CCCV.—*The Intermolecular Condensation of Styryl Ketones. Part II. Styryl Nonyl Ketone and the Formation of Dimerides.*

By Isidor Morris Heilbron and Francis Irving.

In a previous communication (Dickinson, Heilbron, and Irving, J., 1927, 1888), it was shown that certain styryl methyl ketones on treatment with alkali underwent intermolecular condensation with formation of *cyclo*hexenones, whilst treatment with piperidine resulted in the formation of saturated dimerides, probably of *cyclo*butane structure. We have now extended the investigation to a series of styryl nonyl ketones, and in no case has the formation of *cyclo*hexenones been observed, but a number of saturated dimerides have been obtained by the action of alkali.

Methyl nonyl ketone has previously been condensed with benzaldehyde by means of 0·25% alcoholic potassium hydroxide (Carette, *Compt. rend.*, 1900, **131**, 1225), the product being the simple styryl nonyl ketone, m. p. 41—42°. Carette also discovered that by employing hot 1% alcoholic potassium hydroxide, a dimeride melting at 116° was obtained. Styryl nonyl ketone itself on similar treatment was found to yield the same dimeride.

Scholtz and Meyer (*Ber.*, 1910, **43**, 1861) by means of alkali condensed anisaldehyde, piperonal, *p*-tolualdehyde, and cuminal with methyl nonyl ketone, claiming to have obtained the monomeric styryl nonyl ketones in each case. A re-examination of their products has proved, as could be inferred from their high melting points, that the condensation products from *p*-tolualdehyde and cuminal are actually dimerides.

We have further found that whereas *p*-methoxy-, 3 : 4-dimethoxy-, 3 : 4-methylenedioxy-, and *p*-chloro-styryl nonyl ketones are formed when cold, dilute, aqueous alkali or piperidine is used as condensing agent, dimerides are produced by increasing the alkali concentration and preferably carrying out the reaction on the steam-bath instead of at room temperature. *o*- and *m*-Chloro- and *m*-methoxy-benzaldehydes, *o*-tolu- and salicyl-aldehydes did not yield dimerides when treated under such conditions, and it would appear that dimeric forms are more readily produced when the aldehyde is substituted in the para-position.

The dimerides are all colourless substances which react as saturated compounds and are extremely inert towards ketone reagents. Carette (*J. Pharm.*, 1901, **13**, 412) found that bis-(styryl nonyl ketone) failed to react with semicarbazide. We have confirmed this observation, but have succeeded in obtaining a *monoxime* from this compound by prolonged treatment with hydroxylamine. This same inactivity has been noted by Stobbe and Hensel (*Ber.*, 1926, **59**, 2254), who only succeeded in obtaining a monoxime from the dimeride of phenyl 4-methoxystyryl ketone. These dimerides doubtless possess a *cyclo*butane structure similar to the products obtained by the action of short wave-length light or piperidine on unsaturated ketones (Stobbe and Hensel, *loc. cit.*).

EXPERIMENTAL.

Styryl Nonyl Ketone.—Benzaldehyde (2·5 g.) and methyl nonyl ketone (4 g.) were mixed with alcohol (2 c.c.), and piperidine (3 drops) was added. The solution was allowed to stand for several days, small amounts of piperidine being added daily; finally, it was diluted and cooled in a freezing mixture, crystals of styryl nonyl ketone then separating. These were recrystallised from methyl alcohol, appearing in colourless leaflets, m. p. 44° (Carette gives 41—42°; Thoms, *Ber. Deut. pharm. Ges.*, 1901, **11**, 3, gives 44—45°).

Monoxime of Bis-(Styryl Nonyl Ketone).—Bis-(styryl nonyl ketone) (1 mol.), prepared according to the method of Carette (*Compt. rend.*, *loc. cit.*), was refluxed with hydroxylamine (2 mols.) for 2 hours in alcoholic solution, and the product recrystallised from alcohol, fine, colourless needles of the *monoxime* being obtained, m. p. 125—126° (Found: N, 2·7. $C_{36}H_{53}O_2N$ requires N, 2·6%).

Bis-(4-methoxystyryl Nonyl Ketone).—Anisaldehyde (3·2 g.) and methyl nonyl ketone (4 g.) were refluxed for 6 hours with 1% alcoholic potassium hydroxide solution (30 g.). The product was repeatedly crystallised from alcohol, being finally obtained in the form of colourless needles, m. p. 120° [Found: C, 79·3; H, 9·4; *M* (Pregl), 474. $C_{38}H_{56}O_4$ requires C, 79·2; H, 9·7%; *M*, 576]. 4-Methoxystyryl nonyl ketone (Scholtz and Meyer, *loc. cit.*) crystallises in colourless leaflets, m. p. 63°.

3 : 4-*Dimethoxystyryl Nonyl Ketone.*—Veratraldehyde (4 g.) and methyl nonyl ketone (4 g.) were dissolved in alcohol (10 c.c.) together with 2 c.c. of 8% sodium hydroxide solution. Crystals separated after 12 hours, and were purified by recrystallisation from methyl alcohol, a small amount of less soluble dimeride being removed during the process. The *ketone* forms faintly yellow, rhombic plates,

m. p. 61° (yield, 5·5 g.) [Found: C, 75·4; H, 9·5; *M* (Menzies), 314, (Pregl), 323. $C_{20}H_{30}O_3$ requires C, 75·4; H, 9·4%; *M*, 318].

