attempts to effect this reduction but are continuing our efforts.

Experimental

Isobornyl chloride was prepared according to Meerwein and van Emster.[11] The product thus obtained was recrystallized once from *n*-amyl alcohol (dried over calcium oxide) and twice from nitromethane (Eastman Kodak Co. white label) dried over anhydrous calcium sulfate, m.p. 162° (uncor.). It was dried thoroughly in vacuum before use. The camphene used in this synthesis was provided through the courtesy of the Hercules Powder Company Experiment Station.

Bornyl chloride was prepared by the addition of dry HCl to pinene (Hercules grade distilled over sodium) according to the procedure discussed by Thurber and Thielke.[12] It was recrystallized twice from low boiling 30–60° petroleum ether (distilled from sodium), m.p. 131° (uncor.) and stored in a vacuum desiccator over calcium chloride before use.

TABLE II

DIPOLE MOMENT DATA

Compound	Concn., moles/cc. × 10^4	ϵ	η^2	S_0	μ_D
Isobornyl chloride	6.989	2.6121	2.1363	0.0535	2.1
	3.494	2.4167	2.1298		
	1.747	2.3208	2.1269		
	0.874	2.2725	2.1255		
	0.000	2.2250	2.1240		
Bornyl chloride	10.0469	2.7932	2.1392	.0535	2.1
	5.0235	2.5072	2.1322		
	2.5117	2.3650	2.1281		
	1.2558	2.2963	2.1261		
	0.0000	2.2250	2.1240		
	Mole %				
2,6-Dichlorocamphane	1.51	2.5450	2.1298	.0188	4.0
	2.20	2.6534	2.1336		
	4.11	3.0242	2.1406		
	6.05	3.4015	2.1456		
	0.00	2.2372	2.1243		
	Moles/cc. × 10^3				
2,4-Dichlorocamphane	4.5094	2.565	2.1342	.0720	2.5
	2.2547	2.3919	2.1307		
	1.1274	2.3094	2.1281		
	0.5637	2.2687	2.1266		
	0.000	2.2324	2.1252		

2,6-Dichlorocamphane[13] was prepared according to the method of Aschan.[1] For dipole moment measurements it was recrystallized three times from absolute ethanol and stored in a vacuum desiccator over calcium chloride before use, m.p. 170–171° (uncor.).

2,4-Dichlorocamphane was prepared from synthetic camphor (U.S.P. du Pont) by the procedure suggested by Doering and Schoenewaldt.[14] The product was recrystallized twice from absolute methanol saturated with dry hydrogen chloride and stored in a vacuum desiccator over calcium chloride before use, m.p. 178° dec. (uncor.).

Dipole Moment Measurements.—Pure, dry carbon tetrachloride used as the solvent in these experiments was prepared from C.P. Baker grade by the method of Vogel.[15]

The dipole moments were computed from the data shown in Table II, by the method of Guggenheim[16] using the equation

$$\mu_D = 0.0222 \left[\frac{S_0 T}{(\epsilon_0 - 2)(\eta_0^2 - 2)}\right]^{1/2}$$

where

μ_D = the dipole moment in Debyes
S_0 = slope of the plot
T = absolute temp.
ϵ_0 = dielectric of solvent.; ϵ = dielectric of sol.
η_0 = refr. index of solvent; η = refr. index of soln.

Analysis of the error introduced by using this simplified computation according to the suggestion of Palet[17] indicates that an error of no greater than 5% could arise by ignoring consideration of the solution densities in the results reported here. This magnitude of possible error lies beyond the limit which would have significance in our considerations above.

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(11) H. Meerwein and K. van Emster, *Ber.*, **55**, 2526 (1922).

(12) F. H. Thurber and R. C. Thielke, THIS JOURNAL, **53**, 1032 (1931).

(13) This preparation was carried out by Mr. Donald Pascale and Mr. Lloyd Kaplan.

(14) W. von E. Doering and E. F. Schoenewaldt, THIS JOURNAL, **73**, 2333 (1951).

(15) A. I. Vogel, "Textbook of Practical Organic Chemistry," Longmans, Green and Co., New York, N. Y., 1951, p. 174–175.

(16) E. A. Guggenheim, *Trans. Faraday Soc.*, **45**, 714 (1949); J. W. Smith, *ibid.*, **46**, 394 (1950); E. A. Guggenheim, *ibid.*, **47**, 573 (1951).

(17) S. R. Palit, THIS JOURNAL, **74**, 3952 (1952).

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[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF THE UNIVERSITY OF QUEENSLAND]

Some Properties of Isopropenylic Terpenoids

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Approximate values have been calculated for the refractive indices, densities and boiling points of α-citronellol, α-citronellal and certain other acyclic α-terpenoids which are as yet unknown. For this purpose the hydrocarbons 2,6-dimethyloctene-1 and 2,6-dimethyloctene-2 have been prepared and the density and refractive index of 2-methylhexene-1 has been redetermined. In addition the absence of α-citronellal from the essential oil of *Eucalyptus citriodora* Hook has been demonstrated.

After many years of controversy,[1,2] it is now clear that α-citronellol has not as yet been found in nature, although it may be present in samples of citronellol which have been subjected to acid treatment in the course of isolation[3] or purification.[4] It is also true of the other acyclic oxygenated terpenes of "normal" carbon skeleton that in no case has the α-form or isopropenylic isomer been detected in nature.[4–7] Ocimene also, for many years accepted as isopropenylic, has recently been shown to have an isopropylidenic or β-structure.[8,9]

Thus until recently, the α-terpenoids have been unknown except as inseparable contaminants of the

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(1) L. N. Owen and J. L. Simonsen, *Endeavour*, **8**, 26 (1949).

(2) Y-R. Naves, *Perfumery and Essential Oil Record*, **40**, 41 (1949).

(3) Y-R. Naves, *Bull. soc. chim.*, [5] **18**, 506 (1951).

(4) J. Doeuvre, *ibid.*, [5] **3**, 612 (1936).

(5) Y-R. Naves, G. Brus and J. Allard, *Compt. rend.*, **200**, 1112 (1935).

(6) D. Barnard, L. Bateman, A. J. Harding, H. P. Koch, N. Sheppard and G. B. B. M. Sutherland, *J. Chem. Soc.*, 915 (1950).

(7) M. F. Carroll, R. G. Mason, H. W. Thompson and R. C. S. Wood, *ibid.*, 3457 (1950).

(8) G. Dupont and V. Desreux, *Bull. soc. chim.*, [5] **5**, 337 (1938).

(9) M. D. Sutherland, THIS JOURNAL, **74**, 2688 (1952).

