Table I. Summary of Results

	1	2	3	4	5	6	7
Rod temp., °K.[a]	1893	2122	2225	2253	2320	2353	2390
Rod surface area, cm.^{2}	7.5	6.6	6.6	7.5	6.6	7.5	6.9
Carbon evap. rate, g./cm.^{2} sec.[b]	3.3×10^{-13}	8.4×10^{-11}	2.3×10^{-10}	2.3×10^{-9}	8.8×10^{-9}	1.6×10^{-8}	3.5×10^{-8}
Total carbon evaporated, g.	8.9×10^{-9}	2.0×10^{-6}	1.8×10^{-6}	6.2×10^{-5}	2.1×10^{-4}	4.3×10^{-4}	8.7×10^{-4}
Concn. identified products, M[c] Concn. toluene	d	d	2.1×10^{-5}	4.9×10^{-5}	1.1×10^{-4}	d	d
Concn. cycloheptatriene	d	d	$\sim 2 \times 10^{-5}$ [e]	8.6×10^{-4}	4.2×10^{-5}	d	d

[a] Measured by optical pyrometry. [b] The carbon evaporation rate data used were from the work of M. Hock, P. Blackburn, D. Dingledy, and H. Johnston, *J. Phys. Chem.*, **59**, 97 (1955). [c] Product yields were determined by comparison of peak heights from standards; peak heights for toluene and cycloheptatriene are linear in concentration over the concentration range 3×10^{-1} to 3×10^{-5} M. [d] Product yield was less than the limits of detection, which are 8.8×10^{-6} M for toluene and 1.8×10^{-5} M for cycloheptatriene for 2-μl. injections. [e] This yield was just barely above the limit of detection.

of bombarded benzene was collected by vaporization and condensation in a liquid nitrogen cooled cold finger, which was sealed under vacuum. Chromatographic product analyses were performed using silicone oil columns and flame ionization detection. Products were identified by comparison of their relative retention times (relative to the solvent benzene peak) with those of knowns in benzene solution. The experimental results are summarized in Table I.

As is shown in the table, despite a constantly increasing rate of carbon deposition the yields of toluene and cycloheptatriene increased for only the first four runs before falling below their detection limits during the next three runs. Further, whenever the total carbon deposited per irradiation was greater than 3×10^{-6} g.[4] (*i.e.*, runs 4 thru 7), a dark brown material was observed to form on the walls of the bombardment flask during the course of the experiment. Qualitatively, the yield of this material, which was nonvolatile at 1 μ even when heated to *ca.* 50°, increased rapidly with increasing carbon deposition per irradiation. Thus, as the yield of this material increased, the yields of toluene and cycloheptatriene fell below their limits of detection.

That the toluene and cycloheptatriene were not produced by photolysis or pyrolysis of the benzene under the conditions of our experiments is demonstrated by runs 1 and 2 at 1893°K. and 2122°K. In these runs carbon evaporation rates were too low to lead to detectable product levels. However, the operating temperatures of run 1 and particularly of run 2 were not sufficiently different from our normal operating temperatures to effect significantly the yields of products formed by photolysis or pyrolysis. Thus, the failure to detect toluene or cycloheptatriene in either run eliminates the possibility that they were formed by photolysis or pyrolysis.

Skell has reported previously that C_3 from carbon vapor reacts with isobutylene to form 1,1,1′,1′-tetramethylbisethanoallene.[5] The present work provides the first example of reaction of C_1 from carbon vapor with an organic substrate.[5a]

Nuclear transformations have been used extensively to investigate the reactions of hot and moderated carbon atoms with organic substrates.[6] Hot carbon atoms have been found to react with benzene to form radioactively labeled toluene.[7] Accelerated carbon ions, C^+, with kinetic energies as low as 45 e.v., have been shown by Mullen to react with benzene to form both toluene and cycloheptatriene.[8] Our results provide the first demonstration of a reaction between an organic substrate and carbon atoms produced with an initial kinetic energy below 0.3 e.v.

