under similar conditions yields analogous products and provides a similar dependence of product distribution on flow rate of the substrate. Infrared absorption spectra suggest that methylpyrrole and α,β-dimethylacrylonitrile are two of the major "high boiling" products of the reaction but these identifications have not yet been confirmed by comparison with authentic samples.

We are currently undertaking a detailed study of the reaction of "active" nitrogen with conjugated dienes and the results will be reported shortly.

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ATTEMPTED VIOLATIONS OF THE RULE OF TRANS-NUCLEOPHILIC ADDITION

Sir:

The base-catalyzed addition of mesitylenethiol to mesitylacetylene was carried out to determine whether the bulky mesityl groups would affect the behavior of this system as regards the Rule of *trans*-Nucleophilic Addition.[1] However, the adduct, 1-mesityl-2-(mesitylmercapto)-ethene (I, m.p. 44.5–45°; *Anal.* Calcd. for $C_{20}H_{24}S$: C, 81.09; H, 8.11. Found: C, 81.35; H, 7.91), was shown to be of the *cis* configuration, arising from normal *trans* addition of the nucleophile. Although the assignment of configuration is consistent with infrared data (absorption bands of medium intensity at 7.55 and at 14.35 μ and the absence of a band in the 10–10.5 μ region), it is based largely on a comparison of its sulfone derivative (II, m.p. 183–184°; *Anal.* Calcd. for $C_{20}H_{24}O_2S$: C, 73.17; H, 7.32. Found: C, 73.10; H, 7.20) with independently synthesized *trans*- (III, m.p. 116°, strong infrared band at 10.15 μ; *Anal.* Calcd. for $C_{20}H_{24}O_2S$: C, 73.17; H, 7.32. Found: C, 73.00; H, 7.22) 1-mesityl-2-(mesitylsulfonyl)-ethene and ethane (IIa). These were prepared by the reaction sequences

$$\text{MesCH=CH}_2 \xrightarrow[\text{(2) NaOH}]{\text{(1) SO}_3\cdot\text{ dioxane}}$$

$$\text{MesCH=CHSO}_3\text{Na} \xrightarrow{\text{PCl}_5} \text{MesCH=CHSO}_2\text{Cl} \xrightarrow[\text{AlCl}_3]{\text{MesH}} \text{III}$$

$$\text{MesC}\equiv\text{CH} \xrightarrow{n\text{-BuLi}} \xrightarrow{(\text{MesS})_2} \text{MesC}\equiv\text{CSMes} \xrightarrow{\text{H}_2\text{O}_2}$$

$$\text{IV} \xrightarrow[\text{Pd}\cdot\text{C}]{\text{H}_2} \text{IIa}$$

This independent synthesis of compound III was patterned after a synthesis of *trans*-1-phenyl-2-(*p*-tolylsulfonyl)-ethene.[1a] 1-Mesityl-2-mesitylsulfonylacetylene (IV) had m.p. 116–117°. *Anal.* Calcd. for $C_{20}H_{22}O_2S$: C, 73.62; H, 6.75. Found: C, 73.41; H, 6.70.

Additional confirmatory evidence for these configurations was sought by the use of n.m.r. spectroscopy (J_{HH} for III = 15.8 cps.); however, an adequate solvent for II was not found. The coupling constants for the homologous *cis*- and *trans*-1-phenyl-2-(phenylsulfonyl)-ethenes were 12.4 and 15.7 cps., respectively.

Apparently any steric effect on the part of the mesityl groups in this addition is not sufficiently great to violate the Rule of *trans*-Nucleophilic Addition. In fact, we have no strong examples of violations of this rule for additions of negatively-charged nucleophiles to acetylenes.[2] Originally,[3] a partial violation of the rule was claimed for the addition of *p*-toluenethiolate reagent to sodium propiolate, which resulted in a mixture of predominantly *cis*-*p*-tolylmercaptoacrylic acid (V, m.p. 143–144°) and a small amount of the *trans* isomer (VI, m.p. 136–7°).[4,5,6] However, since *cis*-*p*-tolylmercaptoacrylic acid undergoes isomerization in the presence of *p*-toluenethiol and base, the origin of the *trans*-*p*-tolylmercaptoacrylic acid isolated from the reaction mixture is in doubt. It has been shown that the *p*-toluenethiolate reagent causes this isomerization, since neither sodium ethoxide nor refluxing ethanol is sufficient. Also of interest is the fact that the *cis* ester is practically completely isomerized to the *trans* ester on standing in the presence of *p*-toluenethiol. If benzenethiol is used as the isomerizing agent then significant amounts of *p*-toluenethiol appear in the reaction products. This reaction is now under further study in this laboratory.

