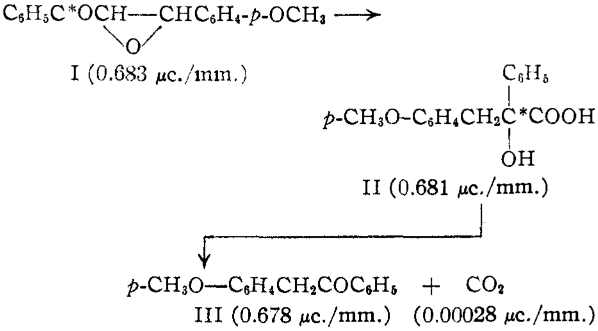
high migratory aptitude for the benzyl group in this rearrangement, or a great difference in the reactivities of the carbonyl groups.

When *p*-methoxybenzylidene-(aceto-1-C^{14})-phenone was prepared as an intermediate in another synthesis, it was of interest to determine its mode of reaction in the base-catalyzed rearrangement.

p-Methoxybenzylidene-(aceto-1-C^{14})-phenone oxide (I) was prepared by condensation of anisaldehyde with (aceto-1-C^{14})-phenone and treatment of the resulting *p*-methoxybenzylidene-(aceto-1-C^{14})-phenone with hydrogen peroxide. Rearrangement of the resulting oxide gave 2-hydroxy-2-phenyl-3-(*p*-methoxyphenyl)-propionic acid, labeled exclusively in the carbinol group, thus demonstrating no phenyl group migration. The radioactivities, reported as microcuries per millimole (μc./mm.) are shown in the reaction scheme below. Degradations and assays were carried out as described previously.[3] The reported radioactivities are subject to an error of ±1%.



Although the *p*-methoxyphenyl group has been shown to migrate less than phenyl in the benzilic acid rearrangement,[4] presumably because of their relative effects on the carbonyl group reactivities, the substitution of a *p*-methoxy group on the potential benzyl group ring of benzylideneacetophenone oxide does not promote phenyl group migration to a discernible level. Although the carbon dioxide obtained in the oxidation of the acid product in the present case contained slightly less radioactivity than did that previously reported, it seems unwise to attach significance to these small numbers.

Experimental

***p*-Methoxybenzylidene-(aceto-1-C^{14})-phenone.**—A 4.05-g. portion of (aceto-1-C^{14})-phenone was condensed with 5.11 g. of anisaldeyde in the presence of ethanolic alkali[5,6] to yield 7.00 g. (87%) of *p*-methoxybenzylidene-(aceto-1-C^{14})-phenone, m.p. 132–134°.

***p*-Methoxybenzylidene-(aceto-1-C^{14})-phenone Oxide (I).**—A 6.7-g. portion of *p*-methoxybenzylidene-(aceto-1-C^{14})-phenone was treated with alkaline hydrogen peroxide[5,6] to obtain 3.58 g. (50%) of I, m.p. 82–83°.

Anal. Calcd. for $C_{16}H_{14}O_3$: C, 75.50; H, 5.55. Found: C, 75.37; H, 5.60.

Radioanal: 0.0276 microcurie C^{14} per 10.26-mg. sample.

2-Hydroxy-2-phenyl-3-(*p*-methoxyphenyl)-propionic Acid (II).—A 3.33-g. sample of I was rearranged by the previously described method to give 1.56 g. (44%) of II, m.p. 192.5–193.0°.

Anal. Calcd. for $C_{16}H_{16}O_4$: C, 70.52; H, 5.92. Found: C, 70.50; H, 5.98.

Radioanal: 0.0527 microcurie C^{14} per 21.37-mg. sample.

***p*-Methoxyphenyl(aceto-1-C^{14})-phenone (III).**—A 0.5-g. sample of II was oxidized as previously described[3] to give 0.358 g. (86%) of *p*-methoxyphenyl-(aceto-1-C^{14})-phenone (III), m.p. 96°, and 0.354 g. (96%) of barium carbonate.

Radioanal: II: 0.0430 microcurie C^{14} per 14.32-mg. sample. $BaCO_3$: 0.00098 microcurie C^{14} per 70-mg. sample.

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[4] J. D. Roberts, D. M. Smith and C. C. Lee, THIS JOURNAL, **73**, 618 (1951).

[5] E. P. Kohler and H. M. Chadwell, "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1941, pp. 78–80.

[6] E. Weitz and A. Scheffer, *Ber.*, **54**, 2338 (1921).

