the experiment, has an absorption maximum at 497 nm, and a half-life of 3 μs. We assign the structure of this product to the 9-fluorenyl radical.[16] This finding suggests that there is either a large solvent effect on carbene reactivity or the fluorenyl radical is formed through rapid hydrogen abstraction by electronically excited DAF.[17] We are continuing to examine the structure, solvent, and temperature dependence of the reactions of ^{1}Fl and ^{3}Fl with the expectation that these studies will lead to a fuller understanding of their chemistry.

Acknowledgments. We thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the National Science Foundation for their support of this work. Special thanks also to James Wehmer for his assistance in setting up and using the laser apparatus.

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(16) I. Norman and G. Porter, *Trans. Faraday Soc.*, **230A**, 399 (1955).

(17) Reactions of electronically excited diazo compounds have been suggested previously: W. J. Baron, M. R. DeCamp, M. E. Hendrick, M. Jones, J., R. H. Levin, and M. B. Sohn, *Carbenes 1973-1975*, **1**, 1 (1973); H. Tomioka, H. Kitagawa, and Y. Izawa, *J. Org. Chem.*, 44, 3072 (1979). A referee has suggested that the short-lived product we observe in CH$_3$CN solution may be ^{3}DAF. We cannot absolutely rule out this possibility. However, if this is the case, then the chemistry previously attributed to singlet carbenes, ether formation and cyclopropanation of olefins in particular, must also proceed from the triplet-excited diazo compound. This conclusion is apparently inconsistent with the observation that carbenes generated from a variety of thermal or photochemical sources give similar products.[18]

(18) R. A. Moss, *Carbenes 1973-1975*, **1**, 1 (1973).

(19) Fellow of the Alfred P. Sloan Foundation 1977-1979; Dreyfus Teacher-Scholar 1979-1984.

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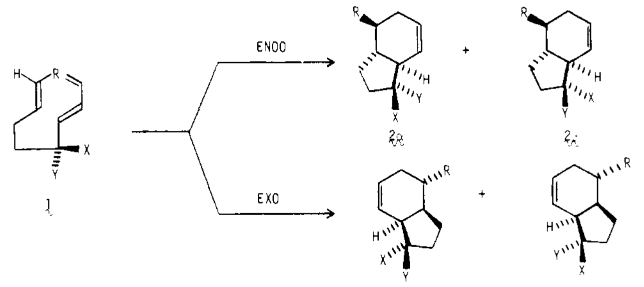
Cytochalasin Support Studies.[1] Chiral and Stereochemical Control via an Intramolecular Diels-Alder Reaction of a (*Z*)-Diene

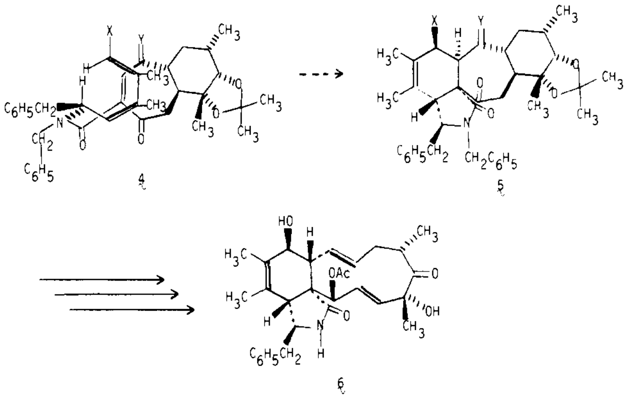
Sir:

The intramolecular Diels-Alder reaction of (*E*)-dienes has become a valuable and often employed strategy at the disposal of the synthetic chemist.[2] A limitation associated with this expedient is that (*E*)-dienes have two relatively easily accessible transition states which, in many instances, afford mixtures of cis and trans fused products (**2** and **3**).[2-5] This situation is further exacerbated by the introduction of an additional asymmetric center at the pentadienylic position of the diene (**1**, X ≠ Y).[6]



