Table II
Asymmetric Reduction of *tert*-Butyl Methyl Ketone by (+)-Tris[(*S*)-2-methylbutyl]aluminum Diethyl Etherate

Run	Solvent	Temp, °C	S Carbinol: Conversion, %[a]	S Carbinol: Chemical purity, %[b]	S Carbinol: Optical rotation: $\alpha^{25}D$, deg, l = 1 (neat)	S Carbinol: Optical rotation: $[\alpha]^{25}D$	S Carbinol: Optical rotation: $[\alpha]^{25}D$[c]	S Carbinol: Optical purity, %[d]	Asymmetric reduction, %[e]
7[f]	Pentane	0	88	74	+0.31	+0.38	+0.51	11.0[g]	11.5
8[h,i]	Benzene	25	90	~100[j]	+0.86	+1.06	+1.06	13.9	14.2
9[h]	Benzene	80	92	94	+0.55	+0.68	+0.72	9.4	9.6
10[i,k,l]	Benzene	25	63	~100[j]	+0.05 (10.87, EtOH)	+0.46	+0.46	11[m]	~11

[a] Based on glpc analyses of the crude product. [b] Estimated by glpc analyses of the product after redistillation, other impurities being the ketone. [c] Corrected for the per cent purity of the carbinol. [d] W. M. Foley, F. J. Welch, E. M. La Combe, and H. S. Mosher, *J. Amer. Chem. Soc.*, **81**, 2779 (1959). [e] Corrected for the minimum optical purity (o.p.) of the organoaluminum compound. [f] Al2MB·Et_2O, o.p. 95.9%. [g] Pure (+)-(*S*)-*tert*-butylmethylcarbinol, $[\alpha]^{25}D$ +1.30° (neat), o.p. 17.0%, showed $[\alpha]^{25}D$ +0.79° in the presence of 22% of the corresponding ketone. [h] Al2MB·Et_2O, o.p. 98.0%. [i] According to Kretchmer's procedure (see ref 5). [j] Recovered by preparative glpc. [k] Al2MB·Et_2O, o.p. 94.4%. [l] In the presence of (*S*)-2-methylbutoxyaluminum species (per cent of alkoxide groups 15.9). [m] Pure (+)-(*S*)-*tert*-butylmethylcarbinol, o.p. 16.5%, showed $[\alpha]^{25}D$ +0.71° (*c* 7.05, EtOH).

As the discrepancy between our result and the result reported in the literature[5] might have arisen from differences in experimental procedures,[6,7] we have carried out the reduction in refluxing benzene[5] (runs 8 and 9, Table II). In addition, we have tested the influence of (*S*)-2-methylbutoxyaluminum species,[8] eventually present in the reaction mixture as oxidation products, on the stereochemistry of the reduction (run 10). In any case *S* carbinol was recovered (Table II). At present we are unable to offer a really satisfactory interpretation about the result reported in the literature.[5]

In conclusion, although the intervention of donor ligands in the reduction controls the extent of stereoselectivity,[2c] at least in the cases investigated the absolute configuration of the carbinol seems to be related only to the structure of the chiral alkyl group bound to the aluminum atom.

Experimental Section[9]

Reduction of Alkyl Methyl Ketones. The following procedure is representative of runs 1–7. A solution of 13.5 mmol of the ketone in 10 ml of anhydrous pentane was added rapidly, under nitrogen, to a solution of 15.0 mmol of the organoaluminum compound in 15 ml of pentane, cooled at 0°, in a flame-dried, two-neck, 100-ml flask fitted with a reflux condenser, a dropping funnel, and a magnetic stirrer. An immediate pale yellow coloration developed and faded quickly. After 2 hr the resulting mixture was cautiously hydrolyzed with dilute sulfuric acid (pH 5) and the organic products were continuously extracted with purified ether. The carbinol was recovered by accurate distillation.

