Azohydrazone Conversion.
II. The Coupling of Diazonium Ion with β-Diketones

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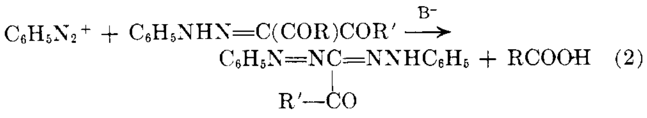
The reaction of the benzenediazonium ion and a β-diketone with 1:1 initial molar ratio in the presence of a weak base yields only a phenylhydrazone. Under otherwise identical conditions but in the presence of a strong base, the reaction of benzenediazonium ion and 1,3-diphenyl-1,3-propanedione produces a di(phenylazo) compound and a formazan together with a phenylhydrazone and the unreacted β-diketone. Such a di(phenylazo) compound, which has not been reported previously, can be further degraded to a formazan in the presence of either an acid or a base. These results suggest that the coupling of the 1,3-diphenyl-1.3-propanedione in the strong base involves a monophenylazo compound as an intermediate which is more reactive than the β-diketone and which can be further coupled to yield a di(phenylazo) compound. Under the same conditions, the direct coupling of the phenylhydrazones yields only a formazan and no di(phenylazo) compound has been isolated; this indicates that such coupling may resemble the coupling of the benzaldehyde phenylhydrazones which proceeds through the formation of an unstable tetrazene.

It is well known that the β-diketones in the presence of a weak base react readily with a diazonium ion to yield the products which are formulated as the monohydrazones[1] (reaction 1). Such hydrazones in the

$$C_6H_5N_2^+ + RCOCH_2COR' \xrightarrow{B^-} C_6H_5N{=}NCH(COR)COR' \longrightarrow C_6H_5NHN{=}C(COR)COR' \quad (1)$$

presence of a strong base can be further coupled to produce a formazan[2,3] (reaction 2). The simultaneous



$$C_6H_5N_2^+ + C_6H_5NHN{=}C(COR)COR' \xrightarrow{B^-} C_6H_5N{=}\underset{R'-CO}{\underset{|}{C}}{=}NNHC_6H_5 + RCOOH \quad (2)$$

coupling and acyl cleavage resembles the Japp–Klingemann type of reactions in which many unstable monoazo intermediates have been isolated.[4–7]

TABLE I

THE COUPLING IN SODIUM ACETATE BUFFERED SOLUTION

Coupling component	Product (m.p., °C.; yield, %[a])	λ_{max_1}, mμ (log ε)	λ_{max_2}, mμ (log ε)	λ_{max_3}, mμ (log ε)	Formula	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	Nitrogen, % Calcd.	Nitrogen, % Found
2,4-Pentanedione, I	2,3,4-pentanetrione-3-phenylhydrazone, IV (89[b]; 85)	242 (4.013)		362 (4.301)	$C_{11}H_{12}N_2O_2$	64.70	64.92	5.88	5.96	13.72	13.70
1-Phenyl-1,3-butanedione, II	1-Phenyl-1,2,3-butanetrione 2-phenylhydrazone, V (98–99[c]; 90)	240 (3.998)	280 (3.799)	365 (4.236)	$C_{16}H_{14}N_2O_2$	72.20	72.33	5.26	5.34	10.53	10.58
1,3-Diphenyl-1,3-propanedione, III	1,3-Diphenyl-1,2,3-propanetrione 2-phenylhydrazone, VI (154–155[d]; 85)	246 (4.250)		378 (4.285)	$C_{21}H_{16}N_2O_2$	76.85	77.01	4.88	4.84	8.54	8.66

[a] Yield for the purified product. [b] C. Beyer and L. Claisen [*Ber.*, **21**, 1697 (1888)] report m.p. 90°. [c] Lit.[b] m.p. 99°. [d] Lit.[b] m.p. 153–154°.

