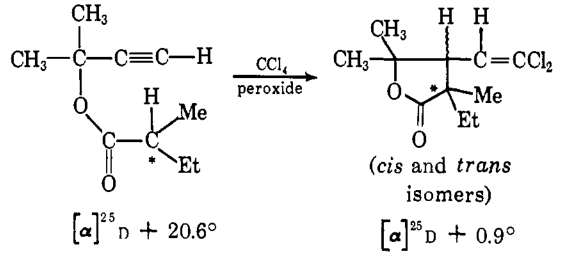
The crucial step of this reaction involves intramolecular 1,5-hydrogen abstraction by a reactive vinyl radical. It is interesting to note that this 1,5-hydrogen shift occurs through a chain containing atoms other than carbon, and that no methyl or acetate 1,2 shift is observed, despite the fact that our system is ideally suited for such a rearrangement. We have found that 1,5-hydrogen migration, as measured by the relative yield of the lactone formed, increases in the order primary < secondary < tertiary ≈ benzylic abstractable hydrogen.

In the addition of carbon tetrachloride to the propionate ester (I, with $R_1 = CH_3$ and $R_2 = H$), the lactone formed consists of only one geometric isomer, presumably the one with *trans* configuration of the methyl and vinyl groups. Since two cyclopentyl isomers were found in the addition of carbon tetrachloride to heptyne-1,[2] we attribute the formation of one single isomeric lactone to thermal equilibration *via* enolization.

Lactone yields of 20–25% have been obtained, but these need not represent the optimum. The ready availability of variously substituted propargyl esters, which can be prepared from numerous propargyl alcohols and a variety of substituted acid chlorides, provides a broad scope for this reaction. Furthermore, this reaction could be extended to the preparation of other heterocyclic systems.

The most interesting feature of our results is that, when an optically active ester is used whose asymmetric center involves the hydrogen to be abstracted, an optically active lactone is obtained. The ester, $[\alpha]^{25}\text{D}$ +20.6° (EtOH), was made from the known optically active acid chloride.[4,5] The lactone, which consisted of *cis* and *trans* isomers, was isolated by vacuum distillation, bp 80–100° (0.4 mm), and was further purified by preparative vpc using an 8-ft 10% Apiezon L on Chromosorb W column at 185°. The isomeric lactones had the characteristic infrared bands at 5.63 and 6.19 μ, and the nmr spectrum of a mixture of the two lactones in about a 3:2 ratio contained two doublets around τ 4 with coupling constants of 10.7 and 10.9 cps, respectively, together with another set of two doublets with the same coupling constants around τ 6.8. *Anal.* Calcd for $C_{11}H_{16}O_2Cl_2$: C, 52.58; H, 6.42; Cl, 28.25. Found: C, 52.56; H, 6.49; Cl, 28.20. The observed optical rotation of the lactones, $[\alpha]^{25}\text{D}$ +0.9°, did not change upon further purification by preparative vpc. The same rotation was also observed when the lactones were dissolved in aqueous KOH, acidified, and then collected by vapor phase chromatography. There was also no significant difference in the specific rotation of the lactones when the reaction was carried out at 60 or at 100° (see Table I).



$[\alpha]^{25}\text{D}$ + 20.6°

(*cis* and *trans* isomers)

$[\alpha]^{25}\text{D}$ + 0.9°

Table I

Reaction conditions	$[\alpha]^{25}\text{D}$ of lactones,[a] deg
60°, KOH extraction, vpc, 0.17 *M* ester	0.90
77°, KOH extraction, vpc, 0.20 *M* ester	0.94, 0.93 (second vpc)
100°, KOH extraction, vpc, 0.28 *M* ester	0.85
77°, 25% C_6H_6, no KOH, vpc, 0.37 *M* ester	0.94

[a] Values have been corrected for differences in optical purity of starting esters.

It is difficult to assess the optical purity of the lactones isolated, especially in view of the possibility of induced asymmetry occurring during the cyclization step. Nevertheless, the residual optical activity clearly demonstrates that free-radical reactions at asymmetric centers can occur without complete racemization. A concerted mechanism in this reaction is unlikely since the hydrogen-abstraction and subsequent cyclization processes occur in two perpendicular planes.