Reduction of *tert*-Butyl Methyl Ketone. Run 8. The ketone (23.1 mmol) in 5 ml of anhydrous benzene was treated with (+)-tris[(*S*)-2-methylbutyl]aluminum diethyl etherate (21.0 mmol), $[\alpha]^{25}D$ +22.25° (*c* 4.07, pentane),[2c] in 50 ml of benzene according to Kretchmer's procedure.[5] After 2 hr the solvent was removed *in vacuo*, and the resulting mixture was added with ether and hydrolyzed with dilute sulfuric acid. The carbinol recovered by continuous extraction was purified by preparative glpc on 500 × 0.80 cm 20% BDS on Chromosorb W 60–80 mesh columns at 120°.

Run 9. A solution of 14.9 mmol of (+)-tris[(*S*)-2-methylbutyl]-aluminum diethyl etherate in 40 ml of anhydrous benzene was added rapidly to a refluxing solution of 16.4 mmol of the ketone in 10 ml of benzene. The solution was maintained at reflux temperature for an additional 2 hr and then worked up as above.

Run 10. A solution of 20.6 mmol of (+)-tris[(*S*)-2-methylbutyl]-aluminum diethyl etherate, $[\alpha]^{25}D$ +21.43° (*c* 4.68, pentane), in 30 ml of dry benzene was cautiously added, at room temperature, with 9.8 mmol of (−)-(*S*)-2-methyl-1-butanol, $[\alpha]^{25}D$ −5.76° (neat), o.p. 99%,[10] followed by 21.6 mmol of the ketone in 30 ml of benzene. The mixture was refluxed for 2 hr and then worked up in the usual manner. Glpc analysis (200 × 0.30 cm 20% Carbowax 1500 on Chromosorb W 60–80 mesh columns at 60°) showed a carbinol:2-methyl-1-butanol ratio of 1.33. Preparative glpc on 270 × 0.80 cm 20% Carbowax 20M on Chromosorb A 45–60 mesh plus 200 × 0.80 cm Carbowax 1500 on Chromosorb W 60–80 mesh columns at 120° afforded pure (+)-(*S*)-*tert*-butylmethylcarbinol.

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Registry No.—Ethyl methyl ketone, 78-93-3; isopropyl methyl ketone, 563-80-4; *tert*-butyl methyl ketone, 75-97-8; (+)-tris[(*S*)-2-methylbutyl]aluminum, 4023-25-0; (+)-tris[(*S*)-2-methylbutyl]-aluminum diethyl etherate, 18902-57-3.

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(8) An asymmetric reduction of the ketone might occur in a competing Meerwein–Ponndorf–Verley process [R. Menicagli, G. P. Giacomelli, and L. Lardicci, *J. Organometal. Chem.*, **50**, C15 (1973)] or through more complex mechanistic pathways involving eventual associates among molecules of AlR_3 and $ROAlR_2$.
(9) (+)-Tris[(*S*)-2-methylbutyl]aluminum and (+)-tris[(*S*)-2-methylbutyl]aluminum diethyl etherate, prepared as previously reported,[2c] were carefully redistilled under nitrogen and stored in sealed glass vials. Optical rotations were taken on a Schmidt-Haensch polarimeter with sensitivity of ±0.005°. Glpc analyses were performed on a C. Erba Fractovap Model GT instrument with flame ionization detectors using, unless otherwise indicate, 200 × 0.30 cm 10% BDS on 60–80 mesh Chromosorb W columns in the range 50–70°. Preparative glpc were carried out on a Perkin-Elmer F 21 instrument.
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Synthesis of Fluoroaromatic Amines

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Fluoroaromatic compounds have proven utility in synthetic[2-4] and theoretical[5-7] organic chemistry, and in can-

