86. *Observations on the Absorption Spectra of Terpenoid Compounds. Part III. The Thiosemicarbazones of Irone, Eucarvone, and some Related Ketones.*

By A. E. GILLAM and T. F. WEST.

The analytical and absorption data for the pairs of thiosemicarbazones obtained from the *d*-irone of English and French origin (Gillam and West, *Nature;* 1941, **148**, 114; this vol., p. 95) indicate the possibility that these samples contain at least two ketones of different empirical formulæ. Further, in conformity with our earlier conclusion that irone is not a dienone like β-ionone but an αβ-unsaturated ketone like α-ionone, the irone thiosemicarbazones are found to exhibit absorption spectra similar to that of α-ionone thiosemicarbazone and different from that of the β-ionone derivative (cf. Ruzicka *et al.*, *Helv. Chim. Acta*, 1933, **16**, 1143; 1940, **23**, 935, 959; 1941, **24**, 1434).

The absorption spectra of the seven-membered ring dienone, eucarvone, and derived ketones and their semicarbazones and thiosemicarbazones are recorded and discussed.

THE various formulations envisaged by Ruzicka and his co-workers to explain the reactions and degradation products of irone have already been considered (Gillam and West, *loc. cit.*) in relation to the observed absorption spectra. While this account was in the press, Ruzicka, Seidel, and Firmenich (*Helv. Chim. Acta*, 1941, **24**, 1434) discussed their own absorption results and considered that structure (I) conformed best with all the available evidence. We therefore now record our accumulated absorption spectra data on the irone thiosemicarbazones and related compounds.

According to Ruzicka and his co-workers (*loc. cit.*), the irone of German origin yielded a thiosemicarbazone melting indefinitely at about 120° whereas this same sample after prolonged boiling with 20% sulphuric acid gave a derivative of m. p. 180°, not depressed by the sample prepared by Chuit (*Rev. Gén. Chim.*, 1903, **6**, 433). The analytical and absorption data obtained upon the thiosemicarbazones derived from samples of natural *d*-irone and the acid-treated product during the course of the present investigation and by earlier workers are summarised in Table I.

TABLE I.

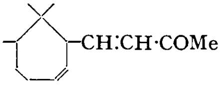
Analytical and Absorption Spectra Data for Irone Thiosemicarbazones.

Origin of parent irone.	Analysis (found), %. C.	H.	N.	M. p.	$\lambda_{max.}$.	$\varepsilon_{max.}$.	Mol. wt. taken.
German[1]	—	—	15·85	181°	—	—	—
Same product[2] recryst. by Ruzicka *et al.* ...	64·30	9·02	—	180°	—	—	—
German[2]	64·64	9·07	14·73	Turbid 110—120°, clear at 130°	—	—	—
German[3]	64·42	8·91	—	Turbid 120—122°, clear at 127°	2980	31,600	279
German[3] from irone boiled with 20% H_2SO_4	64·56	8·92	—	180°	3000	31,600	279
English[4]	64·6	8·4	15·2	185°	3020 2480	32,170 9,370	279
English[4]	65·7	8·9	14·75	112°, clear at 131°	3010 2465	32,450 10,520	293
French[4]	64·75	8·4	15·7	184—185°	3010 2470	32,860 10,460	279
French[4]	65·9	9·3	14·5	115°, clear at 130°	3010 2470	31,200 10,430	293
English from irone boiled with 20% H_2SO_4...	—	—	13·8[5]	156°	3050 2460	29,400 8,730	279

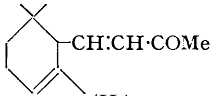
[1] Chuit, *loc. cit.* [2] Ruzicka, Seidel, and Schinz, *Helv. Chim. Acta*, 1933, **16**, 1143. [3] Ruzicka, Seidel, and Firmenich, *ibid.*, 1941, **24**, 1434. [4] Gillam and West, this vol., p. 95. [5] Insufficient material for complete purification.

Hence, the new data provide good analytical evidence for the presence in English and French irone of two ketones possessing different empirical formulæ. This is also supported by the light-absorption data, which show that the four semicarbazones are identical in the locations of their absorption bands; further, the values of the respective molecular extinction coefficients (ε) are approximately equal only when the several molecular weights indicated by the analytical data are used in their calculation (see Tables I and II).

