

the fluoroborate (Et_3N , CH_2Cl_2) as a red liq. With $\text{MeO}_2\text{CC:CCO}_2\text{Me}$ in refluxing xylene, 8-cyanoheptafulvene gave di-Me 1-cyanoazulene-2,3-dicarboxylate, m. 175–6°. CNJN

12771f Aromatic hydrocarbons. Akhmetov, I. G.; et al. U.S.S.R. 213,775 (Cl. C 07c), 12 Feb 1969, Appl. 24 Feb 1967; From *Okrytiya, Izobret., Prom. Obyazys, Tovarnye Znaki* 1969, 46(8), 175. The title compds. are prep'd by hydrogenating pyrolysis resins at 450–950° and at an H pressure of 1–20 atm.

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12772g Purification of products obtained in the ethylation of benzene. Kubica, Jan; Pajak, Maksymilian; Nowinska, Elzbieta; Koszelnik, Stanislaw (Politechnika Wroclawska) Pol. 56,159 (Cl. C 07c), 25 Oct 1968, Appl. 20 Oct 1966; 3 pp. The known method of purification of the title products has been improved. According to the modification the reaction mixt. was fed from the bottom into a column composed of two sections: the bottom section contg. H_2O and the upper section, filled with Raschig rings, contg. 5% NaOH. The modification makes it possible to reduce costs and to simplify the purification process. A block diagram of the system is given. Karol Butkiewicz

12773h Hydrogenation of aromatic compounds by using fluobided alumina catalysts. White, Robert J.; Houston, Robert J. (Chevron Research Co.) U.S. 3,435,085 (Cl. 260–667, C 07c), 25 Mar 1969, Appl. 25 Sep 1967; 2 pp. Aromatics can be hydrogenated in the presence of sulfur over a catalyst contg. a Group VIII hydrogenation metal, preferably Pt, on a non-siliceous alumina support contg. 10–35% F. This catalyst retains a degree of activity in the presence of up to 3% S. The catalyst can be prep'd. by passing a gaseous mixt. of H and HF over the support to which the desired amt. of metal has previously been added. It can also be prep'd. by contacting the support with a soln. of NH_4F , but this catalyst is not as active. Hydrogenation of C_6H_6 contg. 1% S at 725°F. with an alumina catalyst contg. 0.37 wt. % Pt, and 0.5 wt. % F gave a conversion of C_6H_6 of 8 mole %. Hydrogenation of the same feed over a catalyst contg. 0.37% Pt and 17% F gave a conversion of C_6H_6 of 78 mole %. These reactions are conducted at 650°–900°F., 100–4000 psi., a linear hourly space velocity of 0.2–10 and a ratio of H to hydrocarbon of 1:1–20:1. D. E. O'Connor

12774j p-Xylene purification. Antar Petroles de l'Atlantique Fr. 1,526,882 (Cl. C 07c), 31 May 1968, Appl. 12 Sep 1966; 2 pp. p-Xylene of initial purity of 95–8.5% is treated with 0.1–0.3 of its weight of 30% CaCl_2 . Rapid treatment of the crystals in a centrifuge at 20° gives a purity of 99.5% p-xylene.

J. B. Normington

12775k p-Xylenes. Capitano, Peter J.; Angelkorte, Johannes W. (Union Carbide Corp.) U.S. 3,440,295 (Cl. 260–668; C 07c), 22 Apr 1969, Appl. 27 Dec 1966; 4 pp. The efficiency of pyrolysis of p-xylene to yield p-xylenes is approx. doubled by the addn. of radical-forming compds. to scavenge the H. For example, a mixt. of distd. water 4000, AcOH 5.5, and p-xylene 100 g. vapors was fed during 4 hrs. into a pyrolysis tube at 900° and atm. pressure at a rate to give a contact time of 0.050 sec. in the pyrolysis zone to give di-p-xylene 7.40, m. 283–5°, and poly(p-xylene) 7.70 g. (15.10% total yield). A similar pyrolysis of p-xylene with water in the absence of AcOH gave di-p-xylene 2.60 and poly(p-xylene) 5.60 g. (7.70% total yield). Alvin D. Delman