Methylene produced by the photolysis of diazomethane reacts with benzene to give toluene and cycloheptatriene.[9] It is attractive to visualize carbene-like insertion and addition steps in the reactions of carbon atoms with benzene. Indeed, Wolfgang has postulated[6b] and demonstrated[6b] insertion by carbon atoms into C–H and ethylenic double bonds. However, we cannot say where, along the reaction pathways leading to toluene and cycloheptatriene, do the necessary hydrogen abstractions take place. Also, we cannot yet offer a proven explanation for the elimination of the toluene and cycloheptatriene yields and for the formation of the dark brown nonvolatile material when too much carbon (>400 μg.) is deposited in the bombardments.

(6) (a) See review by A. P. Wolf, *Advan. Phys. Org. Chem.*, **2**, 201 (1964); (b) M. Marshall, C. MacKay, and R. Wolfgang, *J. Am. Chem. Soc.*, **86**, 4741 (1964); J. Dubrin, C. MacKay, and R. Wolfgang, *ibid.*, **86**, 4747 (1964), and references cited in these articles.

(7) A. P. Wolf, *Rec. trav. chim.*, **80**, 533 (1961).

(8) R. Lemmon, R. T. Mullen, and F. L. Reynolds, in "Chemical Effects of Nuclear Transformation," Vol. II, International Atomic Energy Agency, Vienna, 1961, pp. 27–35.

(9) *E.g.*, (a) W. E. Doering and L. H. Knox, *J. Am. Chem. Soc.*, **75**, 297 (1953); (b) G. A. Russell and D. G. Hendry, *J. Org. Chem.*, **28**, 1933 (1963).

Jeremy L. Sprung, S. Winstein, W. F. Libby

Contribution No. 1802 from the Department of Chemistry
University of California, Los Angeles, California 90024

On the 260 mμ Cotton Effect in L-Phenylalanine[1]

Sir:

Of late there has been disagreement among several workers[2-5] as to the existence of a Cotton effect for the

(4) It is interesting to note that this amount of carbon contains approximately the same number of carbon fragments as there are surface benzene molecules.

(5) P. S. Skell and L. D. Wescott, *J. Am. Chem. Soc.*, **85**, 1023 (1963).

(5a) NOTE ADDED IN PROOF. Skell and Engel [*ibid.*, **87**, 1135 (1965)] have just reported the reaction of C_1 from a carbon arc with *cis*- and *trans*-2-butenes.

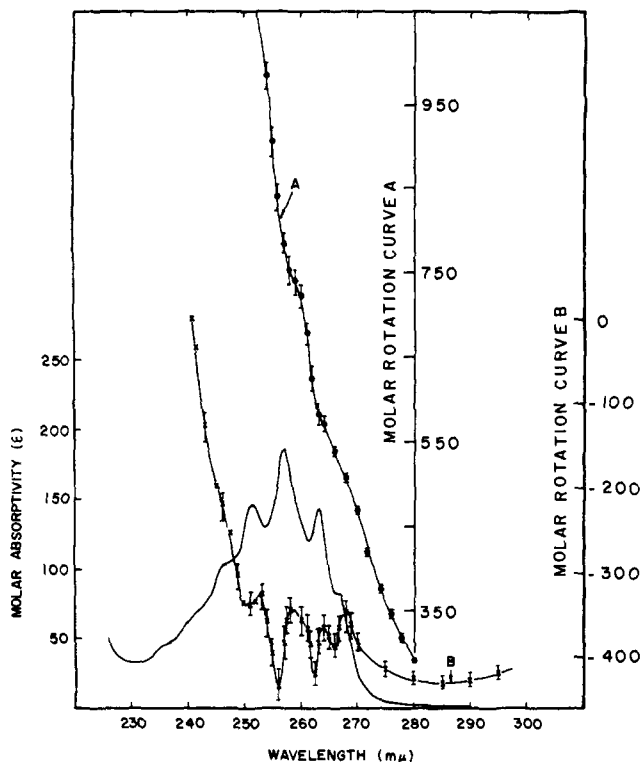(2) J. A. Schellman and C. G. Schellman, *Arch. Biochem. Biophys.*, **65**, 58 (1956).

