(42%) of crystals, mp 54.5–56°. The infrared spectrum showed absorption at 1550 and 1365 ($-NO_2$), 1175 and 1005 cm^{-1} ($-SO_2O$) and the absence of hydroxyl absorption. The nmr spectrum ($CHCl_3$) showed a singlet at δ 1.53 (CH_3C), a singlet at 2.40 ($ArCH_3$), a singlet at 2.93 ($-CH_2S$), a singlet at 3.65 ($-CH_2OTos$) a broad singlet at 4.37 ($-SCH_2Ar$), a singlet at 7.25 ($-SCH_2C_6H_5$) and an A_2B_2 pattern centered at 7.54 ppm for the tosylate aromatic proton resonances, J = 8 cps.

Anal. Calcd for $C_{18}H_{21}NO_5S_2$: C, 54.66; H, 5.35. Found: C, 54.47; H, 5.46.

Preparation of 2-Methyl-2-nitro-3-benzylthiopropanol Tosylate (V) from 2-Methyl-2-nitro-1,3-propanediol Ditosylate (III).—To a solution of sodium benzyl mercaptide in 70 ml of absolute ethanol [prepared from 0.69 g (0.03 g-atom) of sodium and 3.72 g (0.03 mol) of benzyl mercaptan] under a dry nitrogen atmosphere was added 13.3 g (0.03 mol) of 2-methyl-2-nitro-1,3-propanediol ditosylate. The stirred reaction mixture was refluxed overnight under a nitrogen atmosphere. The cooled reaction mixture was concentrated, diluted with water and extracted with ether. The ether extracts were dried ($MgSO_4$) and concentrated to give a yellow oil. The oil was chromatograhed on 50 g of Florisil using a 1:1 mixture of benzene and ethyl acetate as the eluent to afford 7.5 g (63%) of 2-methyl-2-nitro-3-benzylthiopropanol tosylate, mp 50–53°. The infrared spectrum of this product was identical with the spectrum of 2-methyl-2-nitro-3-benzylthiopropanol tosylate prepared from 2-methyl-2-nitro-3-benzylthiopropanol. A mixture of the two products melted at 52–54°.

Reduction of 2-Methyl-2-nitro-3-benzylthiopropanol with Lithium Aluminum Hydride in Ethyl Ether at −15°.—To a solution of 6 g (0.025 mol) of IV in 100 ml of ether cooled by an ice–methanol bath (−15°) was added 2.85 g (0.075 mol) of lithium aluminum hydride in 200 ml of ether. The addition was dropwise over a 1-hr period. The excess lithium aluminum hydride was decomposed by the cautious addition of water and then 400 ml of a 20% potassium sodium tartrate solution was added. The organic layer was separated and the aqueous layer extracted with ether. The combined organic layers were dried over anhydrous sodium sulfate. Concentration of the solution afforded 4.34 g of an oil which was crystallized from an ether cyclohexane mixture to give 34. g (60%) of 2-methyl-2-hydroxylamino-3-benzylthiopropanol (VI), mp 77–82°. The analytical sample prepared by further recrystallization from the same solvent mixture had mp 82–83°.

Anal. Calcd for $C_{11}H_{17}O_2NS$: C, 58.13; H, 7.54. Found: C, 58.23; H, 7.61.

Reduction of 2-Methyl-2-nitro-3-benzylthiopropanol with Zinc and Ammonium Chloride.—To a suspension of 0.721 g (0.003 mol) of 2-methyl-2-nitro-3-benzylthiopropanol in 5 ml of water containing 0.161 g (0.003 mol) of ammonium chloride was added 0.392 g (0.006 mol) of zinc powder, and the mixture was stirred vigorously for 4 hr. The aqueous layer was separated by decantation and the remaining residue was washed with methanol. The methanol washings were concentrated to give a cloudy oil which was dissolved in ether and extracted with 5% hydrochloric acid solution. The acid extracts were made alkaline with sodium bicarbonate and extracted with ether. The ether extracts were dried (Na_2SO_4) and concentrated to give 0.250 g of an oil. Crystallization from cyclohexane afforded 0.200 g (30%) of 2-methyl-2-hydroxylamino-3-benzylthiopropanol, mp 78–81°.

