Appropriate corrections were made for increase in reactant volume due to added titrant.

Registry No.—*syn-syn*-DIA, 26309-06-8; *anti*-1-oximinoacetone, 17280-41-0.

Acknowledgment.—This work was carried out under Contract DA-18-108-AMC-207(A) Task 1C622401A-10204, Department of Defense, whose support is gratefully acknowledged.

α-Methoxy-α-trifluoromethylphenylacetic Acid. Configuration by Asymmetric Synthesis[1]

LADISLAV HUB[2] AND HARRY S. MOSHER*

Department of Chemistry, Stanford University, Stanford, California 94305

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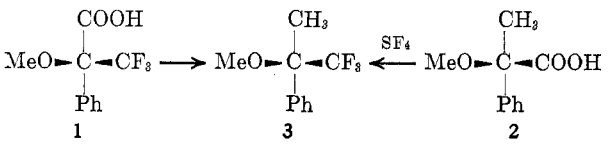
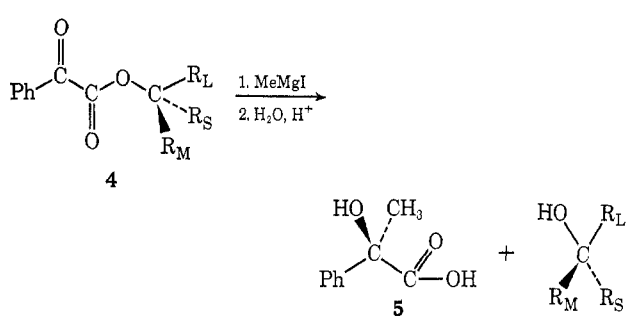
(−)-α-Hydroxy-α-trifluoromethylphenylacetic acid (**13**) has been prepared by asymmetric synthesis involving the reaction of phenylmagnesium bromide with (−)-menthyl trifluoropyruvate [**10**, CF_3COCOO-(−)-menthyl]; 22% asymmetric induction was observed. Application of Prelog's generalization to this system is unambiguous and leads to the assignment of the *S* configuration to this product and to the corresponding methyl ether **1** and methyl ether–methyl ester **14**, in accord with previous work. (−)-Menthyl glyoxylate [HCOCOO-(−)-menthyl] gave 19% asymmetric synthesis of the (*S*)-mandelic ester; this indicates that the nature of the achiral group (CF_3 *vs.* H) has only a minor effect upon the *extent* of asymmetric induction in this system.

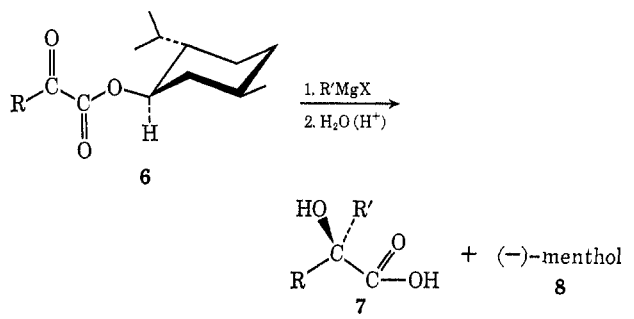
α-Methoxy-α-trifluoromethylphenylacetic acid (**1**, MTPA)[3] is a valuable reagent for the determination of enantiomeric purity of alcohols and amines. Circumstantial evidence for the *S* configuration for (−)-MTPA has been obtained by correlation of the nmr chemical shift of (−)-methyl α-methoxy-α-trifluoromethylphenylacetate in a chiral solvent with that of (*R*)-(−)-methyl mandelate.[4] More recently an extensive study of the circular dichroism of a series of α-substituted phenylacetic acids[5] has convincingly supported this assignment. We had hoped to establish the absolute configuration of MTPA by the conversion of *O*-methylatrolactic acid (**2**) of known configuration into the methyl ether of methylphenyltrifluoromethylcarbinol (**3**) by treatment with sulfur tetrafluoride. This intermediate, **3**, should be readily accessible from MTPA **1**. This approach is similar to that which we have



used to establish the configuration of phenyltrifluoromethylcarbinol and methyltrifluoromethylcarbinol.[6] However repeated attempts to achieve the conversion of **2** to **3** have failed to produce a detectable amount of the trifluoromethyl product **3**; therefore this direct approach has been reluctantly abandoned in favor of the following alternative.