Table I
***N*-Arylhydroxylamine Preparation**

ArNHOH

Ar	Best method	Yield, %	Mp, °C	Lit. mp, °C	Registry no.
Phenyl (**1**)	Zn, NH_4Cl	73	80–81	81[a]	100-65-2
2-Tolyl (**2**)	Zn, NH_4Cl	12	45–46	44[b]	611-22-3
3-Tolyl (**3**)	Zn, NH_4Cl	63	66–68	68[b]	620-25-7
4-Tolyl (**4**)	Zn, NH_4Cl	27	98–99	98[b]	623-10-9
2-Chlorophenyl (**5**)	Zn, NH_4Cl	40	Oil	56[b]	10468-16-3
4-Chlorophenyl (**6**)	Zn, NH_4Cl	13	83–84	86[b]	823-86-9
2-Carboethoxyphenyl (**7**)	Zn, NH_4Cl	65	72–73	74[c]	38476-40-3
1-Napthyl (**8**)	$(NH_4)_2S$	76	78–79	79[d]	607-30-7
2-Napthyl (**9**)	$(NH_4)_2S$	70	135–137	135–137[e]	613-47-8
2-Fluorenyl (**10**)	$(NH_4)_2S$	20	180 dec	170 dec[f]	53-94-1
2-Biphenyl (**11**)	$NaBH_4$[g]	65	Oil	69–71[h]	16169-17-8

[a] Reference 14. [b] Reference 16. [c] Reference 24. [d] R. Willstatter and H. Kubli, *Chem. Ber.*, **41,** 1936 (1908). [e] O. Baudisch and R. Fürst, *Chem. Ber.*, **50,** 324 (1917). [f] P. Lotlikar, E. Miller, J. Miller, and A. Margreth, *Cancer Res.*, **25,** 1743 (1965). [g] Reduction of 2-nitrosobiphenyl. [h] Reference 22.

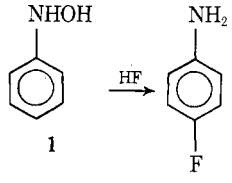
Table II
4-Fluoroaniline Products from *N*-Arylhydroxylamines

$$RArNHOH \xrightarrow{HF} p\text{-}F(R)ArNH_2$$

R	Yield, %	Mp or bp, °C (mm)	Lit. mp or bp, °C (mm)	Registry no.
H (**12**)	43	180 (760)	180–185 (760)[a]	371-40-4
2-CH_3 (**13**)	40	96 (24)	4 (16)[b]	452-71-1
3-CH_3 (**14**)	61	34–36	35[b]	452-69-7
4-CH_3 (**15**)	*c*	*c*	*c*	
2-Cl (**16**)	39	190–192 (756)	192 (760)[b]	2106-02-7
4-Cl (**17**)	Tar			
2-$COOC_2H_5$ (**18**)	29	181–184[d]	185[d]	446-08-2

[a] G. Schiemann and R. Pillansky, *Chem. Ber.*, **62,** 3041 (1929). [b] F. C. Finger, M. J. Gortatowski, R. H. Shiley, and A. H. White, *J. Amer. Chem. Soc.*, **81,** 94 (1959). [c] 4,4′-Azoxytoluene (**19,** 5% yield), mp 61–62° (lit.[27] mp 69–70°). [d] Melting point of 5-fluoroanthranilic acid obtained from hydrolysis of **18,** ref 28.

cer research.[8] The most common method for synthesizing fluoroaromatic compounds has been the Balz–Schiemann and related reactions.[9] Recently some promising new methods have been reported.[10] Two groups have shown that reaction of *N*-phenylhydroxylamine (**1**) with anhydrous hydrogen fluoride produces 4-fluoroaniline (**2**).[11,12]



1 2

We have examined this modification of the Bamberger reaction[13] for the purpose of determining its general synthetic utility for preparing fluoroaromatic amines. The results of our studies are the subject of this paper.

Results and Discussion

***N*-Arylhydroxylamine Synthesis.** The generality of the reaction is highly dependent on the availability of the required *N*-arylhydroxylamines. Zinc dust[14] or ammonium sulfide[15] reduction of the aromatic nitro compounds are the usual methods for preparing *N*-arylhydroxylamines. We have investigated the two methods in detail for several aromatic nitro compounds. The results are given in Table I. Reduction of aromatic nitro compounds with zinc dust–ammonium chloride in heterogeneous aqueous medium was very sensitive to pH. Best results were obtained at pH 6.5–7. Product yields were improved when reaction work-up time was kept short and exposure to laboratory light was minimized. Attempts to prepare *N*-arylhydroxylamines by hydrogenation using an iridium catalyst[16] were unsuccessful. This may be attributed to our inability to correctly prepare the catalyst.[17] Ammonium sulfide was not suitable for the preparation of **1–7.** Usually the starting material was recovered quantitatively.

