a Friedrich condenser and a gas dispersing delivery tube. An oxygen pressure was applied through the condenser and the mixture was placed in a 62.2° thermostat and stirred for six days. At five different times during the run three 1-ml. samples were removed from the mixture for peroxide assay. In the later samples the use of hydrochloric acid increased the titer by about a factor of two over that obtained in acetic acid with no added mineral acid. The final titer was, however, equivalent to only 2.1% of radicals produced in the decomposition. At the end of the run the gas above the reaction mixture was drawn into aqueous silver nitrate and gave a copious precipitate of silver cyanide. Extensive attempts to isolate other products by fractional recrystallization and solvent extraction using petroleum ether, methylene chloride, alcohol and various solvent mixtures led to the isolation of only tetramethylsuccinonitrile and a white, amorphous solid. The latter showed strong infrared absorption at 2240, 1740 and 1680 cm.$^{-1}$ and, in general, had a spectrum similar to that of polymethacrylonitrile.

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AMES, IOWA

## The Configurations of the 3-Methylcyclopentanones and Related Compounds

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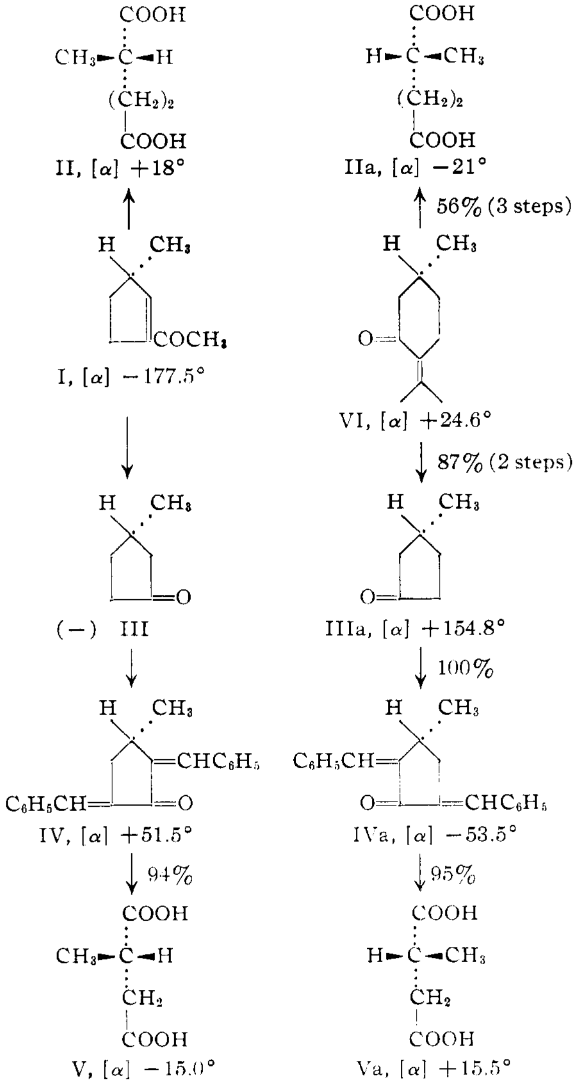
In a recent paper[2] the degradation of nepetonic acid *via* (−)3-methylcyclopentenyl methyl ketone (I) to (+)α-methylglutaric acid (II) and to a 3-methylcyclopentanone (III), which formed a (+)-dibenzylidene derivative IV, was reported. The configuration of II and its relationship to (−)lactic acid has been established by Fredga[3] by his method of quasi-racemates. The configurations of III and IV follow from that of II. The preparation of the enantiomorphs of these compounds from pulegone shows that the latter compound and the principal component of oil of catnip have opposite configurations at the ring carbon carrying the methyl substituent.