In the present paper, the reactions of the diazonium ions with the β-diketones have been studied further and the reaction courses for the formation of formazans are suggested.

Results and Discussion

The results of the coupling of the benzenediazonium ion to several β-diketones in the presence of sodium acetate are summarized in Table I; similar results were also obtained using pyridine as a base. It has been reported[6] that the ultraviolet absorption spectra of the monophenylazo compounds differ from those of the monophenylhydrazones. The azo compounds have a strong K-band at the wave length of 270 to 280 mμ. The monophenylhydrazones give a weak absorption band (or no band) at 284 to 295 mμ and a strong absorption band at a wave length higher than 320 mμ. The ultraviolet absorption spectra of the coupling products, IV–VI of Table I, are similar to those of the typical monophenylhydrazones.[6]

Infrared spectra, Fig. 1, provide additional evidence that compounds IV–VI are phenylhydrazones rather than azo compounds and that an azo-to-hydrazone conversion occurred during the coupling (eq. 1). The β-diketones, which have an α-hydrogen, do not have the –CO stretching band at 5.93 to 5.98 μ, characteristic of normal conjugated ketones, but instead they have a

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(1) M. Parmerter, *Org. Reactions*, **10**, 4 (1959).

(2) E. Bamberger and H. Witter, *Ber.*, **26**, 2786 (1893); *J. prakt. Chem.*, [2]**65**, 123, 139 (1902).

(3) L. Claisen, *Ber.*, **25**, 747 (1892).

(4) R. R. Phillips, *Org. Reactions*, **10**, 143 (1959).

(5) H. Henecka, H. Timmler, R. Lorenz, and W. Geiger, *Ber.*, **90**, 1060 (1957).

(6) H. C. Yao and P. Resnick, *J. Am. Chem. Soc.*, **84**, 3514 (1962).

(7) M. Regitz and B. Eistert, *Ber.*, **96**, 3120 (1963).

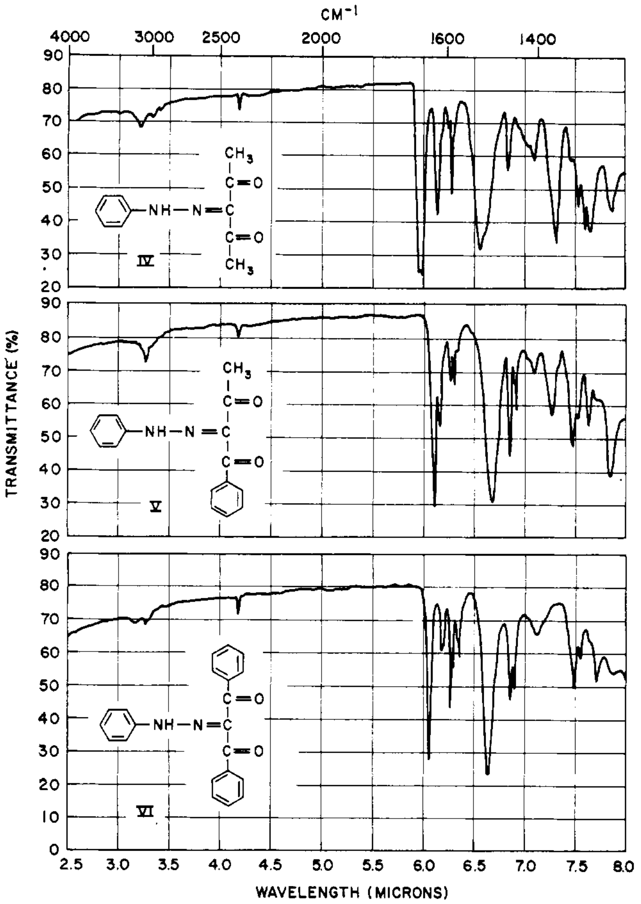
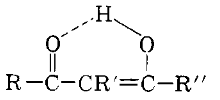
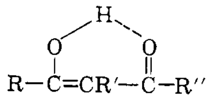


