solved in petroleum ether and freed from iodine by washing once with 0.05 N thiosulfate and twice with water. The solvent was then stripped at room temperature with a rotary evaporator.

Although RSI and to a lesser degree RSBr are thermally unstable, in solution and in the absence of light they can be kept 1 day or more at room temperature without any detectable decomposition. The uv spectrum is a very good probe for decomposition since in each case the spectrum of the decomposed product is quite different from that of the starting material. The stability depends on the concentration. For example, solutions 10^{-2} M of RSI are stable for about 24 hr in the dark before decomposition starts. At the concentrations used in this paper $(1-2 \times 10^{-4}$ M) the solutions are stable 1 week or more and the limited exposure to light in the spectrophotometer is not sufficient to initiate the decomposition. Solutions of RSBr present an even greater stability.

Products.—N-(n-Butyl)triphenylmethylsulfenamide is the only product recovered in the reaction of RSI, RSBr, and RSSCN with n-butylamine. To about 1 g of RSI, RSBr, and RSSCN in 20 ml of benzene, n-butylamine was added (5% excess) while

stirring. The mixture was washed three times with 1 N HCl and three times with water and dried over anhydrous sodium sulfate. The solution was filtered and the solvent stripped in a rotary evaporator. In order to remove all traces of benzene, about 10 ml of petroleum ether was added and evaporated as before. The weight of the oil thus obtained was within 95 and 102% of the stoichiometric yield in sulfenamide. Moreover, the ir spectrum of the oil was identical with that of an authentic sample. After recrystallization from petroleum ether[7] yields of pure, crystalline product ranging from 75 to 85% were obtained.

The Synthesis of *cis*-Pulegol and Its Allylomerization Products, 3-*p*-Menthen-8-ol and 3-*p*-Menthen-8-yl Ethers

E. H. ESCHINASI

*Givaudan Corporation, Clifton, New Jersey 07014*

(−)-*cis*-Pulegol (6) allylomerizes readily to (+)-3-*p*-menthen-8-ol (5), n^{20}D 1.4750, α^{25}D +80°, under mildly acidic conditions. In the presence of alcohols, 3-*p*-menthen-8-yl ethers (4) are also formed, while, in the presence of aluminum isopropoxide (AIP), at temperatures above 100°, both 5 and 6 dehydrate, affording a mixture of 3,8-*p*-menthadiene (2) and 2,4(8)-*p*-menthadiene (3), a fact that may account for the failure of previous workers to isolate pulegols from pulegone (1) by a Meerwein–Pondorff–Verley reduction. *trans*-Pulegol (6a), because of its greater instability, could not be detected from reduction products of 1 under kinetically or thermally controlled conditions.

In the course of an investigation on the nature of some alcohols related to pulegols, we reviewed the possible synthetic routes for *cis*- and *trans*-pulegol (6 and 6a). The AIP reduction of (+)-pulegone (1) at 120–170° according to Short and Read[1] yielded, instead of the desired alcohols, mainly 3,8- and 2,4(8) *p*-menthadiene (2 and 3) and minute amounts (5%) of an alcohol to which they assigned the structure of neoisopulegol.

Lithium aluminum hydride reduction of (+)-pulegone (1) proceeded smoothly and yielded (−)-*cis*-pulegol (6), mp 35.5, α^{25}D −80°, in over 99% yield. Similar results were reported by Porsch, *et al.*,[2] with NaBH₄. However, in an attempt to synthesize *trans*-pulegol (6a) by treating excess triisobutylaluminum (TIBAL) with (+)-pulegone (1), under conditions[3] reported to favor kinetically controlled backside attack leading to an axial OH, we obtained none of the expected *trans*-pulegol (6a) but, instead, (−)-*cis*-pulegol (6), in over 85% yield, together with a small amount (8–10%) of its allylomer, (+)-3-*p*-menthen-8-ol (5). When we carried out the reduction of 1, in isopropyl alcohol (IPA) in the presence of 0.5–1 equiv of AIP at 85° for 4–5 hr, we obtained the following reaction mixture (vpc by order of elution on 20M $^1/_8$-in. column at 200°).

