Y, of the reaction and the conditions under which it occurs, as long as these are the same for $\rho_I$ and $\rho_{II}$.[2] In connection with work on the basicities of substituted azo compounds and on an $H_0$ function in 20% ethanol,[4] we have had occasion to prepare a series of *p*-arylazophenols. We have now determined the acid dissociation constants of the phenolic function of these compounds in an attempt to gain information concerning the transmission of electronic effects through the group X = —N=N-$C_6H_4$—. Such information was of special interest for two reasons; it provided an additional test of the proposed method of calculating the constant ($\pi'$) of eq. 1 by molecular orbital theory, and it provided an interesting comparison with the data available from the consideration of the *p*-arylazo-N,N-dimethylanilines.[2,4d]

## Experimental

**Compounds.**—The preparation and physical properties of the *p*-arylazophenols have been reported in a previous paper.[4b]

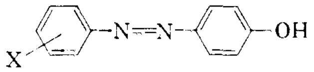
***pK* Determinations.**—The *pK*'s of the *p*-arylazophenols were determined in about $10^{-5}$ *M* solution in 20% ethanol by a standard spectrophotometric method.[5] Standard phosphate and borate buffers made in 20% ethanol were used,[6] and no ionic strength corrections were made. *pK*'s were determined with a Beckman model G *p*H meter, and spectroscopic measurements were made with a Beckman DU quartz spectrophotometer.

## Results and Discussion

The *pK*'s of the *p*-arylazophenols in 20% EtOH are listed in Table I. They are well correlated with the $\sigma$-values[3b] of the substituents in the aryl group with a $\rho = 0.515 \pm 0.019$, $s = 0.011$, $r = 0.998$, $n = 5$ $\log k^0 = 8.393$.[7]

TABLE I

$pK_2$ OF *p*-(ARYLAZO-)-PHENOLS



IN 20% ETHANOL AT 25°

| X | $\sigma$ | $pK_2$ |
|---|---|---|
| 4-$OCH_3$ | −0.268 | 8.54 ± 0.02 |
| 4-$CH_3$ | −0.170 | 8.48 ± .04 |
| H | 0 | 8.38 ± .04 |
| 4-Br | 0.232 | 8.27 ± .02 |
| 3-Br | 0.391 | 8.20 ± .02 |

No data appear to be available for the acid dissociation of simple phenols in the same solvent. Interpolation between reported values yields $\rho_I = 3.10$, $\rho_{II}/\rho_I = 0.16$.[3b] This value is in satisfactory agreement with the molecular orbital value $\pi' = 0.14$[2] for the same group X, and with the value obtained from the basicities of the *p*-aryl-N,N-dimethylanilines $\rho_{II}/\rho_I = 0.13$.[2,8] This latter value, however, requires further comment; it was derived from the $\rho$-value for the first protonation of these bases on the assumption that this reaction involves only the amino group. We have, however, now demonstrated that the conjugate acid of the bases under discussion are tautomeric mixtures of ammonium and azonium forms,[4d] and hence cannot expect a straightforward application of the Hammett equation to these equilibria. Only since substituents do not appear to affect the position of tautomeric equilibrium (*i.e.*, $\rho_T \approx 0$) is our use of the $\rho$ from the basicities of the *p*-aryl-N,N-dimethylanilines for a determination of $\rho_{II}/\rho_I$ for X = —N=N$C_6H_4$— justified, and our comparison of this value with the value from the *p*-arylazophenols and the theoretical value meaningful.

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[4] (a) H. H. Jaffé and R. W. Gardner, THIS JOURNAL, **80**, 319 (1958); (b) S.-J. Yeh and H. H. Jaffé, *ibid.*, **80**, 3274 (c) 3279, (d) 3283 (1959).

[5] L. A. Flexser, L. P. Hammett and A. Dingwall, *ibid.*, **81**, 57, 2103 (1935).

[6] W. M. Clark, "The Determination of Hydrogen Ions," Williams and Wilkins, Baltimore, Md., 3rd. ed., 1928, p. 200.

[7] All symbols have their usual significance; *cf.* ref. 2b.