Reduction of 2-Methyl-2-nitro-3-benzylthiopropanol with Lithium Aluminum Hydride in Refluxing Ethyl Ether.—A solution of 12 g (0.05 mol) of 2-methyl-2-nitro-3-benzylthiopropanol in 50 ml of ether (dried over sodium metal) was added dropwise to an ice-cooled stirred solution–suspension of 5.7 g (0.15 mol) of lithium aluminum hydride in 200 ml of anhydrous ether. After the addition was completed, the reaction mixture was refluxed for 3 hr. The excess lithium aluminum hydride was decomposed with water and 1 l. of a 20% sodium potassium tartrate solution was added. The ether layer was separated and the remaining aqueous layer was extracted with ether. The organic layers were combined and dried ($MgSO_4$). Concentration of the ether afforded 9.9 g of light yellow liquid. Distillation of the liquid under reduced pressure afforded 3.7 g (41%) of colorless product, bp 95° (0.08 mm), $n^{25}D$ 1.5564. The 1-benzylthio-2-propylamine formed a carbonate salt rapidly on exposure to the atmosphere and was thus analyzed as the hydrochloride salt, mp 149–151°. The nmr spectrum (D_2O) showed a doublet at δ 1.44, CH_3 of ($CH_3{}^aCH^b$, $J_{a,b}$ = 7 cps), a doublet at 2.81 , $J_{b,c}$ = 7 cps (slightly perturbed due to the nonequivalence of the methylene protons, $-CH_2$ of $CH^bCH_2{}^cS$), a sextet at 3.57 (CH of $CHCH_2S$ group), a singlet at 3.85 ($-SCH_2Ar$) and a singlet at 7.37 ppm (aromatic protons).

Anal. Calcd for $C_{10}H_{16}ClNS$: C, 55.15; H, 7.41. Found: C, 55.28; H, 7.11.

In a separate experiment the product was isolated in 49% yield as the hydrochloride.

Reduction of 2-Methyl-2-hydroxylamino-3-benzylthiopropanol with Lithium Aluminum Hydride in Refluxing Ethyl Ether.—To a solution–suspension of 0.57 g (0.015 mol) of lithium aluminum hydride in 20 ml of anhydrous ether was added dropwise a solution of 1.14 g (0.005 mol) of VI in 50 ml of ether. After the addition was completed, the mixture was refluxed for 8 hr. The mixture was worked up as in the previous reductions to give 1.07 g of a viscous liquid. This liquid was dissolved in ether and treated with an ethereal solution of *p*-toluenesulfonic acid to give 1.8 g (94%) of 2-methyl-2-amino-3-benzylthiopropanol *p*-toluenesulfonate, mp 133–137°. The analytical sample prepared by recrystallization from an ethanol and ether mixture had mp 134–137°.

Anal. Calcd for $C_{18}H_{25}NS_2O_4$: C, 56.37; H, 6.57; N, 3.65; S, 16.72. Found: C, 56.49; H, 6.58; N, 3.81; S, 16.52.

Registry No.—II, 18386-49-7; III, 18386-50-0; IV, 18386-51-1; V, 18386-52-2; VI, 18354-31-9; VII·HCl, 18354-32-0; VIII·*p*-toluenesulfonate, 18386-53-3.

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Phenylethynylpentafluorobenzene and Phenylethynylpentachlorobenzene

M. D. Rausch, A. Siegel, and L. P. Klemann[1]

Department of Chemistry, University of Massachusetts, Amherst, Massachusetts 01002

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During the course of some current studies concerned with the reductive dimerization of arylacetylenes to dilithium reagents[2] and the conversion of arylacetylenes to aryl-substituted cyclobutadiene–cobalt complexes,[3] we developed a need for several diarylacetylenes in which one of the aryl groups was perhalogenated. Very recently, Filler and Heffern[4] have described a multistep, phosphorane-type route to one of these acetylenes, *viz.*, phenylethynylpentafluorobenzene (1). Other at-

$ArC{\equiv}CC_6H_5$
1, $Ar = C_6F_5$
2, $Ar = C_6Cl_5$

$ArC{\equiv}CC{\equiv}CAr$
3, $Ar = C_6H_5$
4, $Ar = C_6F_5$

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[1] National Science Foundation Graduate Trainee, 1965–1968.

[2] M. D. Rausch and L. P. Klemann, *J. Amer. Chem. Soc.*, **89**, 5732 (1967); unpublished studied by these authors.

[3] M. D. Rausch and R. A. Genetti, *ibid.*, **89**, 5502 (1967); F. Higbie, A. Siegel, and M. D. Rausch, unpublished studies.