Polynuclear nitroaromatic compounds were best reduced using ammonium sulfide.[15] 9-Nitroanthracene yielded only dark, unworkable material. Although we did not optimize the yields of **8, 9,** and **10** owing to their carcinogenic activity, we did find that the ammonium sulfide method was dependable and furnished cleaner products as contrasted with the erratic, low-yield character of the zinc dust reduction method for these compounds.

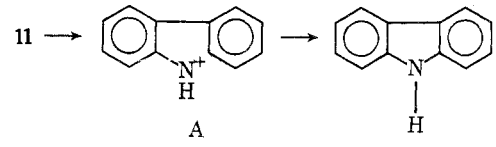
Both the zinc dust and ammonium sulfide reduction methods failed to produce *N*-(2-biphenyl)hydroxylamine (**11**) from 2-nitrobiphenyl. 2,2′-Azoxybiphenyl was the only product isolated. However, reduction of 2-nitrosobiphenyl[18] with 0.25 equiv of sodium borohydride in cold dilute ether solution repeatedly yielded the desired *N*-(2-biphenyl)hydroxylamine in 65% yield. The success of this reaction may be due to the ortho phenyl group preventing further reduction of **11** to 2-aminobiphenyl. Reduction of nitroso compounds with sodium borohydride usually produces the amino compound.[19]

Reactions with Hydrogen Fluoride. *N*-Phenylhydroxylamines (**1–7**) produced *p*-fluoroanilines except when the para position was blocked (**4, 6**). 2-Fluoroanilines were not observed. Products were identified by comparison with authentic samples or with data reported for the authentic compounds. Optimum isolated yields are reported in Table II. Tarry, unworkable material accounted for a material balance. This reaction sequence represents a reasonable synthesis for 4-fluoroanilines even though yields are moderate to low, since starting materials are readily accessible.

Those compounds with substituents in the para position (**4**, **6**) gave mostly tarry material. However, 4,4′-dimethylazoxybenzene was isolated in low yield by sublimation of the tarry product from **4**. No identifiable material was obtained from **6**.

N-(1-Naphthyl)hydroxylamine (**8**) produced only 1,1′-azoxynaphthalene in low yield. No evidence was found for the presence of a fluoroaminonaphthalene, even though the para position is unsubstituted. *N*-(2-Naphthyl)hydroxylamine (**9**) gave mostly 2,2′-azoxynaphthalene and a small amount of 1-fluoro-2-aminonaphthalene. Interestingly, the only fluoroaminonaphthalene produced came from **9**, which has a blocked para position. This contrasts with the results found in the *N*-phenylhydroxylamine series.

N-(2-Biphenyl)hydroxylamine (**11**) reacted with HF to yield a mixture containing carbazole (**20**), 2-amino-5-fluorobiphenyl, and 2,2′-azoxybiphenyl.[20] The production of carbazole suggests the intermediacy of an anilenium ion (A) which undergoes electrophilic cyclization with the ortho phenyl substituent. Reaction of **11** with 20% sulfuric acid solution produced carbazole in low yield.[21,22] Nitrene[22] or protonated hydroxylamine[23] intermediates cannot strictly be excluded at present.



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Experimental Section

All temperature readings are uncorrected. Elemental analysis was performed by Galbraith Laboratories, Knoxville, Tenn. Infrared spectra were recorded on a Perkin-Elmer Model 337 spectrophotometer. Nmr spectra were recorded on a Varian T-60 spectrometer. Mass spectra were recorded on a Varian Mat-111 gc–mass spectrometer. Samples were introduced through the gas chromatograph or in the direct evaporation probe.