Fig. 1.—Infrared absorption spectra of the phenylhydrazones in Fluorolube mull.

very broad band from 6.10 (1640 cm.$^{-1}$) to 6.54 μ (1530 cm.$^{-1}$).[8] This broad band has been attributed to a reduction of the double bond character by resonance between form X and XI. The infrared spectra of the products IV–VI do not possess this broad band (Fig. 1),

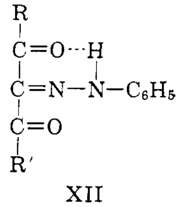

$$\mathrm{R{-}\overset{\overset{O\cdots H}{\|}}{C}{-}CR'{=}\overset{\overset{O}{|}}{C}{-}R''}$$

X


$$\mathrm{R{-}\overset{\overset{O}{|}}{C}{=}CR'{-}\overset{\overset{H\cdots O}{\|}}{C}{-}R''}$$

XI

indicating the absence of an active α-hydrogen in these compounds. Furthermore, it was reported[8] that the normal acetyl CO gives a stretching band at 5.82 μ (1718 cm.$^{-1}$) and the normal benzoyl CO gives a stretching band at 5.95 μ (1681 cm.$^{-1}$). In compounds IV–VI the stretching bands of the acetyl CO and the benzoyl CO were shifted to 5.98 and to 6.10 μ, respectively. Such a shift indicates the effect of conjugation of –CO with a C=N double bond. The stretching bands at 6.15 for IV and at 6.25 μ for VI probably result from the second conjugated –CO involved in a hy-


$$\begin{array}{l}\mathrm{R}\\ \mathrm{|}\\ \mathrm{C{=}O\cdots H}\\ \mathrm{|\qquad\quad |}\\ \mathrm{C{=}N{-}N{-}C_6H_5}\\ \mathrm{|}\\ \mathrm{C{=}O}\\ \mathrm{|}\\ \mathrm{R'}\end{array}$$

XII

TABLE II

THE COUPLING IN STRONG BASE

Component	Product (m.p., °C.; yield, %[a])	$\lambda_{\max_1}$, mμ (log ε)	$\lambda_{\max_2}$, mμ (log ε)	$\lambda_{\max_3}$, mμ (log ε)	Formula	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	Nitrogen, % Calcd.	Nitrogen, % Found	Other product (m.p., °C.; yield, %)
I	1,5-Diphenyl-3-acetylformazan, VII (134–135[b]; 45)	254 (4.008)	300 (4.190)	440 (4.342)	$C_{15}H_{14}N_4O$	67.70	67.78	5.26	5.35	21.04	20.90	IV (87; 20)
II	1,5-Diphenyl-3-benzoylformazan, VIII (141–142[c]; 67)	248 (4.233)	315 (4.196)	440 (4.336)	$C_{20}H_{16}N_4O$	73.20	72.98	4.87	4.88	17.06	17.08	V (98; ~10)
III	2,2-Di-(phenylazo)-1,3-diphenyl-1,3-propanedione IX (120–121; 34)	245 (4.363)	315 (4.085)	420 (4.312)	$C_{27}H_{23}N_4O_2$	75.00	76.06	4.63	4.67	12.96	13.07	VI (154°; 22) VIII (141–142; 7)
IV	VII (135; 42)											
V	VIII (141–142; 60)											
VI	VIII (141–142; 24)											

[a] Yield was estimated from the recrystallized product and was based on the amount of diazonium ion consumed. [b] Lit. (footnote b, Table I) m.p. 134–135°. [c] Lit.[2] m.p. 141–142°.