β-forms of citronellol, citronellal, citronellic acid[10] and nerolidol,[11] detectable only by infrared or Raman spectra or by suitable techniques of ozonization.[2,4] A recent successful attempt[12] to prepare α-citronellol, was assisted by a prior prediction of its physical properties by the approximate method described below, which is based on the differences in molecular volume and molecular refraction of α- and β-olefinic hydrocarbons. To provide a surer basis for these predictions 2,6-dimethyloctene-1 and 2,6-dimethyloctene-2 have been prepared and an anomaly presented by 2-methylhexene-1 has been eliminated. The physical properties of various α-terpenoids have been similarly calculated and should facilitate the isolation and recognition of these substances if they exist in some essential oils, as is likely.

α- and β-Olefins.—An investigation was made to determine if the density and refractive indices of hydrocarbons containing the isopropenyl (or α) structure showed a consistent relationship to the properties of the corresponding saturated hydrocarbons and isopropylidenic (or β) olefins, and whether such a relationship could be extended to the oxygenated terpenes. It was expected that by comparing the properties of hydrocarbons rather than oxygenated compounds, more accurate data would be available and the effect of these differences in structure would be marked and unambiguous. In the refractive index–density chart (Fig. 1a) points are plotted for three series of hydrocarbons $(CH_3)_2$-CH—CH_2—R (I), $CH_2{=}C(CH_3)$—CH_2—R (II) and $(CH_3)_2C{=}CH$—R (III), where R is -Et, -Pr-*n*, -C_4H_9-*n*, -C_5H_{11} (*n* and iso) and -CH_2-CH_2-CH-(CH_3)-Et. The data (squares) for the C_5, C_6, C_7 and C_8 compounds and the C_9-paraffins, are taken from U. S. Bureau of Standards[13] and may be accepted as the best available at the time of compilation (1947). The data for the C_9-olefins, excepting 2-methyloctene-1, are those taken by Egloff[14] from theses (1938) by Rudel and Frank. Some assurance as to reliability is afforded by the close agreement between the values of Frank and those of Mears, *et al.*,[15] for 2-methyloctene-1. The values found by the U. S. Bureau of Standards workers are included in Fig. 1a. The data of Boord,[16] *et al.*, are usedto place a second point (triangle) for 2-methylhexene-2 and circles represent the author's data for 2-methylhexene-1, 2,6-dimethyloctene-1 and 2,6-dimethyloctene-2. The point for 2,6-dimethyloctane represents Enklaar's product from the catalytic reduction of ocimene.[17]

In Fig. 1a each point for a paraffin is identified by an adjacent skeleton formula and a dotted line leads to the point for the corresponding α-olefin and from this to the β-olefin. It is well known[18,19] that these points for series of paraffins lie close to a straight line. Similarly, a straight line drawn through 2-methylbutene-1 and 2,6-dimethyloctene-1 passes close to the points for each of the α-olefins. Another straight line through 2-methylpentene-2 and 2,6-dimethyloctene-2 fits the β-olefins approximately. In the latter cases the agreement is fairly satisfactory excepting only 2-methylbutene-2 and the U. S. Bureau of Standards selected values for the two 2-methylhexenes. It is reasonable to assume that the greater scatter of the points for the olefins as compared with the paraffins is due to the lesser purity of the samples and lower accuracy of the measurements of their properties, and that in general the olefins of each series should lie on or very close to a straight line. 2-Methylbutene-2, however, will undoubtedly remain an exception demonstrating a "first of the series" effect.

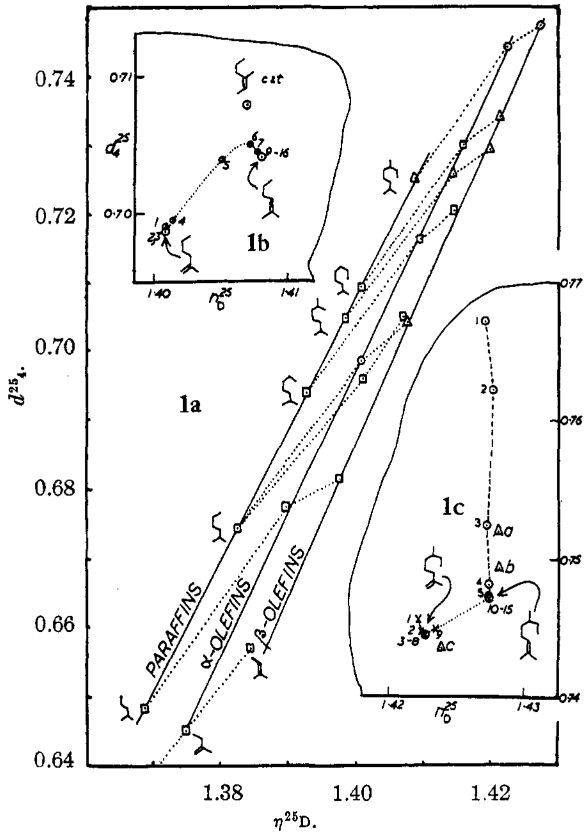

Fig. 1.

The divergence of the methylhexenes using the data of Circular C461 was not unexpected since a low reliability is implied therein for the selected values for these substances. The more recent data of Boord, *et al.*,[16] for 2-methylhexene-2 corrected the anomaly presented by this substance. Reinvestigation of 2-methylhexene-1 has shown that the properties given in Circular C461 for this substance also were seriously in error and that the point for the pure substance lies close to the α-olefin line.

Comparison of the molecular volumes of the α-

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(10) Y-R. Naves, *Perfumery and Essential Oil Record*, **37**, 120 (1946).

(11) Y-R. Naves, *Helv. Chim. Acta*, **30**, 278 (1947).

(12) M. D. Sutherland, THIS JOURNAL, **73**, 2385 (1951).

(13) U. S. Bureau of Standards Circular C461, "Selected Values of Properties of Hydrocarbons."

(14) G. Egloff, "Physical Constants of Hydrocarbons," Vol. I, Reinhold Publishing Corp., New York, N. Y.

(15) T. W. Mears, A. Fookson, P. Pomerantz, E. H. Rich, C. S. Dussinger and F. L. Howard, *J. Research Natl. Bur. Standards*, **44**, 299 (1950).

(16) C. E. Boord, A. L. Herne, K. W. Greenlee, W. I. Perilstein and J. M. Derfer, *Ind. Eng. Chem.*, **41**, 609 (1949).

(17) C. J. Enklaar, *Rec. trav. chim.*, **36**, 215 (1916).

(18) S. S. Kurtz and C. E. Headington, *Ind. Eng. Chem., Anal. Ed.*, **9**, 21 (1937).