The possibility of the existence of isomeric ketones containing six- and seven-membered rings has been envisaged by Ruzicka, Schinz, and Seidel (*Helv. Chim. Acta*, 1940, **23**, 935, 959), but no evidence appears to have been advanced for the possible presence in natural irone of ketones possessing different empirical formulæ.



(I.)



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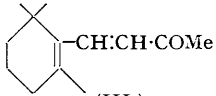


(III.)

Although we had but little irone available, we repeated Ruzicka's experiment on the effect of boiling the ketone with 20% sulphuric acid, and confirmed that the absorption spectrum of the irone changes in the sense that it develops a new absorption maximum near 3100 A. At first sight it might seem that the result of this treatment was an isomerisation to produce a dienone analogous to β-ionone (Ruzicka's β-irone). In our experiments, however, the recovered irone continues to change its light-absorbing properties spontaneously even after the sulphuric acid is removed, and it seems probable that several light-absorbing entities are produced and that some at least of these are labile and tend to disappear on standing. Further, the thiosemicarbazone obtained by us from the acid-treated irone (although not quite pure) absorbed at the same wave-length as the derivatives of the natural ketone. The light-absorption data for the various thiosemicarbazones are shown in Table II, and it will be seen that both irone itself and the acid-treated substance exhibit absorption spectra typical of similar compounds containing the C=C—C=N chromophore such as the thiosemicarbazone of α-ionone (II) in contrast to the compounds derived from β-ionone (III) and eucarvone (IV) which contain the C=C—C=C—C=N chromophore in a similar molecular environment.

In view of the possibility that irone may contain a seven-carbon skeleton (Ruzicka, Seidel, and Firmenich, *loc. cit.*), or alternatively that natural irone may contain a mixture of 7- and 6-carbon-ring isomers, the dienone

TABLE II.

Absorption Spectra of Thiosemicarbazones (in alcohol).

Parent ketone.	Thiosemicarbazone band. $\lambda_{max.}$	ε.	Thiosemicarbazide band. $\lambda_{max.}$	ε.	M. p. of thiosemicarbazone.	M.W. used.
C=C—C=N compounds.						
Irone [1] (German) [2]	3000	31,600	2450	11,700	clear at 127°	279
Irone [1] (acid-treated)	2980	31,600	2450	11,700	179—180°	279
Irone (English)	3020	32,170	2480	9,370	185°	279
Irone (English)	3010	32,450	2465	10,520	clear at 131°	293
Irone (French)	3010	32,860	2470	10,460	184—185°	279
Irone (French)	3010	31,200	2470	10,430	clear at 130°	293
α-Ionone	3025	36,500	2485	9,860	119—120°	265
1-Methyl-Δ¹-*cyclo*hexen-3-one	3025[3]	30,350	2465	9,210	—	—
C=C—C=C—C=N compounds.						
β-Ionone	3140	31,370	2435	7,700	160—161°	265
Eucarvone	3310	22,750	2480	10,200	163—164°	223
Uncombined thiosemicarbazide [2]	—	—	2410	13,800	—	—

[1] Values taken from printed curves, therefore approximate only.

[2] Ruzicka, Seidel, and Firmenich, *loc. cit.*

[3] Unpublished data by Mr. L. K. Evans (Manchestor University).

ketone eucarvone (IV), which is known to contain a 7-carbon-atom ring, provides an interesting model substance. Its absorption spectrum characteristics are given in Table III, and those of its semicarbazone and oxime on p. 486.

The numerical data on eucarvone compare well with published data on similar dienones and their derivatives (cf. Table III), and serve to emphasise the difference between these undoubted dienones and the major constituent of natural irone which has been shown to be an αβ-unsaturated ketone.

TABLE III.

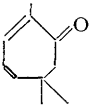
Absorption Spectra of Dienones (in alcohol).

	Original ketone. $\lambda_{max.}$	ε.	Semicarbazone. $\lambda_{max.}$	ε.
Eucarvone	3035	6,300	3090	16,460
			2270	8,030
β-Ionone [1]	2935	8,700	2765	23,300
ψ-Ionone [1]	2910	21,800	2995	45,400
Citrylideneacetaldehyde [1]	2900	15,960	3045	47,200

[1] Data by Burawoy (J., 1941, 23), who noted the exceptionally low value of the wave-length of maximum absorption for β-ionone semicarbazone.

