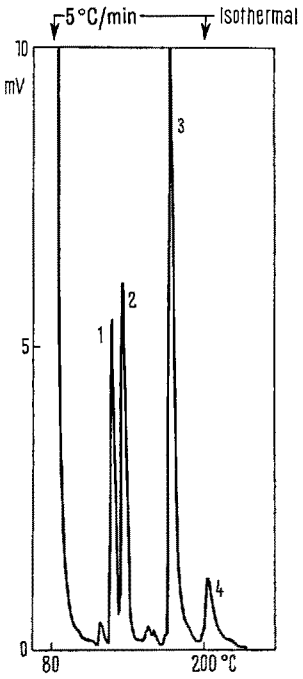
residue was methylated with diazomethane as above. Reproducible yields of 70–100% of the above-mentioned derivatives (except for Glu), identified by their retention times, were obtained. Formation of by-products e.g. acetylamino acetone derivatives[5], was not observed. Glu, however, was transformed into N-acetyl pyroglutamic acid in agreement with the finding of DAKIN and WEST[5]. By brief heating with N HCl prior to the methylation, the normal derivative of Glu appeared in the chromatogram. This treatment was necessary in the presence of Pro, as the retention times of the 2 cyclic derivatives were identical on all the columns studied.



1, valine; 2, leucine; 3, internal standard; 4, valyl-leucine. Column: 1 ft. 3% carbowax 20M.

During an attempt to derivatize the dipeptide Val-Leu for gas-chromatography by the above-mentioned procedure, additional peaks corresponding to the derivatives of Val and Leu were observed. The same result was obtained for other dipeptides and two tripeptides. As the described acetylation procedure is similar to that employed for the racemization of optically active amino acids[3], it is reasonable to assume that the breakdown takes place via oxazolone formation. However, an acetylation of the peptide bond[6], making it labile to water, could also account for the results obtained. With the aid of the calibration values obtained above, the yields of N-acetyl amino acids on treatment of the peptides mentioned with the acetylation mixture could be calculated (Table)[7].

Zusammenfassung. Eine Spaltung von Peptiden tritt auf, wenn versucht wird, gewisse Derivate in an sich üblicher Weise herzustellen. Damit wird auf die Möglichkeit einer Fehlinterpretation hingewiesen.

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Synthesis and Photolysis of 2-Formyl-4,4-Dimethyl-2,5-Cyclohexadienone

It is known that certain substituents influence the pathways of photochemical rearrangements of bicyclic cross-conjugated cyclohexadienones[1,2]. In pursuing our interest in photolytic reactions, we now wish to report the synthesis and photolysis of a monocyclic compound of this type with an electron withdrawing formyl substituent.

Synthesis of 2-formyl-4,4-dimethyl-2,5-cyclohexadienone (III) was carried out by a procedure similar to that employed by EDWARDS et al.[3]. Condensation of I[4] with ethyl formate in the presence of sodium methoxide and reaction of the hydroxymethylene derivative II [b.p. 43–45° (0.1 mm); 69% yield; $\lambda_{max}^{95\%\,EtOH}$ 235 (ε 13,400) and 307 nm (ε 5400); Anal.[5]] with 2,3-dichloro-5,6-dicyanobenzoquinone[6] in dioxane gave III [mp 66.5 to 67°; 61% yield; $\lambda_{max}^{95\%\,EtOH}$ 237 nm (ε 14,350); $\lambda_{max}^{95\%\,EtOH+NaOH}$ 350 nm (ε 13,560); λ_{max}^{KBr} 5.90, 5.98, 6.03, 6.15, and 6.25 μ; $\delta_{TMS}^{CDCl_3}$ 1.40 (s, 6H); H_1:6.3 (doublet, $J_{1-2} = 10$ Hz); H_2:6.9 (2 doublets, $J_{2-3} = 2.5$ Hz); H_3:7.6 (doublet); H_4:10.2 ppm[5]].

A 0.5% solution of III was irradiated in 45% acetic acid using a 450 watt Hanovia high pressure mercury lamp in an all Pyrex cell. UV-absorption after 45 min indicated a 90–95% conversion. Solvent removal in vacuo afforded the crude photoproduct. Efforts to unequivocally characterize the nature of the photoproduct without further chemical transformations were without success. Interpretation of the NMR data indicated an