(19) A. W. Francis, *Ind. Eng. Chem.*, **35**, 443 (1943).

and β-olefins calculated from this selected data shows that the difference ($V_\alpha - V_\beta$) is relatively constant, the values being 0.78, 1.02, 0.87, 0.99, 0.88 and 0.73 ml. in order as listed above. The differences in molecular refraction ($MR_\beta - MR_\alpha$) are also relatively constant, being 0.34, 0.26, 0.17, 0.25, 0.30 and 0.30 ml. in the same order. The erratic nature of the variations in both $V_\alpha - V_\beta$ and $MR_\beta - MR_\alpha$ is probably largely due to deficiencies in the experimental data rather than to an inherent irregularity in the effect of an additional structural unit.

The restriction of these comparisons to hydrocarbons, the carbon skeletons of which are contained within that of 2,6-dimethyloctane minimizes the possibility of interference by structural effects other than the one under consideration. Thus for the diisobutylenes[13] $V_\alpha - V_\beta$ is 1.36 ml. and $MR_\beta - MR_\alpha$ is 0.03 ml.

The Density and Refractive Index of α-Terpenoids.—The applicability of molecular volume differences, derived from hydrocarbons, to oxygenated structures may be tested and justified as an approximation, by comparing $V_{\text{satd.}} - V_\beta$ for the above series of hydrocarbons (9.38, 9.09, 8.85, 8.90, 8.93 and 8.50 ml.) and for I and III where $R = -CH_2-CH_2-CH(CH_3)CH_2-CH_2OH$, (8.33 ml.),[20,21] $R = CH_2-CH_2-CH(CH_3)-CH_2-CH{=}O$ (8.39 ml.),[21,22] $R = CH_2-CH_2-C(OH)(CH_3)-CH{=}CH_2$,[21] (7.01 ml.) and $R = CH_2-CH_2-C(CH_3){=}CH-CHO$ (*trans?*) (7.51 ml.).[23,24]

The differences in molecular refraction $MR_\beta - MR_{\text{satd.}}$ for the same series of hydrocarbons are 0.18, 0.21, 0.29, 0.28, 0.17 and 0.24 ml. whereas for the oxygenated substances indicated, the differences are 0.18, 0.11, −0.18 and +0.36 ml.[23] (−0.26?).[25] The greater variation in molecular volume and refraction differences for the terpenoid pairs compared with the hydrocarbons may reasonably be largely attributed to the impurity of the 2,3-dihydroterpenoids described in the literature, since properties reported by different authors generally show wide variations.

Taking the differences in molecular volume and refraction found for the α- and β-dimethyloctenes (0.73 ml. and 0.30 ml.) as the best available description of the differences to be expected between the acyclic α- and β-terpenoids, the density of each α-isomer can be calculated by assuming for it a molecular volume greater by 0.73 ml. than that of the corresponding β-terpenoid. A value for the refractive index may then be obtained by substituting the density so obtained and a molecular refraction 0.30 ml. less than that observed for the β-isomer in the Lorenz–Lorentz expression. In this way the calculated properties for α-terpenoids recorded in Table I were obtained. Other acyclic terpenoids in which the change from the β- to the α-isomer does not introduce or eliminate conjugation could be treated similarly.

TABLE I

DENSITIES AND REFRACTIVE INDICES OF ACYCLIC α-TERPENOIDS

	β-Terpenoids (obsd.)		α-Terpenoids (calcd.)	
	d^{25}_4	$n^{25}D$	d^{25}_4	$n^{25}D$
Myrcene[a]	0.7847	1.4679	0.7814	1.4622
Ocimene[b]	.7946	1.4836	.7912	1.4778
Citronellol[c]	.8517	1.4529	.8483	1.4477
Citronellal[d]	.8479	1.4448	.8445	1.4396
Citronellic acid[c]	.9224	1.4520	.9187	1.4467
Geraniol[e]	.8758	1.4757	.8722	1.4701
Nerol[e]	.8721	1.4726	.8685	1.4670
Citral a[f]	.8848	1.4876	.8811	1.4818
Citral b[f]	.8829	1.4847	.8792	1.4789
Linalol[c]	.8566	1.4591	.8531	1.4537
Nerolidol[d]	.8743	1.4777	.8718	1.4738

[a] M. D. Sutherland and S. J. Wilson, *Univ. Queensland Papers, Chem. Dept.*, **I**, No. 38, 1950. This paper described myrcene of $\epsilon_{\max}$ 1.84 × 10^4 at 224.5 mμ in alcohol compared with that ($\epsilon_{\max}$ 1.535 × 10^4) of R. D. Walker and J. E. Hawkins, THIS JOURNAL, **74**, 4209 (1952). [b] A. R. Penfold, *Proc. Roy. Soc. New South Wales*, **56**, 197 (1922). [c] Reference 21. [d] Reference 3. [e] Y-R. Naves and P. Ardizio, *Compt. rend.*, **234**, 2433 (1952). [f] Reference 24.

Considering the fallibility of the experimental data, the only approximate additivity of molecular volume and refraction,[26] and the possible errors in the constants of the β-terpenoids, the calculated values for the α-terpenoids are seen to be approximate, and the use of four figures in Table I is only to express the results of calculation. In addition, a further slight uncertainty may be introduced by such effects as the "chromophoric coupling" or pseudocyclization detected by Naves and Ardizio[21] in β-citronellal and β-citronellol, since this would possibly modify the physical constants of the β-isomers as compared with α-isomers.

Two checks on the validity of the calculated properties are available from the literature. A citronellal prepared[7] by dehydration of hydroxydihydrocitronellal and stated to be "almost exclusively in the α-form" showed $n^{25}D$ 1.4428 and d^{25}_4 0.8460 (both corrected to 25°). The point for this substance lies approximately midway between the point for β-citronellal and that calculated for α-citronellal. Since it has been found that the lower reliable limit for detection of β-isomers in α-isomers is approximately 10%[27] and since the preparation was stated to be not quite homogeneous, a purer specimen may give a yet closer agreement. A trace of isopulegol would seriously alter the constants of a sample of otherwise pure α-citronellal. In this regard also, a sample described as pure β-citronellal by the same authors[7] on the basis of hydroxylamine titer and infrared spectrum had a density which is higher by 0.0040 than that of pure β-citronellal.

A sample[12] of α-citronellol ($n^{25}D$ 1.4494, d^{25}_4 0.8484) containing about 5% of β-citronellol shows

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(20) H. Rupe and R. Rinderknecht, *Helv. Chim. Acta*, **7**, 543 (1924), but see ref. 21.

(21) Y-R. Naves and P. Ardizio, *ibid.*, **31**, 1240 (1948).