[8] *Cf.* M. T. Rogers, T. W. Campbell and R. W. Maatman, THIS JOURNAL, **73**, 5122 (1951).

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

# Oxygen Oxidation of Triphenylsilyllithium

BY M. V. GEORGE AND HENRY GILMAN

RECEIVED DECEMBER 27, 1958

Oxidation of triphenylsilyllithium using molecular oxygen has been studied at different temperatures, in tetrahydrofuran as the solvent. Triphenylsilanol, triphenylsilane and small amounts of hexaphenyldisilane were formed in each case, though the yields of these products varied depending on the reaction temperature. A change of the solvent medium to tetrahydropyran did not affect the nature of the reaction products. The oxidation is assumed to proceed through an unstable hydroperoxide salt, followed by the radical decomposition of this intermediate.

Since the early investigations of Bodroux[1] and Bouveault,[2] numerous investigators have studied the reaction of Grignard reagent with molecular oxygen.[3] Wuyts[4] postulated that the oxidation reactions proceed through the formation of peroxide intermediates, and later Porter and Steele[5] suggested the reaction scheme

$$RMgX + O_2 \longrightarrow ROOMgX \xrightarrow{RMgX} 2ROMgX$$

Experimental evidence for this sequence was provided by Walling and Buckler,[6] who in an elegant study, have isolated several intermediate

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[1] F. Bodroux, *Compt. rend.*, **136**, 158 (1903); *Bull. soc. chim.*, [3] **31**, 33 (1904).

[2] L. Bouveault, *ibid.*, [3] **29**, 105 (1903).

[3] For an extensive review on the oxidation of Grignard reagents see, M. S. Kharasch and O. Reinmuth, "Grignard Reactions of Nonmetallic Substances," Prentice-Hall, Inc., New York, N. Y., 1954, pp. 1264-1274.

[4] H. Wuyts, *Bull. soc. chim. Belg.*, **36**, 222 (1927); *Compt. rend.*, **148**, 930 (1909).

[5] C. W. Porter and C. Steele, THIS JOURNAL, **42**, 2650 (1920).

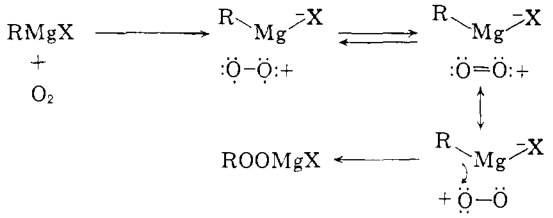
[6] C. Walling and S. A. Buckler, *ibid.*, **77**, 6032 (1955).

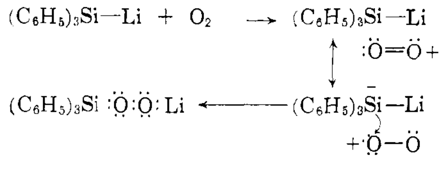
hydroperoxides from the corresponding Grignard reagents.

Müller and Töpel[7] studied the oxidation of several organolithium compounds and have found that the reaction proceeds through a path similar to the Grignard reagents with the formation of intermediate hydroperoxides. Walling and Buckler[6] substantiated this view by isolating *n*-butyl hydroperoxide by the addition of *n*-butyllithium to oxygen-saturated anhydrous ether at −70°. The hydroperoxide formed in 36% yield as compared to 57% from the analogous Grignard reagent.

In view of some special reactions of organosilicon compounds, it seemed of interest to study the oxidation of triphenylsilyllithium with a view to finding out the nature of the products formed and also of the probable course of the reaction. The oxidation reactions were generally carried out with tetrahydrofuran solutions of triphenylsilyllithium, prepared by the lithium cleavage of hexaphenyldisilane.[8,9] When the reaction was carried out at room temperature (25°) a 32.6% yield of triphenylsilanol was obtained. In addition 29.0% of triphenylsilane and 19.3% of hexaphenyldisilane were formed.