***N*-Arylhydroxylamine Preparation. A. Zinc-Dust Reduction.** The preparation of 3-methyl-*N*-phenylhydroxylamine (**3**) will serve to illustrate the general procedure. Zinc dust (124 g, 1.9 mol) was gradually added during a 0.5-hr period to a stirred mixture of *m*-nitrotoluene (115 g, 0.84 mol) and ammonium chloride (50 g, 0.93 mol) in 1.5 l. of water. The pH was kept between 6.5 and 7 by adding small portions of ammonium hydroxide. The reaction temperature increased to approximately 60° and then gradually decreased. At about 45°, the mixture was filtered by suction and the filtrate was thoroughly extracted with a 1:1 benzene–ether mixture. The organic solution was dried by filtration through magnesium sulfate and the solvents were then removed on a rotary evaporator. The remaining yellow material was crystallized from hexane to give 65.0 g (63%) of 3-methyl-*N*-phenylhydroxylamine, mp 67–68°. Compounds **6** and **7** were prepared from 0.127 and 0.59 mol of starting nitroaromatic compound, respectively.

B. Ammonium Sulfide Reduction. *N*-(1-Naphthyl)hydroxylamine (8). A solution of 20.0 g (0.12 mol) of 1-nitronaphthalene in 500 ml of absolute ethanol was cooled to 0°. Ammonia gas was bubbled through the cold solution for about 1 hr. The solution was then saturated with hydrogen sulfide during 1 hr, during which a yellow solid appeared on the sides of the flask. The mixture was stored at 0 to −5° for about 24 hr and then added to 1.2 l. of cold water. Colorless crystals of **8** formed which were collected by suction filtration. Recrystallization from benzene furnished 14.0 g (76%) of **8**, mp 79°.

N-(2-Naphthyl)hydroxylamine (**9**) was prepared from 2-nitronaphthalene (5.8 mmol) using the preceding procedure except that the reaction mixture was stored at 0° for 2 days.

N-(2-Fluorenyl)hydroxylamine (**10**) was prepared from 0.36 mol of 2-nitrofluorene using the procedure for **8** except that a solvent mixture of 300 ml of ethanol and 300 ml of *N*,*N*-dimethylformamide was used.

***N*-(2-Biphenyl)hydroxylamine (11).** 2-Nitrosobiphenyl[18] (5.0 g, 0.27 mol) was dissolved in 500 ml of anhydrous ether under a dry nitrogen atmosphere. The stirred, cooled (0°) mixture was treated with sodium borohydride (0.21 g, 0.0055 mol). The mixture was vigorously stirred for 8 hr. The green color of the solution dissipated and a white solid formed. The mixture was washed with saturated sodium chloride solution and dried by filtration through a cone of magnesium sulfate. Removal of the ether on a rotary evaporator at 0° furnished 3.3 g (65%) of **11** as a yellow semisolid. The compound showed a positive tetrazolium red test. Nmr and ir spectra gave no indication of the presence of any nitroso, azo, or azoxy functions. The material would convert to 2,2′-azoxybiphenyl on exposure to air at room temperature after 0.5 hr. The pure material could be kept several days at −10° under nitrogen in the absence of light.

Yields and melting points of compounds **1**–**11** are reported in Table I.

Tetrazolium Red Test.[25,26] A 0.05-g sample of the compound to be tested was mixed with 0.05 g of 2,3,5-triphenyltetrazolium red in 1.5 ml of 70% ethanol and placed on a clean white porcelain surface. A drop of 2 *N* sodium hydroxide solution was then added. Immediate formation of a bright red color occurred for all of the *N*-arylhydroxylamines. Nitro, amino, nitroso, azo, and azoxy functions did not produce a red color and did not inhibit the color when the hydroxylamino function was present.

