XLVI.—*Some Reactions of Phenyl Propenyl Ketone with Semicarbazides and Thiosemicarbazides.*

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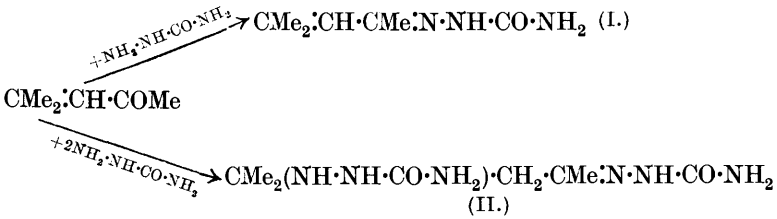
Since circumstances have rendered improbable the continuation of some investigations we had undertaken on the reaction between unsaturated ketones and semicarbazides and thiosemicarbazides, we desire to place on record the results which have been obtained.

It was shown by Rupe and his collaborators (*Ber.*, 1903, **36**, 4377; 1907, **40**, 4764; 1909, **42**, 4503, 4715) that α-unsaturated aliphatic ketones such as mesityl oxide could react with semicarbazide to produce either the semicarbazone (I) or the semicarbazide-semicarbazone (II)



$$\mathrm{CMe_2{:}CH{\cdot}COMe} \xrightarrow{+\mathrm{NH_2{\cdot}NH{\cdot}CO{\cdot}NH_2}} \mathrm{CMe_2{:}CH{\cdot}CMe{:}N{\cdot}NH{\cdot}CO{\cdot}NH_2}$$

(I.)

$$\mathrm{CMe_2{:}CH{\cdot}COMe} \xrightarrow{+2\mathrm{NH_2{\cdot}NH{\cdot}CO{\cdot}NH_2}} \mathrm{CMe_2(NH{\cdot}NH{\cdot}CO{\cdot}NH_2){\cdot}CH_2{\cdot}CMe{:}N{\cdot}NH{\cdot}CO{\cdot}NH_2}$$

(II.)

The view of Rupe and Hinterlach (*Ber.*, 1907, **40**, 4764) that unsaturated aromatic ketones with semicarbazide produce semicarbazones only was modified by the work of Auwers (*Ber.*, 1921, **54**, 987), who found that aromatic unsaturated ketones of the type

$Ar{\cdot}CO{\cdot}CH{:}CHR$ reacted like mesityl oxide; *e.g.*, phenyl propenyl ketone, $Ph{\cdot}CO{\cdot}CH{:}CHMe$, gave both the semicarbazone,

$$PhC({:}N{\cdot}NH{\cdot}CO{\cdot}NH_2){\cdot}CH{:}CHMe,$$

and the semicarbazide-semicarbazone,

$$PhC({:}N{\cdot}NH{\cdot}CO{\cdot}NH_2){\cdot}CH_2{\cdot}CHMe{\cdot}NH{\cdot}NH{\cdot}CO{\cdot}NH_2.$$

Unsaturated aromatic ketones of the type $Ar{\cdot}CH{:}CH{\cdot}COR$ gave, however, semicarbazones only.

We have found that phenyl propenyl ketone, reacting with δ-phenylsemicarbazide or with δ-phenylthiosemicarbazide, gave the *δ-phenylsemicarbazone* or *δ-phenylthiosemicarbazone* only, $PhC({:}N{\cdot}NH{\cdot}CX{\cdot}NHPh){\cdot}CH{:}CHMe$ ($X = O$ or S), the additive compounds not being formed. *p*-Methoxyphenyl propenyl ketone behaved in the same manner with δ-phenylthiosemicarbazide.

The reaction between phenyl propenyl ketone and thiosemicarbazide took an unexpected course, addition at the olefinic linkage occurring with formation of *thiosemicarbazidopropyl phenyl ketone*, $Ph{\cdot}CO{\cdot}CH(NH{\cdot}NH{\cdot}CS{\cdot}NH_2){\cdot}CH_2Me$ or

$$Ph{\cdot}CO{\cdot}CH_2{\cdot}CHMe{\cdot}NH{\cdot}NH{\cdot}CS{\cdot}NH_2,$$

which did not react further with thiosemicarbazide or with semicarbazide but gave *thiosemicarbazidopropyl phenyl ketoxime* with hydroxylamine. A somewhat similar case is reported by Auwers (*loc. cit.*), who found that 4-hydroxy-*m*-tolyl *iso*butenyl ketone gave an additive compound with semicarbazide, formulated as

$$C_6H_3Me(OH){\cdot}CO{\cdot}CH_2{\cdot}CMe_2{\cdot}NH{\cdot}NH{\cdot}CO{\cdot}NH_2,$$

which gave an oxime.

