and 1130 cm^{-1} characteristic of the SO_2 chromophore and a strong band at 745 cm^{-1} in the spectrum of the pure liquid), and its elemental analysis.

Anal. Calcd: C, 19.1; H, 4.8; S, 50.8; O, 25.4. Found: C, 19.1; H, 5.0; S, 50.8; O, 25.2 (direct).

Reaction of Methyl Methanethiolsulfinate with *n*-Pentyl Methanesulfenate.—A solution of 0.50 g (0.0037 mole) of *n*-pentyl methanesulfenate in 5 ml of methylene chloride was cooled to −10° and a solution of 0.41 g (0.0037 mole) of methyl methanethiolsulfinate in 5 ml of methylene chloride was added dropwise with cooling to maintain the reaction temperature at −10°. After the reaction was allowed to stir for 10 min at 0°, a sample of the reaction solution was injected directly into the gas chromatograph. A small amount of sulfenate remained, but dimethyl disulfide and *n*-pentyl methanesulfinate (identified by comparison of their retention times with those of authentic samples) were the major products present. After 0.5 hr, no sulfenate ester could be detected in the reaction mixture.

Oxidations of Methanesulfenate Esters.—To a solution of 1.34 g (0.01 mole) of *n*-pentyl methanesulfenate in 5 ml of methanol was added dropwise 1.05 g (0.0067 mole) of potassium permanganate dissolved in 10 ml of methanol. A brown precipitate, presumably manganese dioxide, formed during the course of the addition. The solution was filtered and a sample was injected into the gas chromatograph. *n*-Pentyl methanesulfinate, identified by comparison of its retention time with that of an authentic sample, was the only volatile product other than methanol in the reaction mixture.

Approximately 1% solutions in methanol of potassium permanganate, sodium dichromate, iodine, and selenium dioxide were prepared and added dropwise to approximately 10% solutions of the three sulfenate esters in methanol. All three esters behaved in a similar manner toward each of the reagents tested. Potassium permanganate gave very rapid decoloration with concomitant manganese dioxide formation. Sodium dichromate solution remained yellow until 1 drop of acetic or hydrochloric acid was added, whereupon the solution turned the pale green color characteristic of chromic ion. The selenium dioxide solutions slowly turned red-orange and deposited a dark red-orange sludge characteristic of selenium. The iodine solutions gave no color change on addition to the ester solutions, even with 1 drop of hydrochloric acid. When a few drops of 5% potassium iodide in 50% acetic acid–water was added to the esters, followed by 1 drop of starch solution, a dark blue color formed in a few seconds, presumably indicating oxidation of iodide ion to iodine.

Acknowledgment.—The authors wish to acknowledge the excellent technical assistance of Messrs. J. F. Ward and H. Lorance.

The Synthesis of 4,6-Dihydrothieno[3,4-*b*]thiophene

D. W. H. MacDowell and Timothy B. Patrick

Department of Chemistry, West Virginia University, Morgantown, West Virginia

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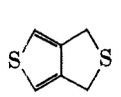
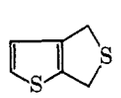
The synthesis of the title compound (II) along with several new 2,3-disubstituted thiophenes is described. Nuclear magnetic resonance and ultraviolet spectra of II are discussed with respect to possible ring strain in the thiophene nucleus.

The synthesis of a thiophene derivative exhibiting a possible ring-strain or Mills–Nixon-type effect has been described by Wynberg and Zwanenburg.[1]

In this work, which reported an elegant synthesis of 1H,3H-thieno[3,4-*c*]thiophene (I), it was claimed that the system containing a five-membered ring fused (3,4) to the thiophene ring exhibited slightly diminished aromatic properties. This was postulated to result possibly from the strain involved in having the two five-membered rings fused together and attention was directed to the desirability of an investigation of compound II. Recently Wynberg and co-workers[2] have synthesized compounds II and IX. The synthesis of II and IX by a different method is reported below.