1 (23.5%)   2 (12.5%)   3 (8.5%)   4, R = Ip (6%)

5 (28%)   6a (0%)   6 (21%)
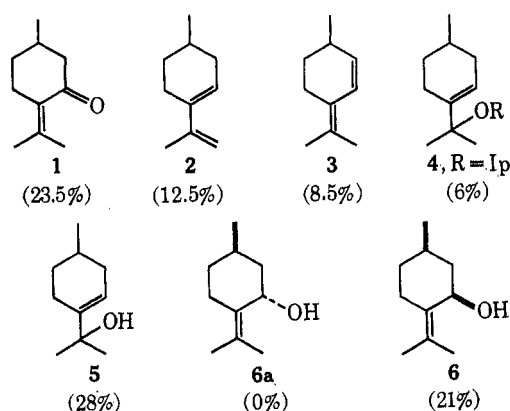
An extension of the reaction time, to complete the conversion of the unreacted pulegone (1), resulted only in larger amounts of 2 and 3 being formed. Unreacted pulegone (1), which made the separation of 3-*p*-menthen-8-ol (5) very difficult, was easily converted into *cis*-pulegol (6) by reduction with LiAlH₄. If, on the other hand, the unreacted pulegone (1) was oximated, with a mixture of NH₂OH·HCl, and sodium acetate in aqueous ethanol (pH 6.5), most of the *cis*-pulegol (6) was

6   →(ph 6.5, H₂O, EtOH)→   5   +   4
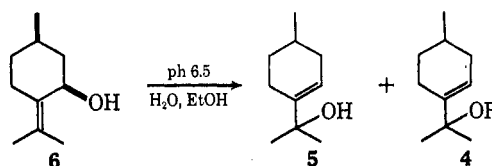
(1) A. G. Short and J. Read, *J. Chem. Soc.* 1306 (1939); see also Read and Grubb, *ibid* , 242 (1934).

(2) F. Porsch, H. Farnow, and H. Winkler, *Dragoco Rept.*, **4**, 75 (1964).

(3) H. Haubenstock and E. G. Davidson, *J. Org. Chem.*, **28**, 2772 (1963).

allylomerized into 3-*p*-menthen-8-ol (5) and 3-*p*-menthen-8-yl ethyl ether (4, R = Et). The facile allylomerization of *cis*-pulegol (6) to 5 could also be carried out, almost quantitatively, in the presence of 20% acetic acid at 70° with little dehydration to 2 and 3.

The identity of *cis*-pulegol (6) was proven both by hydrogenation, in the presence of Pd–C, to menthol and by its nmr spectrum.

The structure of 3-*p*-menthen-8-ol (5) was established by its nmr spectrum and by its hydrogenation with Pd–C into a mixture of 42% *cis*- and 58% *trans*-*p*-menthen-8-ol (7 and 8), identical with that obtained
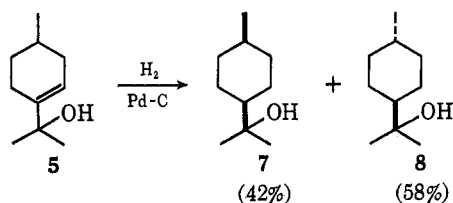
from the hydrogenation of α-terpineol under the same conditions. In addition, the presence of a tertiary OH in 5 was proven by running its nmr spectrum in deuterated DMSO which showed a singlet for the hydroxyl proton at δ 4.23.[4]

Experimental Section

Reduction of (+)-Pulegone with AIP (Meerwein–Pondorff–Verley).—(+)-Pulegone (154 g, 1 M), n^{20}D 1.4871, $[\alpha]^{25}$D +23° (purity by vpc 97%+), 350 ml of absolute isopropyl alcohol (IPA), and 35 g of freshly distilled AIP were heated to reflux under a 2-ft Goodloe column while the pot temperature was maintained at 82° and a distillate was collected at 60–64°. After about 4 hr, 60–70 g of acetone–IPA mixture was collected. The excess IPA was then distilled off (pot temperature reaching 90–95°) under partial vacuum and to the cooled (60°) residue of about 160 g was added 300 g of 50% KOH solution and 50 ml of benzene, under agitation, until solution took place. The top layer was separated and distilled in a modified Claisen–Vigreux flask affording a main cut, bp 70–95° (2 mm), 116 g, n^{20}D 1.4840, consisting of 12.5% 2, 8.5% 3, 6% 4 (R = Ip), 28% 5, 23.5% 1, and 21.5% 6 (vpc 20M 10% column 1/8 in. × 4 m at 150°). The distillate was split in two equal portions and processed as follows.

A. Reduction with LiAlH₄.—The distillate (58 g, n^{20}D 1.4840), in 120 ml of dry ether, containing 23.5% unreacted pulegone (1) and a total of about 50% alcohols 5 and 6 was fed within 5 min into a solution of 4 g of LiAlH₄ in 120 ml of dry ether and heated to reflux for an additional 15 min until the pulegone had completely reacted. The reaction mixture was then decomposed with 10 ml of 50% ethanol followed by 25 ml of water until precipitation of the Al₂O₃. The ether layer was separated and the solvent was evaporated yielding 56 g of crude reaction product consisting of 12.5% 2, 8.5% 3, 6% 4 (R = Ip), 29% 5, and 44% 6.