Dienes possessing *Z* stereochemistry appear far more amenable for product prediction. Because of its geometry, a (*Z*)-diene can only attain a single transition state in the intramolecular Diels-Alder reaction; more importantly, the stereochemical constraints of the reaction are very strongly transmitted to the carbon which is allylic to the diene moiety. Specifically, in the requisite planar *s*-cis conformation, substitutents at the pentadienylic center experience substantial nonbonded interactions with the *Z* hydrogen at the diene terminus.[7] In the case of an unsymmetrically substituted diene (**4**, **15**), it seems apparent that the reaction will follow the pathway which best minimizes this destabilizing interaction. *For chiral dienes, this effect translates into asymmetric induction by the reaction occurring from a single diastereomeric face of the dienophile.*[8-11]

A useful illustration of this concept would be cyclization of *Z*-amide **4** to lactam **5**. Lactam **5** is a potential substrate for an enolate-promoted fragmentation[1] approach to cytochalasin C **6**.[12]



(X = H; OR / Y = O; β-OH, α-H)

As a prelude to the **4** → **5** transformation, we have examined the simpler model system **15**. Synthesis of this material is accomplished as follows: Treatment of the *N*-tosyl derivative of L(−)-phenylalanine **7**[13] with borane-dimethyl sulfide[14] followed

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(1) Paper 2 in this series; for paper 1, see: Clark, D. A.; Fuchs, P. L. *J. Am. Chem. Soc.* **1979**, *101*, 3567.

(2) Recent reviews: (a) Carlson, R. G. *Annu. Rep. Med. Chem.* **1974**, *9*, 270. (b) Oppolzer, W. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 10. (c) Brieger, G.; Bennett, J. N. *Chem. Rev.* **1980**, *80*, 63.

(3) Often the product (**2**) derived from the "endo" transition state (**1a**) is highly favored; however, there are numerous cases[4,5] where mixtures of products or products (**3**) derived only from the "exo" transition state (**1b**) are formed.

(4) (a) Wenkert, E.; Naemura, K. *Synth. Commun.* **1973**, *3*, 45. (b) Bajorek, J. J. S.; Sutherland, J. K. *J. Chem. Soc., Chem. Commun.* **1975**, 1559. (c) Frater, G. *Tetrahedron Lett.* **1976**, 4517. (d) Oppolzer, W.; Achini, R.; Pfenninger, E.; Weber, H. P. *Helv. Chim. Acta* **1976**, *59*, 1186. (e) Oppolzer, W.; Frostle, W. *Ibid.* **1975**, *58*, 590.

(5) (a) Gschwend, H. W.; Lee, A. O.; Meier, H. P. *J. Org. Chem.* **1973**, *38*, 2169. (b) Gschwend, H. W.; Meier, H. P. *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 294. (c) Gschwend, H. W. *Helv. Chim. Acta* **1973**, *56*, 1763.

(6) The Roush dendrobine synthesis provides a well-characterized example of all four possible products being isolated: Roush, W. R. *J. Am. Chem. Soc.* **1978**, *100*, 3599.

(7) It is this interaction that is responsible for the 10^5 times reactivity difference between *trans*- and *cis*-pentadiene: (a) Onishchenko, A. S. In "Diene Synthesis"; Monson, S., Ed.; Jerusalem, 1964; pp 11-18. (b) Sauer, J., *Angew. Chem., Int. Ed. Engl.* **1966**, *5*, 211. (c) *Ibid.* **1967**, *6*, 16.