I



II

Metallation of 3-thiophene aldehyde ethylene acetal[3] (III) followed by formylation with N,N-dimethylformamide gave a 74% yield of 2-formyl-3-thiophene aldehyde ethylene acetal (IV). Hydrolysis of IV with dilute hydrochloric acid furnished 2,3-thiophenedicarboxaldehyde (V) in 80% yield. This compound, prepared independently by us, has also been reported recently by two groups of French workers.[4,5] Conversion of V to VII by way of VI was carried out as indicated in Scheme I. The title compound, 4,6-dihydrothieno[3,4-*b*]thiophene (II), a colorless liquid, bp 70.5–71° (0.7 mm), was prepared in 27% yield by treating VII with sodium sulfide nonahydrate in dimethylformamide solution. The liquid decomposed on standing at room temperature for 1 day, but could be kept with a minimum of decomposition at −5° for several days. Attempts to prepare this compound in methanol solution by the methods of Wynberg and Zwanenburg[1] or Cava[6] gave low yields of mixtures of II and 2,3-bis(methoxymethyl)thiophene (VIII) as evidenced by infrared spectra. The dimethoxy compound (VIII) is readily produced by heating the dibromide (VII) in methanol solution. The 2,3-bis(bromomethyl)thiophene (VII) was treated with the sodium salt of ethyl mercaptan to yield 2,3-bis[(ethylthio)methyl]thiophene (IX) in 67% yield. This compound served as a model compound with which to compare the spectral properties of II.

Discussion

Wynberg and Zwanenburg[1] demonstrated that, on comparison of I with the model (X, Table I) using nmr spectroscopy, the thiophene 2-hydrogen atom was shifted to a higher field while the ultraviolet maximum absorption at 246 mμ was shifted to shorter wavelength. These effects were stated to possibly arise from a small perturbation of the π-orbital delocalization in the thiophene ring.

(1) H. Wynberg and D. J. Zwanenburg, *J. Org. Chem.*, **29**, 1919 (1964).
(2) D. J. Zwanenburg, H. de Haan, and H. Wynberg, *ibid.*, **31**, 3363 (1966).
(3) S. Gronowitz, *Arkiv Kemi*, **20**, 407 (1963).
(4) M. Robba, R. C. Moreau, and B. Roques, *Compt. Rend.*, **259**, 3568 (1964).
(5) P. Pastour, P. Savalle, and P. Eymery, *ibid.*, **260**, 6130 (1965).
(6) M. P. Cava and A. A. Deana, *J. Am. Chem. Soc.*, **81**, 4266 (1959).

SCHEME I

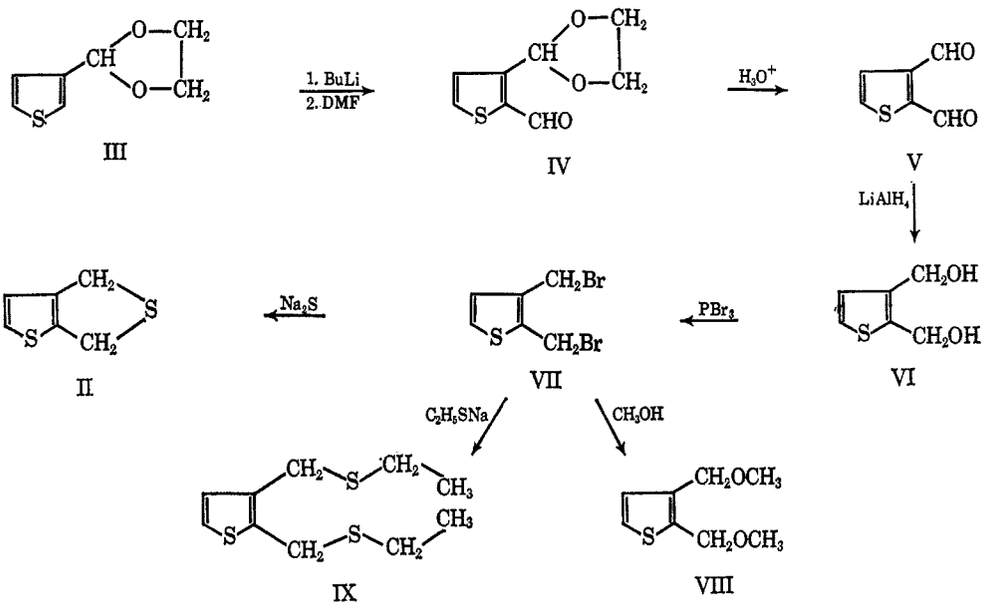
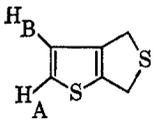
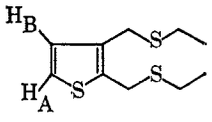
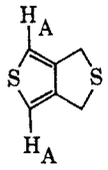
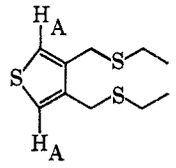