B. Oximation with NH₂OH·HCl, and Sodium Acetate–Ethanol Solution.— The distillate (58 g), as in A, and 10 g of NH₂OH·HCl, 10 g of sodium acetate, 10 ml of water, and 33 ml of ethanol were mixed and agitated at 70° (pH 6.5) for about 2 hr until a sample of the mixture showed the complete disappearance of pulegone (1) (by vpc 20M column at 150°). The reaction mixture was washed twice with 100 ml of water and distilled in a modified Claisen–Vigreux flask yielding a main cut, bp 70–100° (2 mm), 45 g, n^{20}D 1.4750, having the following composition (vpc 20M at 140°): 16% 2, 10.5% 3, 12.5% 4 (R = Et), 7.5% 4 (R = Ip), 51% 5, and 2.5% 6. It was followed

(4) O. L. Chapman and R. W. King, *J. Amer. Chem. Soc.*, **86**, 1256 (1964).

by a second cut of pulegone oxime, 13 g, bp 125–135° (2 mm), n^{20}D 1.5050.

Nester–Faust Distillation.—Both reaction products from A and B were distilled through a Nester–Faust Teflon spinning-band column at a reflux ratio of 200:1 and the following pure products were isolated and their structures were confirmed by nmr and ir spectra.

(+)-3-*p*-Menthen-8-ol (5): bp 104° (15 mm); n^{20}D 1.4750; α^{25}D +80°; nmr (Varian A-60A instrument with TMS as internal standard) in deuterated DMSO showed δ 4.24 (s) for a tertiary OH proton,[4] 5.61–5.86 (broad absorption, 1, vinylic), 1.22–2.41 (m, 14, with *gem* dimethyl), 1.31 (s), 0.97 (d, J = 5 Hz, CH₃CH); ir 6.91, 7.3, 7.4, 8.2, 8.5, 8.7, 8.9, 9, 9.05, 9.15, 11.2, 11.85, 12.32 μ.

3-*p*-Menthen-8-yl ether (4, R = Et): n^{20}D 1.4588; nmr δ 5.63 (broad, s, 1, vinylic), 3.25 (quadruplet, J = 7 Hz, 2, ethoxy methylene), 2.28 (broad m, 7), 1.28 (s, 6, *gem* dimethyl), 1.14 (s of expected t of which 2 outside peaks are masked by other absorption), 0.97 (d, 3, J = 7 Hz, CH₃CH); ir 6.9, 7.1, 7.28, 7.32, 7.4, 7.48, 8.05, 8.12, 8.22, 8.37, 8.7, 9.1, 9.4, 9.85, 10.5, 11.12, 11.3, 12.2, 12.35, 12.6 μ.

3-*p*-Menthen-8-yl isopropyl ether (4, R = Ip): nmr δ 3.20–3.75 (broad heptet, 1, of isopropoxy), 5.68 (broad peak, 1, vinylic); ir 6.85, 6.95, 7.25, 7.3, 7.95, 8, 8.12, 8.26, 8.6, 9, 9.1, 9.25, 9.8, 9.95, 10.2, 11, 11.2, 11.7, 12.4, 12.6 μ.

***cis*-Pulegol (6) by LiAlH₄ Reduction of *d*-Pulegone (1).**—(+)-Pulegone (80 g), n^{20}D 1.4871, $[\alpha]^{25}$D +23°, in 160 ml of ether was reduced within 30 min with 7 g of LiAlH₄ in 120 ml of ether, under essentially the same conditions described under A. Upon evaporation of the ether and distillation through a modified Claisen–Vigreux flask a main cut, bp 75–76° (2 mm), 72 g, n^{20}D 1.4890, $[\alpha]^{25}$D −80°, was obtained; the product crystallized and had mp 34–35.5° (99% pure by vpc). The product obtained by Porsch, *et al.*,[2] with NaBH₄ had mp 31.5–32.5°; $[\alpha]^{25}$D −58.4°; nmr δ 5.48–5.60 (broad absorption, 1), 4.36 (broad t, 1, J = 6 Hz), 1.35–2.99 (broad m, 7, including OH), 0.86–1.28 (m, 9, with *gem* dimethyl), 0.99–1.10 (J = 1 Hz); ir 7.7, 8.85, 9.65, 10.45, 11.05, 11.7 μ.