[4] R. Filler and E. W. Heffern, *J. Org. Chem.*, **32**, 3249 (1967).

tempts[5,6] to form **1** *via* the reaction of phenylethynyllithium and hexafluorobenzene have been reported to be unsatisfactory, due to the ease with which the *p*-fluorine atom in **1** is displaced by additional phenylethynyllithium reagent. It should be mentioned that routes to both bis(pentafluorophenyl)acetylene[4,7,8] and bis(pentachlorophenyl)acetylene[8] have also been described recently.

Earlier studies in our laboratory[9] have shown that the Castro–Stephens procedure[10-12] for the synthesis of diarylacetylenes is applicable to ferrocenyl- and 2-thienylarylacetylenes. In the present note, we describe studies which indicate that this same method represents a convenient route to **1** as well as its chlorinated analog, phenylethynylpentachlorobenzene (**2**).[13]

When iodopentafluorobenzene and phenylethynylcopper(I) were refluxed in pyridine for a period of 10 hr under nitrogen, phenylethynylpentafluorobenzene (**1**) was obtained in 55% yield. A small amount of the oxidative coupling product, diphenylbutadiyne (**3**), was also detected. In general, longer reflux periods resulted in appreciably reduced yields of the desired product, due conceivably to subsequent reactions of **1**.[13] A similar reaction between bromopentafluorobenzene and phenylethynylcopper(I) produced **1** in only 33% yield, and an appreciable amount of diacetylene **3** was formed. These results are in accord with the known halide reactivity series (I > Br > Cl)[12] in reactions of aryl halides with cuprous arylacetylides.

In a reverse manner, a reaction between iodobenzene and pentafluorophenylethynylcopper(I) in refluxing pyridine for 8 hr under nitrogen resulted in the formation of **1** in 74% yield. The oxidative coupling product, perfluorodiphenylbutadiyne (**4**), was not isolated in significant amount from this reaction, although it could readily be prepared by bubbling air through a pyridine solution of ethynylpentafluorobenzene in the presence of cuprous chloride for several hours. Although this alternate route to **1** appears to proceed more smoothly and produces the desired product in higher yield, it is presently handicapped by the limited availability[14] of ethynylpentafluorobenzene.

In several initial reactions involving iodopentachlorobenzene and phenylethynylcopper(I) in refluxing pyridine under nitrogen, the major product was diacetylene **3**, and only low yields of the desired product, phenylethynylpentachlorobenzene (**2**), could be obtained. When extreme care was taken to avoid oxygen from the reaction system by additionally purifying the pyridine *via* a freeze-thaw process, **2** was formed in 49% yield, and only minor amounts of **3** were detected. The conversion of iodopentachlorobenzene into **2** via a concerted displacement process[10-12] is remarkable in view of appreciable steric effects which might be expected to be imposed by the two flanking *o*-chlorine atoms.[15] On the other hand, it has recently been reported that the relative "activating power" of the pentachlorophenyl group in aromatic S_N reactions is appreciably greater than for the pentafluorophenyl group, the former being about as activating as an *o*- or a *p*-nitrophenyl group.[16] Such an effect may possibly account for the reactivity of iodopentachlorobenzene in the Castro–Stephens reaction, although a detailed mechanistic study, including steric factors, would seem necessary before any definitive conclusions could be made. As expected, a reaction between hexachlorobenzene and phenylethynylcopper(I) in refluxing pyridine produced only the oxidative coupling product **3**, and none of the desired acetylene **2** could be detected.

Both unsymmetrical acetylenes **1** and **2** exhibit weak absorptions in the 2200–2250-cm^{-1} region, assignable to $-C\equiv C-$ stretching vibrations, as well as bands characteristic of pentafluorophenyl groups and pentachlorophenyl groups, respectively. Further reactions of these new acetylenes in organic and organometallic systems will be described in subsequent papers.