(22) A. Muller, *Ber.*, **74B**, 1745 (1941); Suzuki, *Chem. News*, **139**, 153 (1929), but see S. Sabetay and J. Bleger, *Bull. soc. chim.*, [4] **43**, 843 (1928).

(23) C. C. Price and J. A. Pappalardo, THIS JOURNAL, **72**, 2614 (1950).

(24) Y-R. Naves, *Bull. Soc. Chim.*, [5] **19**, 521 (1952).

(25) Calculated from refractive index and density data in ref. 23.

(26) S. Glasstone, "Textbook of Physical Chemistry," D. Van Nostrand Co., Inc., New York, N. Y., 1940, pp. 514, 518. A. Weissberger, "Physical Methods of Organic Chemistry," Interscience Publishers, Inc., New York, N. Y., 1949, Vol. 1, Pt. II, p. 1169.

(27) R. L. Werner and M. D. Sutherland, THIS JOURNAL, **74**, 2688 (1951).

close agreement with the calculated density for α-citronellol after correcting for the β-citronellol content but is 0.0015 high in refractive index. This limited experimental data suggests that the calculated properties for α-terpenoids are approximately correct but may possibly be too low by about 0.001 to 0.002 in the refractive index.

The Boiling Points of α-Isomers.—Inspection of the literature[13,14] shows that for I, II and III when R = Me, Et, Pr, Bu and C_5H_{11} (iso), the boiling point of the α-olefin falls, in each case, between the boiling point of the corresponding paraffin and β-olefin and lies closer to the former. For R = C_5H_{11}-*n*, the α-olefin boils slightly closer to III than to I.[14,15] In the case of R = $CH_2CH_2CH(CH_3)C_2H_5$ the boiling point of the paraffin has not been reported at 50 mm. but the α-olefin again boils lower (by 3 ± 0.6°) than the β-olefin.

These examples suggest that each α-isomer will boil below the corresponding β-terpenoid and approximately midway between the β-terpenoid and its 2,3-dihydro derivative. Supporting this conclusion are boiling point differences 1.8° between α- and β-citronellol[12] and 3.8° between dihydrocitronellol and β-citronellol observed under comparable conditions at 10 mm. pressure in a Podbielniak still.[28] This boiling point difference corresponds to a relative volatility[29] of *ca.* 1.1 and should approximate the actual relative volatilities of mixtures of the α- and β-isomers of the acyclic terpene alcohols and aldehydes. In the case of α- and β-citronellic acid and α- and β-nerolidol, an even smaller relative volatility must be anticipated, whereas α- and β-myrcene and α- and β-ocimene should be separable about as readily as the α- and β-2,6-dimethyloctenes (relative volatility *ca.* 1.15[29]) in view of their similar boiling points.

2-Methylhexene-1.—The exceptional positions in Fig. 1a of the points for 2-methylhexene-1 and 2-methylhexene-2 based on data from Circular C461 emphasized the need for more precise data for the two olefins. This was found in the literature[16] for 2-methylhexene-2, but there was no report of both density and refractive index of a sample of the α-olefin.

2-Methylhexanol-2 was dehydrated by refluxing with iodine to yield a mixture of hydrocarbons which on fractional distillation yielded 2-methylhexene-2 closely comparable with that of Boord, *et al.*,[16] and 2-methylhexene-1 the infrared spectrum of which showed strong bands at 882 and 1650 cm.$^{-1}$ due to the isopropenyl group and gave no indications of the presence of impurities.[30] In addition, the refractive index–density curve (Fig. 1b) for the distillate, revealed a hitherto unreported[16,31] third component of the mixture, intermediate in boiling point and refractive index, and higher in density than the α- and β-olefins. This is possibly 3-methylhexene-2 which has the required properties[13] and could be formed by isomerization of the carbonium ion intermediate.[32] The α- and β-olefins were characterized by the preparation of the S-benzylthiouronium salts of the isomeric 3-thia acids resulting from the peroxide-catalyzed additions[33] of thioglycolic acid.

2,6-Dimethyloctene-1 and -2.—Wolff and Thielepape[34] reported the preparation of "2,6-dimethyloctene-1" (actually wholly or largely 2,6-dimethyloctene-2) by heating citronellal hydrazone with sodium ethylate at 170°, the position indicated for the olefinic bond being based on the assumption now known to be incorrect, that natural citronellal was the α-isomer. Kishner[35] prepared an olefin from citronellal hydrazone by distillation from potassium hydroxide and contrary to the statement of Simonsen,[36] demonstrated the β-olefinic structure since a heptanoic acid, acetone and a ketoalcohol $C_{10}H_{20}O_2$ were obtained as products of permanganate oxidation. Dupont and Desreux[37] prepared 2,6-dimethyloctene-2 by partial hydrogenation of myrcene. The three preparations, indicated by points (a), (b) and (c) in Fig. 1c, show poor agreement. Kishner[35] also described materials not indicated in Fig. 1c, which would be expected to be mixtures of the α- and β-olefins from their method of preparation.

A repetition of the preparation using citronellal from the essential oil of *Eucalyptus citriodora* Hook yielded 2,6-dimethyloctene-2 in good yield but with rather different constants from those previously reported. Ozonization yielded 4-methylhexanal and acetone. Addition of thioglycolic acid to the olefin under acid catalysis[33] and under peroxide catalysis[33] yielded two different substituted 3-thia acids characterized as S-benzylthiuronium salts.

A mixture of 2,6-dimethyloctene-2, 2,6-dimethyloctene-1 and 2,6-dimethyloctanol-2 in molar ratio 2.0:1.5:1 was obtained from 2,6-dimethyloctene-2 by the addition of hydrogen chloride followed by treatment with alcoholic alkali. The tertiary alcohol which has an odor strongly resembling linalol, was characterized as the phenylurethan and 4-phenylazophenylurethan. The α-olefin, separated from the β-olefin by high efficiency fractional distillation, yielded 6-methyloctanone and formaldehyde on ozonolysis and was characterized also as the S-benzylthiouronium salt of the peroxide-catalyzed thioglycolic acid adduct.

The derivatives from both the α- and the β-olefin crystallized quickly to constant melting point without giving evidence of separation of diastereoisomers. Disadvantages in this otherwise very convenient method for characterizing olefins were that the maximum depression of melting point obtained from mixtures of the two isomers was only

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[28] Footnote 3 in reference 27.

[29] F. W. Melpolder and C. E. Headington, *Ind. Eng. Chem.*, **39**, 763 (1947).

[30] I wish to thank R. L. Werner of the New South Wales University of Technology, Sydney, for measuring and interpreting these infrared spectra.

[31] J. M. Church with F. C. Whitmore and R. V. McGrew, THIS JOURNAL, **56**, 176 (1934).

