does not dissociate (*e.g.*, eq 2) the B_2H_6–base complex. This demonstrable stability of diborane etherates, as well as the titrimetric observation of diborane aminates,[1] shows that the borane dimer *per se* is acidic. Complexed alkyllithium dimers are even more resistant to dissociation analogous to eq 2.[8] That various electron-deficient dimers *per se* are intrinsically acidic (eq 1) seems rational on theoretical grounds. Previous workers have apparently been forced to write singly bridged species or dissociation of dimers (eq 2) because of their assumption that base only coordinates by σ-bonding directly to the metal atom, which furnishes an unoccupied AO. It is logical to assume that base could also coordinate by π-bonding the intact dimer, which furnishes an unoccupied MO.

Since at least six AO's are available in the four-centered dimer, an ordinary LCAO could be expected to make at least three MO's available for occupancy, but the four atoms of the uncomplexed dimer can furnish only four bonding electrons. An insufficiency of bonding electrons to fill all available MO's of the dimeric species must be the most logical basis of describing this species as electron deficient and as therefore acidic, *i.e.*, susceptible to complexation by an electron donor. As a generalization, Longuet-Higgins suggested[9] that if there are fewer than $2(n - 1)$ electrons bonding an n-centered oligomer, it is electron deficient.[10] Specifically for the four centers of the diborane system, the six possible energy levels estimated (by SCF equations in their LCAO form)[11] suggest that in the three lowest levels only two are strongly bonding and one is approximately nonbonding, and that, among these three, two are σ MO's and one has π symmetry. From considerations of both symmetry and energy levels in such a system, it appears that bonding overlap could occur with a donor furnishing $2p\pi$ electrons either from the nonbonding orbital of a simple Lewis base or from a π MO of an unsaturated system.

It is suggested that oligomeric metal alkyls and hydrides that associate as electron-deficient reagents are appropriately characterized as π acids. Recognition of this characteristic provides a basis for rationalizing the distinctive ability of these reagents to undergo various reactions with nonpolar, unsaturated hydrocarbons, an ability not shared by similar metal organics and hydrides that are not π acids. For example, diborane, aluminum trialkyls, dialkylaluminum hydrides, magnesium dialkyls, and lithium alkyls, all of which can be characterized as oligomeric π acids, all undergo addition to simple olefins, but this addition is not observed with sodium borohydride, dialkylaluminum halides, heavy metal alkyls, and Grignard reagents, none of which are electron-deficient oligomers.

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(8) *Cf.* C. G. Screttas and J. F. Eastham, *J. Am. Chem. Soc.*, **88**, 5668 (1966).

(9) H. C. Longuet-Higgins, *Quart. Rev.* (London), **11**, 121 (1957).

(10) For some consideration of electron deficiency in valence-bond terms, see H. A. Bent, *Chem. Rev.*, **61**, 275 (1961).

(11) W. C. Hamilton, *Proc. Roy. Soc.* (London), **A235**, 395 (1956).

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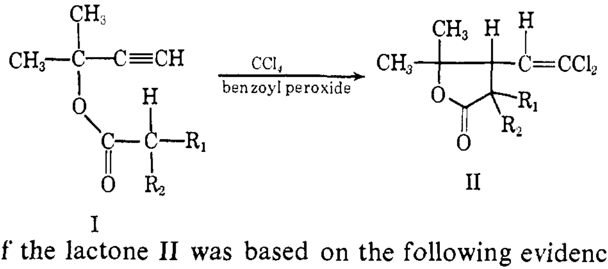
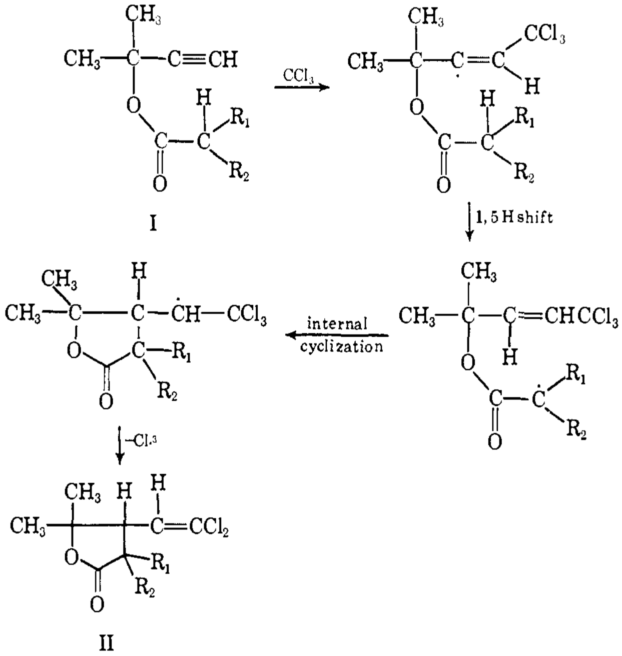
Vinyl Radical Isomerization. II. A New Free-Radical Synthesis of γ-Lactones with Retention of Optical Activity

