constants for bendings and stretch-bend interactions according to methods B and C:

(B) $\quad f_\beta, \; f_{\beta\beta}, \; f_{r\beta}, \; f_{r\beta}', \; f_{d\beta}$

(C) $\quad f_\alpha, \; f_\varphi, \; f_{r\alpha}, \; f_{d\alpha}, \; f_{r\varphi}$

Here r and d refer to $X-Y$ and $X-Z$ stretchings, respectively. All the constants from the latter set (C) may be expressed by those of the former (B), or specifically:

$$f_\alpha = \tfrac{1}{2}(f_\beta + f_{\beta\beta}), \; f_\varphi = 2(f_\beta - f_{\beta\beta}),$$

$$f_{r\alpha} = -\tfrac{1}{2}(f_{r\beta} + f_{r\beta}'), \; f_{d\alpha} = -f_{d\beta}, \quad (7)$$

$$f_{r\varphi} = f_{r\beta} - f_{r\beta}'$$

For ethylene-type molecules (planar symmetric X_2Y_4) one has also seen several treatments of the in-plane bending with unnecessary redundants introduced. Another outstanding example of a molecular model which can be fully treated without redundants is the planar bridged type of Fig. 2 (applicable to beryllium

Fig. 2.

halide dimers [2]). Here one might otherwise expect redundancy both due to the ring formation, and the presence of three coplanar bonds at same atoms.

It should also be mentioned here that many examples in the literature exist, where symmetrically complete sets of valence coordinates are properly omitted, although not always explicity stated. For instance the treatment of the in-plane bendings of benzene in terms of rockings and ring bendings, as given by Wilson *et al.*,[1] does not involve unnecessary redundants. The phosphorus molecule (tetrahedral X_4) is another example; the vibrations are fully described by the six bond stretchings with all angle bendings left out.[3]

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Studies of Spectral Changes in Connexion with the Photoreduction of Benzophenone and 4,4'-Dialkylbenzophenones by Alcohols

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As found by Ciamician and Silber,[1] a solution of benzophenone in ethanol, when exposed to sunlight in a sealed tube, gives benzopinacol, $Ph_2C(OH)C(OH)Ph_2$, and acetaldehyde in nearly quantitative yield. No other reaction products were found. Similar results were obtained by Cohen [2] with different primary and secondary aliphatic alcohols as reductants. The benzopinacol isolated from the irradiated solutions corresponded to between 95 and 100 % of the benzophenone initially present. The results of these early investigations therefore indicated that benzopinacol is the only reduction product of benzophenone which is formed under these conditions.

Later work by Schenck [3] and by Pitts [4] revealed, however, that irradiation of oxygen-free solutions of benzophenone in alcohols, as well as in other solvents that may serve as hydrogen donors, also results in the formation of small quantities of a substance characterized by a strong long-wave absorption band (λ_{max} *ca.* 325 mμ). Since this substance was found to react readily with oxygen and other typical radical reagents, such as DPPH and NO, it was assumed to be of radical nature. The primary products formed in the reaction between a photoactivated benzophenone molecule and, *e.g.*, a molecule of isopropanol, are undoubtedly the free radicals $Me_2\overset{\bullet}{C}OH$ (I) and $Ph_2\overset{\bullet}{C}OH$ (II). The substance with the long-wave absorption band was tentatively suggested to be a free radical formed from II and a molecule of benzophenone, $Ph_2\overset{\bullet}{C}OC(OH)Ph_2$, which is a probable intermediate in the formation of benzopinacol.[3]

In a recent paper we presented the results of a quantitative study of the formation of the "coloured intermediate" in very dilute solutions of benzophenone

in isopropanol.[5] By irradiating with light of known absolute intensity, and measuring the resulting changes in absorbance at suitable wavelengths, it could be shown that only one molecule of benzophenone was consumed in the formation of a molecule of the intermediate. The results also indicated that in sufficiently dilute solutions this substance was the only reaction product formed. From its spectrum and its known chemical properties it was evident that it could not be identified with the mixed pinacol $Ph_2C(OH)C(OH)Me_2$ (III) which might be formed from radicals I and II. As a possible explanation of the results we suggested that conditions in this case might be such as to favour the formation of a charge-transfer complex between the two radicals, in which the primary binding force is due to partial transfer of an electron, instead of a covalent bond.

However, this possibility is precluded by results presented in an important recent paper by Göth, Cerutti and Schmid.[6] These authors irradiated solutions of benzophenone in methanol that were considerably more dilute (ca. 2×10^{-2} M) than those used by Ciamician and by Silber and by Cohen. The results showed that under these conditions the *main* reaction product is the mixed pinacol, $Ph_2C(OH)$-$CH_2(OH)$. On the other hand it has been reported by Schenck[3] that a substance with a long-wave absorption band is formed also in methanol solution.