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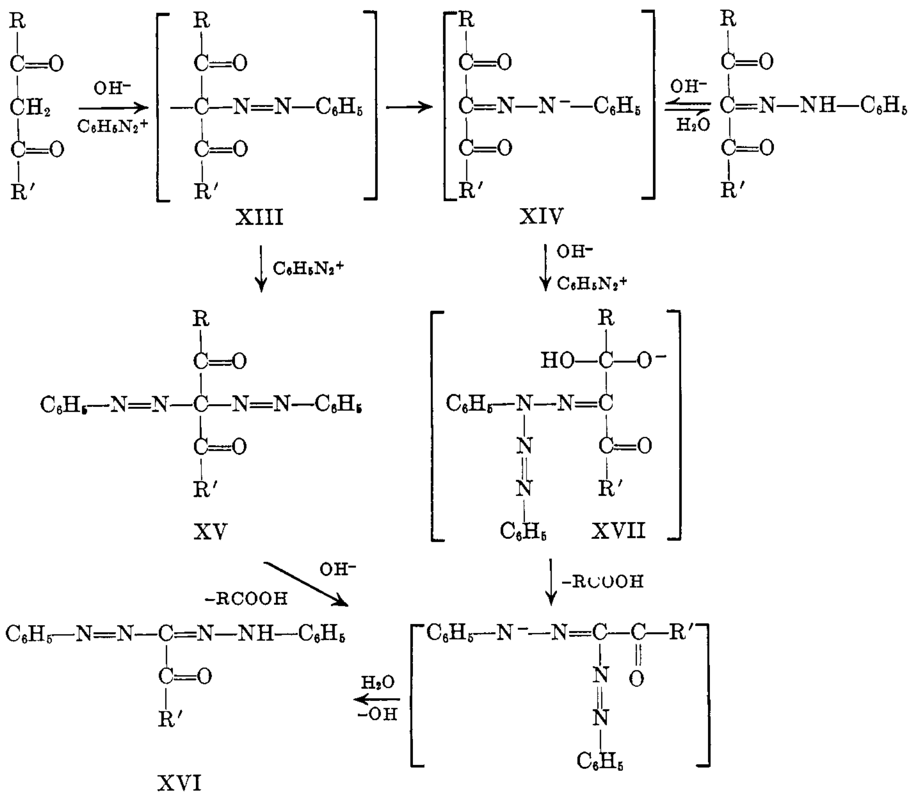
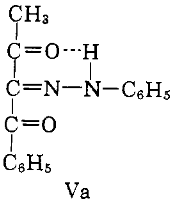
(8) R. S. Rasmussen, D. D. Tunnicliff, and R. R. Brattain, *J. Am. Chem. Soc.*, **71**, 1068 (1949).

SCHEME I

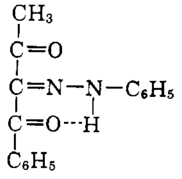


drogen bonding. In addition, the large shift and broadening of the –NH stretching band and the shift and reduction of the second –CO stretching band can result from only a strong hydrogen bonding as shown in XII.

The n.m.r. spectra (Fig. 2) also indicate that these compounds are of the hydrazo form rather than of the azo form. Thus, the azo form which contains a –CH group between the two carbonyl groups should exhibit a peak position similar to that of the methylene proton of acetoacetanilide (at 3.52 p.p.m.)[9] or of 1,3-indanedione (at 3.23 p.p.m.)[9]; such a peak is absent. The n.m.r. spectra also show a separation of the proton peaks at 2.32 and 2.45 p.p.m. of the two acetyl groups in IV (Fig. 2A) which indicates that one of these groups undergoes a shift in chemical environment as a result of hydrogen bonding with the hydrazo NH group. The extremely large chemical shift of the hydrazo NH protons in the spectra of all three compounds further indicates the strong hydrogen bonding of the hydrazo NH group which agrees with the infrared spectral results. In V, which contains one acetyl group and one benzoyl group, the hydrazo NH is hydrogen bonded to the acetyl CO as in Va rather than to the benzoyl CO as in Vb; this is shown by the presence of the hydrazo NH proton peak at 14.70 p.p.m. corresponding to that at 14.68 p.p.m. for IV rather than to that at 13.40 p.p.m. for VI.



