR

Maximum permissible concentration of chloroprene in the atmosphere. A. V. Mnatsakanyan (N. B. Akopyan Inst. Epidemiol. and Hyg., Erevan). *Gigiena i Sanit.* 29(9), 13–18 (1964)(Russ). A concn. of 0.22 mg. chloroprene/m.^{3} was the threshold concn. for decreasing the sulfhydryl concn. in brain homogenates and increasing adenosinetriphosphatase activity in the livers of rats exposed constantly for 60 days; 0.08 mg./m.^{3} is considered a proper max. John Howe Scott

Effect of dichlorobutene on the olfactory organs and ocular analysors. G. V. Deroyan (Med. Inst., Erevan). *Izv. Akad. Nauk Arm. SSR, Biol. Nauki* 17(7), 101–4(1964)(Russ). The threshold concn. for a dichlorobutane (I) effect on the olfactory analysors was investigated with 15 patients and was equal to 0.34 mg./m.^{3} Effect of I on the visual center was examd. on 3 patients. The results indicated that in some cases 0.34 mg./m.^{3} of I produced harmful effects on dark adaptation. A concn. of 0.34 mg./m.^{3} of I in air was considered harmful.
M. Charmandarian

Effects of inorganic fluorides on animals. J. W. Suttie (Univ. of Wisconsin, Madison). *J. Air Pollution Control Assoc.* 14(11), 461–4, 480(1964)(Eng). F^- toxicity in cattle can result from the ingestion of forage contaminated by industrial processes. Cattle are affected when F^- levels in the compact bone exceed 5500 ppm. Marginal toxic effects are noted in animals with F^- concns. in these bones of 4500–5500 ppm. The concn. of F^- in forage that can produce these concns. in the skeleton depends on a no. of factors. Air quality standards based on atm. F^- levels are not feasible for most grazing [illegible]