From the results of Göth, Cerutti and Schmid the conclusion seems inevitable that what is actually formed in extremely dilute solutions of benzophenone in, e.g., isopropanol is a mixture in constant proportions of two isomers, the mixed pinacol III and an isomer with quite different spectral and chemical properties. We are indebted to Professor Douglas C. Neckers of Hope College, Michigan, for the suggestion that this isomer might be the quinoid compound IV, which would result from *para* attack of radical I on radical II.

(IV)
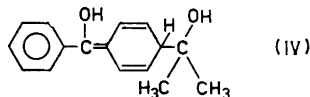
Cf. also a recent paper by Nelsen and Bartlett,[7] and references given therein.

Table 1 gives the results of irradiation experiments with benzophenone and sub-

stituted benzophenones in isopropanol and methanol. Here λ_{max} is the wavelength in $m\mu$ of the maximum in the long-wave absorption band. A_u is the final absorbance of an irradiated solution at a layer thickness of d cm, c_0 its initial concentration in M. The values of A_u/c_0d given in the table refer to λ_{max} and are limiting values, corresponding to $c_0 = 0$, obtained by graphical extrapolation. The experimental technique was essentially that described earlier.[5]

Table 1. Results of irradiation experiments with degassed solutions of benzophenone and substituted benzophenones in isopropanol (IPA) or methanol (MeOH).

Substituents	Alcohol	λ_{max}	A_u/c_0d
None	IPA	322	5200
None	MeOH	315	1300
4,4'-di-*t*-butyl	IPA	349	3800
4,4'-di-*t*-butyl	MeOH	323	600
4,4'-dimethyl	IPA	332	4200

In the case of benzophenone, changing from MeOH to IPA causes an increase in λ_{max} of 7 $m\mu$. The results with 4,4'-di-*t*-butylbenzophenone seem to indicate that the coloured isomer is formed as the result of radical attack in one of the 4-positions rather than in a 2-position, the much larger displacement of λ_{max} probably being connected with increased steric strain due to the greater bulkiness of radical I as compared to H_2COH.

In Fig. 1, curve 1 represents the spectrum obtained on irradiating a 22 μM solution of 4,4'-di-*t*-butylbenzophenone (V) in IPA. Curve 2 shows the spectrum of the same solution after the complete disappearance of the long-wave absorption band as a result of reaction with O_2. In Fig. 2, the changes in absorbance (ΔA) in this process at different wavelengths have been plotted as $\Delta A/(A_u)_{349}$, where $(A_u)_{349}$ is the absorbance of the irradiated solution at 349 $m\mu$ before oxidation. In agreement with the absorption spectrum of V in IPA, the difference spectrum shows a maximum at 265 $m\mu$ and a minimum at 234 $m\mu$, indicating that V is re-formed in the reaction. In fact, the long-wave part of curve 2, Fig. 1, agrees within limits of error with the spectrum of V. Below
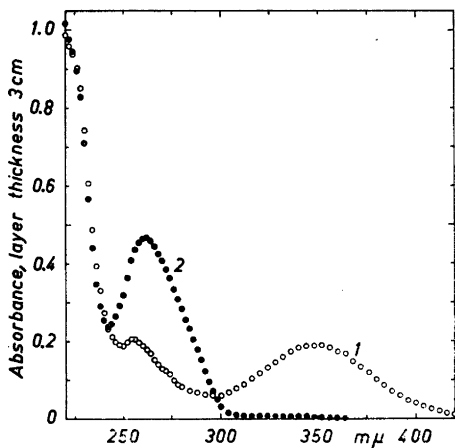
Fig. 1. Absorption spectrum of an irradiated solution of V in IPA before (open circles) and after (filled circles) reaction with O_2.
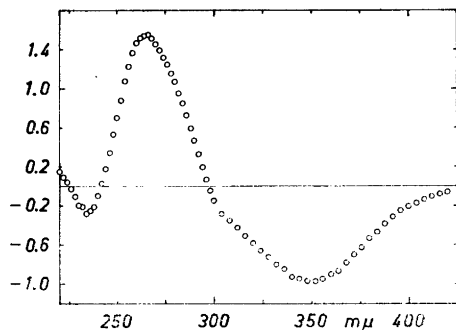

Fig. 2. Difference spectrum, $\Delta A/(A_u)_{349}$, calculated from Fig. 1.

280 mμ, however, additional absorption sets in, giving an excess absorbance at, *e.g.*, 265 mμ of *ca.* 0.07. In this and other similar experiments, that gave closely agreeing results, the oxidation of the coloured isomer was simply the result of slow leakage of air into the evacuated absorption cell, which was kept in a dark room. Markedly different results were obtained when, after the irradiation period, the cell was opened and the solution saturated with air or oxygen. The spectrum of the oxidized solution showed that the yield of V was 10 % higher, and the excess absorbance at 265 mμ amounted to only *ca.* 0.02. This is no more than the

absorbance of the pinacols present, as calculated from the known spectra of the unsubstituted compounds. It may be concluded, therefore, that under these conditions one molecule of V is formed for every molecule of the coloured isomer oxidized. Knowing the absorption spectrum of V in IPA, the molar extinction coefficient of the coloured isomer at 349 mμ may therefore be calculated. The values found averaged 10 300 $M^{-1}cm^{-1}$.