Pulegone (VI) was converted to (−)α-methylglutaric acid (IIa) *via* the ozonolysis of the (−)dibenzylidene derivative of (+)3-methylcyclohexanone; also VI was transformed *via* (+)β-methyladipic acid to (+)3-methylcyclopentanone (IIIa), which yielded the (−)dibenzylidene derivative IVa. The equivalence of the magnitudes of the rotations of the enantiomorphs IV and IVa indicates their optical purity and the rotations of IIIa, IVa and IV establish the direction of rotation of III as (−). The ozonolyses of IV and IVa to the corresponding methylsuccinic acids, V and Va, confirm an earlier[4] configurational relationship of (+)β-methyladipic acid to Va and verify Fredga's conclusion that the methylsuccinic acids and α-methylglutaric acids of opposite rotations have the same configurations.[3,5]

The configuration III assigned to (−)3-methylcyclopentanone is in accord with the calculated configuration of this ketone.[6] It is, however, the reverse of that assigned to this ketone by Hückel.[7]

The orientations of the 2- and 3-substituents relative to the 1-methyl substituent on the cyclopentane nucleus of nepetonic acid and its precursors, nepetalic acid and nepetalactone, have been determined.[2] Consequently, the assignment of configuration III to the 3-methylcyclopentanone derived from these compounds establishes the absolute configurations of their ring substituents as the opposite of those shown in the recent paper.[2]



### Experimental

**(−)α-Methylglutaric Acid (IIa).**—A 26.3-g. sample of (+)pulegone (VI), boiling at 102–102.5° (17 mm.), $n^{24.8}\mathrm{D}$ 1.4853, $\alpha^{25.5}\mathrm{D}$ +22.47° (*l* 1 dm., neat), $[\alpha]^{26.5}\mathrm{D}$ + 24.6° (*c* 2.88, $CHCl_3$), $\lambda_{\max}^{95\%\ \mathrm{EtOH}}$ 252 mμ, log ε 3.85,[8] whose infrared spectrum agreed with the literature[8] and whose red 2,4-dinitrophenylhydrazone melted at 148–149°[8] was hy-

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[2] S. M. McElvain and E. J. Eisenbraun, THIS JOURNAL, **77**, 1599 (1955).

[3] A. Fredga, *Arkiv. Kemi, Mineral. Geol.*, **24A**, No. 32 (1947).

[4] J. von Braun and F. Jostes, *Ber.*, **59**, 1091 (1926).

[5] *Cf.* also V. H. T. James, *Chemistry and Industry*, 1388 (1953).

[6] (a) J. F. Lane, *Science*, **113**, 577 (1951); (b) W. J. Kauzmann, J. E. Walter and H. Eyring, *Chem. Rev.*, **26**, 339 (1940); (c) *cf.* also D. S. Noyce and D. B. Denny, THIS JOURNAL, **76**, 768 (1954).

[7] W. Hückel, "The American FIAT Review I," Vol. 34, M. H. Davidson Co., New Haven, Conn., 1951, p. 79, assigns configuration III to (+)3-methylcyclopentanone; *cf.* also A. Fredga and J. K. Miettinen, *Acta Chem. Scand.*, **1**, 371 (1947).

[8] W. Kuhn and H. Schinz, *Helv. Chim. Acta*, **36**, 161 (1953).

drolyzed[9a,b] to acetone and (+)3-methylcyclohexanone with a mixture of 25 ml. of concentrated hydrochloric acid and 75 ml. of water. The acetone was removed by fractionation as it formed. After removal of the acetone the boiling point rose to 95–98° where (+)3-methylcyclohexanone steam distilled. The ketone was dried and distilled to give 13.3 g. (68.8%) of (+)3-methylcyclohexanone boiling at 166.5–168° (735 mm.), $n^{24.8}_{\mathrm{D}}$ 1.4440, $\alpha^{26}_{\mathrm{D}}$ +12.01° (*l* 1 dm., neat), $[\alpha]^{25}_{\mathrm{D}}$ +14.2° (*c* 4.13, $CHCl_3$) whose infrared spectrum was identical with that of *dl*-3-methylcyclohexanone.

A 2.10-g. sample of (+)3-methylcyclohexanone was converted, in 91% yield, to (−)2,6-dibenzylidene-3-methylcyclohexanone melting at 127–129°,[10a] $[\alpha]^{26}_{\mathrm{D}}$ −42.5° (*c* 0.71, $CHCl_3$),[10b] $\lambda_{\max}^{95\%\ \mathrm{EtOH}}$ 328 mμ, log ε 4.48,[10c] whose infrared and ultraviolet spectra were identical with those of *dl*-2,6-dibenzylidene-3-methylcyclohexanone, m.p. 119–120°.[10c]

A 2.00-g. sample of (−)2,6-dibenzylidene-3-methylcyclohexanone was added to 25 ml. of ethyl acetate and the suspension treated with a stream of oxygen, containing ozone at 0° until all the solid dibenzylidene derivative had dissolved and the color had faded from bright yellow to near colorless. The reaction vessel was cooled to −70° and the ozonization continued until the characteristic blue color due to the presence of excess ozone[11] was observed.