Experimental Section

Phenylacetylene was purchased from Aldrich Chemical Co. and was converted into its copper(I) salt by the method of Castro and Stephens.[10-12] Pentafluorophenylacetylene and its copper(I) salt were prepared by the method of Coe, Plevey, and Tatlow.[14] Pyridine was reagent grade and was dried over potassium hydroxide and refluxed over barium oxide before use. Bromopentafluorobenzene was purchased from the Imperial Smelting Co., Ltd. Iodopentafluorobenzene, bp 162–164°, was prepared in 48% yield by a modification of the method of Vorozhtsov, *et al.*,[17] from pentafluorophenylmagnesium bromide and iodine in ethyl ether solution. Iodopentachlorobenzene was prepared from a reaction between pentachlorophenyllithium (50 mmol)[18] and iodine (31.7 g, 125 mmol) in ethyl ether at −50°. After the reaction mixture had been allowed to warm to room temperature and treated with saturated sodium thiosulfate solution, the ethyl ether portion was washed with water, dried, and evaporated to produce a pale yellow solid. Recrystallization of the solid from hexane gave 11.2 g of crude product, which was sublimed at 135° (0.3 mm) to afford 9.68 g (52%) of iodopentachlorobenzene in the form of white needles, mp 214–216° (lit.[19] mp 207–208°). Elemental analyses were performed by the Schwarzkopf Microanalytical Laboratory, Woodside, N. Y., and by Mr. Charles Meade of the University of Massachusetts Microanalytical Laboratory.

Reaction of Iodobenzene and Pentafluorophenylethynylcopper(I).—Into a 250-ml, three-necked flask equipped with a magnetic stirring bar, reflux condenser and nitrogen inlet were added iodobenzene (1.0 g, 4.9 mmol), pentafluorophenylethynylcopper(I) (1.0 g, 3.9 mmol) and 50 ml of pyridine. The reaction

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(6) P. C. Coe, J. C. Tatlow, and R. C. Terrell, *J. Chem. Soc., C*, 2626 (1967).

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(12) C. E. Castro, E. J. Gaughan, and D. C. Owsley, *ibid.*, **31**, 4071 (1966).

(13) Filler and Heffern[4] have independently investigated the formation of **1** by the Castro–Stephens procedure, using dimethylformamide as the reaction solvent. Their product was obtained in only impure form (20% crude yield), however, and optimum conditions for the synthesis of **1** were not worked out.

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mixture was heated to reflux with stirring under nitrogen for a period of 8 hr, allowed to cool to room temperature, diluted with water, and the hydrolysate was extracted with ethyl ether. The ether extracts were washed successively with water, 5% hydrochloric acid, 5% sodium hydroxide solution, water, and were dried over magnesium sulfate. The ether was removed and the residue was sublimed at 140° (12 mm) to give 0.77 g (74%) of phenylethynylpentafluorobenzene (1), mp 96.5–98°.[20]

Anal. Calcd for $C_{14}H_5F_5$: C, 62.69; H, 1.89; F, 35.42. Found: C, 62.89; H, 2.04; F, 35.43.

The infrared spectrum (KBr) of 1 exhibited major absorptions at 2230, 1500 (broad), 1440, 1110, 1020, 975 (broad), 740 and 680 cm^{-1}.

Perfluorodiphenylbutadiyne (4).—Ethynylpentafluorobenzene (0.20 g, 1.04 mmol) and cuprous chloride (50 mg) were added to 10 ml of pyridine. Dry air was slowly bubbled through the mixture for 3 hr. The mixture was diluted with water and extracted with ethyl ether. The ether extracts were washed with water, 5% hydrochloric acid, water, and were dried. The ether was evaporated and the resulting residue was sublimed at 140° (16 mm) to afford 181 mg (91%) of perfluorodiphenylbutadiyne, mp 104–105°.

Anal. Calcd for $C_{16}F_{10}$: C, 50.28; F, 49.72. Found: C, 50.14; F, 49.92.

Reaction of Iodopentafluorobenzene and Phenylethynylcopper(I).—Iodopentafluorobenzene (8.0 g, 27 mmol) and phenylethynylcopper(I) (4.9 g, 30 mmol) were refluxed in 150 ml of pyridine for a period of 10 hr under nitrogen. After hydrolysis, washing, and drying in the usual manner, the ether was removed and the residue was fractionally sublimed. At 75° (12 mm), diphenylbutadiyne (3) (1.1 g) sublimed; the mp was 85–86° (lit.[21] mp 88°), and a mixture melting point with an authentic sample was undepressed. The remaining product was sublimed at 140° (12 mm) to produce 4.0 g (55%) of phenylethynylpentafluorobenzene (1), mp 93–94°.[20] Thin layer chromatography indicated contamination by trace amounts of diphenylbutadiyne. An infrared spectrum of the product was identical with a spectrum of the product from the reaction of iodobenzene and pentafluorophenylethynylcopper(I).