TABLE I

SPECTRAL DATA

Compd	Solvent	Chemical shift, τ				$\lambda_{max}^{95\% EtOH}$, mμ (ε)
	$(CD_3)_2CO$[a]	2.52	2.60	3.14	3.22 (J = 5 cps)	233 (5200)[a]
	CCl_4[a]	2.74	2.82	3.27	3.35 (J = 5 cps)	
	CCl_4[b]	2.83	2.92	3.36	3.44 (J = 5 cps)	233 (4200)[b]
		doublet		doublet		
	$(CD_3)_2CO$[a]	2.69	2.78	2.96	3.04 (J = 5 cps)	242.5 (8200)[a]
	CCl_4[a]	2.93	3.00	3.09	3.17 (J = 5 cps)	
	CCl_4[b]	2.95	3.02	3.10	3.18 (J = 5 cps)	240.5 (8300)[b]
	$(CH_3)_2CO$[c]	3.02 (singlet)				232 (6100)[c]
	CCl_4[c]	2.75 (singlet)				246 (5600)[c]

[a] This manuscript. [b] Reference 2. [c] Reference 1.

Wynberg and co-workers[2] have recently prepared compounds II and IX and compared their nmr and ultraviolet spectra. Their results together with those obtained in the present paper are contained in Table I.

In our comparison of the nmr spectra of II and IX in two solvents, we have found that the 2-hydrogen atom in II is shifted downfield by 0.19 ppm while the 3-hydrogen atom in II is shifted upfield by 0.18 ppm. The direction of these shifts parallels that found by Wynberg[2] for these compounds. It is difficult to rationalize these shifts on the basis of decreased π-orbital overlap. Abraham and Thomas[7] have recently presented evidence that the ring current in aromatic molecules is not directly related to the resonance energy and that the ring current should only be used to detect aromaticity and not differences in aromaticity. Since the changes in our nmr spectra are small, it is concluded that the changes cannot be adequately explained as being a result of diminished ring current owing to ring strain.

The ultraviolet spectra of I and II when compared with their respective models, show a hypsochromic shift of comparable magnitude in the direction of a diene chromophore. If this change is a result of ring strain then it can be concluded that the amount of ring strain is essentially the same in I and II and that the presence of a double bond common to both rings has not caused any significant difference between I and II.

(7) R. J. Abraham and W. A. Thomas, *J. Chem. Soc.*, B 127 (1966).

Experimental Section

All temperature readings are uncorrected. All elemental analyses were performed by Galbraith Laboratories, Knoxville, Tenn. Nmr spectra were recorded on a Varian HA-60 using tetra-

methylsilane as an internal standard and solvents as specified. The ultraviolet spectra were determined in 95% ethanol on a Bausch and Lomb Spectronic 505 and a Beckman DU spectrophotometer. The infrared spectra were recorded on the Perkin-Elmer Model 21, Perkin-Elmer Model 137, and Perkin-Elmer Model 137 G spectrophotometers.

3-Thiophenealdehyde Ethylene Acetal (III).—The compound was prepared according to the method of Gronowitz[8] in 64% yield, bp 82–84° (1.4 mm) [lit.[3] bp 103–104° (10 mm)], $n^{25}D$ 1.5439. Infrared showed strongest absorptions at 1090 (CO) and 795 cm^{-1} (neat); $\lambda_{max}^{95\% EtOH}$ 236 mμ (ϵ 5860); nmr multiplet at τ 2.4–2.9 (aromatic), singlet at 4.05 (CH), and multiplet 5.95 (CH_2), area ratio, 3:1:4 ($CDCl_3$).