The ozonide was decomposed by dropwise addition of the reaction mixture to a cooled, well stirred mixture of 50 ml. of 30% hydrogen peroxide and 75 ml. of 10% sodium hydroxide solution. After stirring for 2 hr. the reaction mixture was heated on a steam-bath for 1 hr., cooled, acidified with concentrated hydrochloric acid to congo red. It then was extracted continuously with ether for 36 hr. The ether extract was concentrated and the residue subjected to steam distillation until all of the benzoic acid was removed. The remaining solution was evaporated to dryness under diminished pressure, extracted with hot chloroform and filtered. The chloroform solvent was evaporated to give 1.02 g. of tan crystals, m.p. 81–82°, $[\alpha]^{25}_{\mathrm{D}}$ −21.2° (*c* 0.28, $CHCl_3$), which on sublimation gave (−)α-methylglutaric acid (IIa),[3,12] m.p. 82.5–84.5°, $[\alpha]^{25}_{\mathrm{D}}$ −25.2° (*c* 6.79, $CHCl_3$), $[\alpha]^{25}_{\mathrm{D}}$ −24.7° (*c* 2.17, $CHCl_3$); neut. equiv. 73.1 (calcd. 73.1).

The infrared spectrum of IIa, in chloroform, was identical with that of II and with *dl*-α-methylglutaric acid.[2]

(+)α-Methylglutaric acid (II) as obtained from the oxidation of I showed $[\alpha]^{25}_{\mathrm{D}}$ +18° (*c* 6.87, abs. EtOH); however, II prepared from *cis*-nepetolactone[2] showed $[\alpha]^{27}_{\mathrm{D}}$ +24.2° (*c* 2.18, $CHCl_3$), $[\alpha]^{24.8}_{\mathrm{D}}$ + 22.1° (*c* 1.01, abs. EtOH).

(+)**3-Methylcyclopentanone (IIIa).**—A 11.3-g. sample of (+)pulegone (VI) was ozonized at −70° as described above. The product, 10.9 g. of tan-colored semi-solid was distilled at 180° (1 mm.) to give colorless, crystalline (+)β-methyladipic acid,[13] m.p. 85–89°, $[\alpha]^{26}_{\mathrm{D}}$ +9.6° (*c* 4.25, $CHCl_3$).

A 7.0-g. sample of (+)β-methyladipic acid was cyclized in 94.6% yield, according to the procedure of Thorpe and Kon[14] to (+)3-methylcyclopentanone[15] (IIIa), b.p. 143–143.5°, $n^{24.8}_{\mathrm{D}}$ 1.4320, $\alpha^{25}_{\mathrm{D}}$ +143.70° (*l* 1 dm. neat), $[\alpha]^{25}_{\mathrm{D}}$ +154.8° (*c* 0.73, $CHCl_3$). The infrared spectrum of (+)IIIa as the pure liquid was identical with that of *dl*-3-methylcyclopentanone with the exception of a single band at 14.7 μ which was not present in the latter.

**2,5-Dibenzylidene-3-methylcyclopentanone (IVa).**—This compound was prepared in quantitative yield from IIIa; m.p. 150.5–152.5°, $[\alpha]^{26.0}_{\mathrm{D}}$ −53.5° (*c* 0.98, $CHCl_3$), and $\lambda_{\max}^{95\%\ \mathrm{EtOH}}$ 350 mμ, log ε 4.59, agreed with literature values of the enantiomorph IV[2] and the racemate.[2,10c] The infrared spectra of IV and IVa in chloroform were identical.

*Anal.* Calcd. for $C_{20}H_{18}O$: C, 87.55; H, 6.61. Found: C, 87.46; H, 6.64.

**Methylsuccinic Acids (V and Va).**—A 0.427-g. sample of crude IV[2] was ozonized to give 0.194 g. (94%) of (−)-methylsuccinic acid[16] (V), m.p. 111–113°, $[\alpha]^{24.2}_{\mathrm{D}}$ −15.0° (*c* 1.89, abs. EtOH), neut. equiv. 65.2 (calcd. 66.0).

