

in some commercial samples of yeast adenylic acid may be the new adenosinephosphoric acid isomer of Carter and Cohn.<sup>9</sup>

#### Experimental

Formamide was purified by distillation from calcium oxide at a pressure of 1–3 mm., using a still similar to that described by Hickman.<sup>11</sup> The distillate was redistilled from calcium oxide. Dry nitrogen was then bubbled through this second distillate for several hours. The best formamide obtained by this procedure had a specific conductance of  $4 \times 10^{-8}$  ohms<sup>-1</sup> cm.<sup>-1</sup>.<sup>12,13</sup>

N-Methylmorpholine (Carbide and Carbon Chemicals Corp.) was dried over solid potassium hydroxide and then fractionally distilled from barium oxide.

Rotations were measured either with a Schmidt and Haensch or a Rudolph No. 80 polarimeter.

The water content of the various samples was determined<sup>14</sup> by means of the apparatus of Milner and Sherman.<sup>15</sup> The samples were dried *in vacuo* at 110° using Drierite as the desiccant.

(11) Hickman, *Chem. Revs.*, **34**, 55 (1944).

(12) Verhoek, *This Journal*, **58**, 2577 (1936), reports a specific conductance of about  $5 \times 10^{-8}$  ohms<sup>-1</sup> cm.<sup>-1</sup> for formamide purified by his distillation procedure.

(13) We wish to thank Mr. Jonathan S. Dixon for preparing the samples of formamide used in this work.

(14) We wish to thank Miss Dorothy Kuenne for these analyses.

(15) Milner and Sherman, *Ind. Eng. Chem., Anal. Ed.*, **8**, 427 (1936).

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## Emulsion Copolymerization of Butadiene and Styrene at Low Temperatures<sup>1</sup>

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The present work was undertaken in order to develop, if possible, a method for the copolymerization of butadiene and styrene which would be successful at -20°. The recipe in Table I, although not particularly rapid, occasionally gave soluble polymers of high intrinsic viscosity. The

TABLE I  
-20° POLYMERIZATION RECIPE

Water	20.0 g.
Glycerol	20.0
Na <sub>4</sub> P <sub>2</sub> O <sub>7</sub> ·10H <sub>2</sub> O	0.25
Fe(NH <sub>4</sub> ) <sub>2</sub> (SO <sub>4</sub> ) <sub>2</sub> ·6H <sub>2</sub> O	0.25
Potassium oleate	1.0
Benzoyl peroxide	0.1
Styrene	5.0
Butadiene	15.0

polymerizations, however, were not at all reproducible and many identically charged runs gave results ranging all the way from no polymer whatever to polymers with intrinsic viscosities as high as 5. It was suspected that atmospheric oxygen was responsible for this non-reproducibility of results, and every effort was taken to remove all air from the system before polymerization was

(1) This investigation was carried out under the sponsorship of the Office of Rubber Reserve, Reconstruction Finance Corporation, in connection with the Government Synthetic Rubber Program.

started. Air was removed by adding excess butadiene and allowing it to evaporate; it was swept out mechanically with nitrogen; and it was removed along with excess butadiene from the closed system by means of a hypodermic needle inserted through self-sealing polymerization bottle caps. Even with these precautions the results were still quite erratic.

It, therefore, seemed possible that oxygen had already done its damage before all air was removed from the system and such actually proved to be the case. When the *entire* charging technique was carried out under nitrogen this recipe at -20° gave reproducible conversions of soluble copolymers with intrinsic viscosities of between 4.00 and 5.00. It is significant that benzene soluble polymers were obtained even though no modifier was added to the recipe. When the above charging technique was used for polymerization at 0°, 85% conversions were obtained in nine hours. This work is further confirmation of the observation of Hobson and D'Ianni<sup>2</sup> that removal of oxygen from other oxidation-reduction polymerization recipes at 41°F. results in faster polymerizations than are obtained in the presence of oxygen.