If the oxidation of triphenylsilyllithium is assumed to proceed through a route similar to the reaction of Grignard reagents and organolithium compounds, then the first step would be a conversion of the triphenylsilyllithium reagent to the corresponding hydroperoxide salt, by molecular oxygen. The exact mechanism of this oxidation is not too clear. In the case of Grignard reagents Walling and Buckler[6] suggested that the hydroperoxide is formed through a bimolecular association of oxygen and Grignard reagent, followed by a rearrangement. These workers prefer to represent the formation of the final product as taking place through the migration of R with its electron pair as indicated. The oxidation of the silyllithium compound could be represented by a similar scheme.





Another possibility which should not be overlooked is the coördination of one of the oxygen centers with the silicon atom, which could thereby assume a pentacovalent stage in the intermediate complex.

The second step in the oxidation has been assumed to be due to a reaction of the hydroperoxide salt with an additional amount of the Grignard reagent.[5,6,10,11] This ionic mechanism however would not explain the isolation of products like α-phenylethanol from the oxidation of phenylmagnesium bromide[5,12a,b] which on the other hand might be expected from the homolytic decomposition of the intermediate peroxide, followed by a radical attack on the solvent. Russell[13] on the basis of his studies on the autoxidation of 2-nitropropane anion, has suggested that the Grignard oxidation might proceed through an analogous free radical mechanism involving the formation of an intermediate hydroperoxide anion.

One of the products isolated in appreciable quantity from the oxidation of triphenylsilyllithium has been triphenylsilane. The formation of this substance cannot be explained on the basis of an ionic mechanism or by a nucleophilic 1,2-rearrangement of the type reported by Buncel and Davies.[14] It might be possible, on the other hand, to assume that the reaction proceeds by a free radical path, involving the homolytic cleavage of the intermediate hydroperoxide salt. The triphenylsilyl radical thus formed could attack the solvent to give triphenylsilane. No product showing the fate of the ·OLi radical has been isolated. In this connection mention may be made of the earlier work[15] on the peroxide induced oxidation of triphenylsilane. In this study chlorotriphenylsilane was isolated as one of the products from the reaction between di-*t*-butyl peroxide and triphenylsilane in chlorobenzene, which precludes the formation of triphenylsilyl radicals in the reaction medium. It is significant to note that a 19.3% yield of hexaphenyldisilane was also isolated when the oxidation was carried out at 25°. At lower temperatures the yield of this product was slightly lower. The formation of hexaphenyldisilane may result by a dimerization of triphenylsilyl radical, though conclusive evidence is lacking at present for this assumption.

$$(C_6H_5)_3SiOOLi \longrightarrow (C_6H_5)_3SiO\cdot + \cdot OLi$$

$$(C_6H_5)_3SiO\cdot + (C_6H_5)_3SiLi \longrightarrow (C_6H_5)_3SiOLi + (C_6H_5)_3Si\cdot$$

$$(C_6H_5)_3Si\cdot + \text{Solvent} \longrightarrow (C_6H_5)_3SiH$$

The yield of the products of oxidation has been found to vary with the reaction temperature employed. Thus, when the reaction was carrried out at 0° a 47.0% yield of triphenylsilanol was obtained as against 32.6% at 25°. The best yield (60.3%) of triphenylsilanol was obtained when the oxidation was carried out at −25°. This observation is in agreement with the reported variation in

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(7) E. Müller and T. Töpel, *Ber.*, **72**, 273 (1939).

(8) H. Gilman and G. D. Lichtenwalter, THIS JOURNAL, **80**, 608 (1958).

(9) A more convenient method of preparing triphenylsilyllithium by the direct reaction of chlorotriphenylsilane and lithium has been reported recently: H. Gilman, D. J. Peterson and D. Wittenberg, *Chemistry & Industry*, 1479 (1958). This method, however, was avoided in this study because of the possible change in conditions that might arise due to the presence of lithium chloride.

(10) T. W. Campbell, W. Burney and T. L. Jacobs, THIS JOURNAL, **72**, 2735 (1950).

(11) S. Lawesson, N. C. Yang and M. S. Kharasch, Paper presented at the 134th Meeting of the American Chemical Society in Chicago, Ill., 1958.