The retention of optical activity in the lactone can be attributed to rapid trapping of the radical by the internal olefin either before the radical can assume a planar configuration or before rotation about the bond to the carbonyl can take place.

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ene.[2] While such a chain mechanism can be envisioned, a nonchain process cannot be ruled out.

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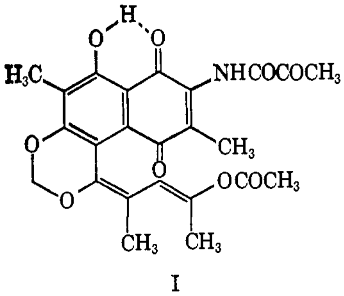
(5) Optical rotations were measured on a Bendix ETL-NPL Type 143A automatic polarimeter and are believed to be accurate to ±3%.

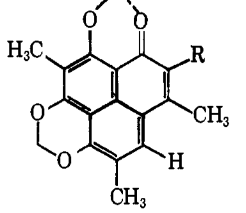
Chemistry of the Streptovaricins. III. Photostreptovarone, a Phenalenone from Photolytic Loss of Acetic Anhydride

Sir:

The isolation[1] and structure[2] of streptovarone (I), the visible chromophore of the streptovaricin antibiotics, have been reported previously. During the structural studies it was noted that, upon standing under fluorescent lights, the dark amber color of solutions of I changed to bright yellow. Repetition of the irradiation under controlled conditions (0.5% methanolic solutions of I, Pyrex container, G.E. sunlamp) gave yellow crystals of the photoproduct, photostreptovarone, in almost quantitative yield We present here evidence assigning structure II (2-pyruv-



I



II, R=NHCOCOCH3
III, R=NH2
IV, R=NHCOCH3
V, R=N(CH3)2

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(1) K. L. Rinehart, Jr., P. K. Martin, and C. E. Coverdale, *J. Am. Chem. Soc.*, **88**, 3149 (1966).

(2) K. L. Rinehart, Jr., C. E. Coverdale, and P. K. Martin, *ibid.*, **88**, 3150 (1966).

amidyl-3,5,8-trimethyl-6,7-methylenedioxy-9-hydroxyphenalen-1-one) to photostreptovarone.

Photostreptovarone, $C_{20}H_{17}NO_6$,[3] mp 260–261°, is converted by acidic methanolysis to pyruvic acid, isolated as methyl pyruvate 2,4-dinitrophenylhydrazone, and deptovarone (*de*pyruvylphotostrep*tovarone*, III), $C_{17}H_{15}NO_4$,[3] fine red crystals, dec ~300°, identified as an amine by characteristic infrared absorptions and its ready conversion to a monoacetyl derivative (IV), $C_{19}H_{17}NO_5$,[3] mp 274–275°, and an N,N-dimethyl derivative (V), $C_{19}H_{19}NO_4$,[3] mp 162–163°.

As expected from the molecular formula of II ($C_4H_6O_2$ lost from I), the principal difference between the nmr spectra of I and II (difficultly soluble) is the absence of two methyl singlets near τ 8.0. In the nmr spectrum of the more soluble III, the remaining methyl groups appear as singlets at τ 7.52 (6 H) and 7.81 (3 H). More significant changes from the spectrum of I are the appearance of an aromatic proton at τ 2.33 (singlet) and a sharp methylenedioxy singlet at τ 4.33.[4] In the spectrum of I, these corresponding protons are found at τ 3.45 (olefin singlet) and 4.5 (very broad absorption due to interconversion of conformers, $\Delta G^{\neq}_{c} \approx 15.2$ kcal/mole[5]). These changes indicate a side-chain phototransformation. The hydroxyl proton appears at τ -6.51 (streptovarone, τ -4.15).

The infrared spectrum of photostreptovarone (II) retains the pyruvamide (3340, 1725, and 1690 cm^{-1}) and hydrogen-bonded ketone (1625 cm^{-1}) absorptions, but lacks the enol acetate (1767 and 1200 cm^{-1}) and nonhydrogen-bonded carbonyl (1677 cm^{-1}) absorptions of streptovarone (I).