(8) There are only three examples of intramolecular Diels-Alder reactions with Z-dienes.[9-11] In their landmark paper, House and Cronin demonstrated that a *Z,E* pair of triene esters cyclize to bicyclic products *at competitive rates*.[9] Their finding indicates that for the (*Z*)-diene the presence of both the diene and dienophile within the same molecule minimizes the steric destabilization of the requisite *s*-cis conformation which is so pronounced in intermolecular Diels-Alder reactions of (*Z*)-dienes.[7] That is, whenever the diene attains the *s*-cis conformation in the intramolecular reaction, it already has the dienophile in close proximity ready to undergo unimolecular cyclization. This must be compared to the intermolecular case where a second-order reaction must be superimposed upon the *s*-cis ⇄ *s*-trans conformational equilibrium. Borch has shown that an unreactive (*Z*)-diene undergoes cis → trans equilibration in preference to direct Diels-Alder cyclization.[10] In another study, Oppolzer has found that a racemic (*Z*)-diene bearing a substituent at the pentadienylic center undergoes a low-yield cyclization at 245 °C to afford a cis-fused bicyclic product (stereochemistry resulting from the pentadienylic center unspecified).[11]

(9) House, H. O.; Cronin, T. H. *J. Org. Chem.* **1965**, *30*, 1061.

(10) Borch, R. F.; Evans, A. J.; Wade, J. J. *J. Am. Chem. Soc.* **1977**, *99*, 1612.

(11) Oppolzer, W.; Fehr, C.; Warneke, J. *Helv. Chim. Acta* **1977**, *60*, 48.

(12) For other synthetic efforts in the cytochalasin area, see ref 4a of Clark, D. A.; Furhs, P. L. *J. Am. Chem. Soc.* **1979**, *101*, 3567. See also: Kim, M. Y.; Wienreb, S. M. *Tetrahedron Lett.* **1979**, 579.

(13) McChesney, E. W.; Swann, W. K. *J. Am. Chem. Soc.* **1937**, *59*, 1116.

(14) Review on BH$_3$·(CH$_3$)$_2$S: Lane, C. F. *Aldrichimica Acta* **1975**, *8*, 20.

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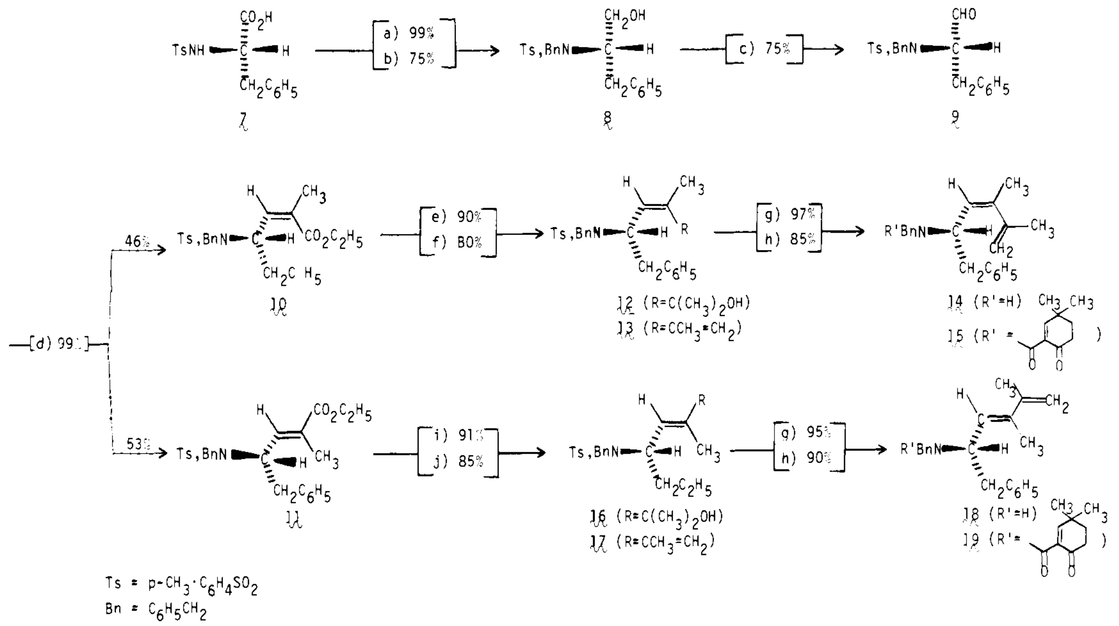
Scheme I



