[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF COLUMBIA UNIVERSITY No. 636]

THE ACTION OF ULTRAVIOLET LIGHT ON TERPENES. I. THE ACTION ON CITRONELLAL

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RECEIVED JULY 21, 1930 PUBLISHED OCTOBER 6, 1930

As is well known,[2] citronellal can be changed into isopulegol or its derivatives by the action of acids or acid anhydrides. In fact, isopulegol is most conveniently prepared in the laboratory by the action of acetic anhydride upon citronellal, and the mechanism of this reaction has been elucidated by Semmler,[2f] who found that the aldehyde was changed first into its enol acetate, which then added a second molecule of acetic acid with formation of a diacetate, this diacetate in turn splitting out a mole of acetic acid again in such manner that ring closure was effected and isopulegol acetate produced.

When such acids as formic or phosphoric are used as condensing agents, hydrates of isopulegol are obtained, as shown by Prins.[2h]

Labbe[3] observed that citronellal on standing gradually changed almost wholly to the isomeric isopulegol. A sample which nearly completely filled its container, after standing for two months, no longer exhaled any citronellal odor or gave any appreciable reaction with bisulfite, but when oxidized with dichromate and sulfuric acid yielded isopulegone.

Sernagiotto[4] likewise noted that when citronellal was exposed to direct sunlight, in the presence of air and moisture, isopulegol was formed, as well as dihydroxycitronellic acid. The conditions under which this experiment and that of Labbe[3] were carried out, however, were such as to make it desirable to ascertain the effect of ultraviolet light alone upon the aldehyde.

For this purpose, citronellal was placed in a closed quartz vessel and exposed to ultraviolet light, the effect of this exposure being followed by noting the gradual rise in the refractive index. Examination of the product showed that a considerable amount of the citronellal had been changed into isopulegol. This conversion must have been due therefore chiefly to the action of the light rays and not to an hydration–dehydration reaction, since all moisture had been excluded.

To prove that under these conditions also the enol form of citronellal

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[1] Rockefeller Foundation Fellow, 1929–1930.

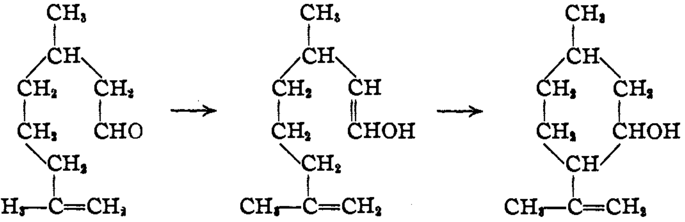
[2] (a) Dodge, THIS JOURNAL, **11**, 464 (1889); (b) Dodge, *ibid.*, **12**, 555 (1890); (c) Tiemann and Schmidt, *Ber.*, **29**, 913 (1896); (d) Barbier and Leser, *Compt. rend.*, **124**, 1308 (1897); (e) Wegscheider and Späth, *Monatsh.*, **30**, 825 (1909); (f) Semmler, *Ber.*, **42**, 2015 (1909); (g) Dodge, THIS JOURNAL, **37**, 2756 (1915); (h) Prins, *Chem. Weekblad*, **14**, 627 (1917).

[3] Labbe, *Bull. soc. chim.*, [3] **21**, 1023 (1899).

[4] Sernagiotto, *Atti accad. Lincei*, [5] **24**, 850 (1915).

was probably the intermediate product, some of this enol acetate was prepared by the method of Semmler[2f] and exposed to the ultraviolet rays. Isopulegol acetate was formed.

It is believed therefore that the effect of the ultraviolet rays upon citronellal (I) is to rearrange it first to the enol formation (II), and then to close the latter to the cyclic isopulegol (III)



I II III

This hypothesis is supported further by the facts that reagents effective in accomplishing this ring closure have been shown to function as enolizing agents, and because the enol being the unstable form of the aldehyde it has been observed by Stoermer[5] that light can change the stable forms of certain compounds into unstable tautomers.

Several investigators[6] have observed that the action of light upon aldehydes often results in the production also of di- and trimolecular polymers. It is worth noting, therefore, that in our own experiments a trimolecular polymer of citronellal was isolated among the products formed by the action of the ultraviolet light. Prins[2h] reported a dimolecular polymer as one of the products when formic acid acted upon citronellal.