Figure 1. Ultraviolet spectrum in H_2O and O.R.D curves for L-phenylalanine. Curve A: 1.39×10^{-2} in 1 N aqueous HCl (1-cm. cell); curve B: 1.26×10^{-3} M in H_2O (10-cm. cell). Vertical lines indicate random experimental error within each set of data. In the case of curve B, because of the small measured rotations due to high dilution, there is also a nonrandom base-line uncertainty corresponding to a possible shift of the entire curve estimated at less than $\pm 50°$.

weak 260 mμ absorption band in the biologically important α-amino acid L-phenylalanine (I). The point of conflict is of some significance and warrants settling, for an accurate description of the optical rotatory dispersion (O.R.D.) and/or circular dichroism (C.D.) of the α-amino acids is a prime prerequisite for the structural interpretation of protein and polypeptide optical activity data.

The Schellmans,[2] using Drude-type analyses, predicted optically active aromatic absorption bands for aromatic amino acids: for L-tyrosine (II) at 272 mμ (0.66 M HCl) and for L-phenylalanine (I) at 253 mμ (0.22 M HCl). The pertinent Cotton effect for II is now well documented experimentally,[3-6] but workers in the United States have heretofore failed to affirm its existence for I.[7] Hooker and Tanford[5] in particular have emphasized this contrast in the behavior of 1 as compared to II and some of its derivatives. It is the purpose of the present note to point out that fundamental considerations governing natural optical activity require that this apparent difference in behavior be not one in kind, but only in degree, and that the ap-

(3) M. Billardon, *Compt. rend.*, 251, 535, 1759 (1960).
(4) E. Iizuka and J. T. Yang, *Biochemistry*, 3, 1519 (1964).
(5) T. M. Hooker and C. Tanford, *J. Am. Chem. Soc.*, 86, 4989 (1964).
(6). G. D. Fasman, E. Bodenheimer, and C. Lindblow, *Biochemistry*, 3, 1665 (1964); S. Beychok and G. D. Fasman, *ibid.*, 3, 1675 (1964).
(7) Billardon[3] published data showing anomalous dispersion in the 260 mμ region for I. In particular, he reported a Cotton effect at the acid pH 1.1 with a peak-trough molar rotation difference of $\sim 200°$. Such results differ markedly from our own findings and those of other workers cited in the present note.

parent behavioral difference really amounts to a question of orders of magnitude that can be qualitatively understood in terms of the local symmetry of the "inherently symmetric, but asymmetrically (more generally, dissymmetrically) perturbed"[8] phenyl chromophore. Toward this end we also present unequivocal experimental evidence for the existence of a 260 mμ Cotton effect for I.

O.R.D. curves (Cary Model 60) and an ultraviolet spectrum (Cary Model 15) for chromatographically pure I from Mann Research Laboratories (Lot 4515) are shown in Figure 1. The O.R.D. curves are plotted on an uncommonly expanded ordinate scale; the visible and near-ultraviolet O.R.D. is so dominated by the transitions below 230 mμ that the extremely weak Cotton effect would be barely discernible on a scale sufficient to display adequately the long wave length singlet aromatic Cotton effect for II. In strongly acid solution (curve A) the Cotton effect is superimposed on a very steep background rotation that almost completely obscures the O.R.D. extrema so prominent in curve B. This explains, in part, why Iizuka and Yang[4] could not decide unequivocally as to the presence of anomalous dispersion for I in the 260 mμ region.

Best resolution was obtained for dilute solutions ($\sim 10^{-3}$ M) in 10-cm. cells with maximum absorbance ~ 2.5 at the peak absorption near 257 mμ (pH 5.9). Repeated runs of the undisturbed sample with the pen response time set at 30 sec. were made in order to average the noise. To test for the possibility of artifacts due to stray light, we measured the O.R.D. of a solution containing L-leucine (III) and DL-phenyl-alanine (IV) that in the 250–300 mμ region had the same background O.R.D. and the same absorbance as the samples used to obtain curve B of the figure; we could detect no Cotton effect in the 260 mμ region for the III–IV solution.