(12) (a) M. S. Kharasch and W. B. Reynolds, THIS JOURNAL, **55**, 1693 (1933); (b) H. Gilman and A. Wood, *ibid.*, **48**, 806 (1926).

(13) G. A. Russell, *ibid.*, **76**, 1595 (1954).

(14) E. Buncel and A. G. Davies, *Chemistry & Industry*, 1052 (1956).

(15) J. Curtice, H. Gilman and G. S. Hammond, THIS JOURNAL, **79**, 4754 (1957).

the yields with temperature of phenolic products, from the oxidation of Grignard reagents.[13,16]

The oxidation of triphenylsilyllithium in tetrahydropyran was examined in order to determine whether a change to this solvent would appreciably alter either the nature of yields or the products. A solution of triphenylsilyllithium in tetrahydropyran for this purpose was prepared by the lithium cleavage of hexaphenyldisilane. The cleavage reaction in this solvent was quite slow and even after 48 hr. of stirring, only a 60.2% yield of the reagent could be obtained. With an extended reaction time (72 hr.) an 81.0% yield of triphenylsilyllithium was obtained. The reagent was found to be fairly stable in this solvent, at room temperature. The oxidation of triphenylsilyllithium in tetrahydropyran, by the usual procedure, gave a 51.9% yield of triphenylsilanol. In this case also triphenylsilane was formed in an appreciable quantity (20.1%). In addition a 4.2% yield of hexaphenyldisilane and 1.6% of hexaphenyldisiloxane were obtained. The hexaphenyldisiloxane might have formed from triphenylsilanol during the work-up of the reaction mixture.

## Experimental

All melting points are uncorrected. Preparations of silyllithium compounds were carried out under an atmosphere of dry, oxygen-free nitrogen.[17] Tetrahydrofuran, boiling at 65–66°, and tetrahydropyran, boiling at 85–86°, were freed from peroxides and moisture before use by refluxing over sodium followed by distillation from lithium aluminum hydride. The oxygen gas employed was purchased from The Ohio Chemical & Mfg. Co. (Cleveland, Ohio) and purified by passage through drying agents.

**Triphenylsilyllithium in Tetrahydrofuran.**—A solution of triphenylsilyllithium in 150 ml. of tetrahydrofuran was prepared by the lithium cleavage of 13.0 g. (0.025 mole) of hexaphenyldisilane using a reported procedure.[8] After stirring the mixture for 12 hr. at room temperature, it was derivatized by treatment with 14.7 g. (0.05 mole) of chlorotriphenylsilane to give a 92.5% yield of hexaphenyldisilane.

In a second run the reaction mixture containing hexaphenyldisilane, lithium and tetrahydrofuran was stirred for 60 hr. at room temperature. Upon treatment with chlorotriphenylsilane 82.1% of hexaphenyldisilane was obtained.

**Reaction of Triphenylsilyllithium with Carbon Dioxide.**—A solution of triphenylsilyllithium (0.05 mole) in 150 ml. of tetrahydrofuran was poured into a slurry of Dry Ice and absolute diethyl ether (100 ml.). The carbonated mixture was hydrolyzed by adding to an excess of ice-cold dilute sulfuric acid (4 *N*). The solution was extracted with ether (300 ml.). Removal of the solvent from the ether extract, after drying over sodium sulfate, gave a white solid. It was treated with 50 ml. of petroleum ether (b.p. 60–70°) to give 12.7 g. (83.4%) of triphenylsilanecarboxylic acid, m.p. 175–176° dec. Recrystallization from a mixture of benzene and petroleum ether (b.p. 60–70°) raised the melting point to 183–184° dec. No depression in the melting point was observed when admixed with an authentic sample of triphenylsilanecarboxylic acid. The infrared spectrum of this compound in carbon disulfide showed absorption bands at 1645 and 1112 cm.$^{-1}$, characteristic of COOH and Si-phenyl groups, respectively.