Sir:

We wish to report a new synthesis of γ-lactones from propargyl esters by free-radical means. The peroxide-initiated addition of CCl_4 to various propargyl esters yielded, besides the normal 1:1 CCl_4:acetylene adducts, γ-butyrolactone derivatives. The assigned structure of the lactone II was based on the following evidence. It was soluble in warm KOH solution and could be recovered upon acidification. It showed an infrared band at 5.62 μ characteristic of γ-lactones, as well as a band at 6.17 μ indicative of the vinylidene chloride group.[1] The nmr spectrum contained a doublet at τ 4.15 with a coupling constant between 9.1 and 10.9 cps, depending on the nature of the R groups. Elemental analyses indicated a compound which corresponded to an addition of CCl_2 to the original ester.



The formation of γ-lactones can best be explained by the following mechanism, which is similar to that proposed for the rearrangement of terminal acetylenes to vinylcyclopentanes.[2]



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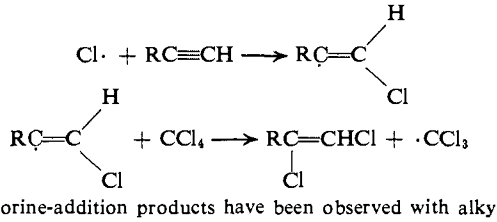
(1) R. Dowbenko, *Tetrahedron*, **21**, 1647 (1965).

(2) E. I. Heiba and R. M. Dessau, *J. Am. Chem. Soc.*, **88**, 1589 (1966).

(3) $CCl_3\cdot$ radical can be regenerated by the following mechanism



$$\mathrm{Cl\cdot + RC{\equiv}CH \longrightarrow R\dot{C}{=}C(H)Cl}$$

$$\mathrm{R\dot{C}{=}C(H)Cl + CCl_4 \longrightarrow RC(Cl){=}CHCl + \cdot CCl_3}$$

Such chlorine-addition products have been observed with alkylacetyl-

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, $[\alpha]^{25}D$ +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, $[\alpha]^{25}D$ +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).

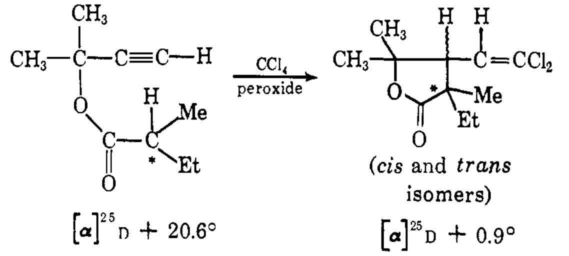


Table I

Reaction conditions	$[\alpha]^{25}D$ 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.

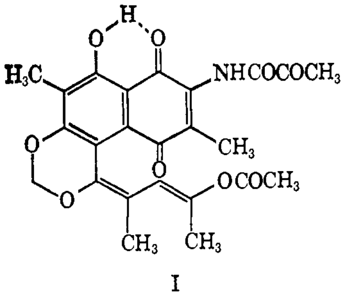
(4) M. S. Kharasch, J. Kuderna, and W. Nudenberg, *J. Org. Chem.*, **19**, 1283 (1954).

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

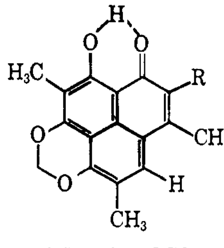
Chemistry of the Streptovaricins. III. Photostreptovarone, a Phenalenone from Photolytic Loss of Acetic Anhydride

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=NHCOCOCH$_3$
III, R=NH$_2$
IV, R=NHCOCH$_3$
V, R=N(CH$_3$)$_2$

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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).