Reduction of Pulegone (1) with Triisobutylaluminum.—To 48 g of a 50% benzene solution of TIBAL (0.12 mol) (Texas Alkyls) in 60 ml of dry benzene was added, under a nitrogen blanket and within 0.5 hr, 15.2 g (0.1 mol) of pulegone, in 50 ml of dry benzene at 35 ± 5° under agitation. A sample of the reaction product, analyzed by vpc (20M column at 175°), indicated that less than 2% ketone 1 was present. The reaction mixture was decomposed with 30% NaOH and distilled in a Claisen–Vigreux flask yielding 14 g, bp 80–84° (2 mm), n^{20}D 1.4880, consisting of 85% 6, 1% 1, 8% 5, 2% 3, and 4% 2.

A. Allylomerization of *cis*-Pulegol (6) to 3-*p*-Menthen-8-ol (5).—*cis*-Pulegol (6) (17 g), mp 34–35°, and 85 g of 20% CH₃COOH were heated under agitation for 20–30 min at 70°, until no more *cis*-pulegol (6) was present. Upon neutralization with 4% NaOH and distillation in a modified Claisen–Vigreux flask, 16 g, bp 70–75° (2 mm), n^{20}D 1.4760, α^{25}D +72°, was obtained which consisted of 8% 2, 1% 3, 88% 5, and 3% unknown.

B. Allylomerization and Etherification of *cis*-Pulegol (6). 1.—To 10 g of *cis*-pulegol (6), 34–35.5°, in 20 g of absolute ethanol was added at room temperature 2 drops of concentrated HCl; after 0.5 hr the reaction mixture consisted of 57% 4 (R = Et) and 43% 5.

2.—A mixture of 20 g of *cis*-pulegol, 20 g of ethanol, 10 ml of water, and 1 ml of acetic acid was heated for 2 hr at 80°; the reaction mixture consisted of 43% 4 (R = Et), 54% 5, traces of 2, and unreacted 6.

Hydrogenation of *cis*-Pulegol (6).—*cis*-Pulegol (6) (10 g), mp 34–35.5°, in 50 ml of ethanol and 1 g of 5% Pd–C catalyst were hydrogenated rapidly (15 min) in a Parr shaker with hydrogen at 50 psi at room temperature and afforded a product (10 g) which crystallized and consisted of 90% methanol, 3% neoisomenthol, and 7% menthone.

Hydrogenation of 3-*p*-Menthen-8-ol (5).—8-*p*-Menthen-8-ol (5) (10 g) in 50 ml of ethanol and 1 g of 5% Pd–C catalyst were shaken in a Parr shaker for 1.5 hr with hydrogen at 50 psi at room temperature and afforded 10 g of a product which consisted of 42% 7 and 58% 8 which were identified by ir and vpc comparison with unambiguous samples of 7 and 8 obtained from the hydrogenation of α-terpineol.

Interaction of AIP with *cis*-Pulegol (6) and 3-*p*-Menthen-8-ol (5). A.—*cis*-Pulegol (6) (5 g), mp 34–35.5°, and 1 g of AIP

were heated in a small modified Claisen–Vigreux flask under a slight (20 mm) vacuum while the IPA formed distilled off. The temperature was maintained for 5 min at 130° and the residue was then decomposed with 30% NaOH to yield about 3 g of reaction product consisting of 58% 2, 39% 3, and traces of unreacted 6.

B.—3-*p*-Menthen-8-ol (5) (5 g) and 1 g of AIP were treated under the same conditions as described in A and afforded 3 g consisting of 60% 2 and 40% 3.

Registry No.—4, R = Et, 24301-81-3; 4, R = IP, 24301-82-4; 5, 24302-23-6; 6, 22472-80-6.

The Additivity of Mass Spectral Substituent Effects.
Cleavage of Benzophenones

MAURICE M. BURSEY[1] AND CHARLES E. TWINE, JR.

Venable Chemical Laboratory, The University of North Carolina, Chapel Hill, North Carolina 27514

It would be of interest to extend mass spectral steric-effect studies to simple cleavage reactions, but in known examples the observed electronic substituent effect is not great, and it can be expected that the effect of steric inhibition of resonance will not be great either. The theory of mass spectra suggests that multiple substitution may cause a great scattering of points about the correlation line against Hammett σ constants compared with the scatter for singly substituted compounds. This work shows that for doubly substituted benzophenones, the increase in scattering is not so large as to preclude observation of a moderate change in relative intensities owing to steric inhibition of resonance.

