solid was placed on a porous plate to remove the residual oils. The colorless solid obtained rapidly decomposed upon standing to a dark oil. The structure of this material was concluded to be *sym*-triphenylcyclopropenyl chloride from the following data. Crystallization of the solid from ethanol–water gave 1,2,3-triphenylcyclopropenyl ethyl ether as white prisms: mp 121–122°; ir (KBr) 5.50 μ; uv (95% ethanol) 317 (ε 21,800), 302 (ε 22,100) 228 (ε 26,500), and 223 mμ (ε 27,600). The nmr spectrum ($CDCl_3$) has a triplet at τ 8.77 (3 H), a quartet at τ 6.32 (2 H), and a multiplet at τ 2.60–2.25 ppm (15 H).

Anal. Calcd for $C_{23}H_{20}O$: C, 88.42; H, 6.45. Found: C, 88.29; H, 6.54.

A 0.5-g sample of 1,2,3-triphenylcyclopropenyl ethyl ether in 50 ml of ether was saturated with hydrogen bromide gas at 0° and was allowed to stand overnight at room temperature. The resulting solid that precipitated was crystallized from acetonitrile to give 0.33 g of triphenylcyclopropenyl bromide. The bromide was identified by comparison of infrared and mixture melting point with those of an authentic sample.[23] The ir spectrum of the bromide was almost identical with that of the original solid.

Reaction of I with Phenylacetylene.—A mixture of 1.0 g of I and 0.7 g of phenylacetylene in 70 ml of benzene was refluxed for 4 hr. The solvent was removed under reduced pressure to give a yellow oil which solidified upon standing. The oily solid was placed on a porous plate to give 0.9 g of a yellow solid. If the crude material is not purified immediately, violent decomposition occurs and a dark oil is produced. The yellow solid was crystallized from cold pentane to give 1-chloro-1,2-diphenylcyclopropene: mp 82–85°; ir 5.50 μ; uv (acetonitrile) λ_{max} 316 (ε 23,400), 301 (ε 29,600), and 288 mμ (ε 23,400). The nmr spectrum ($CDCl_3$) has a singlet at τ 5.05 (1 H) and a multiplet between τ 2.27 and 2.61 (10 H).

The structure of this material was further confirmed by briefly heating the solid in an aqueous ethanol solution. Removal of the solvent and crystallization of the white solid from benzene–hexane gave 0.15 g of bis-Δ′-1,2-diphenylcyclopropenyl ether, mp 164–166° (lit.[24] 163–165). The spectroscopic data obtained were in complete agreement with that reported by Breslow.[33]

Registry No.—I, 4460-46-2; V, 20420-97-7; VII, 20420-98-8; IX, 13668-03-6; 1-Chloro-1,2-diphenylcyclopropene, 20421-00-5.

Acknowledgment.—The authors are indebted to the U. S. Public Health Service (Grant GM 13990-02) for generous support of this research.

[33] R. Breslow, J. Lockhart, and H. W. Chang, *J. Amer. Chem. Soc.*, **83**, 2375 (1961).

Olefin–Tetracyanoethylene Oxide Adducts and Some of Their Derivatives[1a]

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The reaction of tetracyanoethylene oxide with methyl erucate (methyl *cis*-13-docosenoate) and methyl brassidate (methyl *trans*-13-docosenoate) gave 2,2,5,5-tetracyano-3-(11-carbomethoxyundecyl)-4-octyltetrahydrofurans (2 and 3) in good yields. In methanol containing 5% hydrogen chloride, both 2 and 3 undergo partial and selective methanolysis to give 2,5-dicyano-2,5-dicarbomethoxytetrahydrofuran derivatives (4 and 5). The newly formed carbomethoxy groups are *trans* to their adjacent alkyl groups. Both 2 and 3 also are partially and selectively hydrolyzed on the surface of silica gel to give 2,5-dicyano-2,5-dicarbamoyltetrahydrofuran derivatives (10 and 11) in good yields. The newly formed carbamoyl groups have a *cis* relationship to each other.