According to the Prelog generalization,[7] when the small, medium, and large groups (R_S, R_M, R_L) in the alcohol moiety of a chiral benzoylformate ester are as represented in **4**, *R*-(−)-atrolactic acid (**5**) will be produced in excess upon treatment with methylmagnesium iodide. This empirical correlation has been exceedingly reliable for predicting the configuration of secondary carbinols; less use has been made of this generalization for the determination of configuration of α-hydroxy acids, even though the correlation here should be on even firmer ground. For example, the (−)-menthyl group in the keto ester **6** is responsible for the different rates of attack of the reagent on one *vs.* the other diastereotopic faces of the prochiral keto group to give **7** in excess. If R is varied while the chiral "inducing"





(−)-menthyl group is retained, stereoisomers of corresponding configuration should predominate regardless of the nature of the achiral R group. In such comparable reactions the asymmetric reaction is brought about by the same chiral moiety while R, which is achiral, is separated by at least three atoms from the inducing chiral centers. The proximity of R to the

* To whom correspondence should be addressed.

(1) We acknowledge with gratitude support of these studies through NSF Grant 9432.

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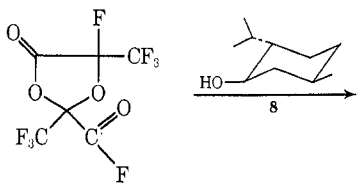
emerging chiral α-hydroxy center may have an effect upon the *extent* of asymmetric synthesis but it certainly should not alter the *sense* of asymmetric synthesis. The same should apply to variations in the R′ group of the reagent. A survey of the available literature confirms that this is so as far as it has been studied.[7,8] For instance, when (−)-menthyl benzoylformate (**6**, R = Ph) is treated with methylmagnesium iodide, (*R*)-(−)-atrolactic acid (**7**, R = Ph; R′ = CH_3) is formed[8b] in 25% excess over the racemate [25% e e (enantiomeric excess)]; when (−)-menthyl pyruvate (**6**, R = CH_3) is treated with phenylmagnesium iodide, (*S*)-(+)-atrolactic acid (**7**, R = CH_3; R′ = Ph) is formed[8g] as predicted (18% e e). Thus by studying the asymmetric reaction of (−)-menthyl trifluoropyruvate (**6**, R = CF_3) with phenylmagnesium bromide (R′ = Ph), additional evidence concerning the configuration of MTPA (**1**) can be obtained. This approach is singularly free of complications from the standpoint of stereochemical interpretation.

Trifluoropyruvyl fluoride and its dimer have been described recently.[9,10] (−)-Menthyl trifluoropyruvate (**10**) was prepared from the dimer of trifluoropyruvyl fluoride [**9**, 4-oxo-2,5-di(trifluoromethyl)-5-fluoro-2-fluorocarbonyl-1,3-dioxolane]. The dioxolane **9** decomposes to trifluoropyruvic acid in the presence of base.[9] The dimer was treated directly with (−)-menthol in the presence of sodium fluoride and a mixture of the desired (−)-menthyl trifluoropyruvate **10** and the menthyl ester, of the dimer (**11**) was obtained. These were separable by gas chromatography. Treatment of



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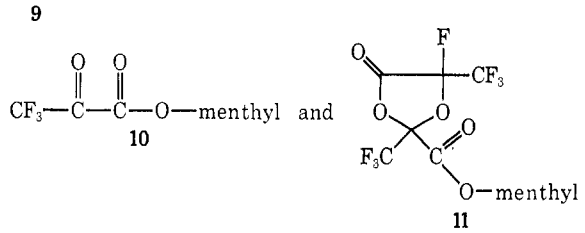
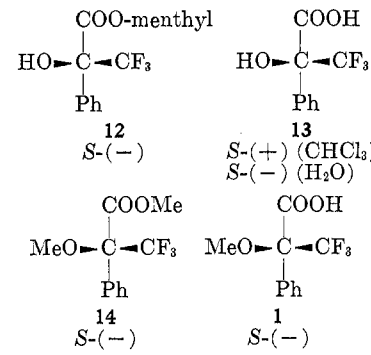