a) $BH_3\cdot(CH_3)_2S$ (2.0 eq), THF, 25°, 48 hr.; b) NaH, THF, 25°, 0.5 hr.; $C_6H_5CH_2Br$, 65°, 36 hr.; c) PCC (3.0 eq), CH_2Cl_2, 25°, 3.5 hr.; d) $[(C_2H_5O)_2P(O)^{\ominus}C(CH_3)\,CO_2C_2H_5]Na^{\oplus}$ (1.5 eq), THF, 0°, 0.5 hr.; 25°, 2 hr.; HPLC (ethyl acetate, hexane, 1:5); e) CH_3MgBr (3.0 eq), ether, -78°→0° (1 hr.); f) CH_3SO_2Cl (5.0 eq), $(C_2H_5)_3N$ (10.0 eq), CH_2Cl_2, 0°, 0.5 hr.; g) 6% Na(Hg), NaH_2PO_4, CH_3OH, 66°, 12 hr.; h) 2-Chloro-1-methylpyridinium iodide, $(C_2H_5)_3N$, CH_2Cl_2, 3,3-dimethyl-6-oxo-cyclohex-1-ene carboxylic acid, 0°, 0.5 hr.; i) CH_3Li (2.5 eq), ether, -78°, 15 min.; j) $POCl_3$, C_6H_5N, 25°, 4 hr.

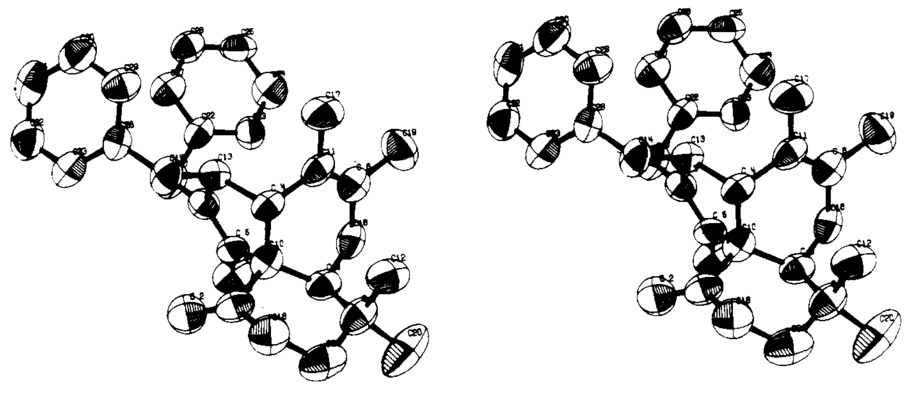


Figure 1.

by *N*-benzylation of the resulting alcohol produced the diprotected chiral alcohol **8**.[15-17] Oxidation of **8** with pyridinium chlorochromate[18] smoothly afforded aldehyde **9**.[15,16] Reaction of **9** with 2-methyl triethylphosphonoacetate yielded an easily separable mixture of esters **10** and **11**.[15,16,19] Treatment of (*Z*)-ester **10** with an excess of methylmagnesium bromide yielded tertiary allylic alcohol **12**[15,16] which, in turn, was dehydrated to the *N*-tosyl (*Z*)-diene **13**.[15,16,20] Reductive detosylation of **13** with sodium amalgam[21] smoothly afforded the *N*-benzyl (*Z*) diene **14**.[15,16,20] Conversion of **14** to the model lactam **15**[15,16] was easily accomplished by reaction of **14** with 3,3-dimethyl-6-oxocyclohex-1-enecarboxylic acid in the presence of the chloropyridinium coupling reagent described by Mukaiyama.[22] The isomeric *E* series (**16**–**19**) was similarily prepared from (*E*)-ester **11**[15,16,20] (Scheme I).