2-Formyl-3-Thiophenealdehyde Ethylene Acetal (IV).—To a stirred solution of 50 g (0.32 mole) of 3-thiophenealdehyde ethylene acetal and 200 ml of anhydrous ether under dry of nitrogen was added 260 ml of freshly prepared *n*-butyllithium (0.33 mole). The addition was carried out in such a manner as to effect a gentle reflux. The contents became cloudy upon addition of the first drop and gradually changed to an orange suspension. The reaction mixture was heated under reflux for 0.5 hr after which a solution of 50 g (0.69 mole) of N,N-dimethylformamide in 100 ml of anhydrous ether was added dropwise over a period of 0.75 hr. The addition of the dimethylformamide caused a thick precipitate to form, and the mixture was stirred vigorously for best results. After complete addition, the contents were stirred at room temperature for 1 hr and then allowed to stand for 16 hr. The entire contents were poured onto ice and allowed to come to room temperature. The organic layer was separated, and the water layer was saturated with sodium chloride and extracted thoroughly with ether. The ether extracts were combined, dried over magnesium sulfate, and concentrated under reduced pressure on a water bath. The residue was distilled under reduced pressure. The pale yellow product was collected at 140–143° (2 mm), 43 g (74%). An analytical sample distilled at 120–121° (0.1 mm); $n^{25}D$ 1.5720; infrared spectrum, strongest absorptions at 1660 (aldehyde (C=O), 1090, and 745 cm^{-1} (neat); $\lambda_{max}^{95\% EtOH}$ 247 mμ (ϵ 1450), 252.5 (3230), 253 (6430), 259 (10,150), 265 (11,900), 267 (12,850), and 291 (s) (6930); nmr ($CDCl_3$) singlet at τ −0.4 (aldehyde), doublets centered at 2.25 and 2.65 (J = 5 cps) (aromatic), and singlets at 3.70 (CH) and 5.55 (CH_2), area ratio 1:1:1:1:4.

Anal. Calcd for $C_8H_8O_3S$: C, 52.16; H, 4.73; S, 17.48. Found: C, 52.04; H, 4.60; S, 17.10.

2,3-Thiophenedicarboxaldehyde (V).—Hydrolysis of 30 g (0.165 mole) of 2-formyl-3-thiophenealdehyde ethylene acetal was carried out by shaking 3-ml portions of the acetal with 7-ml portions of 3 *N* hydrochloric acid at room temperature for 15 min. The solid 2,3-thiophenedicarboxaldehyde was separated by suction filtration. The solid product was washed with cold, dilute sodium bicarbonate solution until no effervescence occurred and was then washed with 10 ml of cold hexane. The resulting yellow solid was dried in air and crystallized from hexane to yield 20 g (88%) of long, white needles, mp 78–79°. An analytical sample was prepared by sublimation, mp 78–79°. The pyridazine derivative melted at 165–165.5° (lit.[8] mp 167°). Oxidation of a small portion of the dialdehyde with silver oxide furnished a nearly quantitative yield of 2,3-thiophenedicarboxylic acid, mp 271–272° dec (lit.[2] mp 271–272° dec), which showed no melting point depression upon admixture with an authentic sample of 2,3-thiophenedicarboxylic acid. Infrared spectrum showed strongest absorptions at 1675 1650 (aldehyde C=O) and 750 cm^{-1} (Nujol); $\lambda_{max}^{95\% EtOH}$ 225 mμ (ϵ 4100), 269 mμ (10,500); nmr ($CDCl_3$) singlets at τ −0.55 and −0.45 (aldehyde), and a multiplet centered at 2.12 (aromatic), area ratio 1:1:2.

Anal. Calcd for $C_6H_4O_2S$: C, 51.41; H, 2.85; S, 22.88. Found: C, 51.29; H, 2.99; S, 22.97.