10 and **11**

(−)-menthyl pyruvate (**10**) with phenylmagnesium bromide gave (−)-menthyl α-trifluoromethyl-α-hydroxyphenylacetate (**7**, R = CF_3; R′ = Ph). Based on the Prelog generalization, this must have the *S* configuration at the position α to the carboxyl group as shown in **12**. The acid **13**, formed on hydrolysis, must



likewise have the *S* configuration. This acid [**13**, (+) in chloroform, (−) in water] was conveniently purified by conversion to the methyl ether–methyl ester (**14**) and preparatively gas chromatographed. The rotation of the methyl α-methoxy-α-trifluoromethylphenylacetate was $[\alpha]^{24}D$ −21.3° (*c* 4.74, acetone) which corresponds to 22% excess of the *S*-(−) enantiomer. It has been shown[8,11] that (−)-**14** gives (−)-**1**, thereby establishing the *S* configuration for (−)-MTPA as previously assigned.[4,5] It is of interest that this per cent asymmetric synthesis is rather close to the 25% found[8b] for (−)-menthyl pyruvate in the comparable asymmetric synthesis.

To obtain further evidence concerning the assumption that the nature of the R group in **6** does not change the stereochemical course of the reaction, we have studied (−)-menthyl glyoxylate (**6**, R = H). Treatment of this with phenylmagnesium bromide gave (−)-menthyl mandelate which was proven to have the *S* configuration by reduction to the known (*S*)-(+)-phenylethylene glycol (19% e e). This not only substantiates the predicted stereochemical course of the reaction but also the prediction that reasonable changes in the R group should have minor influence upon only the *extent* of asymmetric synthesis.

Experimental Section

(−)-Menthyl Trifluoropyruvate (10).—(−)-Menthol (15 g, 96 mmol) was dissolved in glyme (1,2-dimethoxyethane, 100 ml, distilled from lithium aluminum hydride) and sodium fluoride (30 g, 1.25 mol) was added. 4-Oxo-2,5-di(trifluoromethyl)-5-fluoro-2-fluorocarbonyl-1,3-dioxolane[9,10] (**9**, 18 g, 6.25 mmol, crude, bp 57–70°) was slowly added to the well-stirred suspension. After the exothermic reaction subsided, the mixture was stirred overnight. Sodium fluoride was removed by filtration; the solvent was evaporated at reduced pressure and the resulting oil distilled to give 23 g of product, bp 85–87° (1 mm). Preparative gas chromatography (silicone gum rubber SE-60 column, 0.25 in. × 20 ft, 175°, helium flow rate 150 ml/min) showed the presence in approximately equal amounts of two substances, retention times of 24 and 30 min, respectively. The first fraction was menthyl trifluoropyruvate: bp 63–65° (0.7 mm); $[\alpha]^{24}D$ −66.8° (*c* 4.07, CH_3OH); ir spectrum (film) 2950, 1775, 1735, 1455, 1320, 1260, 1170, and 1010 cm^{-1}. The pmr spectrum showed only signals for the menthyl group.

Anal. Calcd for $C_{13}H_{19}O_3F_3$: C, 55.70; H, 6.83; F, 20.33. Found: C, 55.51, 55.61; H, 6.89, 6.85; F, 19.64.

The second fraction was menthyl 4-oxo-2,5-di(trifluoromethyl)-5-fluoro-1,3-dioxolane-5-carboxylate (**11**): bp 65–68° (0.5 mm); $[\alpha]^{24}D$ −45.0° (*c* 10.8, CH_3OH); ir spectrum (film) 2960, 1860, 1770, 1460, 1285, 1225, 1170, 1110, 1070, and 1025 cm^{-1}. The ^{19}F nmr indicated that all four possible stereoisomers, differing in configuration at carbon atoms 2 and 5 of the dioxolane ring, were present in approximately equal amounts.

Anal. Calcd for $C_{16}H_{19}O_5F_7$: C, 45.29; H, 4.51; F, 31.34. Found: C, 45.44; H, 4.50; F, 31.06.

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(10) We are most grateful to Dr. Roy Plunkett and Dr. Harold L. Jackson of the Du Pont Company for a sample of the dimer of trifluoropyruvyl fluoride used in the present study.