The petroleum ether-soluble portion of the residue was chromatographed on alumina. Elution with carbon tetrachloride gave 0.1 g. (0.8%) of hexaphenyldisiloxane, m.p. 225–228° (mixed m.p.). Further elution of the column with methanol gave 0.3 g. (2.2%) of triphenylsilanol, m.p. and mixed m.p. 153–155°.

**Reaction of Triphenylsilyllithium in Tetrahydrofuran, with Oxygen at Room Temperature (25°).**—Oxygen gas was slowly passed through a solution of 0.01 mole of triphenylsilyllithium in 30 ml. of tetrahydrofuran. The reaction was exothermic and the temperature of the mixture was maintained at 25° by outside cooling of the flask. The dark brown color of the silyllithium solution gradually faded and the solution became very pale brown within about 30 minutes. The reaction mixture at this stage gave a negative Color Test I.[18] The solution was poured into ice-cold dilute sulfuric acid. A small quantity of a white insoluble residue was noticed in the hydrolyzed mixture, which was removed by filtration. It melted at 365–367° and did not depress the melting point of an authentic sample of hexaphenyldisilane. The yield of hexaphenyldisilane formed was 0.5 g., 19.3%.

The aqueous filtrate was cautiously extracted with ether and the ether extract was dried over anhydrous sodium sulfate. Removal of the solvent from the ether solution gave a viscous liquid which was chromatographed on alumina. Elution of the column with petroleum ether (b.p. 60–70°) gave 0.8 g. (29.0%) of triphenylsilane, identified by a comparison of the infrared spectrum with that of an authentic sample. The infrared spectrum in carbon tetrachloride showed the –Si–H absorption band at 2140 cm.$^{-1}$, whereas the band characteristic of Si–phenyl group was observed at 1108 cm.$^{-1}$.

On methanol elution of the alumina column, 0.19 g. (32.6%) of triphenylsilanol was obtained, m.p. 153–154° (mixed m.p.). The infrared spectrum of this substance in carbon tetrachloride showed the Si–OH band at 3650 cm.$^{-1}$ and was identical with the spectrum of an authentic sample of triphenylsilanol, in the same solvent.

Repeated elution of the alumina column with methanol gave a small quantity of an unidentified viscous material.

**Reaction of Triphenylsilyllithium in Tetrahydrofuran, with Oxygen at 0°.**—Through a solution of triphenylsilyllithium in tetrahydrofuran (0.04 mole, 100 ml.), kept at 0° by cooling in an ice-bath, oxygen gas was passed for 30 minutes. The reaction mixture gave a negative Color Test I and was hydrolyzed by adding to an excess of ice-cold dilute sulfuric acid. Work-up of the mixture as described in the previous case gave 0.7 g. (6.7%) of hexaphenyldisilane, 1.4 g. (13.4%) of triphenylsilane and 5.2 g. (47.0%) of triphenylsilanol. These products were identified by a comparison of the infrared spectra with those of the authentic samples, and also by mixed melting point determinations.

**Reaction of Triphenylsilyllithium in Tetrahydrofuran, with Oxygen Gas at −25°.**—In a third run oxygen gas was passed through 0.03 mole (105 ml.) of triphenylsilyllithium at −25° for 30 minutes. Work-up of the reaction mixture after hydrolysis gave 0.1 g. (0.6%) of hexaphenyldisilane, m.p. and mixed m.p. 365–367°. Other products isolated were triphenylsilane, 1.0 g. (12.8%), and 5.0 g. (60.3%) of triphenylsilanol.

**Triphenylsilyllithium in Tetrahydropyran.**—To a mixture of 13.0 g. (0.025 mole) of hexaphenyldisilane and 1.0 g. (0.15 g.-atom) of lithium metal 25 ml. of tetrahydropyran was added and the resulting paste was stirred rapidly at room temperature. The mixture became pale yellow after about 30 minutes, indicating the commencement of the cleavage reaction. A further volume of 135 ml. of tetrahydropyran was added to this mixture and the stirring continued for 48 hr. The brown turbid solution gave a positive Color Test I and it was filtered through glass wool.