2,3-Bis(hydroxymethyl)thiophene (VI).—A solution of 5 g (0.035 mole) of 2,3-thiophenedicarboxaldehyde in 100 ml of anhydrous ether was added dropwise at room temperature and at such a rate as to produce a gentle reflux to a suspension of 5 g of powdered lithium aluminum hydride in 100 ml of anhydrous ether contained in a 1-l., three-necked flask. After complete addition, the contents were stirred at room temperature for 12 hr. Twenty milliters of water was then added carefully to the ice-cold reaction mixture, followed by the addition of 20 g of solid ammonium chloride. The contents were made faintly acidic to litmus with 2 *N* sulfuric acid. The gray mixture was then extracted continuously with ether for 12 hr. The ether extract was dried over magnesium sulfate, filtered, and concentrated under reduced pressure on a water bath. To the pink residue obtained upon removal of the ether was added approximately 0.1 g of anhydrous potassium carbonate and the mixture was distilled under reduced pressure. During initial attempts to prepare this alcohol it was found that traces of acid in the product prior to distillation caused extensive decomposition. A colorless, opaque, viscous liquid was collected at 133.5–134.5° (0.25 mm). The product weighed 4.4 g (85%), $n^{24}D$ 1.5793. The liquid did not solidify at −70°. Infrared spectrum showed strongest absorptions at 3200 cm^{-1} (OH) (neat); $\lambda_{max}^{95\% EtOH}$ 236.5 mμ (ϵ 830), 241 (4950), 246 (4250), 251 (s) (2710), 258 (s) 260 (807), 264 (719), 266.5 (645), 269 (870); nmr ($CDCl_3$ with 1 drop of F_3CCOOH) doublets centered at τ 2.85 and 3.06 (J = 5 cps) (aromatic) singlets at 4.73 (OH), 5.42, and 5.53 (methylene), area ratio 1:1:2:4.

Anal. Calcd for $C_6H_8O_2S$: C, 49.98; H, 5.59; S, 22.24. Found: C, 49.90; H, 5.65; S, 22.20.

2,3-Bis(bromomethyl)thiophene (VII).—Into a 100-ml, three-necked flask fitted with an addition funnel, magnetic stirring apparatus, and condenser was introduced a solution of 2 g (0.0135 mole) of 2,3-bis(hydroxymethyl)thiophene in 20 ml of anhydrous ether. A solution of 6 ml of phosphorus tribromide in 19 ml of anhydrous ether was added dropwise at room temperature over a period of 0.5 hr. Each drop of tribromide solution caused a cloudiness to occur in the reaction mixture which disappeared on stirring. After complete addition, the contents were yellow in color and were allowed to stir at room temperature for 8-12 hr. The mixture was carefully poured onto 100 g of ice and while still cold the ether layer was separated and the water layer was saturated with sodium chloride and extracted three times with 20-ml portions of ether. The combined ether extracts were dried and the ether was removed on a rotary solvent evaporator leaving a dark, oily residue which solidified yielding 3.6 g (99%) of a tan solid, melting at 45–48°. One crystallization from hexane at −50° gave 2.9 g (80%), mp 49–50°. An analytical sample prepared by sublimation at 35–40° (0.2 mm) had mp 49–50°. Infrared spectrum showed strongest absorptions at 1200 and 730 cm^{-1} (CCl_4–CS_2); $\lambda_{max}^{95\% EtOH}$ 225 mμ (ϵ 8800) and 250 mμ (ϵ 10,000); nmr ($CDCl_3$) doublets centered at τ 2.72 and 3.00 (J = 6 cps) (aromatic), singlets at 5.29 (CH_2), and 5.50 (CH_2), area ratio 1:1:2:2.

Anal. Calcd for $C_6H_6Br_2S$: C, 26.69; H, 2.24; Br, 59.20; S, 11.88. Found: C, 26.91; H, 2.32; Br, 59.01; S, 11.68.