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(−)-Menthyl trifluoropyruvate forms a hydrate when exposed to air: mp 129–135.5°; ir spectrum ($CHCl_3$ solution) 3450, 2960, 1725, 1450, 1250, 1185, 1140, 1105, 940, and 900 cm^{-1}; $[\alpha]^{24}D$ −116.0° (*c* 2.3, $CHCl_3$). The optical rotation in absolute methanol changes from $[\alpha]^{24}D$ −97° (*c* 6.07, CH_3OH) immediately after solution to an equilibrium value of $[\alpha]^{24}D$ −67.1° (*c* 6.07, CH_3OH) after 3 hr.

Anal. Calcd for $C_{13}H_{19}O_3F_3 \cdot H_2O$: C, 52.34; H, 7.10; F, 19.11. Found: C, 53.24; H, 6.95; F, 18.70.

(*S*)-(−)-Methyl α-Methoxy-α-trifluoromethylphenylacetate (14).—To the cooled ethereal solution of the Grignard reagent from bromobenzene (2.2 g, 14 mmol in ether) and sublimed magnesium (0.5 g, 20 mmol) was added a solution of (−)-menthyl trifluoropyruvate (3 g, 10.7 mmol) in anhydrous ether. After the reaction mixture was refluxed for 30 min, it was decomposed with dilute sulfuric acid and extracted with ether. The combined ethereal extracts were successively washed with water, sodium bicarbonate solution, and water. The ether was evaporated to give a slightly yellow oil which was saponified with 50% aqueous ethanolic sodium hydroxide by refluxing for 3 hr. The ethanol was removed by vacuum evaporation and the residue taken up in water and the solution extracted several times with ether to remove menthol. The water layer was acidified and extracted with ether to give 1.35 g (57% yield) of α-trifluoromethyl-α-hydroxyphenylacetic acid (**13**) as a slightly brown solid which was methylated without purification by dissolving in glyme (20 ml), adding a suspension of sodium hydride (0.3 g, 12.5 mmol) in glyme and treating with dimethyl sulfate (1.8 g, 14.3 mmol) at room temperature for 4 hr. Unreacted dimethyl sulfate and sodium hydride were decomposed in the cold with 10 ml of ammonium hydroxide; the mixture was acidified with cold, dilute sulfuric acid followed by extraction with ether. Evaporation of the ethereal solution after washing with sodium bicarbonate and drying (Na_2SO_4) gave an oil which yielded upon distillation 0.9 g (62% yield) of (−)-methyl α-methoxy-α-trifluoromethylphenylacetate (**14**), bp 72–75° (0.5 mm). Traces of impurities were removed by preparative gas chromatography (silicone QFl column, 0.25 in. × 20 ft, 200°) to give purified **14**, $[\alpha]^{24}D$ −21.8° (*c* 6.48, acetone), which corresponds to 22.7% excess of the (*S*)-(−) enantiomer. The nmr and ir spectra were identical with those from an authentic sample.[3,11]

This experiment was repeated under the same conditions to give methyl α-methoxy-α-trifluoromethylphenylacetate, $[\alpha]^{24}D$ −21.3° (*c* 4.74, acetone), corresponding to 22.2% enantiomeric excess, in an overall yield of 70%.

(−)-Menthyl Glyoxylate.—A solution of 1 equiv of (−)-menthol in chloroform was slowly added to a chloroform solution of oxalyl chloride. The mixture was heated at 60° for 3 hr, the solvent evaporated under vacuum, and the residue distilled to give menthyl oxalyl chloride, bp 80° (0.3 mm), 80% yield [lit.[12] bp 123–125° (8–9 mm)].

(−)-Menthyl oxalyl chloride (30 g) in 150 ml of benzene under nitrogen was refluxed while 10% excess of tri-*n*-butyltin hydride [39 g, bp 85–95° (1 mm), prepared[13] by reduction of tri-*n*-butyltin chloride with lithium aluminum hydride] dissolved in 50 ml of benzene was slowly added. After 2 hr at reflux, the solvent was removed under reduced pressure and the residue distilled. The first fraction, (−)-menthyl glyoxylate, 14.9 g (58%), bp 102–103° (1.5 mm), $[\alpha]^{24}D$ −65.0° (*c* 9.02, CH_3OH), showed only trace impurities by glc [bis-(2-ethylhexyl)tetrachlorophthalate column, 0.25 in. × 10 ft, 135°]. The second fraction, 10.5 g, bp 103–115° (1 mm), was mostly (−)-menthyl glyoxylate but was contaminated with tri-*n*-butyltin chloride. The addition of 2 ml of water to this fraction caused the formation of a white solid which was recrystallized from petroleum ether (bp 60–68°) to give 6.9 g (24%) of (−)-menthyl glyoxylate hydrate, mp 79–80°, $[\alpha]^{22}D$ −84.9° (*c* 3.44, $CHCl_3$).