Reaction of Bromopentafluorobenzene and Phenylethynylcopper(I).—Bromopentafluorobenzene (5.0 g, 20 mmol) and phenylethynylcopper(I) (3.25 g, 20 mmol) were refluxed in 100 ml of pyridine for a period of 12 hr under nitrogen. After hydrolysis, washing, and drying in the usual manner, evaporation of the solvent left 5.0 g of a tan residue. Thin layer chromatography indicated two components. Accordingly, a 100-mg portion of the residue was subjected to preparative thin layer chromatography on silica gel using pentane as eluent. The bands which separated were extracted with ethyl ether. Evaporation of the solvent containing the component of lower R_f deposited 35 mg of diphenylbutadiyne, mp 85–86°. The solvent containing the band of higher R_f was evaporated to give 35 mg of phenylethynylpentafluorobenzene (1), mp 92–93°; this amount corresponds to a 33% yield of the product in the original reaction.

Reaction of Iodopentachlorobenzene and Phenylethynylcopper(I).—Iodopentachlorobenzene (7.52 g, 20 mmol), phenylethynylcopper(I) (6.58 g, 40 mmol) and 225 ml of dry, degassed (three freeze–thaw cycles) pyridine were refluxed for 21 hr under nitrogen. The reaction mixture was cooled, poured into 500 ml of ice–water, and extracted with 900 ml of dichloromethane. The extracts were washed as described above and were subsequently dried over sodium sulfate. Evaporation gave a brown residue which was washed with 75 ml of cold (−60°) pentane and filtered, leaving 3.93 g of a tan solid. This material was sublimed at 80° (0.1 mm) to remove trace amounts of diphenylbutadiyne. Continued sublimation at 175° (0.1 mm) afforded 3.41 g (49%) of white crystals of phenylethynylpentachlorobenzene (2), mp 218–220°.

Anal. Calcd for $C_{14}H_5Cl_5$: C, 47.98; H, 1.44; Cl, 50.58. Found: C, 48.00; H, 1.47; Cl, 50.53.

The infrared spectrum (KBr) exhibited major absorptions at 2220, 1490, 1460, 1400, 1345, 1300, 1276, 745, 710 and 680 cm^{-1}. A small amount of diphenylbutadiyne was observed in the pentane extract after evaporation.

Registry No.—1, 13509-88-1; 2, 18320-78-0; 4, 18320-79-1.

Acknowledgments.—The authors are indebted to the National Science Foundation and to the Donors of the Petroleum Research Fund, administered by the American Chemical Society, for grants in support of this research.

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[20] Wiles and Massey[5] report a melting point for 1 of 93°; Filler and Heffern[4] report mp 108.5–109.5°. The melting point of 1 prepared in our studies varied slightly from run to run, due possibly to the presence of very small amounts of either diacetylene 3 or 4 resulting from an oxidative coupling process.

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Optically Active Nuclear Magnetic Resonance Solvents. VIII. Resolution of 2,2,2-Trifluorophenylethanol

W. H. PIRKLE, S. D. BEARE, AND T. G. BURLINGAME

Department of Chemistry and Chemical Engineering, University of Illinois, Urbana, Illinois 61801

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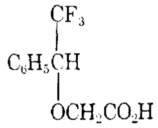
With the reports[1,2] that the optical purities and absolute configurations of a number of amines and sulfoxides may be determined by nmr spectroscopy in optically active 2,2,2-trifluorophenylethanol (1) as solvent, the convenient and efficient resolution herein reported for this carbinol should be of general interest. This carbinol has previously been resolved by Feigl and Mosher[3] through a lengthy series of fractional crystallizations of the diastereomeric 3β-acetoxy-Δ^5-etienates, an approach which ultimately affords the pure enantiomers, α^{25}D +41.14° and α^{26}D −41.18° (neat, l = 1) in low yields.

Typically, alcohols having no other "handles" are converted into acid phthalates or acid succinates, resolved as such, and recovered from the esters after hydrolysis. However, the esters of acidic alcohols generally hydrolyze readily,[4] and this is the result of attempts to resolve the acid phthalate of 1 with optically active bases.[5] This problem has been avoided by converting 1 into a more stable resolvable derivative, 2,2,2-trifluorophenylethoxyacetic acid (2), prepared from

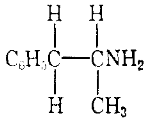
$C_6H_5CH(CF_3)OH$

1



$C_6H_5CH(CF_3)OCH_2CO_2H$

2



$C_6H_5CH_2CH(CH_3)NH_2$

3

1 and ethyl bromoacetate *via* the Williamson synthesis. One of the diastereomeric salts of 2 and amphetamine (3), both enantiomers of which are readily available,

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