To understand the extreme weakness of the 260 mμ Cotton effect in 1, consider a benzene ring substituted such that the *effective* local symmetry is C_{2v}. If one constructs the π-molecular orbitals of the system solely from linear combinations of $2p_z$ atomic orbitals of carbon, then all π–π^* transitions from the ground state have their nonvanishing electric dipole transition moments $\mathbf{\mu}_e$ directed in the plane of the ring, and their nonvanishing magnetic dipole transition moments $\mathbf{\mu}_m$ directed perpendicular to that plane.[9] Hence no amount of mixing of the π–π^* transitions among themselves can lead to a nonvanishing scalar product $\mathbf{\mu}_e \cdot \mathbf{\mu}_m$, and hence to optically active π–π^* transitions. In other words, the dissymmetric molecular environment provided for the aromatic chromophore by the amino acid substituent in I and II is ineffective for the generation of a π–π^* Cotton effect if π-states of the sort just described are the only states involved. Further, if one can ignore the possibility of charge transfer between or the mixing of transitions between the aromatic and amino acid groups, then the only way the requisite in-plane $\mathbf{\mu}_m$ can be achieved is by mixing the π–π^* transitions with some perpendicular transi-

(8) A. Moscowitz, *Tetrahedron*, 13, 48 (1961); A. Moscowitz, K. Mislow, M. A. W. Glass, and C. Djerassi, *J. Am. Chem. Soc.*, 84, 1945 (1962); A. Moscowitz, W. C. Kreuger, I. T. Kay, G. Skewes, and S. Bruckenstein, *Proc. Natl. Acad. Sci. U. S.*, 52, 1190 (1964).
(9) D. J. Caldwell and H. Eyring, *Ann. Rev. Phys. Chem.*, 15, 281 (1964).

tion of the aromatic chromophore, *e.g.*, a σ–π^* or n–π^* transition, or expanding the basis set and invoking, *e.g.*, 3d orbitals. In tyrosine, the oxygen atom of the aromatic chromophore is a ready source of nonbonding orbitals for n–π^* transitions, and the long wave length aromatic Cotton effect is detectable without difficulty.[3-6] In phenylalanine, where the 260 mμ u_e is itself only very weakly allowed to begin with, this important mechanism for producing a properly directed u_m is absent, and only the less effective mechanisms of mixing with σ–π^* transitions or transitions involving 3d or higher oribitals are available. In view of this situation, the exceptional faintness of the 260 mμ Cotton effect in I becomes understandable.[9a]

(9a) Note Added in Proof. Since the time of submission of this communication, Hooker and Tanford (private communication) have corroborated the existence of the 260 mμ Cotton effect for I.

(10) Fellow of the Alfred P. Sloan Foundation.

(11) On leave from Chemical Laboratory IV, H. C. Oersted Institute, Copenhagen, Denmark.

Albert Moscowitz,[10] Andreas Rosenberg, Aage E. Hansen[11]

Departments of Chemistry and Laboratory Medicine
University of Minnesota, Minneapolis, Minnesota 55455

Carbon–Carbon Bond Reduction by Complex Metal Hydrides. II. Novel Origin of Cyclopropanes[1]

Sir:

We wish to report that reduction of allylic alcohols by lithium aluminum hydride[2] can be carried beyond the saturated alcohol stage to give cyclopropanes as the ultimate reaction products. We have investigated the behavior of cinnamyl derivatives in greater detail.

A mixture of *cis* and *trans* ethyl α,β-dimethyl-3,4-dichlorocinnamate (Ia) after reduction in refluxing tetrahydrofuran, under nitrogen, for 1 hr. with a 100% excess of lithium aluminum hydride, followed by neutral or base work-up, gave 45% yield[3] of a hydrocarbon, b.p. 78–80° (0.1 mm.). *Anal.* Calcd. for $C_{11}H_{12}Cl_2$: C, 61.42; H, 5.62; Cl, 32.96. Found: C, 61.62; H, 5.81; Cl, 32.68. The n.m.r. spectrum exhibited, in addition to the expected three-proton splitting pattern in the aromatic region, complex absorption corresponding to a total of nine hydrogens at τ 8.7–9.8. This region included a three-proton singlet at τ 8.77 and complex absorption corresponding to one proton at τ 9.4–9.8, peaking strongly at 9.67,[4] suggesting structure IVa for the hydrocarbon. This assignment of structure and stereochemistry was confirmed by an independent synthesis of IVa in 15% yield *via* the Simmons–Smith reaction,[5] employing

(1) For part I, see M. J. Jorgenson, *Tetrahedron Letters*, 13, 559 (1962).

(2) (a) N. G. Gaylord, "Reduction with Complex Metal Hydrides," Interscience Publishers, Inc., New York, N. Y., 1956, Chapter 15; (b) F. A. Hochstein and W. G. Brown, *J. Am. Chem. Soc.*, 70, 3484 (1948); R. F. Nystrom and W. G. Brown, *ibid.*, 69, 1197 (1947).