A 2.80-g. sample of crude IVa, m.p. 148.5–150°, $[\alpha]^{26}_{\mathrm{D}}$ −52.2° (*c* 1.15, $CHCl_3$) was ozonized to yield 1.28 g. (95%) of (+)methylsuccinic acid[16] (Va), which melted at 113–115° after sublimation, $[\alpha]^{25.5}_{\mathrm{D}}$ +15.5° (*c* 2.82 abs. EtOH), neut. equiv. 65.8 (66.0). In a similar manner a 1.70-g. sample of IVa, m.p. 150.5–152.5°, $[\alpha]^{26}_{\mathrm{D}}$ −53.2° (*c* 1.14, $CHCl_3$), after four recrystallizations from 95% ethanol, gave (+) methylsuccinic acid[4,16] Va, m.p. 113–114°, $[\alpha]^{25.5}_{\mathrm{D}}$ +15.5° (*c* 2.71 abs. EtOH), neut. equiv. 66.4 (calcd. 66.0).

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[9] (a) O. Wallach, *Ann.*, **289**, 337 (1896); (b) R. Adams, *et al.*, THIS JOURNAL, **64**, 2087 (1942).

[10] (a) O. Wallach, *Ber.*, **29**, 1596 (1896); (b) F. Nerdel and C. Kresse, *Z. Elektrochem.*, **56**, 234 (1952); (c) H. S. French and L. Wiley, THIS JOURNAL, **71**, 3702 (1949).

[11] E. R. H. Jones, *et al.*, *J. Chem. Soc.*, 4890 (1952).

[12] I. Scheer, R. B. Kostic and E. Mosettig, THIS JOURNAL, **75**, 4871 (1953).

[13] This acid, m.p. 86–88°, $[\alpha]^{26}_{\mathrm{D}}$ +11.5° (*c* 9.38, $CHCl_3$) was also prepared, in low yield and less conveniently, by oxidizing menthone according to the method of W. Semmler, *Ber.*, **25**, 3513 (1892); the menthone was obtained by the oxidation of (−)menthol according to the method of E. R. H. Jones, *et al.* (*J. Chem. Soc.*, 2548 (1953)).

[14] J. F. Thorpe and G. A. R. Kon, "Organic Syntheses," Coll. Vol. I, 2nd Ed., John Wiley and Sons, Inc., New York, N. Y., 1941, p. 192.

[15] G. H. Stempel, *et al.*, THIS JOURNAL, **67**, 344 (1945).

[16] A. Fredga, *Arkiv. Kemi, Mineral., Geol.*, **15B**, No. 23 (1942).

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## Coupling Reaction of Phenols and Phenol Alcohols with Diazonium Compounds

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The reaction of phenol alcohols with like species to form resins is of considerable interest and commercial significance. Because of its apparent parallelism, the reaction of diazonium compounds with phenol alcohols (methylolphenols) has been widely studied in an effort to determine the relative reactivities of various resin intermediates and the relative reactivities of the several positions in the phenolic nucleus.

Ziegler and Zigeuner[1] have conducted the most complete studies of this reaction, although several others have been cited by Hultzsch.[2] Their method involved isolation, identification and measurement of yield of azo compound formed when the coupling reagent reacted with a methylolphenol. They found it possible to replace a methylol group in either the *ortho* or *para* position. The reaction also is analogous to the replacement of the substituent group in phenol aldehydes, phenolcarboxylic acids and phenolsulfonic acids.[2]

When the *para* position is not blocked by halogen or alkyl, reaction occurs preferentially in the *para* position. When a choice exists between replacement of an *o*-hydrogen atom or an *o*-methylol group in the same molecule, the methylol group is displaced, formaldehyde being eliminated in the reaction. From these experiments it has sometimes been concluded, logically but incorrectly, that the order of ease of replacement is *p*-methylol, *p*-hydrogen, *o*-methylol, *o*-hydrogen atom.[3] However, the experiments of Ziegler and Zigeuner did not include any examples of competition between displacement of a methylol group and displacement of

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[1] (a) E. Ziegler and G. Zigeuner, *Monatsh.*, **79**, 42 (1948); (b) **79**, 89 (1948); (c) **79**, 358, 363 (1948).

[2] K. Hultzsch, "Chemie der Phenolharze," Springer, Berlin, 1950, p. 35.

[3] G. Sprengling, paper presented before Division of Paint, Varnish and Plastics Chemistry, 118th Meeting, Am. Chem. Soc., Chicago, Ill., 1950.