Carveol and Carveol Acetate

BY ROBERT H. REITSEMA

RECEIVED OCTOBER 31, 1952

Two important constituents of spearmint oil, carveol and carveol acetate have been prepared by a convenient method. The reduction of carvone to carveol using aluminum isopropoxide has been reported several times.[1–3] It seemed of interest to investigate this reduction using lithium aluminum hydride as the reducing agent to compare yields and the nature of the isomers obtained.

The yield of crude carveol, $[\alpha]_D$ −36.2°, obtained was 92.8% of the theoretical amount. Reduction with aluminum isopropoxide has been reported to give carveol mixtures with rotations of 100.9–108.2°[2] and −109.0°[3] from *d*-carvone and *l*-carvone, respectively. This would indicate that nearly equal amounts of the *cis* and *trans* isomers formed since *d*-carvone leads to *d*-*cis*-carveol, $[\alpha]_D$ 23.9°, and *d*-*trans*-carveol, $[\alpha]_D$ 213.1°. Lithium aluminum hydride gives predominantly the *cis* configuration as can be seen from the rotation of the crude mixture which is $[\alpha]_D$ −36.2°. This would be the most favored configuration assuming that attack takes place at the less hindered side of the carbonyl group. The mixture was investigated by isolation of *l*-*cis*-carveol 3,5-dinitrobenzoate and by separation of the *p*-nitrobenzoate into the *cis* and *trans* isomers.

Experimental

Carvone was isolated from spearmint oil with sodium bisulfite and redistilled giving a product boiling 103–104.5° (11 mm.), α_D −59.55°. To 3.1 g. (0.33 equiv.) of lithium aluminum hydride in 75 ml. of anhydrous ether was added dropwise 45.0 g. (0.3 mole) of this carvone in 75 ml. of anhydrous ether. After all the carvone had been added, the mixture was boiled under reflux for an additional hour. About 15 ml. of water was added cautiously, followed by 200 ml. of 10% hydrochloric acid. The ether layer was separated and the aqueous extracts were dried over anhydrous sodium sulfate. Ether was evaporated leaving 43.9 g. (96%) oil, $[\alpha]_D$ −33.1°, n^{24}_D 1.4922. Distillation of the oil gave 92.9% of the theoretical amount of carveol, b.p. 109–111° (12 mm.), $[\alpha]_D$ −36.2°, n^{20}_D 1.4955, d^{25}_{25} 0.9527. This compares with *l*-*cis*-carveol, b.p. 101° (10 mm.), $[\alpha]_D$ 23.9°, n^{25}_D 1.4959, d^{25}_4 0.9521.[2]

To 1.0 g. of the product in 3 ml. of dry pyridine was added 1.7 g. of 3,5-dinitrobenzoyl chloride. The mixture was stirred thoroughly, allowed to cool to room temperature and poured into 1.5 ml. of water. The resulting oil was slurried with 10 ml. of 5% sodium carbonate giving a white solid which was washed with water and recrystallized from ethanol three times giving 0.68 g., m.p. 91–92.5°, $[\alpha]_D$ 45.0° ($CHCl_3$, *c* 3). This compares with the report[2] for

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[1] W. Ponndorf, *Z. angew. Chem.*, **39**, 138 (1926).

[2] R. G. Johnson and J. Read, *J. Chem. Soc.*, 233 (1934).

[3] T. Nagasawa, *Repts. Osaka Imp. Ind. Research Inst.*, **19**, No. 4 (1938); *C. A.*, **34**, 219[8] (1940).

the *d-cis*-carveol derivative, m.p. 92.5°, $[\alpha]_D$ 44.2° ($CHCl_3$, *c* 2).

In a similar manner the *p*-nitrobenzoate was prepared giving a mixture melting mainly at 27–28° and completely melted at 70–72°. Recrystallization gave a mixture of transparent plates, m.p. 26–28°, and a powder, m.p. 75–78°, after mechanical separation. This compares with the report[3] of the *d-cis* derivative m.p. 26.5–28° and the *d-trans* derivative, m.p. 77°.

Boiling 10.78 g. of the carveol mixture with 10 ml. of acetic anhydride and 1.0 g. of anhydrous sodium acetate for two hours gave on distillation 9.56 g. of carveol acetate, b.p. 110–113° (12 mm.), $n^{20}D$ 1.4760, αD −33.2°.

Oxidation of 6.0 g. of the carveol mixture in 12.5 ml. of glacial acetic acid with 5.4 g. of chromic anhydride in 12.5 ml. of acetic anhydride at 13–17° gave carvone, αD −54.6°, $n^{20}D$ 1.4959. This indicates that little isomerization of the ring structure occurred during the reduction and subsequent oxidation.[4,5]

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[4] This reaction was carried out by Mr. V. J. Baarman.

[5] Unless otherwise indicated all notations taken on homogeneous materials.