The enantiomeric homogeneity of dienes **13** and **17** (Scheme I) was established from their conversion to alcohol **8** without loss of enantiomeric integrity (>95% from $[\alpha]^{25}{}_D$ and ^1H NMR chiral shift reagent comparisons[17]).

$$\mathbf{13,17}\ \xrightarrow{\left[\begin{array}{c}(1)\ O_3,\ C_2H_5OH,\ -78\ ^\circ C\\(2)\ NaBH_4,C_2H_5OH,\ 25\ ^\circ C\\75\%\end{array}\right]}\ \mathbf{8}$$

Heating a 0.01 M solution of (*Z*)-amide **15** in toluene at reflux for 40 h produced tricyclic **22** [mp 133–133.5 °C, $[\alpha]^{25}{}_D$ +107.5° ± 2.0° (*c* 0.55, $CHCl_3$)] in 95% yield. It is interesting to note

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(15) The ^1H NMR, ^{13}C NMR, and exact mass spectral data are completely in accord with the structure assigned. Yields refer to isolated material of >95% purity.

(16) $[\alpha]^{25}{}_D$ ($CHCl_3$): **8**, -53.5° (*c* 1.96); **9**, -117.6° (*c* 2.03); **10**, +34.7° (*c* 2.53); **11**, +38.3° (*c* 2.92); **12**, -22.2° (*c* 2.25); **13**, -13.0° (*c* 1.08); **14**, -3.0° (*c* 1.74); **15**, +13.7° (*c* 0.95); **16**, +6.7° (*c* 0.57); **17**, +47.6° (*c* 2.20); **18**, -6.4° (*c* 0.77); **22**, +107.5° (*c* 0.55).

(17) The ^1H NMR (360-MHz) spectrum of racemic **8** containing 10 mol % of tris[3-[(trifluoromethyl)hydroxymethylene]-*d*-camphorato]europium(III) showed diastereotopic resonance pairs at 8.01 (d, *J* = 7.9 Hz) and 8.05 (d, *J* = 7.9 Hz), 7.81 (d, *J* = 6.6 Hz) and 7.71 (d, *J* = 6.9 Hz), 5.25 (d, *J* = 16.2 Hz) and 5.20 (d, *J* = 15.6 Hz), and 4.95 (d, *J* = 16.2 Hz) and 4.91 (d, *J* = 15.6 Hz) ppm while that of **8**, derived from either **7** or from dienes **13** and **17** by ozonolysis, showed only the later, higher field signals of each resonance pair.

(18) Corey, E. J.; Suggs, J. W. *Tetrahedron Lett.* **1975**, 2647.

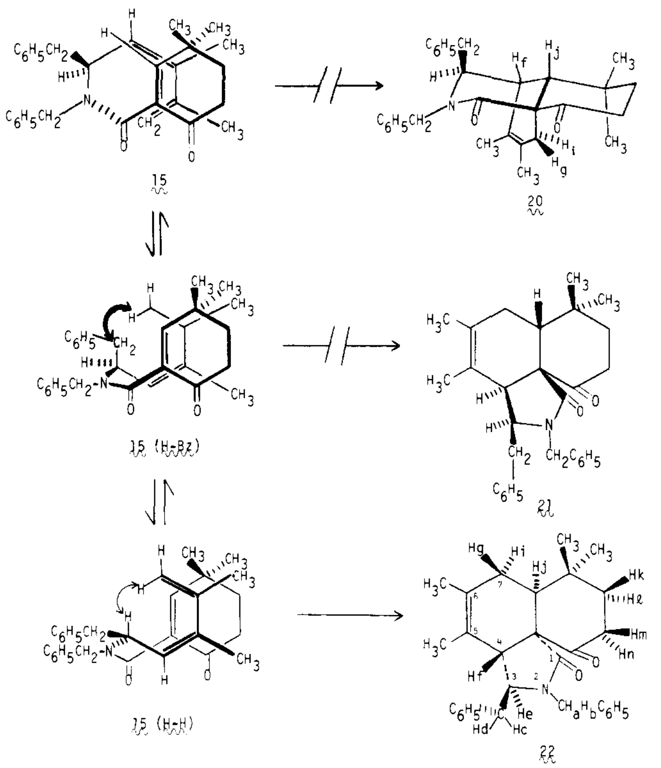
(19) **10**: $\delta(CDCl_3)$ 4.87 (1 H, dd, *J* = 1.5, 10 Hz); 1.67 (3 H, d, *J* = 1.5 Hz). **11**: δ ($CDCl_3$) 6.55 (1 H, dd, *J* = 1.5, 10 Hz); 1.22 (3 H, d, *J* = 1.5 Hz).