Bis-(3 : 4-*dimethoxystyryl Nonyl Ketone*).—Veratraldehyde (4 g.) and methyl nonyl ketone (4 g.) were refluxed with 1% alcoholic potassium hydroxide (25 g.) for 4 hours. The crude product was repeatedly recrystallised from alcohol, separating in colourless needles, m. p. 135° [Found: C, 75·5; H, 9·2; *M* (Menzies), 646. $C_{40}H_{60}O_6$ requires C, 75·4; H, 9·4%; *M*, 636].

Bis-(3 : 4-*methylenedioxystyryl Nonyl Ketone*).—Piperonal (4 g.) and methyl nonyl ketone (4 g.) were refluxed with 2% alcoholic potassium hydroxide (40 c.c.) for 6 hours. The product which separated on cooling was repeatedly crystallised from alcohol, and obtained finally in fine, colourless needles, m. p. 128° [Found: C, 75·6; H, 8·5; *M* (Menzies), 608. $C_{38}H_{52}O_6$ requires C, 75·5; H, 8·6%; *M*, 604]. Scholtz and Meyer (*loc. cit.*) describe **3** : 4-methylenedioxystyryl nonyl ketone as forming pale yellow needles, m. p. 56°.

Bis-(4-*methylstyryl Nonyl Ketone*).—This was first prepared by Scholtz and Meyer (*loc. cit.*) by the addition of 15% sodium hydroxide solution to an alcoholic solution of *p*-tolualdehyde and methyl nonyl ketone, and allowing the solution to stand at room temperature. These authors, however, described the compound as 4-methylstyryl nonyl ketone, m. p. 129°. We have prepared the compound by a similar method, but find it to melt at 134—135° [Found: *M* (Pregl), 425. $C_{38}H_{56}O_2$ requires *M*, 544].

4-iso*Propylstyryl Nonyl Ketone*.—Cuminaldehyde (2 g.) and methyl nonyl ketone (2·5 g.) were dissolved in alcohol (5 c.c.), and 6 drops of 8% sodium hydroxide added. After 2 days, the solution was cooled in ice and salt, and the separated product recrystallised from methyl alcohol, appearing as colourless plates, m. p. 40° [Found: C, 83·9; H, 10·9; *M* (Pregl), 297. $C_{21}H_{32}O$ requires C, 84·0; H, 10·7%; *M*, 300].

Bis-(4-iso*propylstyryl Nonyl Ketone*).—This compound was obtained by Scholtz and Meyer (*loc. cit.*) by the action of 15% sodium hydroxide on cuminaldehyde and methyl nonyl ketone in cold alcoholic solution, and was described as 4-*iso*propylstyryl nonyl ketone, m. p. 144°. We have prepared the compound by a similar method, but find it to be a dimeride, m. p. 150° [Found: C, 84·1; H, 10·7; *M* (Menzies), 605. $C_{42}H_{64}O_2$ requires C, 84·0; H, 10·7%; *M*, 600].

4-*Chlorostyryl Nonyl Ketone*.—*p*-Chlorobenzaldehyde (2 g.) and methyl nonyl ketone (2·5 g.) were dissolved in alcohol (45 c.c.), and 1 c.c. of 8% sodium hydroxide was added. The product separated after standing for 24 hours at room temperature, and was recrystallised from alcohol, forming colourless plates, m. p. 62—63° (yield, 2·5 g.) [Found : C, 73·5 ; H, 8·7 ; *M* (Menzies), 294. $C_{18}H_{25}OCl$ requires C, 73·8 ; H, 8·5% ; *M*, 293].

Bis-(4*-chlorostyryl Nonyl Ketone*).—*p*-Chlorobenzaldehyde (2 g.) and methyl nonyl ketone (2·5 g.) were refluxed for 4 hours with 1% alcoholic potassium hydroxide (40 c.c.). The separated product was recrystallised from alcohol, colourless, fine needles being obtained, m. p. 126—127° [Found : C, 73·7 ; H, 8·3 ; *M* (Menzies), 614. $C_{36}H_{50}O_2Cl_2$ requires C, 73·8 ; H, 8·5% ; *M*, 585].

3-*Chlorostyryl Nonyl Ketone*.—This compound was prepared by a method similar to that employed for the 4-chloro-derivative. The product obtained by cooling in ice gave colourless plates on recrystallisation from methyl alcohol, m. p. 57° (Found : C, 74·0 ; H, 8·6%).

2-*Chlorostyryl Nonyl Ketone Semicarbazone*.—*o* - Chlorobenzaldehyde (2 g.) and methyl nonyl ketone (2·5 g.) were treated with 0·25% alcoholic potassium hydroxide (20 c.c.) for 7 days. The crude condensation product could not be induced to solidify, and for identification was converted into its *semicarbazone*, which separated from alcohol in colourless needles, m. p. 123—124° (Found : N, 12·1. $C_{19}H_{28}ON_3Cl$ requires N, 12·0%).

2-*Hydroxystyryl Nonyl Ketone*.—Salicylaldehyde (5 g.) and methyl nonyl ketone (7 g.) were dissolved in absolute alcohol, and sodium hydroxide (30 c.c. of 30%) was added. After standing at room temperature for 5 days, the dark solution was diluted with water and rendered neutral with carbon dioxide. The crude product separated from methyl alcohol (charcoal) in colourless leaflets, m. p. 79° (yield, 5·5 g.) (Found : C, 78·7 ; H, 9·4. $C_{18}H_{26}O_2$ requires C, 78·7 ; H, 9·5%).

THE UNIVERSITY, LIVERPOOL. [*Received, June* 6*th,* 1928.]