On chemical evidence formula (V) was assigned by Wallach to the dihydroeucarvone obtained by reducing eucarvone with sodium and alcohol to dihydroeucarveol and oxidising this with chromic acid. The absorption spectrum confirms the absence of a conjugated system (see Experimental). On the other hand, structure (VI) was ascribed to the β-dihydroeucarvone obtained by reducing eucarvoxime with hydrogen in the presence of a palladium catalyst. The absorption spectrum of this compound clearly shows it to be an αβ-unsaturated ketone, and further, as a compound containing a disubstituted C=C—C=O chromophore, it should absorb at 2390 ± 50 A. (Woodward, *J. Amer. Chem. Soc.*, 1941, **63**, 1123). Its intense short-wave absorption band is actually situated at 2395 A., which makes it a very typical member of its class. This is of considerable interest, since the chromophore has a 7-carbon-atom ring whereas the rule was developed on data involving acyclic and 6-atom-ring compounds, and it has already been shown that at least two αβ-unsaturated ketones in a 5-carbon-atom-ring environment are exceptions to Woodward's rule (Gillam and West, J., 1941, 811, and unpublished observation).

The semicarbazone of β-dihydroeucarvone, is also perfectly typical of such derivatives of αβ-unsaturated ketones, absorbing as it does at 2645 A. (ε = 18,500).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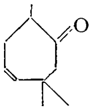
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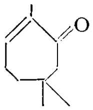
(VI.)

EXPERIMENTAL.

Analyses are by Drs. Weiler and Strauss, Oxford.

Irone Thiosemicarbazones.—The preparation of the four compounds has been described in this vol., p. 95.

α-Ionone Thiosemicarbazone.—A sample prepared according to Chuit's method (*loc. cit.*), after repeated recrystallisation, had m. p. 121—122° and showed maximum absorption at 3020 A. (ε = 31,600) and 2475 A. (ε = 9720). A purer sample was obtained thus : α-ionone (1 g.) in ethyl alcohol (10 ml.) was added to a solution of thiosemicarbazide (0·7 g.) in water (5 ml.) containing a trace of hydrochloric acid. After being boiled under reflux (15 mins.), the solution was poured into cold water, and the thick oil extracted with ether. The ethereal solution was washed repeatedly with water, and the residue (1·6 g.) remaining after removal of the ether was extracted six times with light petroleum. The product (1·3 g.) had m. p. 104—108°, raised by two recrystallisations from aqueous methanol and two from light petroleum to 119—120°, unchanged by further recrystallisation (Found : N, 15·7. Calc. for $C_{14}H_{23}N_3S$: N, 15·85%). It showed maximum absorption at 3025 A. (ε = 36,500) and 2485 A. (ε = 9860).

β-Ionone Thiosemicarbazone.—A sample prepared according to Chuit (*loc. cit.*) had m. p. 160—161° (Chuit gives 158°) and showed maximum absorption at 3130 A. (ε = 31,200) and 2440 A. (ε = 8150), and another sample prepared as described for eucarvone thiosemicarbazone had m. p. 160—161° (Found : N, 15·6%) and displayed maximum absorption at 3150 A. (ε = 31,540) and 2430 A. (ε = 7300).

Treatment of Irone with Sulphuric Acid.—Irone (0·74 g.), derived from the English oil of orris (Gillam and West, this vol., p. 95), was refluxed for 10 hours in a nitrogen atmosphere, the oil extracted with ether, and the solution washed first with sodium bicarbonate and then with water. The ether was removed, and the oil distilled, giving 0·33 g. having b. p. 110—115°/2 mm., $n_D^{21·5°}$ 1·5110, showing maximum absorption at 3100 A. (ε = 3250) ; after standing for 3 days the alcoholic solution gave a value of ε = 2250 at 2970 A., and after 7 days ε = 1725 at 2700—3000 A.