Anal. Calcd for $C_{12}H_{20}O_3 \cdot H_2O$: C, 62.58; H, 9.63. Found: C, 62.85; H, 9.66.

The third fraction, bp 115–120° (1 mm), was primarily tri-*n*-butyltin chloride.

(−)-Menthyl glyoxylate gave the following: ir spectrum (film) 2950, 2920, 2860, 1800 (w), 1750, 1720 (s), 1450, 1290, 1220, and 975 cm^{-1}; nmr spectrum (neat, 60 MHz) δ 9.35 (s, 1 H), 4.8 (sextet, 1 H), 0.7–2.3 (broad, menthyl group). The nmr spectrum of the hydrate ($CDCl_3$) showed δ 5.27 (s, 1 H), 4.6 (broad, 3 H, reduced to a singlet, 1 H by washing with D_2O), and the characteristic menthyl group signals. The 2,4-dinitrophenylhydrazone, mp 145–146°, $[\alpha]^{24}D$ −105° (*c* 2.77, $CHCl_3$), was prepared in the usual way.

Anal. Calcd for $C_{18}H_{24}N_4O_6$: C, 55.09; H, 6.17; N, 14.25. Found: C, 55.33; H, 6.14; N, 14.05.

Reaction of (−)-Menthyl Glyoxylate with Methylmagnesium Iodide.—An ethereal solution of the Grignard reagent from 3.5 g of methyl iodide was added to an ether solution of 4.25 g of (−)-menthyl glyoxylate at 0°. The reaction was refluxed for 10 hr and hydrolyzed with a saturated ammonium chloride solution. The washed (H_2O, $NaHCO_3$, H_2O) and dried (Na_2SO_4) ether extracts were evaporated; the residue was distilled to give 3.1 g of menthyl lactate, bp 80–85° (1 mm). The per cent asymmetric synthesis was determined as follows by conversion to 1,1-diphenylpropane-1,2-diol (whose absolute configuration and enantiomeric purity are known[14]). An ether solution of the total menthyl lactate from the above experiment was added to an ethereal phenyl Grignard solution made from 13 g of phenyl bromide and 3.4 g of sublimed magnesium. The reaction mixture was refluxed for 12 hr and hydrolyzed with cold saturated ammonium chloride solution. The washed (H_2O) and dried (Na_2SO_4) ether layer was evaporated and the residue was steam distilled to remove menthol and biphenyl. The nonvolatile oil was taken into ether solution which was dried (Na_2SO_4) and evaporated to give an oil, 1.25 g, 41%, which was purified by silica gel column chromatography using benzene solvent; 1.08 g of pure diol, mp 88–92°, $[\alpha]^{24}D$ −24.3° (*c* 3.54, benzene), which corresponds to 16% of the rotation of the pure isomer [lit.[14] mp 92–93°, $[\alpha]^{20}D$ +149.8° (*c* 2.43, benzene)], was obtained. The spectra were as follows: ir (benzene) 3570 (s), 2980, 2930 (w), 1490, 1450 (s), 1100, 890, and 690 cm^{-1}; nmr (60 MHz, acetone-d_6) δ 7.8–70 (aromatic protons, 10 H), 4.85 (q, 1 H, J = 6 Hz), 1.03 (d, 3 H, J = 6 Hz), 4.5 (s, 1 H), and 3.0–3.8 (broad, 2 H). These last two signals disappeared upon D_2O exchange.

The asymmetric synthesis was first carried out as above but with hydrolysis of the Grignard reactions using dilute sulfuric acid, instead of saturated ammonium chloride solution, to give a 45% overall yield of 1,1-diphenylpropane-1,2-diol, mp 86–90°, $[\alpha]^{24}D$ −19.3° (*c* 2.02, benzene), corresponding to 13% asymmetric synthesis.

