Addition of the silver salt of (−)-*trans*-cyclobutane-1,2-dicarboxylic acid[4] having $[\alpha]^{25}_{D}$ −83.4° (water) (about 46% racemic) to the theoretical amount of bromine in refluxing carbon tetrachloride[2] gave as 32% of the neutral product *trans*-1,2-dibromocyclobutane, distilled through a semimicro column at 20 mm. with a pot temperature of 120°. The purest fraction contained 4% (by vapor chromatographic analysis) of a higher boiling, unsaturated, unidentified contaminant, and had $[\alpha]^{27}_{D}-6.0°$ (carbon tetrachloride), m.p. −38 to −22°, and n^{25}_{D} 1.5358. *Anal.* Calcd. for $C_4H_6Br_2$: C, 22.46; H, 2.83. Found: C, 22.74; H, 2.87. (Buchman[2] had shown that the dibromide product from racemic *trans*-dicarboxylate was identical with that from addition of bromine to cyclobutene, and reported for the dibromide b.p. 72–4°/20mm., n^{25}_{D} 1.5343, m.p. −1° to +1°.) It was shown that the unknown contaminant was not responsible for the optical activity of the dibromide, since a higher boiling fraction of the reaction product (5 mm., pot temp. 150°) contained about 55% of the unknown and yet possessed $[\alpha]^{27}_{D}$ −3.3° (carbon tetrachloride).

It may be concluded that the reaction does not proceed entirely, if at all, through symmetrical intermediates such as II or IV, if we assume that neither asymmetric addition of bromine atoms to these intermediates nor asymmetric destruction of racemic dibromide in the reaction mixture occurs. These reasonable assumptions will be checked by further experiments, which should also reveal the optical yield and stereochemistry (double retention or double inversion) of the reaction.

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Ortho Alkylation of Aniline with Styrene

Sir:

Recent publications[1,2] on the *ortho* alkylation of aromatic amines in the presence of aluminum anilide type catalysts prompt us to report some unusual results which were obtained during a reinvestigation of the Hofmann-Martius[3] and Reilly-Hickinbottom[4] rearrangements. Hickinbottom[5] discovered that a mixture of aniline and its hydrochloride reacted with styrene at 200–240° (sealed tube) in 6 hr. to give a 28.4% yield of α-phenethylated anilines, 7.5% *ortho*, 17.7% *para* and 3.2% N, by isolation. Under what presumably were identical conditions, we consistently obtained an 82–85% yield of monoalkylated aniline which promptly crystallized to give a 74–77% isolated yield of *ortho-α-phenethylaniline*, m.p. and mixed m.p. 58.5–59.0°. Infrared analysis showed only 5–10% of the *para* isomer in the crude product; *N*-α-phenethylaniline was apparent (infrared) after 1 but not 6 hr. Aniline and α-phenethyl chloride gave similar, but not identical results; no alkylation of aniline by styrene was observed without the hydrochloride being present. But *N*-α-phenethylanilinium chloride, under essentially identical conditions, gave only 19–24% of mono-C-alkylate, 60–70% the *para* isomer.

We have no explanation at present for the discrepancy between our results and those of Hickinbottom. Complete details, and a rationalization of the different isomer distributions obtained by direct alkylation and by rearrangement of the anilinium salt, will be published shortly. The scope of this *ortho* alkylation is being investigated further.

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Synthesis of 2-Heptafluorobutyrylthiophene

Sir:

The preparation of 2-heptafluorobutyrylthiophene has been accomplished by the Grignard method after previous failures using other synthetic techniques. Although aliphatic acids have been successfully condensed with thiophene using P_2O_5 as the condensation agent,[1,2] the use of a totally fluorinated acid such as heptafluorobutyric acid resulted only in its conversion to the acid anhydride by the condensation agent. The use of the anhydride was also unsuccessful. It has also been found that the acylation of thiophene with organic

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acid anhydrides may be effected by the use of catalytic amounts of substances such as iodine or hydriodic acid,[3] zinc chloride,[4] phosphorus pentoxide,[5] and stannic chloride or BF_3-etherate.[6] As in the previous case, the use of a fluorinated anhydride, such as heptafluorobutyric anhydride, in the acylation reaction with the above catalysts, gave no product or produced only tars. Similar results were encountered by a Friedel-Crafts type reaction in the presence of aluminum chloride.[7] This reaction was carried out at low temperature using the acid chloride as the acylating agent without the use of solvent and also in the presence of nitrobenzene.

We now wish to describe the synthesis of 2-heptafluorobutyrylthiophene which may be generally applicable to condensation reactions involving a fluoro-alkyl group and a cyclic-type compound. Thiophene magnesium bromide was first prepared from 2-bromothiophene and magnesium by the standard Grignard method. The volatile heptafluorobutyryl chloride was then prepared by the slow addition of heptafluorobutyric acid to phosphorus pentachloride using a Dry Ice–alcohol trap. The Grignard was added slowly to a mixture of the acid chloride and ether over a period of 90 min. and then refluxed for several hours. The contents were added to a 10% ice–NH_4Cl solution. The separated ether layer was neutralized with 10% K_2CO_3 and finally dried over anhydrous sodium sulfate. Distillation gave a 32% yield of ketone, b.p. 91.5–92.1° at 32 mm.

Anal. Calcd. for $C_8H_3OF_7S$: C, 34.29; H, 1.08; F, 47.47. Found: C, 34.13; H, 1.25; F, 46.85.

The compound was characterized by the 2,4-dinitrophenylhydrazone, m.p. 90.2–90.8°.

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