Va



Vb

Although the coupling of a 1:1 molar ratio of benzenediazonium ion to β-diketones in weak base produces the phenylhydrazones in almost quantitative yields, additional products are formed and unreacted diketones are recovered in strong base. Table II summarizes results of the reactions of benzenediazonium ions in strong base with both the β-diketones and the phenylhydrazones prepared from them. The products arising from these reactions can be accounted for by Scheme I.

When R and R′ are both phenyl groups then the 2,2-di(phenylazo) compound can be isolated. Thus, when 1,3-diphenyl-1,3-propanedione (III) is treated with benzenediazonium ion then the 2,2-di(phenylazo)-1,3-diphenyl-1,3-propanedione (IX) is obtained along with the 1,3-diphenyl-1,2,3-propanetrione 2-phenylhydrazone (VI), 1,5-diphenyl-3-benzoylformazan (VIII), and some unreacted β-diketone. When either R or R′ or both are methyl groups then the corresponding 2,2-diphenylazo compound cannot be isolated and higher yields of the formazans are obtained. Presumably, the acetyl groups undergo hydrolytic cleavage more readily than benzoyl groups in the presence of strong base as has been observed in the Japp–Klingemann type of reaction.[4–7] The isolations in this work of 1,5-diphenyl-3-benzoylformazan (VIII) from the coupling of 1-phenyl-1,3-butanedione (II) and of 1-phenyl-1,2,3-butanetrione 2-phenylhydrazone provide additional evidence that the benzoyl group undergoes cleavage less readily than the acetyl group. However, the benzoyl group will also cleave at about 50° in the presence of an acid or a base and 1,5-diphenyl-3-benzoylformazan is formed from the di(phenylazo) compound IX.

The coupling of benzenediazonium ion to 1,3-diphenyl-1,2,3-propanetrione 2-phenylhydrazone in

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[9] "N.m.r. Spectra Catalog," Varian Associates, Spectrum No. 256 and 224.

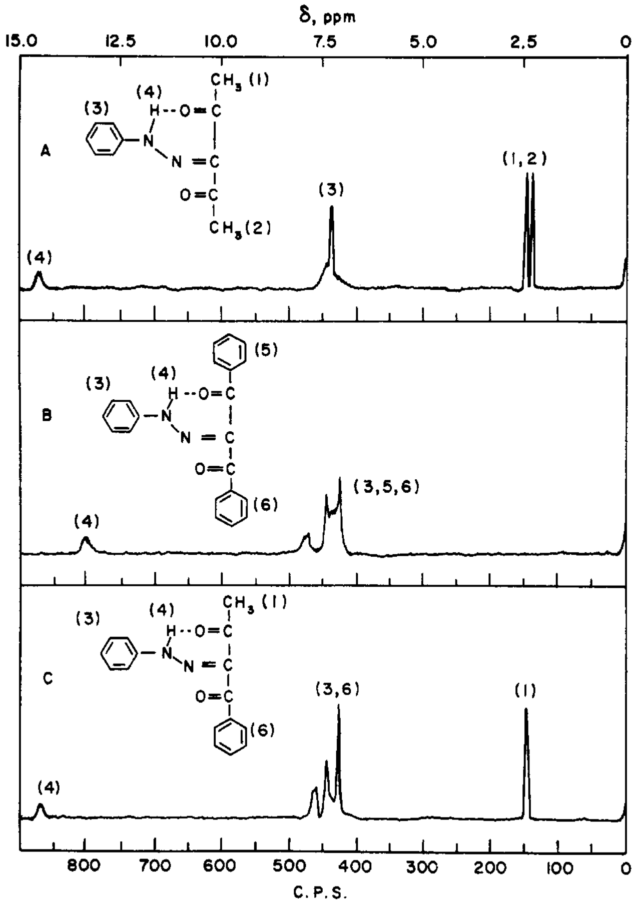

Fig. 2.—N.m.r. spectra of the phenylhydrazones in carbon disulfide solution (tetramethylsilane as internal reference).