When treated with thiosemicarbazide according to the method of Ruzicka *et al.* (1933, *loc. cit.*) the bulk of the irone was recovered unchanged. Accordingly, recovered irone (0·21 g.) in methyl alcohol (7·5 ml.) was refluxed for 1 hour with a solution of thiosemicarbazide (0·15 g.) in water (2·5 ml.) in the presence of a trace of hydrochloric acid. When worked up as for α-ionone thiosemicarbazone, the crude thiosemicarbazone (0·06 g.) had m. p. 135° (sintering at 125°), raised by recrystallisation from methyl alcohol to 156° (sintering at 150°) (25 mg.) (Found : N, 13·8%). It showed maximum absorption at 3050 A. (ε = 29,400) (cf. Table I). When mixed with the thiosemicarbazone, m. p. 185°, the product melted at 176° (sintering at 162°).

The unreacted irone recovered during the light petroleum washing (0·075 g.) showed maximum absorption at 3100 A. (ε = 4450).

Eucarvone and its Derivatives.—The eucarvone was prepared from carvone according to Wallach's modifications (*Annalen*, 1905, **339**, 104) of Baeyer's method (*Ber.*, 1894, **27**, 810), and had b. p. 87—89°/7 mm., $n_D^{22°}$ 1·5085, $d_{15°}^{23°}$ 0·9056, α_D + 1·5° ; it showed maximum absorption at 3035 A. (alcohol) (ε = 6000). The semicarbazone (Baeyer, *loc. cit.*), m. p. 185—186°, showed maximum absorption at 3090 A. (ε = 16,460) and 2270 A. (ε = 8030) ; the eucarvone regenerated from it as described by Wallach had b. p. 85—86°/5 mm., $n_D^{20°}$ 1·5100, α_D ± 0° (*c*, 5 in alcohol) ; $\lambda_{max.}$ 3035 A. (alcohol) (ε = 6300).

Eucarvone (1·8 g.) in ethyl alcohol (20 ml.) was added to a solution of thiosemicarbazide (1·25 g.) in water (10 ml.) containing a trace of hydrochloric acid, the solution refluxed for 5 hours, poured into water, and the precipitated thiosemicarbazone extracted with ether. Removal of the solvent from the dried ethereal solution gave a solid (2·1 g.), m. p. 154—156° ; after recrystallisation from methyl alcohol, the white crystalline *eucarvone thiosemicarbazone* (1·2 g.) has m. p. 163—164°, unchanged by further recrystallisation (Found : N, 19·1. $C_{11}H_{17}N_3S$ requires N, 18·9%). This sample showed maximum absorption at 3310 A. (alcohol) (ε = 22,750) and 2480 A. (ε = 10,200).

The Dihydroeucarvones.—Eucarvone was reduced to dihydroeucarveol and this was oxidised to dihydroeucarvone with chromic acid (Baeyer, *Ber.*, 1894, **27**, 1915 ; Wallach, *Annalen*, 1899, **305**, 239). The semicarbazone, after repeated recrystallisation from methyl alcohol, had m. p. 190—191° and was used to regenerate the α-dihydroeucarvone by steam-distillation in the presence of phthalic acid. This had b. p. 44—45°/0·5 mm., $n_D^{17°}$ 1·4671, $d_{15°}^{20°}$ 0·938, and showed maximum absorption at 2910 A. (ε = 33), the band being typical, in both location and intensity, of an unconjugated carbonyl group.

Eucarvoxime, m. p. 106°, prepared as described by Wallach (*ibid.*), showed maximum absorption at 2920 A. (ε = 10,500). It was reduced in the presence of a colloidal palladium catalyst (Paal) and treated as described by Wallach (*Annalen*, 1914, **403**, 91). The semicarbazone of the ketone obtained had m. p. 201°, and showed maximum absorption at 2645 A. (ε = 18,500) ; it was used to regenerate β-dihydroeucarvone by steam-distillation in the presence of dilute sulphuric acid. This had b. p. 54°/1·5 mm., $n_D^{22°}$ 1·4793, and showed maximum absorption at 2395 A. (ε = 7250) and 3080 A. (ε = 137).

Determinations of absorption spectra were made on a Hilger E_3 quartz spectrograph in conjunction with a Spekker photometer, standard methods being used.

THE UNIVERSITY, MANCHESTER.
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