The formation of benzoyl ions in the mass spectra of singly substituted benzophenones can be correlated remarkably well with Hammett σ constants.[2] This general type of correlation, in which the relative intensities of benzoyl ion [A^+] with respect to the intensities of the molecular ions [M^+] are plotted against substituent constants as in eq 1, where $Z = [A^+]/[M^+]$, has been found for unsubstituted ions in the spectra of

$$\log (Z/Z_0) = \rho\sigma \qquad (1)$$

other aromatic compounds.[3] An interesting observation made recently is that *ortho*-substituent effects on ion intensities calculated in this fashion may be correlated[4] with *ortho*-substituent constants derived[5] from rates of gas-phase ester pyrolyses; the good correlation supports the validity of the interpretation of the pyrolysis data.

The relationship of eq 1 does not follow[6] from the quasiequilibrium theory of mass spectra,[7] and other explanations have been suggested. It is generally recognized that the equation of relative "rates" of mass spectral processes with intensity ratios is a simplification, and that other factors, notably appearance potentials of fragment ions[8] and the energy distribution of the molecular ions,[9] in principle govern the intensities of peaks in such a fashion that a Hammett plot may be extracted from them. These factors have been summarized.[10-12] Recently attempts have

been made to work backward from the existence of correlations with σ constants in mass spectra, specifically correlations of ion intensities, ionization potentials, and appearance potentials of fragments, to derive the form which the energy distribution of molecular ions must have to meet the requirement of an exact fit of the ion intensity data to eq 1.[13] The restrictions imposed for mathematical tractability make this solution of mostly theoretical interest, but the calculation shows that reasonable distributions produced from consideration of the physical processes occurring in electron impact and the energy distribution in the original molecule[14] are fairly similar in form to this distribution, and allows the hope that further refinement of the model employed will give a better understanding of the importance of the energy distribution.

One would anticipate, on the basis of the good correlation of *meta*- and *para*-substituent constants with relative intensities in benzophenone spectra[2] and on the basis that the correlation can be extended remarkably well to *ortho* substituents,[4] that a good correlation could be routinely expected. The present considerations of substituent effects on ion intensities, irrespective of their author, would all predict this in the first approximation, for substituent effects would be expected to be cumulative on electron density, affecting ionization potentials and bond energies in closely similar patterns. It is more important to consider why substituent effects may *not* be cumulative in ion intensity data. The major reason would be the fact that the introduction of more substituents into the aromatic ring affords more routes for decomposition, which will then compete more effectively with formation of the ion of interest, benzoyl. Fewer ions will then decompose by the desired route, and the degree of correlation will be reduced. Further, the introduction of additional complex substituents could alter the effective number of degrees of freedom in the molecular ion to the extent that ion intensities will be noticeably affected. In practice, this alteration has been observed for metastable

(1) Research Fellow of the Alfred P. Sloan Foundation, 1969–1971.
(2) M. M. Bursey and F. W. McLafferty, *J. Amer. Chem. Soc.*, **88**, 529 (1966).
(3) For a review, see M. M. Bursey, *Org. Mass Spectrom.*, **1**, 31 (1968).
(4) K. K. Lum and G. G. Smith, *J. Org. Chem.*, **34**, 2095 (1969).
(5) G. G. Smith, K. K. Lum, J. A. Kirby, and J. Posposil, *ibid.*, **34**, 2090 (1969).
(6) M. S. Chin and A. G. Harrison, *Org. Mass Spectrom.*, **2**, 1073 (1969). We thank Professor Harrison for a copy of this manuscript before publication.
(7) H. M. Rosenstock, M. B. Wallenstein, A. L. Wahrhaftig, and H. Eyring, *Proc. Nat. Acad. Sci. U. S.*, **38**, 667 (1952).
(8) T. W. Bentley, R. A. W. Johnstone, and D. W. Payling, *J. Amer. Chem. Soc.*, **91**, 3978 (1969).
(9) R. S. Ward, R. G. Cooks, and D. H. Williams, *ibid.*, **91**, 2727 (1969).
(10) F. W. McLafferty, *Chem. Commun.*, 956 (1968).
(11) R. G. Cooks, I. Howe, and D. H. Williams, *Org. Mass Spectrom.*, **2**, 137 (1969).
(12) M. M. Bursey and M. K. Hoffman, "Mass Spectrometry, 1970," G. W. A. Milne, Ed., John Wiley & Sons, Inc., New York, N. Y., in press.

(13) R. P. Buck and M. M. Bursey, *Org. Mass Spectrom.*, **3**, 387 (1970).
(14) M. L. Vestal, *J. Chem. Phys.*, **43**, 1356 (1965).