strong base produces only the formazan and no 2,2-di-(phenylazo)-1,3-diphenyl-1,3-propanedione. Thus, the coupling with the phenylhydrazones appears to proceed *via* a pathway different from that with the β-diketones. A possible alternate route is *via* a tetrazene intermediate XVII similar to that postulated for the coupling of the diazonium ion to the benzaldehyde phenylhydrazones to form a formazan.[1,10–12] These tetrazenes are very unstable and readily rearrange at room temperature to the formazans. In the coupling of the hydrazones IV–VI such rearrangement is accompanied by an acyl cleavage. Attempts to isolate tetrazene intermediates were not successful in this study.

Experimental

Reagents.—2,4-Pentanedione (Matheson Coleman and Bell) was redistilled, and 1-phenyl-1,3-butanedione (Eastman) and 1,3-diphenyl-1,3-propanedione (Matheson Coleman and Bell) were recrystallized from benzene before use.

The Coupling Reactions in Aqueous Pyridine Solution. A.—The general procedure described in the previous paper[6] was used for the coupling of benzenediazonium chloride to the β-diketones (I–III of Table I). With an initial molar ratio of the reactants of 1:1 (β-diketone to diazonium salt), the products were only phenylhydrazones IV–VI which were obtained in 80–90% yield.

B.—Using the above procedure, the coupling reaction of benzenediazonium chloride to the phenylhydrazones IV–VI does not occur. Unreacted phenylhydrazones are recovered.

The Coupling Reactions in Sodium Acetate Buffered Solution. A. For β-Diketones.—β-Diketone (0.05 mole) was dissolved in 400 ml. of methanol solution containing 2 g. of sodium hydroxide and 15 g. of sodium acetate and the solution was diluted with water to about 800 ml. The solution was stirred and cooled to below 5°. A diazonium ion solution was prepared by dissolving 4.7 g. (0.05 mole) of aniline in 40 ml. of 5 *N* hydrochloric acid, cooling to 0°, and adding a saturated aqueous solution of 3.5 g. of sodium nitrite; it was then added dropwise with stirring to the β-diketone solution. During the addition, a yellow solid precipitated. It was collected, washed, and recrystallized from benzene and pentane. The results are shown in Table I.

B. For Phenylhydrazones IV–VI of Table I.—Using the procedure employed for sodium acetate buffered solutions, the coupling reaction of benzenediazonium salt to the phenylhydrazones did not occur. Unreacted phenylhydrazones were recovered.

The Coupling Reaction in Presence of Excess Sodium Hydroxide. A. For β-Diketones.—A solution of 11.2 g. (0.05 mole) of 1,3-diphenyl-1,3-propanedione (III) in 400 ml. of methanol was mixed with 500 ml. of aqueous sodium hydroxide (10.5 g. of NaOH) solution. The solution was cooled to below 5°. A diazonium chloride solution prepared from 4.7 g. (0.05 mole) of aniline was then added dropwise with stirring. During the addition of the diazonium salt, the solution turned orange, and a red solid gradually precipitated. After the red precipitate was collected, the filtrate was acidified with hydrochloric acid and about 2.8 g. of the unreacted β-diketone III was precipitated out as a white solid. The red precipitate was separated into three components as follows. It was washed with water and extracted with ether. The undissolved yellow residue was collected, recrystallized from benzene and pentane, and 3.6 g. of 1,3-diphenyl-1,2,3-propanetrione 2-phenylhydrazone (VI, yellow solid, m.p. 153°) was obtained. The ethereal extract was washed with water several times and dried with anhydrous magnesium sulfate. After the ether was evaporated, the residue was recrystallized from hexane to give orange crystals (IX, 3.7 g., m.p. 120–121°). Further concentration of the hexane solution yielded the red crystals which after recrystallization from methanol gave long needles (VIII, 0.6 g., m.p. 141–142°). Compound VIII which has the empirical formula $C_{20}H_{16}N_4O$ is 1,5-diphenyl-3-3-benzoylformazan and is identical with the product from the coupling of benzenediazonium ion to 1-phenyl-1,3-butanedione, to 1-phenyl-1,2,3-butanetrione 2-phenylhydrazone, or to 1,3-diphenyl-1,2,3-propanetrione 2-phenylhydrazone (Table II) in the presence of sodium hydroxide. Compound IX has the empirical formula of $C_{27}H_{20}N_4O_2$ (Table II) and is easily hydrolyzed in the presence of either a base or an acid to yield 1,5-diphenyl-3-benzoylformazan. Such evidence indicates that compound IX is 2,2-di(phenylazo)-1,3-diphenyl-1,3-propanedione.