12776m Alkylation of aromatics using a halogen-containing aluminosilicate-alumina catalyst. Mitsche, Roy T. (Universal Oil Products Co.) U.S. 3,436,432 (Cl. 260–671; C 07c), 01 Apr 1969, Appl. 27 Jun 1966–29 Mar 1968; 4 pp. Alkylation of aromatic hydrocarbons was carried out using as catalyst a halogen-contg. suspension of cryst. aluminosilicate in an alumina matrix. Thus, Al (99.99% pure) was digested in HCl to produce a sol of wt. ratio Al-Cl ~1.15 and sp. gr. 1.3450. An aq. soln. (700 ml.) contg. 28% hexamethylenetetramine was mixed with 700 ml. of the sol soln., 10 g. of the H form of synthetic mordenite (11.6% Al_2O_3 , 87.7% SiO_2 and 0.2% Na; particle size, 57.6%, 0–20 μ) was dispersed in the sol. The resulting sol was added to a forming oil at 95° to form particles of 1/16 in. diam.; the particles were aged overnight in oil and then 3 hrs. in an ammonia soln. at 95°, partially washed with H_2O , dried, and calcined 4 hrs. at 600° to give 350 ml. catalyst, which was treated with 250 ml. soln. contg. 8.4 ml. concd. HCl, the water evapd., and the catalyst was then oxidized in the presence of HCl vapor to yield a material contg. 0.75% Cl and 5% mordenite. Using this catalyst at 500 psig. and 150°, the alkylation of benzene with ethylene was carried out in substantially complete conversion to give primarily ethylbenzene and diethylbenzene.

D. E. O'Connor

12777n Diethylbenzene. Mamedov, A. A.; Pinoker, A. E.; Teslenko, E. P.; Khodos, T. K. (State Scientific-Research and Design Institute of the Nitrogen Industry, Dnepropetrovsk) U.S.S.R. 237,133 (Cl. C 07c), 12 Feb 1969, Appl. 15 Jan 1968; From *Okrytiya, Izobret., Prom. Obyazys, Tovarnye Znaki* 1969, 46(8), 18. Diethylbenzene is prep'd. by disproportionation of EtPh during heating in the presence of AlCl_3 , 1,1-Diphenyl-

ethane, or its homologs, is added as 5 wt. % of the AlCl_3 to aid catalytic action.

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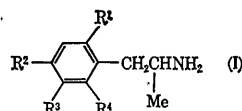
12778p Alkylated aromatic hydrocarbons. Takeda, Yoshiyuki (Mitsubishi Chemical Industries Co., Ltd.) Japan. 69 06,807 (Cl. 16 C 1), 25 Mar 1969, Appl. 21 Dec 1966; 5 pp. By using a liq. catalyst prep'd. from org. aluminum compds., $\text{R}_n\text{Al-X}_{3-n}$ (where R is alkyl, aryl, or arylalkyl having C_{1-12} , X is halogen, and n is 0.5–3, and TiX_3), the title compds. are prep'd. by reaction of an aromatic hydrocarbon, which has at least one H able to be substituted with alkyl, with an olefin in hydrocarbon solvent. Thus, a mixt. of 25.0 g. sesquithialuminum chloride and 76.4 g. TiCl_4 in 750 ml. benzene was mixed well and kept at room temp. 1 hr. under argon atm., then filtered. The filtrate was made up to 1300 g. with benzene and charged in an autoclave. Ethylene was introduced into the autoclave up to 2.3–2.5 kg./ cm^2 and the reaction was carried out 4 hrs. at 50–5° with shaking (500–600 rpm.). After reaction, the catalyst was decomp'd. with addn. of 1000 g. MeOH. The oily product (2916 g.) was washed three times with 500 cc. of 3N HCl, three times with 500 cc. of 3N NaOH, three times with H_2O , then distd. to give 850 g. at 80°/760 mm. to 203°/2 mm. and 110 g. high boiling residue. Rectification of the distillate gave 32.3 g. C_2 side chain, 66.7 g. C_4 , 99.8 g. C_6 , 127.5 g. C_8 , 142.8 g. C_{10} , 145.4 g. C_{12} , 120.8 g. C_{14} , and 78.7 g. C_{16} . Y. Tsuji

12779q Dehydrogenation catalyst. Bogdanova, O. K.; Belomestnykh, I. P.; Voikina, N. V.; Kuznetsova, M. S.; Torsunova, N. T. (Zelinskii, N. D., Institute of Organic Chemistry) U.S.S.R. 237,114 (Cl. B 01j), 12 Feb 1969, Appl. 05 Nov 1967; From *Okrytiya, Izobret., Prom. Obyazys, Tovarnye Znaki* 1969, 46(8), 15. The title catalyst for prep'g. styrene by oxidative dehydrogenation of EtPh is produced from compds. of Mo, Co or Fe with an MgO or Al_2O_3 carrier. The carrier is satd. with an aq. Mo, Co, or Fe salt soln., with subsequent drying and air treatment at 500–550°.