Another complication in this system is the low solubility of V, which was overlooked by the experimenters (R.F.H., R.B.K. and D.L.G.),[3] who noted more facile over-all conversion of VI than of V to the methylthiochromone by the two stage treatment at 0° with thionyl chloride followed by aluminum chloride. Actually, it now appears that for homogeneous systems with V and VI and with solutions of the corresponding acyl chlorides the *cis* structures do indeed cyclize most readily.[6]

In addition to infrared spectral interpretations,[5] reduction data,[5] isomerization data,[5,6] and formation of V and VI from the geometrically analogous chloroacrylic acids,[5,6,7] nuclear magnetic resonance studies[8] are consistent with *cis* and *trans* configurations for V and VI, respectively.[9] In fact, n.m.r. data appear to be the most reliable

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[1] (a) W. E. Truce and J. A. Simms, THIS JOURNAL, **78**, 2756 (1956); (b) S. I. Miller, *ibid.*, **78**, 6091 (1956).

[2] In a sense, the second stage of nucleophilic displacements proceeding *via* a "benzyne" intermediate can be considered to be a violation of the Rule of *trans*-Nucleophilic Addition.

[3] W. E. Truce, *et al.*, *ibid.*, **79**, 1770, 5311 (1957); **81**, 4931 (1959).

[4] In regard to an earlier claim [W. J. Croxall and F. L. Freimiller, U. S. Patent 2,532,292 (1950); *C. A.*, **45**, 3420 (1951)] that *cis* and *trans*-β-*p*-tolylmercaptoacrylic acids had m.p. 104–107° and 136–137°, respectively, it was shown that the lower melting material was a mixture of the geometrical isomers.

[5] F. Montanari, *Tetrahedron Letters*, [4] 18 (1960).

[6] Unpublished work from this laboratory.

[7] There is a mounting body of evidence that nucleophilic displacements on activated haloölefinic systems proceed with retention of configuration, a phenomenon which was discussed initially for the chlorocrotonate system by E. Jones and C. A. Vernon [*Nature*, **176**, 791 (1955)].

[8] The authors wish to express their gratitude to Mr. William Baitinger of this laboratory for the determination of the nuclear magnetic resonance spectra.

[9] Inasmuch as the highly *tentative* assignments of configurations in the phenylpropiolic acid system [THIS JOURNAL, **81**, 5795 (1959)] were based largely on analogy to the propiolic acid system, a more complete investigation of that area is in progress. Also, the nuclear magnetic resonance spectra and dipole moments of most of our ethylenic compounds are being determined by B. G. and these data will be published separately.

physical evidence for the configurational assignments for V, VI and their corresponding esters. The proton–proton coupling constants for the vinylic hydrogens in V (J_{HH} = 9.7 ± 0.5 cps.; ester 10.4 cps.) and VI (J_{HH} = 15.4 ± 0.5 cps.; ester 14.9 cps.) are in agreement with the observation that *trans* ethenes of this type invariably have higher coupling constants than do the corresponding *cis* isomers. Infrared evidence can be ambiguous (*e.g.*, both geometrically isomeric ethyl *p*-tolylmercaptoacrylates show medium to strong absorption in the region of approx. 10.3–10.6 μ) and definite correlations between spectra and structures should be made with caution. Similarly, dipole moment studies can aid in structural assignments, but a background of model compounds must first be measured in order to isolate the various individual "group" effects.

These results demonstrate that the driving force for thiolates to add in a trans manner is so strong as even to overcome the adverse steric and electronic factors in the present examples.

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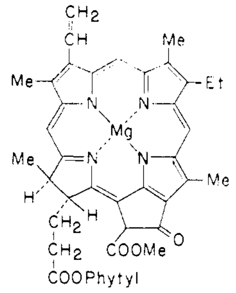
THE TOTAL SYNTHESIS OF CHLOROPHYLL

Sir:

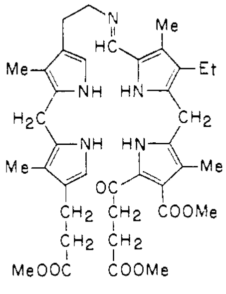
The chemical study of the ubiquitous green pigment of the plant world, chlorophyll *a*, was initiated with the classical investigations of Willstätter just after the turn of the century. The subsequent researches of Stoll and of Conant, and the massive contributions of the Munich school, were crowned by the proposal of a complete structure in 1940 by Hans Fischer. With the addition of stereochemical and other definitive detail during the last few years by Linstead and the Imperial College school, the structural investigations had culminated in the expression I.[1] We now wish to record the total synthesis of chlorophyll *a*, by methods which confirm the structure I in every respect.