Adducts of tetracyanoethylene oxide (TCNEO, **1**) *via* the unusual *cis* cycloaddition to olefins, acetylenes, and aromatics[2-4] are products having potential for further modifications to provide compounds of diverse functionality. We have prepared TCNEO adducts **2** and **3** of methyl erucate and methyl brassidate, the respective *cis* and *trans* isomers of methyl 13-docosenoate. Homogeneity of each adduct was determined by tlc on silica gel, on which the two can be readily resolved. The adducts were isomeric 2,2,5,5-tetracyano-3-(11-carbomethoxyundecyl)-4-octyltetrahydrofurans, as judged by ir, nmr, and elemental analyses.

Esters.—In contrast with the complete methanolysis of TCNEO adducts obtained by somewhat different conditions,[2] we found that both adducts may undergo partial and selective methanolysis. Reaction at room temperature with methanol containing 5% hydrogen chloride converts **2** and **3** to **4** and **5**, respectively, in 90% yield. Their ir and nmr spectra are consistent for dicyanodicarbomethoxytetrahydrofuran derivatives.

The methanolysis products of the two TCNEO adducts could have their respective ring substituents in several different geometric configurations. However, most of these can be excluded as likely possibilities. Since the cycloaddition of TCNEO to olefins is *cis*,[2,3] we may reasonably assume that the ring alkyl substituents have a *cis* relationship in compounds **2** and **4** and a *trans* relationship in compounds **3** and **5**. Chemical shift values for the ring protons, when compared with literature values,[2] are consistent with this interpretation. Nmr analyses of both methanolysis products **4** and **5** show that the six protons associated with the carbomethoxy groups on the rings occur as a sharp singlet[5] (τ 6.09 and 6.08, respectively). Thus, in both **4** and **5**, the two carbomethoxy groups on the ring appear to be in magnetically equivalent environments. The two ring protons in **4** and **5** are also magnetically equivalent (multiplets at τ 7.20 and 7.37, respectively). These observations imply that, in compounds **4** and **5**, one carbomethoxy is attached at position 2 and the other at position 5. If *gem* functions were present, the ring protons could be expected to have greatly different chemical shift values due to the marked difference in diamagnetic anisotropy of the cyano and carbomethoxy groups. Also, each carbomethoxy group should have identical geometric relationships with its adjacent ring alkyl substituent. Apparently the methanolysis reaction has considerable stereoselectivity.

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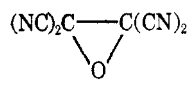
[1] (a) Presented in part at the 58th Annual Meeting of the American Oil Chemists' Society, New Orleans, La., May 7–10, 1967. (b) This is a laboratory of the Northern Utilization Research and Development Division, Agricultural Research Service, U. S. Department of Agriculture.

[2] W. J. Linn and R. E. Benson, *J. Amer. Chem. Soc.*, **87**, 3657 (1965).

[3] W. J. Linn, *ibid.*, **87**, 3665 (1965).

[4] P. Brown and R. C. Cookson, *Proc. Chem. Soc.*, 185 (1964).

[5] The band width at half peak height is approximately 1 Hz.



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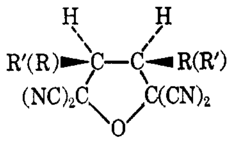

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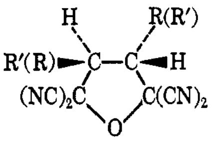

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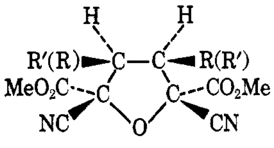

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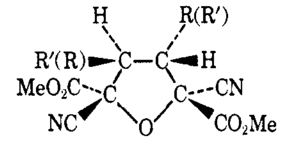

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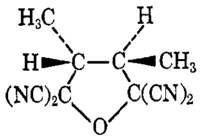

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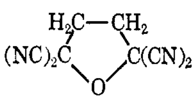

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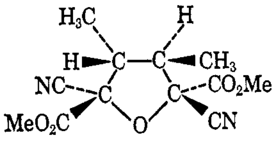

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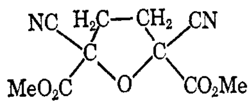

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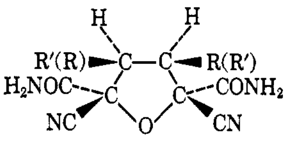

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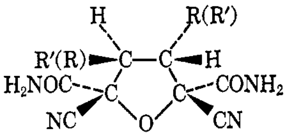

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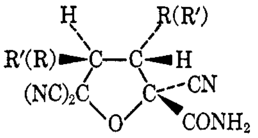