The Vapor Pressures of Some Substituted Benzotrifluorides[1]

BY SAMUEL KARDON AND JOHN H. SAYLOR

RECEIVED JANUARY 16, 1953

The measurements reported in this note resulted from a continuation of a general program in this Laboratory concerning the solubility and other physical properties of organic fluorine compounds.

TABLE I

PHYSICAL CONSTANTS AND CONSTANTS OF THE VAPOR PRESSURE EQUATION

Benzotrifluoride	B.p., °C. Calcd.	F.p., °C. Obsd.	Dep.	$\eta^{20°}D$	$\eta^{30°}D$	$\epsilon^{30°}$	A	B	C
m-Nitro	202.75	−1.32	0.06	1.4719	1.4675	17	7.18025	1710.60	195.12
m-Amino	191.13	5.65	.01	1.4788	1.4750		7.17030	1650.21	193.58
3-Nitro-4-chloro	222.58	−2.54	.04	1.4895	1.4853	12.8	7.15778	1738.71	183.95
2-Chloro-5-nitro	231.88	21.7	.5		1.5043	9.8	7.15409	1779.91	184.64

Experimental

Materials.—The compounds were supplied by the Hooker Electrochemical Company and were further purified by distillation at reduced pressure (controlled to ±0.1 mm.) in a silvered vacuum-jacketed glass column packed with 1/8" glass helices. The fractions used were characterized by measuring refractive indices, dielectric constants and freezing points. The dielectric constants were measured by the heterodyne beat method. The apparatus was calibrated with benzene and chlorobenzene and has been found to give good results in measuring dielectric constants of highly purified materials with values up to approximately 15. The freezing points were determined as previously described.[2]

Vapor Pressures.—The apparatus which was previously used by Potter[2] was employed. It was a modification of the boiling point apparatus described by Rossini and coworkers.[3]

Results

Fifteen to twenty individual measurements were made on each compound from approximately 5 to 740 mm. The data were fitted by the method of least squares to the equation

$$\log p = \frac{-B}{t + C} + A$$

where p is the pressure in mm. and t is the temperature in degrees centigrade.

The standard deviation between the observed pressures and those calculated from the equation ranged from 0.09 to 0.11 mm.

Table I gives the boiling points calculated from the vapor pressure equation, the freezing points, the freezing point depressions, the refractive indices (η), the dielectric constants (ϵ) and the values of the three constants in the above equation. The value given for the dielectric constant of *m*-nitrobenzotrifluoride is not considered as reliable as those for the other compounds.

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[1] Part of the work reported was carried out under Contract N6ori-107, T. O. II with the Office of Naval Research. Taken from the thesis submitted by Samuel Kardon to the Graduate School of Duke University in partial fulfillment of the requirements for the degree of Master of Arts, June 1952.

[2] J. C. Potter and J. H. Saylor, THIS JOURNAL, **73**, 90 (1951).

[3] C. B. Willingham, W. J. Taylor, J. M. Pignocco and F. D. Rossini, *J. Research Natl. Bur. Standards*, **35**, 219 (1945).

Polyalkylene Sulfides. XII.[1] Termination by Disulfide Formation[2]

BY C. S. MARVEL, C. W. HINMAN AND H. K. INSKIP

RECEIVED DECEMBER 18, 1952

It has been observed[3] that 96–98% of the thiol groups have reacted in 8 to 16 minutes when hexamethylenedithiol and biallyl polymerize in a persulfate initiated reaction at 30°. The complete disappearance of thiol groups occurs only after many hours. The polymer formed in the first few minutes has an inherent viscosity of 0.4 to 0.7 and that obtained after a much longer reaction time has an inherent viscosity of about 1.0. Other dithiols and diolefins show a similar behavior. This has suggested to us that the slow reaction may be an oxidation of terminal thiol groups in the polymers first formed, to yield a disulfide which thus terminates further polymerization.

Evidence of the presence of disulfide links in the polymers of higher inherent viscosity produced in the above reaction has now been obtained. If one of the polymers produced in the long reaction time is reduced by amalgamated zinc and hydrochloric acid in hot xylene solution, it is cleaved to a polymer of lower inherent viscosity. This reduction product can be reoxidized with iodine to produce a poly-

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[1] For the eleventh communication on this topic, see C. S. Marvel and H. N. Cripps, *J. Polymer Sci.*, **9**, 53 (1952).

[2] The work discussed herein was performed as a part of the research project sponsored by the Reconstruction Finance Corporation, Office of Synthetic Rubber, in connection with the Government Synthetic Rubber Program.

[3] C. S. Marvel and A. H. Markhart, Jr., THIS JOURNAL, **73**, 1064 (1951).