That "citronellal," as ordinarily obtained, is probably an equilibrium mixture of two structural isomers, one, the so-called "alpha" or "limonene" form, corresponding to Formula (I) above, and the other, the "beta," "terpinolene" or "rhodinal" form, $(CH_3)_2C{=}CH(CH_2)_2CH(CH_3)CH_2$-CHO, seems indicated by the reports of various workers.[2h,7]

The nature of the citronellal used in our experiments is described beyond. Although both forms yield isopulegol when treated with strong

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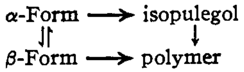
[5] (a) Stoermer and Simon, *Ann.*, **342,** 11 (1905); (b) Stoermer, *Ber.*, **42,** 4867 (1909).

[6] (a) Benrath, *J. prakt. Chem.*, [2] **72,** 220 (1905); (b) Ciamician and Silber, *Ber.*, **44,** 1558 (1911); (c) Benrath, *J. prakt. Chem.*, [2] **86,** 336 (1912); (d) Franke and Pollitzer, *Sitz. Akad. Wiss. Wien*, Abt. IIb, 122, 183 (1913); *Monatsh.*, **34,** 797 (1913); (e) Stobbe and Lippold, *J. prakt. Chem.*, [2] **90,** 277, 280 (1914).

[7] (a) Semmler, *Ber.*, **26,** 2257 (1893); (b) Barbier and Bouveault, *Compt. rend.*, **122,** 737 (1896); (c) Tiemann and Schmidt, *Ber.*, **30,** 33 (1897); (d) Harries and Roeder, *ibid.*, **32,** 3357 (1899); (e) Bouveault, *Bull. soc. chim.*, [3] **23,** 458, 463 (1900); (f) Harries and Schauwecker, *Ber.* **34,** 1498, 2981 (1901); (g) Harries and Himmelmann, *ibid.*, **41,** 2187 (1908); (h) Harries, *Schimmel's Ber.*, October, **1915,** p. 78; (i) Grignard and Doeuvre, *Compt. rend.*, **187,** 270 (1928); (j) Grignard and Doeuvre, *ibid.*, **187,** 330 (1928); (k) Verley, *Bull. soc. chim.*, [3] **43,** 845 (1928); (l) Doeuvre, *ibid.*, [3] **47,** 323 (1930).

acids, it is our belief that, under the action of ultraviolet light, the alpha tends to produce isopulegol mainly and the beta the polymer



If, then, light alone is capable of changing citronellal into isopulegol and higher polymers, it is of considerable significance for phytochemistry and botany as a plausible, or at least possible, explanation of the origin of certain cyclic terpenes found in the vegetable kingdom.

Experimental Part

Apparatus.—The source of the ultraviolet light was a mercury vapor lamp manufactured by the Hanovia Chemical and Manufacturing Company, of Newark, N. J., and known as the "Advanced Research Lamp," with an average life of about 4000 hours. The container for the material to be exposed to the rays was a quartz box, 10 × 5 × 1 cm., furnished with quartz inlet and outlet tubes, which were kept closed with rubber tubing during the experiments. This box was placed four inches from the burner and its temperature was maintained at 45–50° by a stream of air. In Runs A and B, Table I, the box was filled completely by the citronellal. In Run C, the quantity of aldehyde available was not enough for this, so the space remaining was filled with dry carbon dioxide, to prevent oxidation, and this was done also in Run B after the removal of the sample for analysis following fifty hours' exposure.

Citronellal.—A high-class commercial article, supplied through the courtesy of Fritzsche Brothers, of New York, was used as initial material; b. p. 200–202°, d^{20} 0.8578, n_D^{22} 1.44991, α_D^{30} $+4°22'$ (l = 0.5 dm.).

To determine the amount of non-volatile impurities present, 5 g. of the aldehyde was distilled with steam. What remained in the distilling flask was extracted repeatedly with ether, the ether extracts dried and the ether driven off. There remained 0.02 g. of a yellow oil, equivalent to 0.4% of the original aldehyde.

The determination of the non-aldehydic content of the volatile material was based upon the experiments of Tiemann and Schmidt[7c] which proved that citronellal condenses quantitatively with semicarbazide under proper conditions. Three grams of the steam-distilled aldehyde, which had been dried with anhydrous sodium sulfate, was poured into an aqueous solution of 3 g. of semicarbazide hydrochloride and 3 g. of anhydrous sodium acetate. Alcohol was added to this solution until it became slightly opalescent. The mixture was kept at room temperature overnight, then heated for six hours at 60–70°, after which it was transferred to a larger flask and distilled with steam. The oil driven over by the steam was collected with ether, the ether extracts dried with anhydrous sodium sulfate and the ether removed. There remained 0.25 g. of oil, or 8.3% of the original aldehyde.