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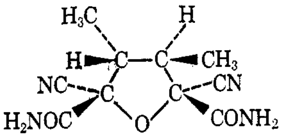

13

$R = CH_3(CH_2)_7$-
$R' = MeO_2C(CH_2)_{11}$-

The nmr spectrum of an admixture of **4** and **5** showed singlets at τ 6.10 and 6.07 corresponding to the ring carbomethoxy groups of the respective compounds. Evidently the small differences observed between these signals in the separate spectra are real, and, in addition to being attached to different carbon atoms, it is probable for steric reasons that the newly formed carbomethoxy groups are *trans* to their adjacent alkyl groups. For each, the present nmr data do not rule out the possibility that the carbomethoxy groups are *cis* to their adjacent alkyl groups.

On steric grounds, one might assume that carbomethoxy groups would be generated in these selective methanolysis reactions from nitrile groups that are *trans* to adjacent alkyl groups. Therefore, the two products would have the structures as shown for **4** and **5**. To test this hypothesis and to gain greater insight into the steric course of the reaction, two model compounds were prepared by methanolysis of the known[2] *trans*-3,4-dimethyl-2,2,5,5-tetracyanotetrahydrofuran (**6**) and 2,2,-5,5-tetracyanotetrahydrofuran (**7**).

The diester product **8** from **6** gives a six-proton singlet at τ 6.03,[5] corresponding to carbomethoxy protons. According to our reasoning, the carbomethoxy groups should be generated *trans* to their adjacent methyl groups. In contrast, the four cyano groups of **7** should have equivalent reactivity. If a monoester species actually is formed, the methanolysis of the second nitrile group might occur selectively so as to favor formation of the product with *trans* carbomethoxy groups. In fact, the nmr spectrum of product **9** shows two sharp bands corresponding to the carbomethoxy protons. The major band[5] occurs at τ 6.03, which is coincident with that of *trans*-dimethyl compound **8**. We believe that the second band[5] at τ 6.06 is due to the isomer of **9** having *cis* carbomethoxy groups.

Additional support for the conclusions concerning products of the selective methanolysis is provided in the following section on amides.

Amides.— In early phase of our investigation, we attempted to purify reaction product **2** from TCNEO and methyl erucate by chromatography on silica gel. The yield of adduct by this procedure was considerably less than anticipated, and almost all fractions contained some amide as determined by ir. A large amount of product of greater polarity than the starting material could be removed from the silica gel columns, and the ir spectrum of this polar fraction revealed bands corresponding to amide absorption. Since the initial mixture had no amide absorption in the ir, the hydrolysis reaction probably occurred during a short residence time on silica gel.

This fact was established by spotting pure adduct **2** on a tlc plate, waiting about 2 min, and then spotting the pure adduct in a second place on the plate. The chromatogram was developed with an irrigant (chloroform/acetonitrile) containing about 1% acetic acid to eliminate streaking. The first applied material was resolved into two spots, while the second was homogeneous. In the absence of acetic acid, streaking occurred with the pure adduct. This streaking implies that hydrolysis occurs during development of the chromatogram.

For larger scale reactions, adducts **2** and **3** were mixed neat with silica gel. Adduct **2** reacted more readily than did adduct **3**, which did not react appreciably during conventional tlc. These reaction differences probably reflect steric inhibition exerted by the bulky *trans* alkyl groups present in **3**. We observed that silica gel was not unique in its ability to catalyze this reaction. Neutral alumina and washed sand also hydrolyzed the nitriles to amides.

Although examples described in the Experimental Section involve addition of water to the silica gel, the reactions proceed equally well on silica gel samples activated as received from the suppliers or water-washed silica gels activated by heating for several hours at 120°. Acetonitrile, malononitrile, and 1,11-undecanedinitrile yielded little or no amide when treated with silica gel; therefore, this silica-catalyzed hydrolysis of nitriles is not general in scope. In its facility, this reaction parallels the solid phase catalysis reported by Cook, Forbes, and Khan.[6] They found that a variety of nitriles are

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(6) M. J. Cook, E. J. Forbes, and G. M. Khan, *Chem. Commun.*, 121 (1966).

converted to amides when agitated in methylene chloride with solid manganese dioxide. In contrast, the hydrolysis of nitriles to amides in solution frequently involves quite rigorous acid or alkali treatment.