[32] D. P. Stevenson, C. O. Wagner, D. Beeck and J. W. Otras, *ibid.*, **74**, 3274 (1952).

[33] J. R. Cunneen, *J. Chem. Soc.*, 36 (1947).

[34] L. Wolff and E. Thielepape, *Ann.*, **394**, 103 (1912); Beilstein's "Handbuch der Organischen Chemie," Vol. 1, First Suplt., p. 96.

[35] N. M. Kishner, *J. Russ. Phys. Chem. Soc.*, **43**, 951 (1911); Beilstein's "Handbuch der organischen Chemie," Vol. 1, First Suplt., p. 96.

[36] J. L. Simonsen, "The Terpenes," Vol. 1, 2nd ed., Cambridge University Press, Cambridge, 1947, p. 76.

[37] G. Dupont and V. Desreux, *Compt. rend.*, **203**, 733 (1936).

about two degrees and the melting points obtained were somewhat dependent on the technique used.

The infrared spectrum[30] of the α-olefin showed bands of high intensity at 884 and 1648 cm.$^{-1}$ characteristic of the isopropenyl group, while the β-olefin showed bands of medium intensity, at 835 and 1671 cm.$^{-1}$, and was free from α-olefin.

α-Citronellal Content of the Essential Oil of *Eucalyptus citriodora* Hook.—The proportion of α-citronellal in the original essential oil was estimated by separating and measuring the α-olefin in the crude hydrocarbon obtained by the Kishner reduction. The crude citronellal used for conversion to the hydrazone was distilled from the essential oil over a wide boiling range sufficient to ensure the inclusion of any α-citronellal if the predictions made above with regard to boiling point are correct. It was converted to the hydrazone and to the hydrocarbon in such a manner as to avoid preferential loss of the α-isomer and shift of the (isolated) olefinic bond.[38] A careful distillation of the crude olefins was carried out at high reflux ratio in order to concentrate the lower boiling α-olefin in the earliest fractions. Although 7% of the charge distilled before the density became identical with that of 2,6-dimethyloctene-2, this was due to the presence of unidentified substances of higher density. As suggested by the refractive index–density curve (Fig. 1c) and determined by a quantitative ozonization procedure, the quantity of 2,6-dimethyloctene-1 in the early fractions did not exceed one-tenth of one per cent. of the charge. While it is possible that some or all of the formaldehyde obtained by ozonization was derived from a substance other than 2,6-dimethyloctene-2, it is probable that the α-olefin, if present in the crude hydrocarbon, would not be entirely concentrated in the early fractions and a rather indefinite quantity would tail off into later fractions as a trace impurity.

Nevertheless, the conclusion may be drawn that the proportion of α-citronellal in *E. citriodora* oil is certainly less than one-half of one per cent., in agreement with the results of Naves.[2] The present determination, however, does not assume that isolation through the crystalline bisulfite compound,[2,3,7] or purification through the crystalline semicarbazone[6] effects no change in the proportion of isomers.

Experimental

2-Methylhexanol-2.—This substance, b.p. 142.5–143°, d^{25}_4 0.8098, n^{25}_{D} 1.4161, from *n*-butylmagnesium bromide and acetone was fractionated through a 20-inch column of glass helices.

The phenylurethan, m.p. 67.5–68°, crystallized from petroleum ether (b.p. 60–70°).

Anal. Calcd. for $C_{14}H_{21}O_2N$: C, 71.45; H, 8.99. Found: C, 71.6; H, 9.04.

The phenylazophenylurethan, m.p. 99–99.5°, formed orange rosettes from petroleum ether (b.p. 60–70°).

Anal. Calcd. for $C_{20}H_{25}O_2N_3$: C, 70.8; H, 7.42. Found: C, 71.1; H, 7.35.

Methylhexenes.—2-Methylhexanol-2 (152 ml.) was dehydrated to a mixture of heptenes (155 ml., n^{18}_{D} 1.4095) by distilling from iodine at atmospheric pressure using a fractionating column to return unreacted alcohol.[31] Mixed heptenes (n^{19}_{D} 1.4104) were also obtained by the dehydration of the Grignard product which had been purified only by the removal of distillate until the boiling point of 2-methylhexanol-2 was reached. The two preparations mixed in equal quantities were distilled at atmospheric pressure through a 72-inch Podbielniak "Hypercal" still at reflux ratio of 60. The distillate was collected in 10-ml. fractions, the density and refractive index of each fraction being measured (see Fig. 1b). The proportions of the olefins, indicated in Fig. 1b, is not the true ratio owing to the development of a fault in the fraction-changing mechanism. 2-Methylhexene-1, b.p. 91.5° (760 mm.), n^{25}_{D} 1.4008 and d^{25}_4 0.6987. Braun, *et al.*,[39] found b.p. 91.8° (760 mm.) and n^{20}_{D} 1.4033. 2-Methylhexene-2, b.p. 95.1° (760 mm.), n^{25}_{D} 1.4080 and d^{25}_n 0.7041. Boord, *et al.*,[16] found b.p. 95.41° (760 mm.), n^{20}_{D} 1.4103 and d^{20}_4 0.7081.

The densities were measured with pycnometers holding 3–5 ml., and the refractive indices with a Pulfrich refractometer. The temperature of the 25° bath varied within 0.03° and was measured with a thermometer checked against the sodium sulfate monohydrate transition point.

4-Isopropyl-3-thiaheptanoic Acid.—Thioglycolic acid (3.5 ml.) and 2-methylhexene-2 (7.0 ml. ≡ 1.0 mole) became miscible only after shaking with a trace of ascaridole.[33] After standing overnight and washing with water, the reaction mixture yielded by distillation unreacted hydrocarbon, an intermediate fraction and 4.80 g. (= 50% yield) of **4-isopropyl-3-thiaheptanoic acid,** a faintly yellowish oil of b.p. 144–145° (5 mm.), d^{25}_4 1.008 and n^{25}_{D} 1.4743.

Anal. Calcd. for $C_9H_{18}O_2S$: C, 56.8; H, 9.54. Found: C, 57.0; H, 9.33.

Potentiometric titration of the acid partitioned between equal volumes of water and petrol ether showed that about 99.5% of the acid was neutralized at *p*H 6.9.

A gum, presumably the sulfone,[33] was obtained by oxidation with aqueous permanganate, but could not be crystallized.

The S-benzylthiuronium salt, m.p. 155° (immersed at 150°), was obtained as colorless plates from acetone–methanol mixture. The melting point was affected somewhat by the rate of heating and temperature of immersion.

Anal. Calcd. for $C_{17}H_{28}O_2N_2S_2$: C, 57.3; H, 7.91. Found: C, 57.0; H, 7.85.