#### Experimental

**Polymerization at -20°.**—A solution of 2.5 g. of finely pulverized sodium pyrophosphate decahydrate in 105 ml. of redistilled water was prepared. This solution was poured directly into a clean 28-oz. ginger ale bottle which had previously been flushed out with nitrogen and placed on a steam cone. Nitrogen was kept streaming into the bottle during all the charging period until after the addition of butadiene. Then 2.5 g. of pulverized ferrous ammonium sulfate hexahydrate dissolved in 35 ml. of redistilled water was added through a funnel to the bottle. A cloudy precipitate formed in the solution, which was heated slowly with hand agitation to about 60°. Meanwhile, 10 g. of dry potassium oleate (pH 10) was dissolved in 60 ml. of redistilled water with slight warming if necessary and then 200 g. of glycerol was added with stirring to the soap solution. When the activator solution had come to temperature, the soap-water-glycerol solution was added to it and the bottle, after preliminary cooling under the water-tap, was placed in an ice-salt-bath. (The flow of nitrogen into the bottle was maintained.) After the temperature of the contents had reached 0°, 50 ml. of styrene containing 1.0 g. of benzoyl peroxide was added, and then about 175 g. (an excess) of butadiene. The excess butadiene was evaporated to proper weight (150 g. of butadiene), the bottle was crimp-capped, and the contents were allowed to polymerize with tumbling in a -20° bath for twenty-four to forty-two and one-half hours. The latex formed was added with mechanical agitation to

TABLE II  
POLYMERIZATION AT -20°

Run	Polymerization time in hours	Conversion, %	Static solubility in benzene	[ $\eta$ ]
1	42.5	69.2	81	5.08
2	42.5	69.2	80.5	5.05
3	24	36.5	92	4.12
4	24	36.5	92	4.07
5	31.5	58.5	90.5	4.87
6	31.5	58.5	91.5	4.90

(2) Hobson and D'Ianni, *Ind. Eng. Chem.*, in press.

75 ml. of a water suspension of phenyl- $\beta$ -naphthylamine and was coagulated with salt-dilute acid solution, washed with tap water, and dried overnight at 70°.

The results of some typical runs are listed in Table II.

The polymers obtained were essentially gel-free even though no modifier was used. No microgel was detected by centrifuging or by cold-milling.

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### The Mechanism of Elimination of Hydrogen Bromide from $\alpha$ -Bromo Ketosteroids through Formation of Hydrazones

BY VERNON R. MATTOX AND EDWARD C. KENDALL

Recently a reaction has been described in which the atom of bromine in 4-bromo-3-ketosteroids was removed as hydrogen bromide with the introduction of a double bond at C<sub>4</sub>-C<sub>5</sub> as a sequel to formation of the 3-(2,4-dinitrophenylhydrazone).<sup>1</sup> Discussion of the mechanism of the reaction was limited to the statement that "the reactivity of the bromine at C<sub>4</sub> is greatly increased through formation of a hydrazone at C<sub>3</sub>."

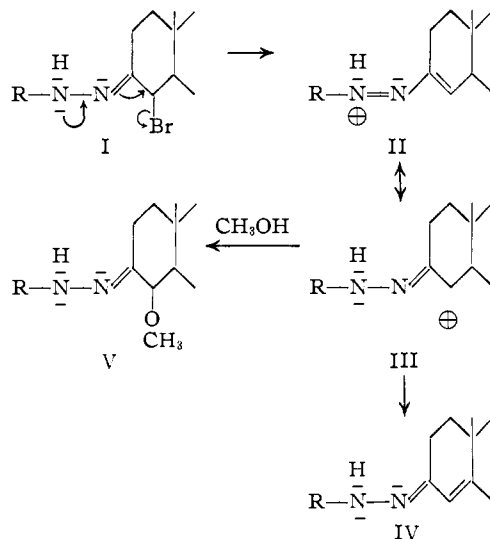
Djerassi has extended the reaction to other 3-keto  $\alpha$ -bromo steroids and has suggested a mechanism<sup>2</sup> for the elimination of hydrogen bromide and the formation of an unsaturated hydrazone in acetic acid.