EXPERIMENTAL.

Phenyl propenyl ketone was prepared by Kohler's method (*Amer. Chem. J.*, 1909, **42**, 395), the exposure to sunlight being 1 hour, not 15 minutes as recommended by Kohler.

δ-Phenylsemicarbazide hydrochloride was prepared by Borsche's method (*Ber.*, 1905, **38**, 83). In working up the solution obtained by the hydrolysis of acetone-δ-phenylsemicarbazone with 5% hydrochloric acid, better yields were obtained by fractionally concentrating the solution under reduced pressure; each crop of crystals was washed with a little hydrochloric acid, the washings being added to the filtrate. The hydrochloride was crystallised from absolute alcohol; from these mother-liquors the remainder of the salt was precipitated by ether, diphenylcarbamide and colouring matter remaining in solution.

Phenyl Propenyl Ketone.—Reaction with δ-phenylsemicarbazide. The ketone (1 mol.) was added to the filtered solution prepared from δ-phenylsemicarbazide hydrochloride and potassium acetate (2·5 mols. of each) in the minimum quantity of alcohol. After a week the deposited *phenyl propenyl ketone δ-phenylsemicarbazone* was collected. It crystallised from absolute alcohol in fine needles, m. p. 212°, soluble in alcohol, benzene and light petroleum, very soluble in chloroform (Found : N, 15·1, 15·0. $C_{17}H_{17}ON_3$ requires N, 15·1%). Excess of δ-phenylsemicarbazide gave the same result.

With δ-phenylthiosemicarbazide. An alcoholic solution of the two reactants (equimolecular quantities) deposited a yellow crystalline mass which was collected after 5 days and dissolved in benzene. On addition of this solution to light petroleum, colourless crystals, m. p. 140°, of *phenyl propenyl ketone δ-phenylthiosemicarbazone* separated, soluble in alcohol, benzene and chloroform (Found : N, 14·4; S, 10·8. $C_{17}H_{17}N_3S$ requires N, 14·2; S, 10·8%). The substance became yellow in light without alteration in m. p. Excess of δ-phenylthiosemicarbazide gave the same result.

With thiosemicarbazide. An aqueous-alcoholic solution of the two reactants (equimolecular quantities) was kept for over a week; the resulting *thiosemicarbazidopropyl phenyl ketone* was then collected, further quantities being obtained from the solution by concentration under reduced pressure. Recrystallisation from alcohol or from chloroform–light petroleum gave small prisms, m. p. 140°, soluble in alcohol and chloroform, slightly soluble in light petroleum, almost insoluble in benzene (Found : N, 17·7; S, 13·0, 13·1; *M*, cryoscopic in nitrobenzene, 282, 285. $C_{11}H_{15}ON_3S$ requires N, 17·7; S, 13·5%; *M*, 237). Excess of thiosemicarbazide gave the same result. The *oxime*, a crystalline powder, m. p. 165°, prepared from the ketone, hydroxylamine hydrochloride, and potassium acetate in hot alcoholic solution, separated on cooling and was crystallised by addition of light petroleum to the absolute alcoholic solution. It was soluble in alcohol and slightly soluble in benzene, ether, and light petroleum (Found : C, 52·5; H, 6·9; S, 12·4. $C_{11}H_{16}ON_4S$ requires C, 52·4; H, 6·3; S, 12·7%).

p-*Methoxyphenyl propenyl ketone δ-phenylsemicarbazone*, prepared in the same way as the phenyl propenyl ketone derivative, was phototropic, and sparingly soluble in the usual organic solvents but very soluble in pyridine. It crystallised from alcohol–pyridine in needles, m. p. 249° (Found : N, 13·7, 13·5. $C_{18}H_{19}O_2N_3$ requires N, 13·6%).

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