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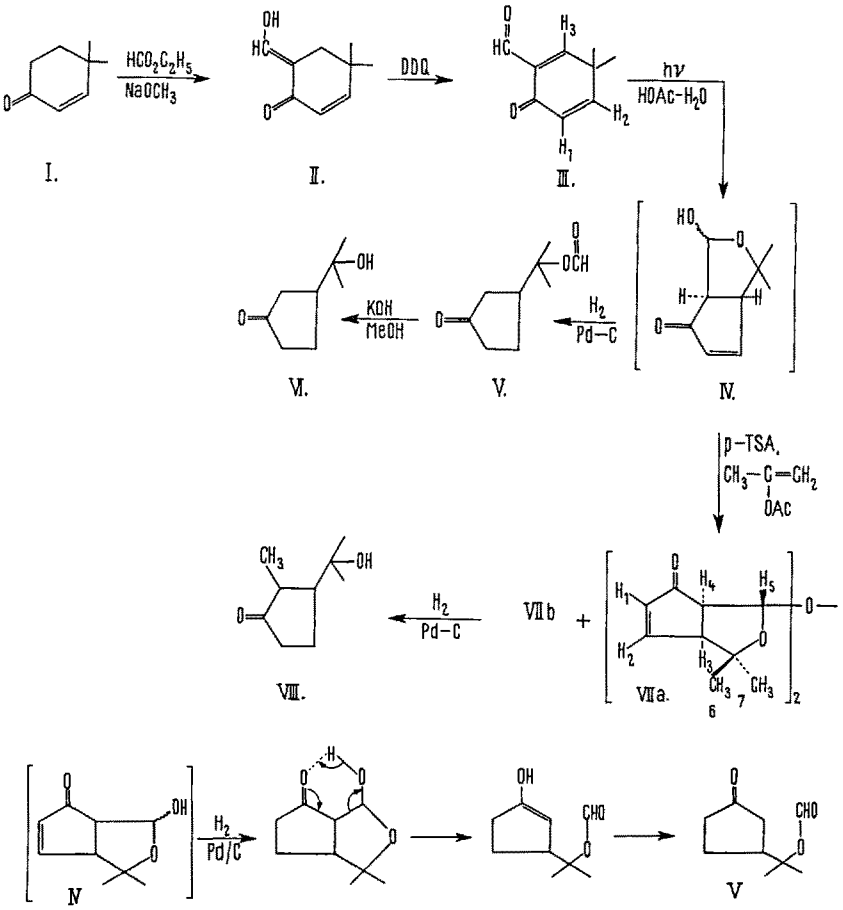
exceptionally pure product; nonequivalent methyl groups, vinyl protons, a multiplet integrating for two and one exchangeable proton suggested structure IV. Reactions of the crude photoproduct were supportive of this structure. Catalytic hydrogenation (10% Pd/C) of the photoproduct in methanol gave the ketoformate V [b.p. 110 to 115° (0.15 mm); 70% yield; λ_{max}^{NEAT} 5.74 and 5.79 μ; $\delta_{TMS}^{CDCl_3}$ 1.64 (s, 6H), 1.8–2.5 (broad, 7H) and 8.04 ppm (s, 1H). Hydrolysis of V at room temperature in 2.5% KOH in methanol (3 days) gave a light yellow oil VI [liquid, purified by GLC; 37% yield; λ_{max}^{NEAT} 2.91 and 5.78 μ; $\delta_{TMS}^{CDCl_3}$ 1.17 (s, 6H), 1.65–2.35 (m, 7H) 2.65 ppm (s, 1H)].

The proposed structure of the photoproduct IV was supported by the chemical reactions and the spectral data. The remarkable similarity of the NMR of the photoproduct and the dimeric ether VIIa was particularly informative, the only difference being one exchangeable proton (–OH). The absence of VIIa in the photoproduct was indicated by spectral data, thin layer and column chromatography. The formation of VIIa from the photoproduct can be rationalized by elimination of water from 2 molecules of IV. Since the photoproduct after treatment with isopropenyl acetate no longer had an acidic proton available for rearrangement, hydrogenolysis took place giving rise to the methyl ketoalcohol (VIII). The formation of the ketoformate V can be rationalized as follows:



Treatment of the crude photoproduct IV with isopropenyl acetate containing a trace of *p*-toluenesulfonic acid gave the dimeric ether VIIa [mp 196–197°; 20% yield; $\lambda_{max}^{CCl_4}$ 5.80, 7.20, 7.30 and 10.10 μ; $\lambda_{max}^{95\%\,EtOH}$ 223 nm (ε 16,300); $\delta_{TMS}^{CDCl_3}$ H_1: 6.15 (2 doublets, J_{1-2} = 6, J_{1-3} = 1.5 Hz); H_2: 7.16 (2 doublets, J_{2-3} = 2.5 Hz); H_3: 3.38 (2 triplets, J_{3-4} = 6.0 Hz); H_4: 3.05 (2 doublets, J_{4-5} = < 0.5 Hz); H_5: 5.37 (s); 6-CH_3: 1.26 (s); 7-CH_3: 1.58 ppm (s)]. The residue, VIIb, remaining after isolation of VIIa and having an NMR practically identical with VIIa was hydrogenated (10% Pd/C in methanol) and gave the methyl ketoalcohol VIII [b.p. 100–105°; 50% yield; λ_{max}^{NEAT} 5.80 and 2.77–3.22 μ (broad –OH); $\delta_{TMS}^{CDCl_3}$ 1.4–2.55 (broad, 7H); 1.05–1.40 ppm (unresolved multiplet, 9H)].

Basic hydrolysis of V gave the expected keto-alcohol VI.

This work further supports the generally accepted ZIMMERMANN-SCHUSTER zwitterionic intermediates in dienone photochemistry[1].

Résumé. On a étudié la photolyse du 2-formyl-4,4-diméthyl-2,5-cyclohexadiénone dans l'acide acétique aqueux. La constitution du produit principal de cette réaction a été élucidée sur la base de transformation successive. On a montré qu'il s'agissait d'un semi-acétal interne. La formation de ce composé peut être interprété sur la base de l'amphotère ionique intermédiaire selon ZIMMERMANN-SCHUSTER.

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