In conducting the runs recorded in Table I, the change in refractive index of the citronellal was determined with a Pulfrich refractometer at the intervals indicated. It will be noted that indices recorded in Runs B and C are mostly lower than in Run A, for the same total exposure, and this we believe can be ascribed, in part at least, to the decreasing activity of the lamp with use.

After exposure, as shown in Table I, samples were removed and analyzed for non-volatile and for volatile non-aldehydic content by the methods given above. The refractive index for the volatile non-aldehydic material obtained was also recorded. These data are given in Table II.

Examination of the volatile non-aldehydic material separated (from Run A after

177.5 hours' exposure, which amounted to 27.9%.—It was distilled under reduced pressure. Practically all came over at 90–91° at 9 mm. pressure and showed the properties of isopulegol, including d^{20} 0.9125 and n^{22}_{D} 1.47078, as compared with $d^{17.5}$ 0.9154 and n^{20}_{D} 1.47292 as recorded for isopulegol in the literature.[7c]

This product (3.2 g.) was oxidized to isopulegone by potassium dichromate and sulfuric acid, as described by Tiemann and Schmidt,[7c,8] except that sodium bicarbonate was added to the oxidized mixture before it was distilled with steam. The ketone recovered (2 g.) was converted into its semicarbazone which, after two recrystallizations from dilute alcohol, formed colorless needles, m. p. 183° (uncorr.), in agreement with the figure given in the literature[9] for the inactive isopulegone semicarbazone.

Anal. Calcd. for $C_{11}H_{19}ON_3$: N, 20.10. Found: N, 19.95.

Tiemann and Schmidt obtained the active semicarbazone by their process.

Examination of that Portion of the Exposed Aldehyde which was not Volatile with Steam.—This portion was recovered, by the method already described, by ether extraction of the mixture remaining in the distilling flask after subjecting to steam distillation that sample of exposed citronellal (Run A) used above for the determination of volatile non-aldehydic constituents. The viscous yellow oil (62.1%) left after the evaporation of the dried ether could not be distilled without decomposition. After being kept in an evacuated desiccator for several weeks, to remove all traces of ether or moisture, it was analyzed and its molecular weight determined.

Anal. Calcd. for $(C_{10}H_{18}O)_x$: C, 77.92; H, 11.69. Found: C, 78.23; H, 11.50. Mol. wt. found, 466.7 and 460.8; calcd. for $C_{30}H_{54}O_3$, 462.4.

These results lead to the conclusion that the product was a trimolecular polymer of citronellal.

Examination of the curve plotted from Run A discloses some irregularity and flattening in the middle region, and it was to learn more about this that Run B was carried out and the content of volatile non-aldehydic and of non-volatile material determined after 50 and after 118 hours' exposure (see Table II). These results indicate a condition approaching

TABLE I

EXPERIMENTAL RESULTS

Citronellal,[10] n^{20}_{D} 1.4461 Isopulegol,[7c] n^{20}_{D} 1.47292

Run A		Run A		Run B		Run C	
Total hours exposed	n^{22}_{D}	Total hours exposed	n^{22}_{D}	Total hours exposed	n^{22}_{D}	Total hours exposed	n^{22}_{D}
0	1.44991	88	1.46566	6.5	1.45031	20	1.45271
8.5	1.44981	99	1.46763	16.5	1.45151	40	1.45441
18	1.45091	109	1.46862	26	1.45281		
21.5	1.45101	120	1.47009	33	1.45371		
28	1.45291	129.5	1.47107	50	1.45561		
38	1.45571	139	1.47205	63	1.45711		
48	1.45761	148.5	1.47312	75	1.45811		
55	1.46199	160.5	1.47362	87	1.45921		
62	1.46347	167.5	1.47470	100	1.46283		
76	1.46497	177.5	1.47523	118	1.46318		

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[8] Tiemann and Schmidt, *Ber.*, **32**, 3257 (1899).

[9] (a) Harries and Roeder, *ibid.*, **32**, 3371 (1899); (b) Wallach, *Ann.*, **365**, 252 (1909).

[10] Tiemann, *Ber.*, **32**, 818 (1899).