Diamide **10** was obtained from **2**, and in addition to diamide **11**, a small yield of monoamide **12** was isolated from the reaction mixture after silica gel treatment of **3**.

Diamide products **10** and **11** have nmr spectra consistent with 2,5-dicyano-2,5-dicarbamoyltetrahydrofuran derivatives. The alkyl substituents must be oriented as in **2** and **3**. The two ring protons in **10** and **11** appear to be in magnetically equivalent environments (multiplets at τ 7.31 and 7.34, respectively). In contrast, the amide protons are in different environments. Amide **10** has two broad singlets of nearly equal intensity, whereas amide **11** has three broad singlets of unequal intensity (τ 3.31, 1.5 H; τ 2.57, 0.6 H; and τ 2.20, 0.9 H). The signal for the fourth proton may be so broad that it is not detected.

These hydrolysis reactions probably involve compound interaction with water adsorbed on the silica gel surface. If the tetranitrile compounds are adsorbed at the silica surface and then displaced by solvent or by desorption and diffusion, the amide groups should be generated with a *cis* relationship in most of the diamide molecules formed. Therefore, amide groups in **10** should be in a greatly different environment from those in **11**. In product **10**, amide groups would be *trans* to their adjacent alkyl groups, whereas in product **11** one amide group would be *trans* and the other would be *cis* to its adjacent alkyl group. In a study that has some parallel to ours, Ciganek[7] has reported a selective hydrolysis of 7,7-dicyanonorcaradiene with alkaline hydrogen peroxide.

In an effort to determine whether the amide groups in **10** and **11** are *cis* or *trans*, both products were allowed to react with methanol containing 5% hydrogen chloride under the same conditions used to prepare **4** and **5**. The reaction with **10** was not complete, but the corresponding ester was isolated by column chromatography. This ester had ir and nmr spectra identical with those of **4**. In contrast, the amide groups of **11** were not converted to ester groups in a clear-cut manner. A small sample of amide **11** gave several products (at least six by tlc). The major one probably contains two nitrile groups, one amide group, and one ester group on the tetrahydrofuran ring. Its ir spectrum showed amide bands of lower intensity than in the parent compound **11**. The other major change in the spectrum was an increase in intensity and broadening of the absorption band at 1250-1290 cm^{-1}. The nmr spectrum, compared to that of the parent amide **11**, showed a diminution of the three amide bands and of the deshielded methylene multiplet at about τ 8.0. A band also appeared at τ 6.05, but it was not of sufficient intensity to account for one new methoxyl group per molecule.

Hydrogen-Bonding Studies.—Additional insight into the suggested selectivity in the nitrile hydrolysis is gained by ir spectra of amide products **10, 11,** and **12** at concentration levels ranging from 0.02 to 0.0004 *M*.

Band assignments were made in accordance with the discussion by Jones and Sandorfy.[8] The tetrahydrofuran monoamide trinitrile, **12**, is without detectable associated N–H stretching bands at concentrations of 0.02 to 0.0004 *M* in chloroform solution. In carbon tetrachloride solution, **12** has appreciable associated N–H bands only at the 0.02 *M* concentration.

These data suggest that in either chloroform or carbon tetrachloride, amide **12** occurs mainly, if not entirely, as the monomer at concentrations of 0.004 *M* or less. Also, at least in chloroform, there is no detectable N–H intramolecular association with π bonds of the nitriles or with electron pairs of ring oxygen.

It seems likely that at concentrations of less than 0.004 *M*, at any rate, the appreciable N–H association found for amides **10** and **11** is due to intramolecular hydrogen bonding. This bonding must involve interaction between the two amide groups. From this interpretation, it follows that the two amide groups in both **10** and **11** must be *cis* as shown.

It has been suggested that the association bands of amides chiefly involve –N-H···O=C– rather than –NH···N– linkages.[8] This bonding would require one carbonyl oxygen to achieve a preferred conformation projecting over the plane of the tetrahydrofuran ring. The amide group *cis* to its adjacent alkyl group in compound **11** should experience steric interactions causing restricted rotation about its carbon–carbon bond. This restricted rotation, together with hydrogen bonding effects, should cause considerable preference for one conformation.