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12780h Aminated benzenes. Barker, Robert S. (Halcon International, Inc.) U.S. 3,442,950 (Cl. 260–576; C 07c), 06 May 1969, Appl. 08 Jun 1962–16 Feb 1967; 2 pp. The title compds. were prep'd. by the catalytic reaction of cyclohexanol (I) and cyclohexanone (II) with an aminating agent in the presence of an initially added quantity of H. A Pt-C catalyst was soaked in excess 0.1N NaOH, washed until the pH of the washings was ~7.5, placed in the reactor, and treated from 150 to 300° with a slow stream of H. A mixt. contg. NH_3 , H, I, and II in molar ratio of 16:1:1:0.2 was passed over the catalyst at 315° and 12 psig. at liq. hourly space velocity 0.5 to give a I-II conversion of 100%. The effluent after the removal of H_2O contained 89% PhNH_2 , 5% cyclohexylamine, 5% C_6H_6 , and 1% high boilers. MeNH_2 , H and I in the mole ratio of 5:5:1 passed over Pd-SiO₂ catalyst at 330° gave 70% PhNHMe . The process is diagrammatically described. Sister Miriam Grace Solomon

12781j Substituted α -methyl- β -phenylethylamines as central nervous system stimulants. Shulgin, Alexander T. (Dow Chemical Co.) Brit. 1,147,739 (Cl. C 07c), 02 Apr 1969, US Appl. 29 Dec 1966; 8 pp. The title compds. of formula I have stimulant properties and are prep'd. by redn. of the corresponding 2-nitropropenes with LiAlH_4 . A soln. of 50 g. 1-(4-ethyl-2,5-dimethoxyphenyl)-2-nitropropene in 50 ml. Et_2O was



added dropwise over 3 hrs. to a refluxing suspension of 20 g. LiAlH_4 in 1.5 l. Et_2O , and the mixt. refluxed overnight, and worked up to give I ($\text{R}^1 = \text{R}^3 = \text{MeO}$, $\text{R}^2 = \text{Et}$, $\text{R}^4 = \text{H}$). HCl (III), m. 195° (AcOEt), base m. 61–1.5°. The following I were similarly prep'd. (R^1 , R^2 , R^3 , R^4 , salt, and m.p. salt given): MeO , Me_2C , MeO , H, HCl, 168°; MeO , Me, MeO , H, base, 60.5–61°; EtO , Me, EtO , H, HCl, 161–2°; MeO , C_6H_{13} , MeO , H, —; EtO , Me, H, MeO , HCl, 186–7.5°; MeO , Me, H, MeO , HCl, 193–5°; MeO , Et, MeO , H, acid sulfate, —; EtO , Me, MeO , H, citrate, —; MeO , Pr, MeO , H, HCl, 182.5–83°; BuO , C_6H_{13} , BuO , H, acetate, —; BuO , Bu, H, BuO, —; and MeO , Me, MeO , H, acetate, —. III at 0.05 mg./kg. showed strong CNS stimulation in rabbits. P. Mamalis

12782k Benzotrichloride from toluene. Israel Mining Industries-Institute for Research and Development Israeli 24,329 (Cl. C 07c), 27 Mar 1969, Appl. 16 Sep 1965; 13 pp. Toluene (640 ml.) was boiled and Cl gas passed in as the mixt. was irradiated with a 25 w. Hg-vapor lamp. After 18 hrs. the mixt. had turned dark, so a 2nd 175 w. Hg lamp was directed at the adaptor where the reflux occurred, and the temp. maintained 8 hrs. at 185° and 8 hrs. at 200°; the products b. <145°/3 mm. were distd. to give 4.5% PhCH_2Cl and 79.2% PhCHCl_2 . No PhCCl_3 was obtained. When the distillate was refluxed in a stream of Cl, irradiated with a 175 w. Hg lamp, and 0.1% tetramethylthiuram disulfide (I) added to the mixt., it was found to contain after distn. 88% PhCCl_3 . Similarly, PhCH_2Cl was converted into PhCCl_3 by the addn. of I and treatment as above.