TABLE II

RESULTS OF EXPERIMENTS

Run	Total hours of exposure	Non-volatile, %	Volatile non-aldehydic %	Volatile non-aldehydic n_D^{22}
	0	0.4	8.3	1.46387
C	20	12	18.7	1.46852
C	40	20	28.1	1.47051
B	50	34.4	32.1	1.46783
B	118	34.4	34.4	1.46931 (n_D^{26})
A	177.5	62.1	27.9	1.47078

The refractive index of the volatile non-aldehydic portion was determined on the distilled oil in Run A, but on the undistilled material from Runs B and C.

equilibrium in this region. The variation in the refractive index during this period of temporary equilibrium may be due to a change in the character of this non-volatile material, rather than in its total amount, after which change the curve resumes its normal course. Similarly, the fall in volatile non-aldehydic ingredients after 118 hours' exposure is believed to be due to polymerization of the isopulegol.

The Action of Ultraviolet Light upon the Enol Acetate of Citronellal.—This was prepared by the method of Semmler[2f] and showed the following constants: b. p. (10 mm.) 110–115°, d^{20} 0.9068, n_D^{28} 1.44801.

Fifteen grams of this acetate was placed in the quartz box, the remaining space in the box being filled with dry carbon dioxide, and was exposed to the ultraviolet light, the changes produced in the enol acetate being followed by determining the changes in its density. The results are presented in Table III.

TABLE III

EXPERIMENTAL DATA

Total hours exposed	d^{20}
0	0.9068
7	.9078
16	.9102
26	.9122
38	.9236
46	.9238

Citronellal enol acetate,[2f] d^{20} 0.902, n_D 1.45762. Isopulegol acetate,[2f] d^{20} 0.925, n_D 1.459

Upon the conclusion of this exposure, 14 g. of the exposed enol acetate was repeatedly distilled under diminished pressure. On the sixth distillation, the following fractions were collected.

Fraction	B. p. at 10 mm., °C.	Amt., g.	d^{20}	n_D^{23}
1	90–105	1.5	0.9168	1.45541
2	105–107	7	.9278	1.45691
3	107–125	3	.9054	1.45341

There remained in the distilling flask only a small quantity of viscous oil.

Fraction 1 was not examined, but its high density would indicate that it was composed chiefly of isopulegol acetate.

Fraction 2 was analyzed with the following results.

Anal. Calcd. for $C_{12}H_{20}O_2$: C, 73.47; H, 10.20. Found: C, 73.0; H, 10.14.

These analytical figures, taken together with the density and refractive index of this fraction, supported the conclusion that it was mainly isopulegol acetate. It (4 g.) was therefore saponified by an alcoholic potassium hydroxide solution and the mixture distilled with steam. The volatile oil was extracted from the distillate with ether, the ether evaporated and the residual isopulegol oxidized by dichromate and sulfuric acid to the isopulegone, whose semicarbazone was prepared and melted at 183° (uncorr.). This product, when mixed with the inactive isopulegone semicarbazone obtained from citronellal itself, as already reported, showed no change in melting point.

Fraction 3 contained unchanged enol acetate.

Summary

1. Citronellal can be changed to isopulegol by the action of ultraviolet light, a fact which is of considerable significance to phytochemistry as well as to botany.

2. The mechanism of the reaction is believed to consist first in the rearrangement of the aldehyde into its enol formation, which then closes to the cyclic isopulegol, since it is shown that citronellal enol acetate also can be converted into isopulegol acetate by ultraviolet light.

New York, N. Y.

[Contribution from the Chemical Laboratory of the University of Illinois]

STEREOCHEMISTRY OF DIPHENYLBENZENES. PREPARATION OF STEREOISOMERIC 3,6-DI-(2,4-DIMETHYLPHENYL)-2,5-DIBROMOHYDROQUINONES AND THEIR DERIVATIVES. IX[1]

By E. Browning[2] and Roger Adams

Received July 25, 1930 Published October 6, 1930

In a recent article[3] on the isomerism of diphenyl compounds it was pointed out that interesting possibilities for stereoisomerism existed in diphenylbenzene derivatives if the same conditions were found in these latter molecules that produced isomerism in diphenyl derivatives. Thus, for example, in a molecule of type (I) in which each of the two end benzene rings are asymmetric in themselves and similar to each other, meso and racemic modifications should exist. The meso form is of peculiar interest

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[1] For article No. VIII in this series see Stanley and Adams, This Journal, **52**, November, 1930.

[2] This communication is the abstract of a thesis submitted by E. Browning in partial fulfilment of the requirements for the degree of Doctor of Philosophy in Chemistry at the University of Illinois.

[3] Stanley and Adams, *Rec. trav. chim.*, **48**, 1035 (1929).