2,4-Pentanedione and 1-phenyl-1,3-butanedione are more reactive than 1,3-diphenyl-1,3-propanedione; they were coupled under the same conditions but in the presence of half of the amount of sodium hydroxide. The results are shown in Table II.

B. For the Phenylhydrazones.—A solution of 8.2 g. (0.025 mole) of 1,3-diphenyl-1,2,3-propanetrione 2-phenylhydrazone (VI) in 400 ml. of methanol was mixed with 200 ml. of aqueous sodium hydroxide (10.5 g. of NaOH) solution. The solid was completely dissolved and the solution became red. The solution was cooled to below 5°. A diazonium chloride solution prepared from 2.4 g. (0.025 mole) of aniline was then added dropwise with stirring. After the addition, the solution was stirred for 0.5 hr. and then filtered. The solid was washed with water and then extracted with about 150 ml. of ether. After the ether was evaporated the residue was recrystallized from hexane to give red crystals (VIII, 1.9 g., m.p. 141–142°, red needles from methanol). The filtrate of the coupled solution was neutralized with dilute hydrochloric acid. A precipitate was formed which was filtered, washed with water, and recrystallized from benzene and pentane mixture. About 4.8 g. of the phenylhydrazone VI was recovered unreacted.

The phenylhydrazones IV and V were coupled with benzenediazonium salt using the same procedure as for the phenylhydrazone VI. The results are shown in Table II.

The Hydrolytic Cleavage of 2,2-Di(phenylazo)-1,3-diphenyl-1,3-propanedione (IX). A. With Base.—Aqueous sodium hydroxide solution (1 ml., 1%) was added to 50 ml. of methanol-water (4:1) solution containing 0.2 g. of IX. The solution was warmed to about 50° and then cooled with ice. The solid precip-

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(10) H. Von Pechmann, *Ber.*, **27**, 1679 (1894).

(11) M. Bush and R. Schmidt, *J. prakt. Chem.*, **127**, 131, 182 (1931).

(12) H. Hauptmann and A. C. DeM. Perisse, *Experientia*, **10**, 60 (1954); *Ber.*, **89**, 1081 (1956).

itated from the solution was filtered, washed with water, and recrystallized from methanol. About 0.06 g. of red needles were obtained which melted at 141–142°. The infrared spectra and the ultimate composition of this product are the same as those of VIII.

Anal. Calcd. for $C_{20}H_{16}N_4O$: C, 73.2; H, 4.87; N, 17.06. Found: C, 73.0; H, 4.92; N, 17.02.

B. **With Acid.**—Three drops of concentrated H_2SO_4 was added to 50 ml. of methanol–water (4:1) solution containing 0.2 g. of IX. The solution was boiled for about 15 min. and cooled. The solid precipitate was filtered, washed with water, and recrystallized from methanol to yield about 0.09 g. of red needles, m.p. 141–142°. The infrared spectra and the ultimate composition of this product are the same as those of VIII.

Anal. Calcd. for $C_{20}H_{16}N_4O$: C, 73.2; H, 4.87; N, 17.06. Found: C, 72.92; H, 4.83; N, 17.00.