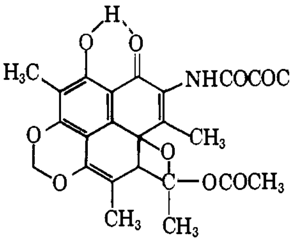
Both nmr and infrared data are in good agreement with structure II. For comparison, the simplest analog, 9-hydroxyphenalen-1-one (VI, synthesized according to Loudon and Razdan[6]), gives a carbonyl band at 1625 cm^{-1} and C-4 proton absorption at τ 2.27 (assigned by factoring the complex AB_2 region of the spectrum of VI[7]). More pertinent is the close similarity of the ultraviolet spectra of II–IV to those of VI and the more complex 9-hydroxyphenalen-1-one derivative atrovenetin triacetate[8] (Table I) and the similar chemical behavior of the chelated hydroxyl group of II–IV and VI: red-brown ferric chloride test,[9] negative boric acid–acetic anhydride test,[10] and lack of reactivity toward acetylation and methylation. The hydroxyl proton of VI is found at τ -6.21.

Table I. Spectra of 9-Hydroxyphenalen-1-ones in Ethanol

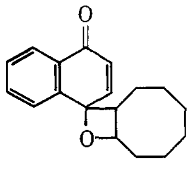
Compound	λ_{max}, mμ (ϵ)
Photostreptovarone (II)	447 (12,400), 427 (14,400), 407 (12,000), 372 (17,100), 275 (infl), 265 (infl), 237 (31,500)
Deptovarone (III)	460 (4200), 391 (9200), 374 (9200), 288 (4300), 252 (21,000)
Deptovarone (III) (0.1 *N* HCl–ethanol)	448 (4600), 423 (3700), 372 (infl), 360 (7200), 324 (4200), 260 (16,500), 233 (24,000)
Acetyldeptovarone (IV)	445 (10,100), 428 (13,300), 407 (11,700), 373 (17,300), 280 (infl), 265 (infl), 233 (29,100)
9-Hydroxyphenalen-1-one (VI)[a]	440 (12,000), 430 (7400), 415 (8900), 350 (17,800), 265 (8900), 235 (12,600)
Atrovenetin triacetate[a]	433 (19,500), 409 (15,800), 390 (infl), 350–347 (12,000), 275 (17,000), 247 (infl)

[a] Data from ref 8.

The elements lost ($C_4H_6O_3$) upon the irradiation of streptovarone are formally those of acetic anhydride. Such a loss might involve an intermediate such as VII. Although VII has not been isolated, acetic anhydride has been obtained [characterized by glpc retention time (20% S.E. 30 on Chromosorb W column) and infrared and nmr spectra]. Moreover, the intermediate VII resembles the spirooxetans (*e.g.*, VIII) isolated by Bryce-Smith and Gilbert[11] upon irradiation of quinones in the presence of olefins.



VII



VIII

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(3) Microanalyses and mass spectra agree with the molecular formulas.

(4) A model is provided by 1,8-methylenedioxynaphthalene, whose spectrum contains a two-proton singlet at τ 4.57.

(5) We thank Dr. J. M. Lehn, Université de Strasbourg, for determination of the temperature-dependent spectra.

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(12) Public Health Service Predoctoral Fellow and Monsanto Summer Fellow.

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Synthetic Reactions by a Complex Catalyst. VI. A Novel Hydrosilation of Isocyanide by Copper Catalyst

Sir:

In the course of studies upon synthetic reactions of compounds of carbon having lone-pair electrons,[1] we have recently found that, in the presence of copper catalyst, isocyanide reacts with primary and secondary amines,[1a] alcohols,[1d] and thiols[2] to produce the corresponding derivatives of formimidic acid. These reactions involve insertion of isocyanide into nitrogen–hydrogen, oxygen–hydrogen, and sulfur–hydrogen linkages, respectively; on the other hand, these are con-

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(2) T. Saegusa, Y. Ito, S. Kobayashi, K. Hirota, and Y. Okumura, to be published.