S-Benzylthiuronium 5-Methyl-3-thianonanoate.—2-Methylhexene-1 (1.0 ml.) and thioglycolic acid (1.0 ml. ≡ 2.09 moles) when shaken with a trace of ascaridole, mixed with warming. After standing overnight, the mixture was diluted with 20 cc. of petroleum ether (b.p. 40–60°) and extracted with five equal volumes of water when a test indicated complete removal of unreacted thioglycolic acid. The petroleum ether layer was then shaken with 10 ml. of water containing brom thymol blue, while 2 *N* NaOH solution was added drop by drop till the aqueous layer turned green (3.5 ml. required ≡ 98% yield). The aqueous layer was run into a solution of S-benzylthiuronium chloride (1.4 g. ≡ 3.5 ml. 2 *N* NaOH) yielding a heavy precipitate which was filtered after standing at 0° for several hours. Washing with acetone removed most of the adsorbed indicator and left 2.28 g. of crude salt, m.p. 149–149.5° (immersed at 147°). Crystallization to constant melting point from acetone containing a little methanol yielded colorless plates, m.p. 151–151.5° (immersed at 148°).

Anal. Calcd. for $C_{17}H_{28}N_2S_2O_2$: C, 57.3; H, 7.91. Found: C, 57.0; H, 7.85.

Crude Citronellal.—The samples of the essential oil of *Eucalyptus citriodora* were distilled in the field by Mr. J. R. Archbold, from leaf collected at Howard, Queensland.

A citronellal–isopulegol mixture, b.p. 85–86° (10 mm.), was easily separated from this oil in a 22-inch Lecky–Ewell type still. Distillation of this mixture in various stills at 10 or 20 mm. pressure effected no worthwhile separation. The crude citronellal for determination of the α-isomer content was obtained from the essential oil by rejecting only those materials boiling below 80° and above 87° at 10 mm. pressure at total reflux. A typical product (n^{25}_{D} 1.4486, d^{25}_4 0.8568 and $[\alpha]_{\text{D}}$ +2.4°) contained 84% of citronellal as determined by an oximation method.[40] Several batches of

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(38) L. Bateman, J. I. Cunneen and E. S. Waight, *J. Chem. Soc.*, 1714 (1952).

(39) W. G. Braun, D. F. Spooner and M. R. Fenske, *Anal. Chem.*, **22**, 1074 (1950).

(40) Essential Oil Subcomm. Report, No. 10, *Analyst*, **57**, 773 (1932).

oil varied in the rotation of the citronellal and the proportion of isopulegol.

Citronellal Hydrazone.—Hydrazine hydrate (380 ml.) was refluxed in a 20-inch glass-helices still, while 385 ml. of crude (84%) of citronellal dripped in through the reflux condenser in the course of ten hours. Occasionally when the boiling point dropped below 110°, the addition of citronellal was stopped while a distillate of aqueous hydrazine was removed to raise the boiling point to above 115° again. This yielded 80 ml. of aqueous distillate and 16 ml. of oily distillate which was added to the oily layer in the pot. This colorless oil was separated from the hydrazine hydrate layer, and 7 ml. of hydrazine hydrate was distilled from it by lowering the pressure to below 1 mm. at room temperature for one-half hour. The residual clear colorless oil had $d^{25}{}_4$ 0.9063 and $n^{25}\mathrm{D}$ 1.4798.

Distillation of a sample from a claisen flask at 1 mm. pressure yielded an isopulegol fraction, a hydrazone fraction, b.p. 90–95°, $n^{25}\mathrm{D}$ 1.482, and citronellal azine, b.p. 160–162°, $n^{25}\mathrm{D}$ 1.483 and $d^{25}{}_4$ 0.863. The literature[35] reports, b.p. 125–140° (15 mm.) for the hydrazone and b.p. 209–213° (25 mm.) for the azine. The hydrazone fraction on redistillation gave some hydrazone but rather more of freshly formed azine.

Conversion to Hydrocarbon.—Crude hydrazone (202 ml.) dripped at 50 ml. per hour onto 50 g. of potassium hydroxide pellets in a distilling flask heated in an oil-bath at 210°. The distillate consisted of 8 ml. of aqueous layer and 190 ml. of crude product which after washing with water and drying, had $n^{25}\mathrm{D}$ 1.4350 and $d^{25}{}_4$ 0.7741. Hydrazone (102 ml.) treated at 200° yielded 92 ml. of crude hydrocarbon of $n^{25}\mathrm{D}$ 1.4315. A slower rate of addition gave material of $n^{25}\mathrm{D}$ 1.4310, and a faster rate gave $n^{25}\mathrm{D}$ 1.4340. At 220°, 100 ml. gave 92 ml. of $n^{25}\mathrm{D}$ 1.4363 and $d^{25}{}_4$ 0.7773. Probable causes of this variation are incomplete distillation of the isopulegol at the lower temperatures and increased volatilization of unreacted hydrazone at higher temperatures.

Various batches of crude product (428 ml.) were combined and distilled at 50 mm. pressure through a 20-inch Lecky–Ewell type still at low reflux ratio. From an initial boiling point of 80°, crude hydrocarbon (364 ml., $n^{25}\mathrm{D}$ 1.4225, $d^{25}{}_4$ 0.7500) distilled to a sharp break at 86°. Distillation continued at 10 mm. pressure and a reflux ratio of 15, yielded 38 ml. of isopulegol (a mixture of isomers, middle fraction, b.p. 85° (10 mm.), $n^{25}\mathrm{D}$ 1.4690, $d^{25}{}_4$ 0.9070, $[\alpha]\mathrm{D}$ −0.6°), 6 ml. of higher-boiling constituents of *E. citriodora* oil and 17 ml. of azine. The yield of hydrocarbon based on the citronellal content of the crude citronellal was 95% of the theoretical yield. Of the isopulegol present in the crude citronellal, approximately 75% was recovered.