The prepared triphenylsilyllithium was derivatized by treatment with 14.7 g. (0.05 mole) of chlorotriphenylsilane to give 15.6 g. (60.2%) of hexaphenyldisilane, m.p. and mixed m.p. 364–366°.

In a second run the lithium cleavage of hexaphenyldisilane in tetrahydropyran was allowed to proceed for 72 hr. at room temperature. Derivatization with chlorotriphenylsilane gave 81.0% of hexaphenyldisilane.

**Reaction of Triphenylsilyllithium in Tetrahydropyran with Oxygen at 0°.**—Through 0.023 mole of a tetrahydropyran solution (110 ml.) of triphenylsilyllithium, kept cooled at 0° in an ice-bath, oxygen gas was passed for 30 minutes. The mixture gave a negative Color Test I and the solution was acid-hydrolyzed by pouring into ice-cold dilute sulfuric acid. The hydrolyzed solution was worked up as in the previous cases to give 0.5 g. (4.2%) of hexaphenyldisilane, m.p. and mixed m.p. 365–367°. In addition 1.2 g. (20.1%) of triphenylsilane and 3.3 g. (51.9%) of triphenylsilanol were also obtained. A small quantity (0.2

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[16] M. D. Ivanoff, *Bull. soc. chim.*, [4] **39**, 47 (1926).

[17] L. J. Brady, *Ind. Eng. Chem., Anal. Ed.*, **20**, 1034 (1948).

[18] H. Gilman and F. Schulze, THIS JOURNAL, **47**, 2002 (1925).

g., 1.6%) of hexaphenyldisiloxane, m.p. 226–228° (mixed m.p.) could be isolated as one of the products from this run.

**Acknowledgment.**—This research was supported by the United States Air Force under Contract AF 33(616)-3510 monitored by Materials Laboratory, Directorate of Laboratories, Wright Air Development Center, Wright Patterson AFB, Ohio. Infrared analyses were obtained through the courtesy of the Institute for Atomic Research, Iowa State College, and special acknowledgment is made to Dr. V. A. Fassel and Mr. R. Kniseley for the spectra.

AMES, IOWA

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[CONTRIBUTION FROM THE MERCK SHARP & DOHME RESEARCH LABORATORIES, MERCK & CO., INC.]

# Selective Sodium Borohydride Reductions in Aqueous Dimethylformamide Solution. Neighboring Group Effects in the Cortical Side Chain[1]

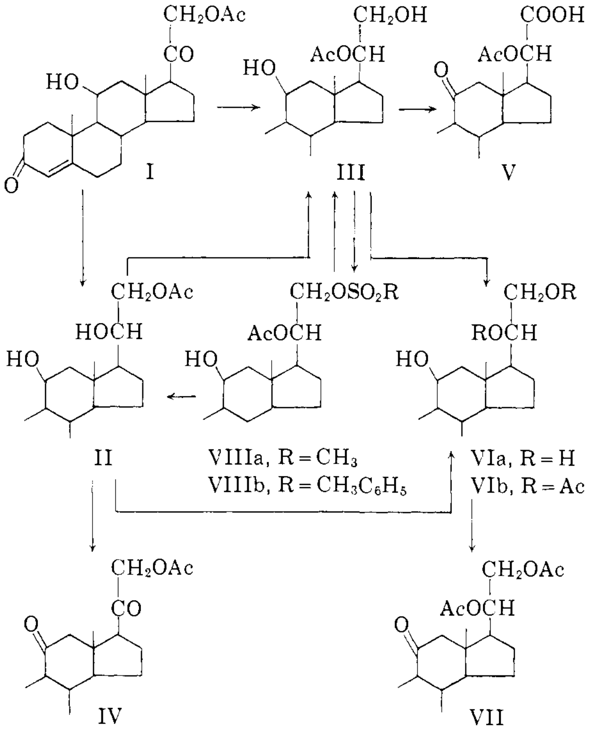
BY D. TAUB, R. D. HOFFSOMMER AND N. L. WENDLER

RECEIVED DECEMBER 20, 1958

Sodium borohydride reduction of corticosterone 21-acetate (I) in aqueous dimethylformamide proceeded largely with acetyl migration to give the $20\beta$-acetate 21-ol III as well as the $20\beta$-ol-21-acetate II. The 21-mesylate-$20\beta$-acetate VIIIa on demesylation gave mixtures of II and III in which II predominated. Similar sodium borohydride reductions of hydrocortisone 21-acetate (XI) and cortisone 21-acetate (XIII) led directly to Reichstein's Substances E and U 21-acetates, respectively.