For **11** and **12**, there is a two-proton multiplet corresponding to a greatly deshielded methylene. The multiplets centered at τ 7.94 and 7.97, respectively, are probably deshielded by amide carbonyl.[9] In addition to a preferred conformation of the amide groups, this deshielding effect would require a preferred orientation of one alkyl group. Presumably this alkyl group is on the same side of the tetrahydrofuran ring as the amide groups. Spectra of more model compounds would be needed for an unambiguous assignment of the deshielded proton pair. However, examination of molecular models prompts the suggestion that the methylene in question is β to the tetrahydrofuran ring. Both diester **8** and diamide **13** give AX_3 $A'X'_3$ spectra[10] with their respective dimethyl multiplets occurring with nearly identical chemical shift values of τ 8.63 and 8.66. Since the methyl proton shift values of both **8** and **13** are $X_3X'_3$ spectra rather than M_3X_3, we conclude that protons of substituents α to the ring are essentially affected equally by amide groups. Therefore, it seems unlikely that the preferentially deshielded methylenes (τ 7.94 and 7.97) of compounds **11** and **12** are those α to the tetrahydrofuran ring.

Quenched Infrared Nitrile Absorptions.—Compounds **4, 5, 8-11,** and **13**, which have either two disubstituted cyano acetamides or two disubstituted methyl cyano acetate groups, lack ir absorption bands owing to the nitrile groups (*ca.* 2250 cm^{-1}). Such nitriles (one substituent is an ether oxygen) have been discussed

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[7] E. Ciganek, *J. Amer. Chem. Soc.*, **89**, 1458 (1967).

[8] R. N. Jones and C. Sandorfy, "Techniques of Organic Chemistry, Chemical Applications of Spectroscopy," Vol. IX, W. West, Ed., Interscience Publishers, Inc., New York, N. Y., 1956, p 509 ff.

[9] G. J. Karabatsos, G. C. Sonnichsen, N. Hsi, and D. J. Fenoglio, *J. Amer. Chem. Soc.*, **89**, 5067 (1967).

[10] For discussions of $AX_3A'X'_3$ spectra, see A. A. Bothner-By and C. Naar-Colin, *ibid.*, **84**, 743 (1962), and F. A. L. Anet, *ibid.*, **84**, 747 (1962).

in the literature, and there is ample precedent for the absence of nitrile absorption.[11–13]

Experimental Section

Melting points were taken on a Fisher–Johns[14] block. Ir spectra were determined with an infracord Model 337 spectrophotometer; nmr spectra were determined with a Varian A-60 or an HA-100 spectrometer on solutions containing tetramethylsilane. Fractionation and purity of materials were monitored by tlc on silica gel. Spots were developed by charing with chromic acid at about 160°. TCNEO (1) was prepared by the action of aqueous hydrogen peroxide on tetracyanoethylene in acetonitrile as described by Linn, Webster, and Benson.[15] Adducts of 1 with olefins were prepared in toluene by the procedure of Linn and Benson.[2]

2,2,5,5-Tetracyano-3-(11-carbomethoxyundecyl)-4-octyltetrahydrofurans (**2** and **3**).—A typical preparation of adduct from methyl erucate (methyl *cis*-13-docosenoate) is described as follows: 0.6 g of TCNEO was refluxed for 16 hr with 1.7 g of methyl erucate in toluene. The solvent was removed *in vacuo* and the residue was partitioned countercurrently between hexane and acetonitrile. Adduct **2** (2.1 g, 100%) was obtained from the acetonitrile phases: ir (neat) 2250 ($C{\equiv}N$), 1730 ($C{=}O$), 1075, 1018 cm^{-1}; nmr (CCl_4) τ 9.10 (t, 3, CH_3), 8.0–8.95 (m, 34, CH_2), 7.76 (t, 2, CH_2CO), 6.83 (m, 2, ring CH), and 6.38 ppm (s, 3, OCH_3).

Anal. Calcd for $C_{29}H_{44}N_4O_3$: C, 70.13; H, 8.93; N, 11.28. Found: C, 70.68; H, 9.00; N, 11.13.