We wish to report some additional observations on the reaction of hydrazines with  $\alpha$ -bromo-ketosteroids, and to suggest that the mechanism for the activation of the atom of bromine and the subsequent reactions which occur is as follows: (1) the hydrazone I is formed with the atom of bromine still intact, (2) an attack of the solvent on the bromine occurs and electrons are donated by the atom of nitrogen alpha to the phenyl group to form a resonance hybrid to which structures II and the carbonium ion III contribute, and (3) the carbonium ion is stabilized either through loss of a proton and formation of a double bond to give IV or through the addition of a negative group to give the C<sub>4</sub> substituent V. This mechanism correlates the reactivity of the halogen atom in I with that of other compounds<sup>3</sup> in which the halogen atom is alpha to a double bond or conjugated system that can act as an electron donor.

The essential difference between this mechanism and the one suggested by Djerassi is that (1) the bromine is not lost until after the hydrazone is formed, and therefore a hydroxy imino structure is not involved, and (2) with the hydrazone grouping as an intermediate the atom of nitrogen alpha to the phenyl group is the principal donor of electrons.

Hydrogen bonding between the atom of nitrogen alpha to the phenyl group and the bromine

- (1) Mattox and Kendall, *THIS JOURNAL*, **70**, 882 (1948).
- (2) Djerassi, *ibid.*, **71**, 1003 (1949).
- (3) Hughes, *Trans. Faraday Soc.*, **37**, 603 (1941).



appears not to be essential, for  $\alpha,\alpha$ -diphenylhydrazine removes hydrogen bromide from 4-bromo-3-ketosteroids. However, with the diphenylhydrazine, structure I could be formed as with mono substituted hydrazines. With disubstituted hydrazines and 2-bromo-3-ketosteroids, Djerassi<sup>2</sup> has obtained similar results.

The formation of an unsaturated hydrazone with loss of hydrogen chloride from a chloroaldehyde by treatment with 2,4-dichlorophenylhydrazine has been reported by Chattaway and Irving.<sup>4</sup> van Alphen<sup>5</sup> has clarified earlier investigations<sup>6</sup> concerned with the removal of hydrogen chloride from chloroacetoacetic ester with phenylhydrazine. In this instance an azo compound is formed. It appears probable that a structure analogous to I is an intermediate, but since an atom of hydrogen beta to the ketone is not available a proton is lost from the atom of nitrogen alpha to the phenyl group. van Alphen<sup>7</sup> also showed that phenacyl chloride in ethanol lost hydrogen chloride when treated with phenylhydrazine to yield [1,3-diphenyl-(1,2-diazacyclobutene-2)]. Djerassi,<sup>8</sup> on the other hand, observed that 2,4-dinitrophenylhydrazine did not remove hydrogen bromide from phenacyl bromide.

When semicarbazide was added to an acetic acid solution of methyl 3,11-diketo-4,12-( $\alpha$ )-dibromocholanate, a yellow color developed rapidly and faded within an hour or two to give a colorless semicarbazone of the  $\Delta^4$ -steroid. When methanol was used as the solvent, the semicarbazone of the 4-methoxy steroid<sup>9</sup> was ob-

- (4) Chattaway and Irving, *J. Chem. Soc.*, 88 (1930).
- (5) van Alphen, *Rec. trav. chim.*, **64**, 109 (1945); **64**, 305 (1945).
- (6) Bender, *Ber.*, **20**, 2747 (1887); Freer, *Am. Chem. J.*, **21**, 14 (1899).
- (7) van Alphen, *Rec. trav. chim.*, **65**, 112 (1946).
- (8) Personal communication.
- (9) The structure of this compound was shown by conversion with pyruvic acid to methyl 3,11-diketo-4-methoxy-12( $\alpha$ )-bromocholanate: unpublished work.