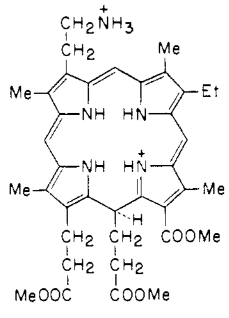
I

2 - (β,β - Dicyanovinyl) - 3,5 - dimethyl - 4 - ethylpyrrole[2] was converted by sulfuryl chloride in acetic acid at 55° to 2-(β,β-dicyanovinyl)-3-methyl-4-ethyl-5-chloromethylpyrrole [m.p. 189–192°], and thence, by condensation with 3-carbethoxy-4-methylpyrrole[3] in hot aqueous ethanolic hydrochloric acid to 3′,4-dimethyl-3-ethyl-4′-carbethoxy-5-(β,β-dicyanovinyl)-dipyrrylmethane [m.p. 195–197°], which, with β-carbomethoxypropionyl chloride in dichloromethane in the presence of anhydrous zinc chloride, gave 3′,4-dimethyl-3-ethyl-4′-carbethoxy - 5 - (β,β - dicyanovinyl) - 5′ - (β - carbomethoxypropionyl)-dipyrrylmethane [m.p. 134–135°]. The acid obtained from the latter by cleavage and hydrolysis with hot 33% aqueous sodium hydroxide was converted by diazomethane to 3′,4-dimethyl-3-ethyl-4′-carbomethoxy-5-formyl-5′ - (β - carbomethoxypropionyl) - dipyrrylmethane [m.p. 203–204°], which, condensed with ethylamine in the presence of acetic acid, gave 3′,4-dimethyl - 3 - ethyl - 4′ - carbomethoxy - 5 - (N - ethylformimino) - 5′ - (β - carbomethoxypropionyl)-dipyrrylmethane [m.p. 85–87°], whose hydrobromide [m.p. 100°], with hydrogen sulfide in benzene/methanol in the presence of sodium methoxide, yielded 3′,4-dimethyl-3-ethyl-4′-carbomethoxy-5-thioformyl - 5′ - (β - carbomethoxypropionyl) - dipyrrylmethane [m.p. 145–146°].

2,5-Dicarboxy-3-methyl-4-formylpyrrole[4] was converted, by condensation with nitromethane in boiling ethanol in the presence of diethylamine, to 2,5 - dicarboxy - 3 - methyl - 4 - (β - nitrovinyl) - pyrrole [m.p. > 300°, $\lambda\lambda_{max}$ mμ: 219, 272, 335], and thence, by reduction with sodium borohydride in aqueous sodium bicarbonate, to 2,5-dicarboxy-3-methyl-4-(β-nitroethyl)-pyrrole [m.p. 244–245°], which was decarboxylated in fused sodium acetate/potassium acetate at 120° to 3-methyl-4-(β-nitroethyl)-pyrrole [b.p. 93° (0.04 mm.), n_D^{25} 1.5200]. The nitro compound was hydrogenated in methanol over reduced platinum oxide to give 3-methyl-4-(β-aminoethyl)-pyrrole [b.p. 80° (0.10 mm.), n_D^{23} 1.5331], which, condensed with 2-formyl-3-methyl-4-(β-carbomethoxyethyl)-pyrrole[5] in methanolic hydrogen bromide, gave 3,3′-dimethyl-4-(β-aminoethyl) - 4′ - (β - carbomethoxyethoxyethyl) - dipyrromethene dihydrobromide [monohydrate, d.p. 200–201°]. The methene was reduced in aqueous



II



III

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[1] (a) *Cf.* A. Stoll and E. Wiedemann, *Fortschr. chem. Forsch.*, **2**(3), 538 (1952); (b) G. E. Ficken, R. B. Johns and R. P. Linstead, *J. Chem. Soc.*, 2273 (1956); (c) J. W. K. Burrell, L. M. Jackman and B. C. L. Weedon, *Proc. Chem. Soc.*, 263 (1959).

[2] H. Fischer and M. Neber, *Ann.*, **496**, 1 (1932).

[3] A. Treibs, R. Schmidt and R. Zinsmeister, *Ber.*, **90**, 79 (1957).

[4] H. Fischer and K. Zeile, *Ann.*, **483**, 266 (1930).

[5] H. Fischer and Z. Csukás, *Ann.*, **508**, 175 (1934).