Adduct **3** (0.65 g, 92%) was prepared by reaction of TCNEO (0.20 g) with methyl brassidate (0.53 g) (methyl *trans*-13-docosenoate): ir (neat) 2250 ($C{\equiv}N$), 1730 ($C{=}O$), 1115, 1068, 1010 cm^{-1}; nmr (CCl_4) τ 9.12 (t, 3, CH_3), 7.90–8.90 (m, 34, CH_2), 7.79 (t, 2, CH_2CO), 7.22 (m, 2, ring CH), and 6.42 ppm (s, 3, OCH_3).

Anal. Calcd for $C_{29}H_{44}N_4O_3$: C, 70.13; H, 8.93; N, 11.28. Found: C, 70.36; H, 8.95; N, 11.21.

Chromatography of adduct **3** and in particular of adduct **2** on thin layers of silica gel revealed that the adducts react with silica gel.

2,5-Dicyano-2,5-dicarbomethoxy-3-(11-carbomethoxyundecyl)-4-octyltetrahydrofurans (**4** and **5**).—The erucate adduct **2** (0.332 g), chilled in an ice bath, was mixed with 10 ml of 5% hydrogen chloride in methanol. The mixture became homogeneous after about 10 min; then it was held at room temperature for 20 hr. Volatile solvent was removed *in vacuo*, water (5 ml) was added, and the product was extracted with four 5-ml portions of ether. The solvent was removed *in vacuo* to give 0.332 g of **4**. Chromatography on silica gel and two treatments with charcoal gave 0.238 g of **4**: ir (neat) 1750 ($C{=}O$, broad), 1092, 1070, 797 cm^{-1}; nmr (CCl_4) τ 9.10 (t, 3, CH_3), 8.0–8.9 (m, 34, CH_2), 7.76 (t, 2, CH_2CO), 7.20 (m, 2, ring CH), 6.39 (s, 3, OCH_3) and 6.09 ppm (s, 6, OCH_3).

Anal. Calcd for $C_{31}H_{50}N_2O_7$: C, 66.16; H, 8.96; N, 4.98. Found: C, 65.34; H, 8.83; N, 4.96.

The brassidate adduct **3** (0.193 g) was esterified as above to give 0.198 g of **5**. Chromatography on silica gel gave 0.132 g of pure **5**: ir (neat) 1750 ($C{=}O$, broad), 1120, 1075, 1045, 815, 790, 780 cm^{-1}; nmr (CCl_4) τ 9.12 (t, 3, CH_3), 8.0–9.0 (m, 34, CH_2), 7.78 (t, 2, CH_2CO), 7.37 (m, 2, ring CH), 6.40 (s, 3, OCH_3), and 6.08 ppm (s, 6, OCH_3).

Anal. Calcd for $C_{31}H_{50}N_2O_7$: C, 66.16· H, 8.96; N, 4.98. Found: C, 67.01; H, 9.06; N, 4.84.

***trans*-3,4-Dimethyl-2,5-dicyano-2,5-dicarbomethoxytetrahydrofuran** (**8**).—*trans*-3,4-Dimethyl-2,2,5,5-tetracyanotetrahydrofuran (**6**, 0.124 g) was let stand with methanol containing 5% hydrogen chloride as described before. The crude product (0.141 g) was chromatographed on silica gel. Selected fractions were combined to give 0.134 g of pure **8**: mp 111.5–114°; ir (Fluorolub mull) 1770 and 1745 ($C{=}O$), 1050, 1028, 812 cm^{-1}; nmr ($CDCl_3$) τ 8.63 (m, 6, CH_3), 7.41 (m, 2, CH), and 6.03 ppm (s, 6, OCH_3).

Anal. Calcd for $C_{12}H_{14}N_2O_5$: C, 54.13; H, 5.30; N, 10.52. Found: C, 54.33; H, 5.48; N, 10.54.

2,5-Dicyano-2,5-dicarbomethoxytetrahydrofuran (**9**).—2,2,5,5-Tetracyanotetranydrofuran (**7**, 0.168 g) was let stand with methanol containing 5% hydrogen chloride as described previously. The crude product (0.203 g) was purified by silica gel chromatography to give selected fractions of pure **9** (0.144 g): ir (neat) 1760 (broad, $C{=}O$), 1089, 1049, 796 cm^{-1}; nmr ($CDCl_3$) τ 7.14 (s, 4, CH_2) 6.06 and 6.03 ppm, major band (2s, 6, OCH_3).

Anal. Calcd for $C_{10}H_{10}N_2O_5$: N, 11.76. Found: N, 10.77.