Reaction of Phenylmagnesium Bromide with (−)-Menthyl Glyoxylate.—The ethereal phenyl Grignard solution prepared from 5.3 g of bromobenzene was added to a cold, ether solution containing 6 g of (−)-menthyl glyoxylate. After refluxing overnight, the reaction mixture was hydrolyzed with saturated ammonium chloride solution and the water layer extracted with ether. The combined ether extracts were washed (H_2O), dried (Na_2SO_4), and evaporated to give a residue of menthyl mandelate, 8.3 g. One-half of this residue was reduced with lithium aluminum hydride, 0.7 g, in ether. The reaction mixture was decomposed with water and 15% sodium hydroxide. The precipitated hydroxides were removed by filtration, and the residue, after evaporating with ether, was purified by silica gel column chromatography. Menthol was removed by chloroform elution and the phenylethylene glycol with methanol elution to give 0.6 g, 35% yield, which was further purified by sublimation: mp 58–62°; $[\alpha]^{24}D$ +12.4° (*c* 9.07, $CHCl_3$). This corresponds to 19.4% asymmetric synthesis based on the reported value[8a,15] for (*S*)-(+)-phenylethylene glycol of $[\alpha]^{23}D$ +63.8° (*c* 9.5, $CHCl_3$), mp 66–67°. The racemic diol has a melting point of 69–70°.[16] It has been reported[17] that the maximum rotation of phenylethylene glycol should be 30% higher than this; however, we have confirmed Bakshi and Turner's value by means of nmr studies of the MTPA derivative.[18]

The second half of the reaction product from phenylmagnesium bromide and (−)-menthyl glyoxylate was treated with excess phenylmagnesium bromide. However the triphenylethane-1,2-diol obtained (2.7 g, mp 150–155°, $[\alpha]^{22}D$ −5.2° (*c* 2.68, acetone), corresponded to 2.4% enantiomeric purity based on the rotation of $[\alpha]D$ +218.9° (*c* 2, acetone).[19] It was concluded that extensive racemization of this glycol had occurred.

DL-Methylphenyltrifluoromethylcarbinyl Methyl Ether (3).—

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DL-Methylphenyltrifluoromethylcarbinol[20,21] (5.7 g), bp 95–100° (20 mm), prepared in 89% yield by the action of phenylmagnesium bromide on methyl trifluoromethyl ketone and in 90% yield by the action of methylmagnesium iodide on phenyl trifluoromethyl ketone) was treated in ether solution (30 ml) with sodium hydride (4.0 g, 50% mineral oil dispersion) followed by refluxing (1 hr) with dimethyl sulfate (4 g) to give the methyl ether **3** (6.1 g). This product showed no unreacted carbinol by vpc analysis (UCON LB 1715, 5 ft × 0.25 in., 150°, helium flow rate 30 ml/min, retention time 4 min): nmr ($CDCl_3$) δ 1.78 (q, 3 H, J = 0.8 Hz, long range CF_3 coupling), 3.22 (s, 3 H), 7.2 ppm (broad, 5 H, aromatic).

Anal. Calcd for $C_{10}H_{11}F_3O$: C, 58.81; H, 5.43. Found: C, 58.98; H, 5.51.

This material was used as a calibration standard for vpc and thin layer chromatography (tlc) studies in connection with the following sulfur tetrafluoride reactions.

Reactions of Sulfur Tetrafluoride with DL-*O*-Methylatrolactic Acid 2.—A stainless steel hydrogenation-type autoclave, 150-ml capacity, was charged with *O*-methylatrolactic acid[22] (2.0 g) and cooled to −60°. Sulfur tetrafluoride (25 g) was condensed in the autoclave followed by hydrogen fluoride (29 g) and the mixture was shaken at 20–25° for 24 hr. The reaction mixture was processed as indicated previously.[23] No starting material was recovered but no methylphenyltrifluoromethylcarbinyl methyl ether could be detected by tlc. Essentially the same procedure was conducted at 50° for 22 hr and at 90° for 3 days. In these runs a spot was observed on tlc with the same R_f value as the desired ether, but preparative silica gel chromatography failed to isolate any of the desired ether. Further experiments in which SF_4 was added to the acid sample **2** in water to generate the HF *in situ* were likewise unsuccessful, leading in some cases to block residues and in others to mixtures like the above which contained no starting acid but in which the ether could not be detected.

Registry No.—**3**, 26315-60-6; **6** (R = H), 26315-61-7; **6** 2,4-DNP, 26315-62-8; **10**, 26315-63-9; **11**, 26315-64-0; **14**, 26164-19-2.