On the other hand, as appears from Table 1, the extrapolated value of $A_u/c_0 d$ at the same wavelength is only 3800 $M^{-1}cm^{-1}$. This shows that the coloured isomer formed in extremely dilute solutions of V in IPA corresponds to *ca.* 37 % of the ketone consumed.

The reaction of the coloured isomer with oxygen was found to be slow. Whether the solution was saturated with O_2 or with air, a first-order rate constant $= 0.11$ hour^{-1} was obtained.

The results obtained by treating the irradiated solutions with O_2 or air were confirmed by an experiment of a different kind. The cell containing the solution was filled with nitrogen and a drop of a solution of HCl in IPA was added, giving a concentration of HCl in the irradiated solution of *ca.* 50 μM. This also resulted in the gradual disappearance of the long-wave absorption band and the reappearance of the spectrum of V. The calculated value of the molar extinction coefficient of the coloured isomer at 349 mμ was 9900 $M^{-1}cm^{-1}$.

Preliminary results with benzophenone in IPA seem to indicate that the irradiated solutions contain, besides IV, small quantities of a compound with maximum absorbance at *ca.* 270 mμ, which is more resistant to attack by O_2 and by HCl than IV.

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Metabolism of Progesterone by Streptomyces griseus

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The microbial side chain degradation of progesterone, leading to testosterone, Δ^4-androstene-3,17-dione, and testololactone or their 1-dehydroderivatives, is well known.[1-5] The cleavage of the side chain is suggested to proceed in a way, similar to the non-enzymatic action of peracids on ketones, [5] as shown in Fig. 1. Formation of the intermediate testosterone acetate from progesterone has only been demonstrated in *Cladosporium resinae* (Fonken *et al.*).[6] In some other microorganisms high esterase activity is believed to prevent accumulation of this compound [6,7] and therefore only the later products in this reaction sequence have been detected.

As one part of a study, regarding the progesterone metabolism of some different microorganisms, the fungus *Streptomyces griseus* was investigated. Upon incubation of progesterone with this fungus three products were demonstrated: testosterone acetate (main product), testosterone and Δ^4-androstene-3,17-dione.

Experimental. A spore culture of *Streptomyces griseus* was obtained as a gift from AB KABI, Stockholm. The fungus was grown up on beer-wort-distilled water 1:1 in cotton-plugged Erlenmeyer flasks on a shaking table at 25−27°C. After completed fermentation the mycelia were harvested, washed with distilled water and resuspended to original density in 0.1 M Na_2HPO_4 (pH 8.3). The suspension was distributed in 50 ml portions into 200 ml Erlenmeyer flasks and the steroid substrate (29.0 mg of progesterone, dissolved in 1.0 ml of methanol) was pipetted into each flask. The flasks were stopped with cotton plugs and the incubation took place on a shaking table at 25−27°C.

At definite time intervals duplicate flasks were withdrawn and the steroids were extracted with two 50 ml portions of chloroform. By evaporation at 50°C the extracts were concentrated to 50 ml volume and 0.5 ml aliquots of these solutions were analyzed by thin-layer chromatography (TLC) and gas-liquid chromatography (GLC).
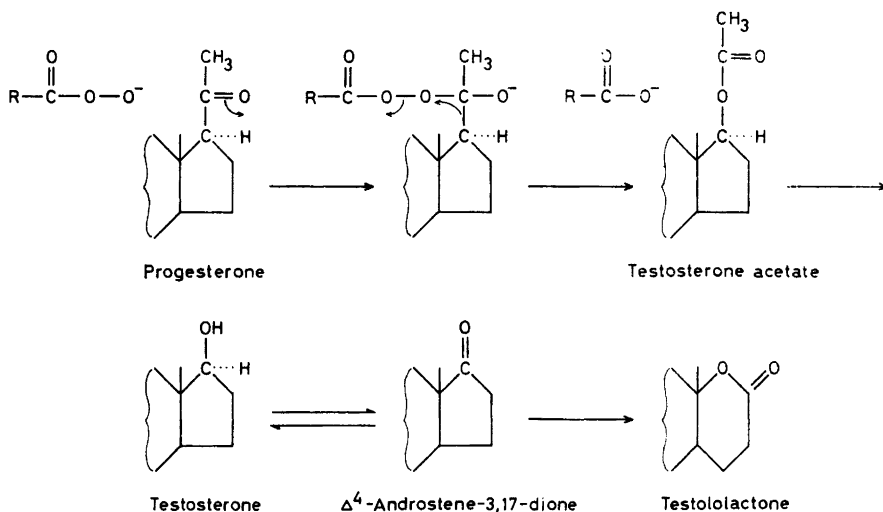

Fig. 1. Pathway of the microbial side chain degradation of progesterone.