(3) The balance consisted of 3- and 4-chloro-α,β-dimethylcinnamyl and hydrocinnamyl alcohols, formed from the reduction of one of the chlorines in the benzene ring. Loss of one chlorine reduces the rate of subsequent cyclopropane formation substantially; less than 5% of monochlorocyclopropane products were formed.

(4) The complex spectrum is caused by virtual coupling of the ring protons with one methyl group *via* the tertiary hydrogen (*cf.* the spectrum of deuterated VII).

(5) The procedure of R. S. Shank and H. Shechter, *J. Org. Chem.*, 24, 1825 (1959), was employed.

hydrocarbon V (Ar = 3,4-dichlorophenyl) as starting material.

The double bond reduction of the parent ester Ib took place at a slower rate. In refluxing dimethoxyethane both *cis* and *trans* esters Ib were reduced to the same cyclopropane IVb within 20 hr. At intermediate intervals the conversion to cyclopropane was incomplete; the balance of the product consisted in the case of the *cis* isomer of *threo* alcohol III[6] (R = CH_3, Ar = phenyl), in the case of the *trans* isomer of small amounts of the same alcohol III and larger amounts of α,β-dimethylcinnamyl alcohol. A mixture of *cis* and *trans* esters Ic, in refluxing tetrahydrofuran, gave cyclopropane IVc in 10 hr.

Ethyl cinnamate is reduced to hydrocinnamyl alcohol within 30 min. at room temperature in ether.[2] Under these conditions no cyclopropane formation was observed. We have found that more vigorous conditions lead to the formation of phenylcyclopropane (IVd), a 70-hr. reflux in dimethoxyethane yielding 28%[7] IVd.

The following interpretation is offered for the mechanistic origin of cyclopropanes. It is evident that cyclopropanes result from a reaction taking place subsequent to the formation of an aluminate intermediate.[2b] This reaction may proceed *via* an internal displacement sequence, in a lithium salt formed from reorganization of the aluminate intermediate, or it may take place *via* a concerted loss of an aluminate species. Steric and electronic factors exert strong control over the reaction; a quantitative correlation of these effects with reaction rate is in progress.
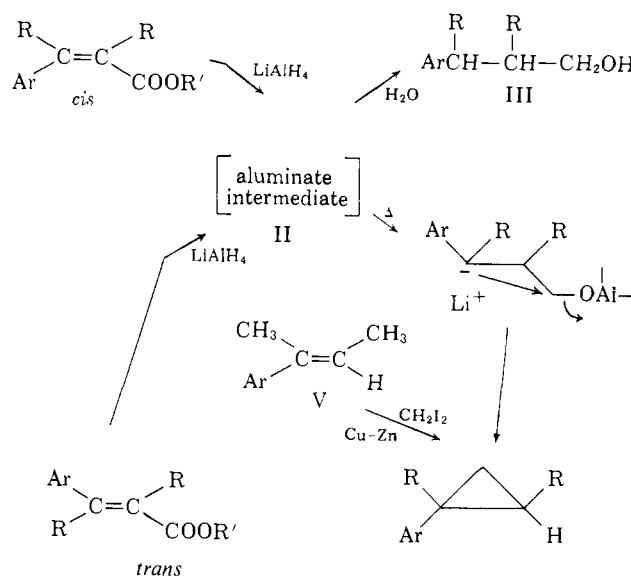
Ia, R = CH_3; R' = CH_2CH_3;
    Ar = 3,4-dichlorophenyl
b, R = R' = CH_3;
    Ar = phenyl
c, R = CH_3; R' = CH_2CH_3;
    Ar = 4-chlorophenyl
d, R = H; R' = CH_2CH_3;
    Ar = phenyl

IVa, R = CH_3; Ar = 3,4-dichlorophenyl
b, R = CH_3; Ar = phenyl
c, R = CH_3; Ar = 4-chlorophenyl
d, R = H; Ar = phenyl

(6) The implications of this stereochemistry with regard to the structure of the intermediate and the mechanism of the reduction will be elaborated in a subsequent publication.

(7) Since the second step appears to be pyrolytic in nature, the experimental procedure should be adaptable to give higher yields in shorter time.