4,6-Dihydrothieno[3,4-*b*]thiophene (II).—Into a 250-ml, one-necked flask fitted with a condenser and magnetic stirring apparatus was introduced 2.0 g (0.0083 mole) of sodium sulfide nonhydrate, 2.0 g (0.0074 mole) of 2,3-bis(bromomethyl)thiophene, and 100 ml of N,N-dimethylformamide. The mixture was stirred at 90–100° for 12 hr during which time the contents became dark in color. The dimethylformamide was removed under reduced pressure on a water bath until the residue occupied a volume of 5–10 ml. Twenty milliters of water was added and the mixture was extracted four times with 20-ml portions of ether. The combined ether extracts were dried over magnesium sulfate and concentrated at room temperature under reduced pressure. The dark residue was vacuum distilled at 61–63° (0.7 mm) yielding 0.4 g (27%) of pale yellow liquid. After passage over alumina (hexane) and redistillation at 70.5–71° (0.7 mm) 0.3 g (23%) of clear, colorless product, $n^{29}D$ 1.6261, was obtained. Infrared spectrum showed strongest absorptions at 2900, 1145, 828, and 700 cm^{-1} (neat); $\lambda_{max}^{95\% EtOH}$ 233 mμ (ϵ 5200); nmr (a, deuterioacetone) two doublets at τ 2.52 and 2.60, 3.14 and 3.22 (J = 5 cps) (aromatic), and a complex multiplet at 5.88–6.08 (methylene), area ratio 1:1:4; (b, carbon tetrachloride) two doublets at τ 2.74 and 2.82, 3.27 and 3.35 (J = 5 cps), and a multiplet at 5.88–6.12, area ratio 1:1:4.

Anal. Calcd for $C_6H_6S_2$: C, 50.67; H, 4.25; S, 45.08. Found: C, 50.62; H, 4.17; S, 44.97.

2,3-Bis(methoxymethyl)thiophene (VIII).—A solution of 1.5 g of 2,3-bis(bromomethyl)thiophene (0.0056 mole) in 50 ml of methanol was heated under reflux for 5 min. The methanol was removed under reduced pressure and the residue was taken up in ether. The ether was dried and removed under reduced pressure leaving a small residue which was distilled under reduced pressure. The clear, white product was collected at 51–52° (0.1 mm). The product weighed 0.35 g (36%). Infrared spectrum showed strongest absorptions at 1080 (CO) and 695 cm^{-1}

(8) M. Robba, R. C. Moreau, and B. Roques, *Compt. Rend.*, **259**, 4726 (1964).

(neat); nmr ($CDCl_3$) doublets centered at τ 2.73 and 2.96 (J = 5 cps) (aromatic), singlets at 5.36 and 5.45 (CH_2), and singlets at 6.61 and 6.65 (CH_3), area ratio 1:1:2:2:3:3.

Anal. Calcd for $C_8H_{12}O_2S$: C, 55.78; H, 7.02; S, 18.62. Found: C, 55.65; H, 6.93; S, 18.49.

2,3-Bis[(ethylthio)methyl]thiophene (IX).—In a 100-ml, one-necked flask fitted with a condenser and magnetic stirring apparatus was introduced 30 ml of anhydrous tetrahydrofuran and 1.1 g (0.018 mole) of ethyl mercaptan. One gram (0.02 mole) of 50% suspension of sodium hydride in mineral oil was washed free of mineral oil with anhydrous ether and added to the reaction mixture and stirred for 10 min. A solution of 2 g (0.0074 mole) of 2,3-bis(bromomethyl)thiophene in 30 ml of anhydrous tetrahydrofuran was added all at once and the contents were heated under reflux for 16 hr. After cooling, the reaction mixture was filtered and the solvent was removed under reduced pressure. The residue was vacuum distilled and the product was collected at 115–118° (0.45 mm) as a clear, colorless liquid weighing 1.1 g (69%). For analysis a solution of the sample in hexane was passed over alumina and the product redistilled at 135–136° (0.7 mm), $n^{24}D$ 1.5709. Infrared spectrum showed strongest absorptions at 2900, 1440, and 705 cm^{-1} (neat); $\lambda_{max}^{95\%\ EtOH}$ 242.5 mμ (ϵ 8200); nmr (a, deuterioacetone) two doublets at τ 2.69 and 2.78, 2.96 and 3.04 (J = 5 cps) (aromatic), two singlets at 6.00 and 6.22 (methylene), two superimposed quadruplets at 7.3–7.7 (methylene), and two superimposed triplets at 8.65–8.9 (methyl) (J = 7 cps), area ratio 1:1:2:2:4:6; (b, carbon tetrachloride) τ 2.93 and 3.00, 3.09 and 3.17, singlets at 6.16 and 6.34, quadruplets at 7.33–7.75, and triplets at 8.65–8.9, area ratio 1:1:2:2:4:6.