Fractional Distillation of Crude Hydrocarbon.—Crude hydrocarbon (330 ml.) was refluxed eight hours in a 72-inch "Hypercal" Podbielniak still at 50 mm. pressure, after which the distillate was collected at a reflux ratio of approximately 140,[41] with frequent returns to total reflux. The refractive index and density of the early fractions are plotted (dashed curve) in Fig. 1c. Fraction 1, b.p. 76.9–79.6°, 2.0 ml., $[\alpha]\mathrm{D}$ +1.85°, and fraction 2, b.p. 79.6–80.0°, 1.7 ml., and fraction 3, b.p. 80.0–82.1°, 4.7 ml., were united and the composite examined for terminal methylene groups by a technique modified from that of Doeuvre[4] and that of Naves[42] principally in the very convenient use of propionic acid as solvent for the ozonation. The formaldehyde yield was 3% of the theory for 2,6-dimethyloctene-1. Treatment of the bulk of the sample with thioglycolic acid in presence of peroxide followed by steam distillation after dilution with water, yielded a smaller volume of oil, which by successive treatments was almost completely consumed, leaving no residue of saturated hydrocarbons. Another sample, ozonized and treated to remove carbonyl and acidic substances similarly left no unreactive residue, and hence *p*-menthane is not a constituent of the mixture. Later fractions were of 5-ml. volume and by fraction 7 the physical constants had arrived at those of pure 2,6-dimethyloctene-2, b.p. 82.3 ± 0.3° (50 mm.), $n^{25}\mathrm{D}$ 1.4275, $d^{25}{}_4$ 0.7472 (corrected for buoyancy) and $[\alpha]^{25}\mathrm{D}$ +2.44° (not optically pure; Kishner[35] found $[\alpha]^{20}\mathrm{D}$ +9.28° for hydrocarbon from *d*-citronellal).

Ozonolysis of 2,6-Dimethyloctene-2.—The olefin (17.5 g., $[\alpha]^{25}\mathrm{D}$ +0.65°) was ozonized and the products were worked up in a manner similar to that described later under the ozonolysis of 2,6-dimethyloctene-1. Distillation of the steam volatile oil at atmospheric pressure through a short column yielded acetone, higher-boiling materials which were not investigated and 8.55 g. (60% yield) of crude **4-methylhexanal** of boiling range 140–149°. A central fraction, b.p. 144–145° (760 mm.), obtained on redistillation, had $n^{25}\mathrm{D}$ 1.412, $d^{25}{}_4$ 0.824 and $[\alpha]^{25}\mathrm{D}$ +1.3° (not optically pure).

Anal. Calcd. for $C_7H_{14}O$: C, 73.6; H, 12.4. Found: C, 73.7; H, 12.3.

The 2,4-dinitrophenylhydrazone, m.p. 88.5–89°, crystallized in yellow plates from ethanol.

Anal. Calcd. for $C_{13}H_{18}N_4O_4$: C, 53.1; H, 6.19. Found: C, 53.3; H, 6.20.

The aldimethone, m.p. 125–126°, crystallized from methanol.

Anal. Calcd. for $C_{23}H_{36}O_4$: C, 73.3; H, 9.64. Found: C, 73.5; H, 9.52.

Thioglycolic Acid Adducts of 2,6-Dimethyloctene-2. (a) **Peroxide Catalysis.**—Olefin (2.0 ml.) and thioglycolic acid (1.0 ml. ≡ 1.35 moles) reacted only after a trace of ascaridole had been added, miscibility being complete in an hour. After standing overnight, the mixture was diluted with petroleum ether (b.p. 40–60°) and worked up as was the derivative from 2-methylhexene-1.

The acid obtained in 87% yield as the sodium salt was converted to colorless crystals (3.15 g.) of **S-benzylthiuronium 7-methyl-4-isopropyl-3-thianonanoate** which melted at 132–133° when immersed at 130°. Crystallization from methanol containing some acetone yielded 0.94 g. of m.p. 137–137.5°. Recrystallization from acetone or ethyl acetate did not change this melting point.

Anal. Calcd. for $C_{20}H_{34}O_2N_2S_2$: C, 60.3; H, 8.60. Found: C, 59.9; H, 8.38.

(b) **Acid Catalysis.**—Olefin (14 g.) was stirred at 0° with 37.5 g. of concd. sulfuric acid and 12.5 g. of water for two hours while 4.6 g. of thioglycolic acid dripped in to give a 25% yield of the thia acid.[33] **S-Benzylthiuronium 4,4,8-trimethyl-3-thiadecanoate** crystallized from acetone as colorless plates of m.p. 147–148° (immersed at 142°).

Anal. Calcd. for $C_{20}H_{34}O_2N_2S_2$: C, 60.3; H, 8.60. Found: C, 60.7; H, 8.65.

Isomerization of 2,6-Dimethyloctene-2.—The olefin (350 ml.) in an equal volume of ether, was saturated at room temperature with hydrogen chloride. The solvent and excess hydrogen chloride were boiled off on the water-bath and the residue run into sodium hydroxide (200 g. ≡ 2.7 moles) dissolved in 90% ethanol. After refluxing overnight, the alcohol was distilled off through a fractionating column leaving an aqueous layer and 335 ml. of oil which was separated by fractional distillation at 50 mm. pressure into mixed hydrocarbons (b.p. 80–84° (50 mm.)) and 2,6-dimethyloctanol-2.

2,6-Dimethyloctanol-2.—Redistillation at 10 mm. pressure in the Lecky–Ewell type still yielded constant-boiling material of which a central fraction had b.p. 80.5° (10 mm.), $n^{25}\mathrm{D}$ 1.4220, $d^{25}{}_4$ 0.8023. The alcohol, which has an odor similar to that of linalol, was found to be readily dehydrated by distillation from iodine or *p*-toluenesulfonic acid.

Anal. Calcd. for $C_{10}H_{22}O$: C, 75.9; H, 14.0. Found: C, 76.2; H, 13.7.

The phenylurethan crystallized as needles of m.p. 83–83.5° from petroleum ether.

Anal. Calcd. for $C_{17}H_{27}O_2N$: C, 73.6; H, 9.81. Found: C, 73.4; H, 9.59.

The 4-phenylazophenylurethan crystallized as orange needles of m.p. 121.5–122° from petroleum ether.

Anal. Calcd. for $C_{23}H_{31}O_2N_3$: C, 72.4; H, 8.19. Found: C, 72.3; H, 7.85.

Fractional Distillation of Mixed Olefins.—Of the olefin mixture, 250 ml. were fractionated in the Podbielniak "Hypercal" still at 50 mm. pressure and true reflux ratio 90 to 100. The refractive index–density curve (dotted curve) for this distillation (Fig. 1c) demonstrates that the mixture consisted almost entirely of 2,6-dimethyloctene-1 (fractions

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[41] This is the true reflux ratio, calculated from the apparent reflux ratio by taking into account the cup volume of the needle valve seat and the boilup measured under the conditions of distillation.

[42] Y-R. Naves, *Helv. Chim. Acta*, **32**, 1151 (1949).

3–8) and 2,6-dimethyloctene-2 (fractions 10–15) with a trace of another substance of lower boiling point in fractions 1 and 2 (b.p. 76.8–79.3° (50 mm.)). The pot residue (7% of the charge) was not examined. Fractionation of another sample of this mixture at 20 mm. pressure was less satisfactory, three intermediate fractions being obtained, probably because of a lower column efficiency due to the reduction in pressure.