The Spectral Results.—Ultraviolet spectra were measured in methanol solution with a Cary 14 spectrophotometer, infrared spectra were obtained in a Fluorolube mull with a Perkin-Elmer 237 spectrophotometer, and n.m.r. spectra were obtained in carbon disulfide solution with a Varian A-60 analytical n.m.r. spectrometer.

Acknowledgment.—The author is indebted to Dr. C. H. Ruof for his help in preparing this paper and wishes to thank Mr. J. L. Parsons for the discussion of the infrared absorption spectra.

The Reduction of 12-Keto Steroids[1]

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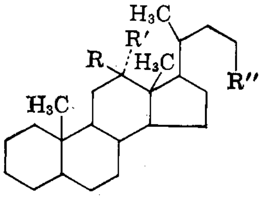
In contrast to the accepted generalization, it has been found that reduction of certain 12-keto steroids with lithium–liquid ammonia or sodium in alcohol affords predominantly the axial alcohol. It has been found that this anomaly is apparently a function of the structure of the side chain attached at C-17, and may be associated with a shielding of the oxygen in the 12-position by the C-21 methyl group. Other reactions in support of this hypothesis are discussed.

It has been generally accepted that the reduction of cyclic ketones by either sodium in alcohol, or lithium–liquid ammonia–alcohol gives rise exclusively or almost exclusively to the alcohol containing the thermodynamically more stable equatorial hydroxyl group.[2–6] These methods have found rather extensive use in steroid chemistry, and, in fact, provide the only practicable method for the preparation of steroid 11α-ols.[7–13] Although in the case of some bridged bicyclic ketones it has been found that sodium in alcohol reduction leads to a preponderance of the thermodynamically less stable alcohol[14] and although the reduction of camphor with potassium, rubidium, or cesium in liquid ammonia with ethanol as a proton source gives principally the less stable *exo* alcohol,[14] it seems to be generally accepted that reduction of cyclic ketones in general, and steroidal ketones in particular with either of the above reagents gives principally the more stable of a pair of epimeric alcohols, almost invariably the equatorial isomer.

In direct contrast to the above generalizations we found in attempting to prepare 12β-hydroxycholanic acid (Ia) by either lithium–liquid ammonia or sodium–*n*-propyl alcohol reduction of 12-ketocholanic acid[15] (Ib) the only isolable product was the 12α- (axial) ol, isolated as the methyl ester (Ic). Initially it was felt that these anomalous reductions were caused by an electrostatic effect associated with the carboxylate anion, and in order to check this hypothesis 12-cholanone (Id), prepared by oxidation of 12α-cholanol[16] (Ie), was subjected to reduction under similar conditions. Once again the axial alcohol was the principal product. From the lithium–liquid ammonia reduction, the 12α-ol was obtained in 71% yield, while sodium–*n*-propyl alcohol reduction gave the α–β-ol in a ratio of 1.7:1. The structure of 12β-cholanol (If) was confirmed by its oxidation to 12-cholanone, and analytical data.



Ia, R = OH; R′ = H; R″ = CO_2H
b, R, R′ = O; R″ = CO_2H
c, R = H; R′ = OH; R″ = CO_2CH_3
d, R, R′ = O; R″ = CH_3
e, R′ = H; R′ = OH; R″ = CH_3
f, R = OH; R′ = H; R″ = CH_3

At this stage there appeared to be several possible alternative explanations for these somewhat puzzling reductions. First, the possibility that the stereochemis-

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(1) A preliminary communication discussing a portion of this work appeared: J. W. Huffman, D. M. Alabran, and T. W. Bethea, *J. Org. Chem.*, **27**, 3381 (1962).

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(6) W. G. Dauben and K. S. Pitzer in "Steric Effects in Organic Chemistry," M. S. Newman, Ed., John Wiley and Sons, Inc., New York, N. Y., 1956, p. 47.

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