(20) Confirmation of the olefin geometry assigned to **13** and **14** and **17** and **18** was provided by the consistently higher field shifts (mutual shielding) in the ^{13}C NMR of the vinyl methyl group and the asymmetric carbon atom in the *E* isomers.

(21) Trost, B. M.; Arndt, H. C.; Strege, P. F. *Tetrahedron Lett.* **1976**, 3477.

(22) Bald, E.; Saigo, K.; Mukaiyama, T. *Chem. Lett.* **1975**, 1163.

Scheme II



that under identical conditions the isomeric *E*-amide **19** (Scheme I) is recovered largely unchanged. The structure of lactam **22**, although firmly supported by spectral analysis,[15,23] was additionally verified by X-ray analysis (Figure 1).[24] This finding indicates that cyclization has occurred specifically via the indicated **15** (H–H) transition state[25] with the exclusion of alternate products **20** and **21** (Scheme II).

Acknowledgments. We thank the National Science Foundation (CHE 79-03953) and the National Institute of Health (AI-13073) for their generous support of this work. The carbon-13 NMR data reported in this investigation were obtained on the departmental CFT-20 instrument provided by NSF Grant 7842. We thank Preston Conrad for providing those spectra. We also thank the Purdue University Bioligical Magnetic Resonance Laboratory (NIH RR01077) for access to the 360-MHz ^{1}H NMR spectrometer and John Saddler for providing those spectra.

Supplementary Material Available: Listings of observed and calculated structural factors and bond lengths and bond angles (18 pages). Ordering information is given on any current masthead page.

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[23] For **22** atoms have been numbered according to the cytochalasin numbering system: ν_{max} (CHCl$_3$) 5.88, 5.95 μm; ^{1}H NMR (360 MHz, CDCl$_3$) δ 7.25–7.10 (m, 10 H, aryl), 5.17 (d, J_{ab} = 15.4 Hz, H$_a$), 3.91 (d, J_{ab} = 15.4 Hz, H$_b$), 3.20 (dd, J_{ce} = 5.3 Hz, J_{de} = 9.8 Hz, J_{ef} <1 Hz, H$_e$), 3.05 (dd, J_{ce} = 5.3 Hz, J_{cd} = 13.2 Hz, H$_c$), 2.81 (ddd, J_{mn} = J_{kn} = 14.2 Hz, J_{ln} = 5.8 Hz, Hn), 2.51 (d, J_{gj} = 6.4 Hz, H$_j$), 2.50 (dd, J_{cd} = 13.2 Hz, J_{de} = 9.8 Hz, H$_d$), 2.45 (ddd, J_{mn} = 14.2 Hz, J_{km} = 4.0 Hz, J_{lm} = 4.5 Hz, H_m), 2.39 (br s, J_{ef} < 1 Hz, H$_f$), 2.11 (ddq, J_{gi} = 17.5 Hz, J_{gj} = 6.4 Hz, $J_{CH_3(5)g}$ = 1.5 Hz, H$_g$), 1.89 (d, J_{gi} = 17.5 Hz, H$_i$), 1.88 (ddd, J_{kl} = 15.5 Hz, J_{km} = 4.0 Hz, J_{kn} = 14.2 Hz, H$_k$), 1.74 (ddd, J_{kl} = 15.5 Hz, J_{lm} = 4.5 Hz, J_{ln} = 5.8 Hz, H$_l$), 1.55 (brs, C$_6$–CH$_3$), 1.05 (s, CH$_3$), 0.90 (d, $J_{CH_3(5)g}$ = 1.5 Hz C$_5$–CH$_3$), 0.82 (s, CH$_3$); ^{13}C NMR (CDCl$_3$) δ 212.0 (s), 172.7 (s), 138.0 (s), 136.5 (s), 129.5 (d), 128.7 (d), 128.4 (d), 128.0 (s), 127.7 (d), 127.3 (d), 126.7 (d), 123.2 (s), 62.8 (d), 62.1 (s), 44.9 (d), 44.6 (t), 43.8 (d), 41.7 (t), 39.0 (t), 36.2 (t), 33.2 (s), 30.7 (q), 29.6 (t), 23.1 (q), 19.8 (q), 16.1 (q). Anal. Found: C, 81.75; H, 8.12; N, 3.16. $C_{30}H_{35}NO_2$ requires C, 81.59; H, 7.99; N, 3.17.