2,5-Dicyano-2,5-dicarbamoyl-3-(11-carbomethoxyundecyl)-4-octyltetrahydrofuran (**10** and **11**).—Erucate adduct **2** (0.314 g) was mixed with 5 g of 30–60 mesh silica gel and 1.0 g of water, and then left for 18 hr. The product was fractionated on a silica gel column. Similar fractions were combined and then decolorized in an acetone slurry of charcoal. Decolorized **10** (0.238 g, 70%) was further purified by silica gel chromatography to give 0.120 g of pure amorphous solid. The solid, which was opalescent to transparent on the melting point block, became more transparent as the temperature increased and fluid at 72.5°: ir ($CHCl_3$) 3509, 3479, 3400, 3330, 3284, 3170, 1710 (broad, $C{=}O$), 1590, 1082 cm^{-1}; nmr ($CDCl_3$) τ 9.12 (t, 3, CH_3), 7.9-8.9 (m, 34, CH_2), 7.69 (t, 2, CH_2CO), 7.31 (m, 2, ring CH), 6.32 (s, 3, OCH_3), 2.25 and 2.89 ppm [2s (broad), 4, NH_2].

Anal. Calcd for $C_{29}H_{48}N_4O_5$: C, 65.38; H, 9.08; N, 10.52. Found: C, 65.91; H, 9.27; N, 10.36.

The brassidate adduct **3** (0.211 g) was mixed with silica gel as above except that the contact time was 120 hr. Tlc of the products revealed six spots. The major material (**11**, 0.106 g, 47%) was isolated by chromatography on silica gel. One additional fractionation gave selected fractions (0.042 g) of pure **11**. The nearly transparent amorphous solid became rapidly fluid at 103°: ir ($CHCl_3$) 3510, 3480, 3397, 3332, 3292, 3176, 1720 (broad, $C{=}O$), 1592, 1117, 1072, 1028 cm^{-1}; nmr ($CDCl_3$) τ 9.12 (t, 3, CH_3), 8.05–8.95 (m, 32, CH_2), 7.94 (m, 2, CH_2), 7.71 (t, 2, CH_2CO), 7.34 (m, 2, ring CH), 6.36 (s, 3, OCH_3), and 3.31, 2.57, 2.20 ppm [3s (broad), 3, NH_2].

A small sample (0.011 g) of product **12**, which has a higher R_f than **11**, was isolated from some chromatographic fractions as a semisolid: ir (neat) 3440, 3352, 3290, 3188, 2247 ($C{\equiv}N$), 1720 (broad $C{=}O$), 1594, 1114, 1065, 1020 cm^{-1}; nmr ($CDCl_3$) τ 9.12 (t, 3, CH_3), 8.05–8.90 (m, 32, CH_2), 7.97 (m, 2, CH_2), 7.00–7.82 [overlapping m and t (7.70), 4, ring CH and CH_2CO], 6.36 (s, 3, OCH_3), 3.90 and 3.62 ppm [2s (broad), 2 (1.6), NH_2].

***trans*-3,4-Dimethyl-2,5-dicyano-2,5-dicarbamoyltetrahydrofuran** (**13**).—*trans*-3,4-Dimethyl-2,2,5,5-tetracyanotetrahydrofuran (**6**, 0.114 g) was stored with silica gel as described before. Chromatography on a silica gel column gave 0.126 g of **13**: mp 197–199° with some sublimation beginning at 180°; ir (Fluorolub mull) 3470, 3445, 3335, 3255, 3190, 1710, 1685, 1590, 1064, 1040, 1010, 803, 770 cm^{-1}; nmr ($CD_3C{\equiv}N$) τ 8.66 (m, 6, CH_3), 7.56 (m, 2, CH), 3.55, 3.05, 2.44 ppm [3s (broad), 4, NH_2].

Anal. Calcd for $C_{10}H_{12}N_4O_3$: C, 50.84; H, 5.12; N, 23.72. Found: C, 50.82; H, 5.43; N, 23.81.

Registry No.—**2**, 20407-00-5; **3**, 20462-29-7; **4**, 20407-01-6; **5**, 20407-02-7; **8**, 20407-03-8; **9**, 20407-05-0; **10**, 20407-07-2; **11**, 20407-10-7; **12**, 20407-11-8; **13**, 20407-12-9.

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