Anal. Calcd for $C_{10}H_{16}S_3$: C, 51.67; H, 6.94; S, 41.39. Found: C, 51.83; H, 6.82; S, 41.30.

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The Alkylation of Benzene with 1,2-Dichloroalkanes

DEREK L. RANSLEY

Chevron Research Company, Richmond, California

Received April 7, 1966

Benzene has been alkylated with 1,2-dichloro-4-methylpentane, 1,2-dichlorohexane, 1,2-dichlorobutane, and 1,2-dichloropropane with either aluminum chloride or liquid hydrogen fluoride catalysts. The products obtained are consistent with a mechanism in which the secondary chloride reacts initially to give preferentially the 1-chlorophenylalkane in which the phenyl group is in the penultimate position. Subsequent products are determined largely by the influence of the phenyl group in assisting ionization of the primary chloride which, in turn, is dependent on the relative positions of the phenyl and chloro groups. Other features which affect the product distribution are also discussed.

A study has been made of the products found in the alkylation of benzene with several 1,2-dichloroalkanes. The reactions were performed using liquid hydrogen fluoride and also aluminum chloride catalysts.

The hydrogen fluoride reactions were carried out under a pressure of dry hydrogen chloride at temperatures greater than 80°. The aluminum chloride reactions were performed by adding the catalyst to a 1 M solution of the dichloride in benzene at 25°. In the latter reactions almost complete dichloride conversion was obtained.

The products were isolated by distillation or by preparative gas chromatography and identified by nuclear magnetic resonance (nmr), infrared, and mass spectroscopy. All of the spectral evidence was consistent with the structures assigned and is presented in Table I.

Results

1,2-Dichloro-4-methylpentane (1).—After 6 hr at 90° with liquid hydrogen fluoride 1 yielded 1-chloro-4-methyl-4-phenylpentane (2, Chart I) as the major product (~80%). The conversion was too low (~15%) to permit identification of other products on the scale employed. From the addition of 9.3 mole % aluminum chloride to 1, the products 3–7 (weight per cent) were identified after 3 hr.

Two further reactions were run on a 0.01-mole scale in which it was demonstrated that the addition of aluminum chloride, in the absence of benzene, caused the transformation of 2 to 4 and 4 to 5.

1,2-Dichlorohexane (8).—The hydrogen fluoride catalyzed reaction of benzene with 8 gave a low conversion, but an almost quantitative yield, of 1-chloro-5-phenylhexane (9, Chart II). The conversion at 80° was only 5% after 5 hr.

CHART I

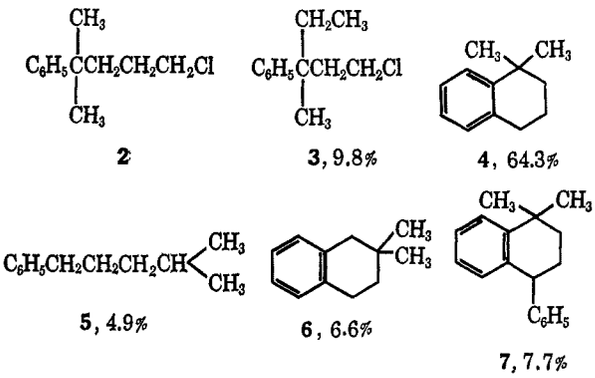
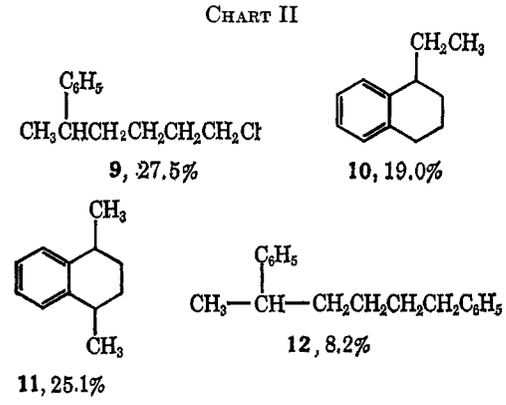


CHART II



Treatment of 8 with 8.8 mole % aluminum chloride for 6 hr gave products 9–12 (weight per cent shown),