Reaction of *N*-Phenylhydroxylamines 1–7 with Liquid Hydrogen Fluoride. The preparation of 2-chloro-4-fluoroaniline (**16**) will be used as a representative reaction. To 100 ml (5.0 mol) of hydrogen fluoride freshly condensed in a polyethylene container at −60° was added 3.61 g (0.025 mol) of 2-chloro-*N*-phenylhydroxylamine (**5**) in 0.5 g portions with swirling of the container after each addition. The dark mixture was allowed to stand overnight while the hydrogen fluoride evaporated (in a hood!). During this time approximately 20 ml of water condensed in the container. Ether (30–50 ml) was added and ammonia was bubbled into the mixture until a basic indication was obtained toward litmus. The organic layer was separated and combined with an ether extract of the aqueous layer. The organic solution was washed with saturated sodium chloride solution and dried by filtration through magnesium sulfate. Evaporation of the ether on a rotary evaporator furnished a red oil. Distillation in a short-path apparatus gave 1.42 g (39%) of **16**, n^{25}D 1.5570.

Only tarry material was obtained from the reaction of **4** with HF. Chromatography on Florisil using hexane furnished a red oil, which was purified by molecular distillation in a semimicro sublimation apparatus. The yellow solid obtained was 4,4′-azoxytoluene (**19**, 5%), mp 61–62° (lit.[27] mp 69–70°). Ir, nmr, and mass spectra of **19** were identical with those of an authentic sample.

Ethyl 5-fluoroanthranilate was purified by chromatography on a 6 × 1 in. column of Florisil using hexane as the eluting solvent: ir (neat) 3490, 3380 (NH_2), and 1700 cm^{-1} (C=O); nmr (CCl_4) δ 1.4–1.6 (t, 3 H, CH_3, J = 7 Hz), 4.3–4.7 (q, 2 H, CH_2, J = Hz), 5.6–6.2 (broad, 2 H, NH_2), and 6.6–8.2 (m, 3 H, aromatic). *Anal.* Calcd for $C_9H_{10}O_2NF$: C, 59.0; H, 5.5; N, 7.6; F, 10.4. Found: C, 59.1; H, 5.5; N, 7.6; F, 10.0. Hydrolysis of 0.2 g of **18** with sodium carbonate solution at 30° overnight followed by acidification to pH 3 gave 5-fluoroanthranilic acid (90%) as a tan solid, mp 181–184° (lit.[28] mp 185°).

Reaction of *N*-(1-Naphthyl)hydroxylamine (8) with Hydrogen Fluoride. Five grams (0.031 mol) of **8** was added slowly to 100 ml of hydrogen fluoride at −60°. A black mixture resulted immediately. After standing overnight, the mixture was neutralized with sodium bicarbonate solution. The basic solution was extracted with ether. After the usual work-up, the ether was evaporated to give black crystals. Attempts to purify the substance were unsuccessful. A mass spectrum of the crude material showed the presence of 1,1′-azoxynaphthalene as compared with a mass spectrum of an authentic sample. The addition of acetone or methylene chloride as cosolvents produced the same result.

Reaction of *N*-(2-Naphthyl)hydroxylamine (9) with Hydrogen Fluoride. *N*-(2-Naphthyl)hydroxylamine (**9**, 0.62 g, 0.0039 mol) was slowly added to 150 ml of freshly condensed hydrogen fluoride at −60°. After the solution had stood overnight, ether was added and the contents were neutralized with ammonia. The mixture was filtered, leaving a small amount of dark residue. The ether solution was separated and combined with an ether extract of the aqueous layer. After drying ($MgSO_4$) and removal of the ether, a brown semisolid remained. Injection of a benzene solution of the semisolid into the gc–mass spectrometer (5 ft × 0.25 in. column of 3% SE-30 on Chromosorb W at 150° and 15 ml/min He flow) showed one major eluent, identified as 1-fluoro-2-aminonaphthalene by comparison of its mass spectrum (*m*/*e* 161, parent) with that of an authentic sample.[29]

The yield was 10% as determined by glpc. Several other unidentified substances were present in very small amounts.