[24] The crystal structure of an earlier, racemic version of tricyclic compound **22** was determined by using standard procedures. Crystals of **22** belong to space group $P2_1a$ with a = 17.602, b = 15.312, and c = 9.486 Å and β = 97.62°. The structure was solved by using the MULTAN program and refined to an R of 0.14, at which point refinement was terminated. A difference fourier map revealed no peaks larger than 0.45 e/Å^3. Figure 1 shows an ORTEP stereo plot of the structure of **22**.

[25] It seems quite likely that the bulky *N*-benzyl substituent is serving to destabilize nonreactive conformers in a manner similar to that found by Gschwend in his studies with *E*-amides (ref 5).

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[30] A. P. Sloan Fellow 1977–1979.

Effect of Photoelectrode Crystal Structure on Output Stability of Cd(Se,Te)/Polysulfide Photoelectrochemical Cells

Sir:

Cadmium chalcogenides have received a great deal of attention as photoelectrodes in polychalcogenide redox couple containing photoelectrochemical cells since the stabilizing effect of these redox couples on them was discovered.[1-3] Most of the attention was focused on CdSe, for which *long-term* output stability in polysulfide solutions (with or without added Se) was achieved by using single crystals,[4] pressed pellets,[5] and electroplated[1,6] or painted[7] thin layers. Stabilization of the low-band-gap material CdTe (E_G = 1.45 eV vs. 1.75 eV for CdSe, at room temperature) was achieved at low-output currents only, i.e., short-circuit currents below those expected at reasonable quantum efficiencies under solar illumination conditions.[1,8,9] Under such conditions, CdTe thin layers in polysulfide solution[1,8,10] and polytelluride solution[1,8] and single crystals in selenide or telluride solution[9] were stable at low photocurrent densities.

We report here on thin-film polycrystalline Cd(Se,Te) alloy photoelectrodes, which show output stability comparable to CdSe photoelectrodes[6] when possessing the hexagonal (wurtzite) structure and which have optical band gaps similar to that of pure CdTe.[11] CdSe and CdTe form homogeneous alloys over the whole composition range,[11,12] with the alloy adopting the cubic (sphalerite) or hexagonal (wurtzite) structure, depending on the composition and conditions of preparation. Figure 1 shows the variation of the optical band gap (absorption edge) of the alloys as a function of composition and crystal structure.[11] Similar behavior is observed for Cd(S,Te) alloys[11,13] while Cd(S,Se) alloys show monotonic dependence of their band gaps on composition.[11] The latter alloys have been used successfully as photoelectrodes in polysulfide solution.[14] Both the cubic and the hexagonal forms

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[1] Hodes, G.; Manassen, J.; Cahen, D. *Nature* (*London*) **1976**, *261*, 403; *Bull. Isr. Phys. Soc.* **1976**, *22*, 100.

[2] Ellis, A. B.; Kaiser, S. W.; Wrighton, M. S. *J. Am. Chem. Soc.* **1976**, *98*, 1635; *Ibid.* **1976**, *98*, 6855.

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