2,6-Dimethyloctene-1.—This olefin is a pleasant smelling mobile liquid of b.p. 79.3 ± 0.3° (50 mm.), $n^{25}\text{D}$ 1.4226, d^{25}_4 0.7443 (corrected for buoyancy) and $[\alpha]^{27}\text{D}$ +1.80° (not optically pure and corresponding to $[\alpha]^{27}\text{D}$ +2.34° for 2,6-dimethyloctene-2).

Anal. Calcd. for $C_{10}H_{20}$: C, 85.7; H, 14.35. Found: C, 85.8; H, 14.35.

Ozonolysis of 2,6-Dimethyloctene-1.—The olefin (15 ml., $[\alpha]^{27}\text{D}$ +1.80°) in 50 ml. of acetic acid was cooled in ice-water and 17 l. per hour of ozonized oxygen (7.7% by weight of O_3) was passed for 2.5 hours when the production of fog ceased. The solution was poured into 250 ml. of water and the aqueous layer was separated and refluxed under an oil-trap. The water-insoluble ozonide was washed with a little water into a flask containing an excess of zinc dust and a trace of silver nitrate and hydroquinone. The suspension was brought to the boil while being vigorously stirred and was then also refluxed under the oil-trap. The total oil (12.5 ml.) obtained yielded 8.35 g. (74% yield) of crude ketone b.p. 68–75° (10 mm.). Redistillation yielded **6-methyloctanone-2**, b.p. 70–71° (10 mm.), $n^{25}\text{D}$ 1.420, d^{25}_4 0.822 and $[\alpha]\text{D}$ +1.4° (not optically pure).

Anal. Calcd. for $C_9H_{18}O$: C, 76.2; H, 12.75. Found: C, 76.5; H, 12.4.

The 2,4-dinitrophenylhydrazone, m.p. 61–62°, crystallized from ethanol.

Anal. Calcd. for $C_{15}H_{22}O_4N_4$: C, 55.9; H, 6.87. Found: C, 56.0; H, 6.95.

The semicarbazone, m.p. 130.5–131.5°, crystallized from ethanol.

Anal. Calcd. for $C_{10}H_{21}N_3O$: C, 60.25; H, 10.62. Found: C, 60.3; H, 10.6.

Thioglycolic Acid Adduct of 2,6-Dimethyloctene-1.—By the method described, 3.78 g. (67% yield) of crude **S-benzylthiuronium 5,9-dimethyl-3-thiahendecanoate**, m.p. 138–139°, was obtained from 2.0 g. of olefin. Crystallization from acetone raised the melting point to 145–145.5° (immersed at 140°), but examination of the mother liquors did not reveal a second component of different melting point.

Anal. Calcd. for $C_{20}H_{34}N_2O_2S_2$: C, 60.3; H, 8.60. Found: C, 59.9; H, 8.30.

BRISBANE, AUSTRALIA

[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

Grignard Reactions Involving Opening of the Furan Ring

BY REYNOLD C. FUSON AND HARLAN P. WALLINGFORD[1]

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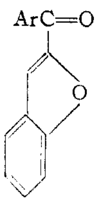
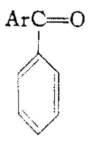
2-Mesitoylfuran reacts with mesitylmagnesium bromide, with opening of the furan ring, to form 1,5-dimesityl-2,4-pentadien-2-ol-1-one. 2-Duroylfuran gives a similar product.

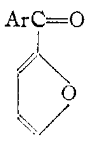
In earlier studies[2] it was found that, by imposing steric hindrance on the carbonyl group, certain furyl ketones could be made to react in the 1,4-manner with Grignard reagents. The 2-benzofuryl ketones I are examples. Subsequent work with hindered ketones in the benzene series II has shown that certain reagents attack the *p*-position even when the *o*-positions are unoccupied, *i.e.*, reactions corresponding to 1,6-addition take precedence over 1,4-addition when both are possible.[3] This same choice is offered by the 2-furyl ketones III, in which the 5-position corresponds to the *p*-position of the phenyl ketones II. Thus 2-mesitoylfuran (III, Ar = Mes) is analogous to the *p*-methoxyphenyl ketones IV. However, it has the possible advantage that the ether oxygen atom, together with that of the carbonyl group, may form a chelate ring involving magnesium.



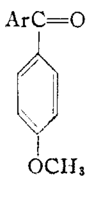
I



II



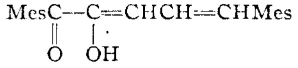
III



IV

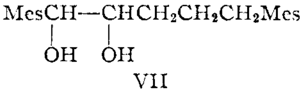
When treated with mesitylmagnesium bromide 2-mesitoylfuran was found to be attacked at the 5-position, the reaction involving opening of the ring to produce 1,5-dimesityl-2,4-pentadien-2-ol-1-one (V). The opening of the ring corresponds to methoxyl displacement in the *p*-methoxyphenyl series.[4] An analogous pentadienolone (VI) was produced when 2-duroylfuran was allowed to react with the mesityl reagent.

Catalytic hydrogenation converted the dimesitylpentadienolone (V) to the corresponding 1,2-glycol VII. The carbon skeleton was established by reduction of the glycol to the parent hydrocarbon VIII, which was prepared by an independent method. The keto enol V was identified by comparison with an authentic specimen made by the oxidation of 1,5-dimesityl-2,4-pentadien-1-one.[5] The two samples have identical infrared spectra and a mixed melting point determination showed no depression.



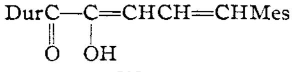
$$\underset{\underset{O}{\|}}{MesC}-\underset{\underset{OH}{|}}{C}=CHCH=CHMes$$

V



$$Mes\underset{\underset{OH}{|}}{CH}-\underset{\underset{OH}{|}}{C}HCH_2CH_2CH_2Mes$$

VII



$$\underset{\underset{O}{\|}}{DurC}-\underset{\underset{OH}{|}}{C}=CHCH=CHMes$$

VI

$Mes(CH_2)_5Mes$

VIII

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[1] du Pont Fellow, 1951–1952.

[2] (a) R. C. Fuson, E. W. Kaiser and S. B. Speck, *J. Org. Chem.*, **6**, 845 (1941); (b) R. E. Lutz and W. G. Reveley, THIS JOURNAL, **63**, 3178 (1941).

[3] For a leading reference, see R. C. Fuson and R. Tull, *ibid.*, **71**, 2543 (1949).

[4] R. C. Fuson and R. Gaertner, *J. Org. Chem.*, **13**, 496 (1948).

[5] R. C. Fuson, H. O. House and L. R. Melby, THIS JOURNAL, **75**, 5952 (1953).