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The Peroxide-Initiated Decarbonylation of 9-Carbazolylacetaldehyde. A Possible Free-Radical Displacement[1a]

BRUNO M. VITTIMBERGA AND MATTHEW L. HERZ[1b]

Department of Chemistry, University of Rhode Island, Kingston, Rhode Island 02881

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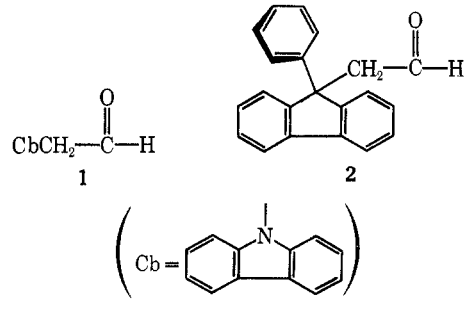
The peroxide initiated decarbonylation of 9-carbazolylacetaldehyde was studied in *o*-dichlorobenzene at 140 and 170° in an effort to observe a free radical N → C migration. No migration was detected. A reaction did occur, however, with the formation of 9-methylcarbazole, 1,2-dicarbazol-9-ylethene, and dicarbazol-9-ylmethane. Evidence is presented to support the structures of these compounds and the mechanism of their formation.

As part of a study on free-radical migration reactions,[2,3] we were prompted to investigate the peroxide-initiated decarbonylation of 9-carbazolylacetaldehyde (**1**). It was hoped that the stabilizing forces in this molecule would contribute to the first example of a nitrogen to carbon free-radical migration.[4]

This system was chosen because of its similarity to 9-phenyl-9-fluorenylacetaldehyde (**2**) which on decarbonylation was found to give a smooth conversion to



9-phenylphenanthrene.[5] Similar rearrangement in **1** would reduce ring strain with the simultaneous formation of the strongly stabilized free radical of the type R—CH_2—N—Ar.

The desired rearrangement would be expected to occur irreversibly[6] and most probably lead to the formation of the stable aromatic compound, phenanthridine, in a manner similar to the reaction of **2**. Radical stabilization and relief of ring strain, which are not necessary for carbon-to-carbon migration,[7] could provide the necessary driving force for nitrogen-to-carbon homolytic phenyl migration.

The aldehyde, **1**, was synthesized by an alkaline permanganate oxidation of 9-allylcarbazole[8] to yield 1-carbazol-9-yl-2,3-dihydroxypropane. This glycol was further oxidized with periodic acid to yield **1** the structure of which was verified by infrared, nmr and elemental analyses.

The di-*t*-butyl peroxide (DTBP) initiated decarbonylation was carried out both in the presence of oxygen and in deoxygenated systems. The results appear in Table I. When the decarbonylation was carried out in the presence of excess oxygen under the various conditions described in Table I (runs 1, 2, and 3), the only product

(1) (a) Based on the Ph.D. Thesis of M. L. Herz, University of Rhode Island, 1969. U.S. Army Natick Laboratory, Natick, Mass. (b) American Hoeshst Fellow, 1967–1968.

(2) For a review, see C. Walling, "Molecular Rearrangements," Vol. I, P. de Mayo, Ed., Interscience, New York, N. Y., 1963, p 409 ff.

(3) (a) J. W. Wilt and M. Stumpf, *J. Org. Chem.*, **30**, 1256 (1965); (b) J. W. Wilt and O. Koluve, *J. Amer. Chem. Soc.*, **87**, 2071 (1965); (c) J. W. Wilt, O. Koluve, and J. F. Kraemer, *ibid.*, **91**, 2624 (1969).

(4) A possible 1,3-N → C migration has recently been described by R. W. Binkley, *Tetrahedron Lett.*, 1893 (1969).

(5) B. M. Vittimberga, *ibid.*, 2383 (1965).

(6) W. Rickatson and T. S. Stevens, *J. Chem. Soc.*, 3960 (1963).

(7) (a) W. H. Urry and N. Nicholaides, *J. Amer. Chem. Soc.*, **74**, 5163 (1952). (b) F. H. Seubold, *ibid.*, **75**, 2532 (1953); (c) L. H. Slaugh, *ibid.*, **81**, 2262 (1959).

(8) This compound was prepared using a modification of the procedure of B. Levy, *Monatsh. Chem.*, **33**, 182 (1912).