The present work originated in an attempt to modify the procedure of Norymberski and Woods[2] for the preferential reduction of the 20-keto group of cortical steroids in the presence of the $\Delta^4$-3-keto and/or 11-keto groupings, such that concomitant loss of easily hydrolyzable ester functions elsewhere in the molecule would not occur. Under the conditions employed by Norymberski and Woods (1.5 mols of sodium borohydride per mol of steroid in methanol at 0° for one hour) the 21-acetate function of 21-acetoxy-20-keto steroids readily undergoes methanolysis and the principal products, produced in moderate yields, are $20\beta$-21-diols[3] or, following mild acetylation, the corresponding diacetates.[2]

In preliminary studies we found that reduction of 20-ketoacetoxy systems in aqueous dimethylformamide proceeds more slowly than in methanol but without loss of acetate functionality.[3c] These conditions were applied in detail to the reduction of corticosterone acetate (I) in the interest of obtaining the corresponding 21-monoacetate II.[4] When compound I was treated with sodium borohydride in 50% aqueous dimethylformamide, a new substance, m.p. 234–240°, which partly precipitated during the reduction, was formed in 75–80% yield. Its analysis, infrared and ultraviolet absorption spectra were in conformity with those expected for structure II and it readily formed monomesylate and monotosylate derivatives. However, $CrO_3$ oxidation of the reduction product did not produce 11-dehydrocorticosterone acetate (IV) as would be expected from II. The oxidation product was an *acetoxy acid* formulated as V on the basis of its properties and analysis.



The substance, m.p. 234–240°, must therefore have a 20-acetate-21-ol part structure.[5] The $20\beta$-acetate-21-ol formulation III was shown to be

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[1] Presented in part at the 132nd Meeting of the American Chemical Society, September 1957, New York, N. Y. (Abstracts, p. 23P).

[2] J. K. Norymberski and C. F. Woods, *J. Chem. Soc.*, 3426 (1955).

[3] (a) See for example: C. M. Southcott, H. E. Bandy, S. E. Newsom and M. Darrach, *Can. J. Biochem. Physiol.*, **34** 913 (1956). (b) It should be noted that the $17\beta$-acetoxy function in $C_{19}$-steroids is stable to sodium borohydride in aqueous methanol (E. Elisberg, H. Vanderhaeghe and T. F. Gallagher, THIS JOURNAL, **74**, 2814 (1952).

[3c] N. L. Wendler, R. P. Graber and G. G. Hazen, *Tetrahedron*, **3**, 144 (1958).

[4] 21-Monoacetates may be obtained from the corresponding 20,21-diols of 3-keto-$\Delta^4$-pregnenes in low yield by partial acetylation and chromatography [*e.g.*, L. H. Sarett, THIS JOURNAL, **68**, 2478 (1946)] and similarly from $17\alpha$,20,21-triols [*e.g.*, Huang-Minlon and R. H. Pettebone, *ibid.*, **74**, 1562 (1952)]. Catalytic reduction of the 20-carbonyl group, which proceeds in good yield to the corresponding $20\beta$-hydroxy compound without loss of the 21-acetate function [L. H. Sarett, *ibid.*, **71**, 1169 (1949)], is not applicable to $\Delta^4$-3-keto systems since reduction of A-ring functionality would occur also.

[5] Acetyl migration from $C_{18}$ to $C_{17}$ was recently observed during the sodium borohydride reduction of *d,l*-ethylenedioxy-5-androstene-$11\beta$,18-diol-17-one 18-acetate by P. Wieland, K. Heusler and A. Wettstein, *Helv. Chim. Acta*, **41**, 1657 (1958).