Subjection of the brown semisolid to chromatography on a 10 × 1 in. column of alumina using hexane as the eluting solvent and adding benzene as the chromatography proceeded produced 0.29 g (50%) of 2,2′-azoxynaphthalene: mp 163° (lit.[30] mp 164°); nmr ($CDCl_3$) δ 7.2–8.2 (aromatic); ir (KBr) 1475 cm^{-1} (N=NO).

Reaction of *N*-(2-Biphenyl)hydroxylamine (11) with Hydrogen Fluoride. Freshly prepared **11** (1.82 g, 9.8 mmol) was slowly added to 100 ml of freshly condensed hydrogen fluoride at −60°. The mixture initially showed a blue color which changed to black after standing for several hours. After evaporation of the hydrogen fluoride, water (30 ml) and ether (30 ml) were added and the contents were neutralized with ammonia gas. The mixture was filtered to give a dark brown residue. The residue was shown to be carbazole (**23**) by comparison of its mass spectrum, infrared spectrum, and thin layer chromatography (silica gel) R_f data with those of an authentic sample of carbazole. The crude yield was 0.25 g (15%).

The filtrate was extracted with ether. The separated organic mixture was dried ($MgSO_4$) and concentrated on a rotary evaporator to give a brown oil. Chromatography on a 10 × 1 in. column of alumina using 1:1 benzene–hexane produced 1.0 g (60%) of 2,2′-azoxybiphenyl: mp 156° (lit.[31] mp 158°); nmr ($CDCl_3$) δ 7.2–7.5 (aromatic); ir (KBr) 1480 cm^{-1} (N=NO). These spectra were identical with those of authentic material.

A second eluent was obtained as a semisolid. It was identified as 5-fluoro-2-aminobiphenyl by comparison with an authentic sample.[32] The crude yield was 0.37 g (20%): mp 55–65; nmr ($CDCl_3$) δ 3.5–3.7 (broad, 2 H, NH_2) and 6.7–7.6 (m, 8 H, aromatic); ir (KBr) 3400, 3380 (NH_2), 830, 750 cm^{-1} (aromatic).

Reaction of *N*-(2-Biphenyl)hydroxylamine (11) with Sulfuric Acid. A mixture of 0.1 g (0.5 mmol) of **11** and 2 ml of 20% sulfuric acid was stored at room temperature for 1 hr. The resulting green mixture was extracted with chloroform. The dried ($MgSO_4$) chloroform solution was concentrated to give a dark green residue. Thin layer chromatography and mass spectral analysis (*m/e* 167, parent) were identical with those of authentic carbazole. The yield was 10%.

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Registry No.—Hydrogen fluoride, 7664-39-3.

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Synthesis of Cyclopropylmethanol Derivatives Bearing Electronegative Substituents[1a]

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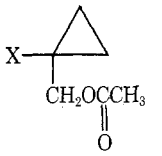
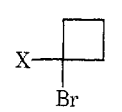
In this note we report a convenient synthesis of cyclopropylmethanol acetates bearing electron-withdrawing substituents at the 1 position. The data base for cyclopropylcarbinyl cation chemistry, for example, is provided in overwhelming part by experiments performed on carbon skeletons carrying electron-donating substituents.[2] Recent studies in the bicyclo[2.2.1]heptyl system have highlighted some interesting effects of electronegative substituents on the chemistry of the 2-cation.[3] Thus, one rationale for exploring synthetic approaches to electronegatively substituted cyclopropylcarbinyl derivatives lies in the proposition that such compounds should be of interest in the further elucidation of the chemistry of cyclopropylcarbinyl reactive intermediates.

The starting materials for the preparations of **1** were the known cyclobutyl derivatives **2** and conversions into **1**



1a, X = COC_6H_5
b, X = CO_2CH_3
c, X = $CONH_2$
d, X = NO_2



2a, X = COC_6H_5
b, X = CO_2CH_3
c, X = $CONH_2$
d, X = NO_2
e, X = NO

were accomplished by heating each starting material in glacial acetic acid containing an excess of silver acetate.