Diels–Alder Reactions of α-Terpinene with α,β-Unsaturated Nitriles

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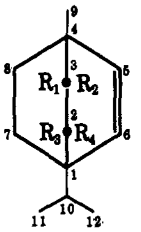
The addition of acrylonitrile, fumaronitrile, and tetracyanoethylene to α-terpinene was investigated. The four possible acrylonitrile adducts and the two possible fumaronitrile adducts were isolated and their structures (III–VIII) were established, chiefly on the basis of differences in long-range shielding effects in the n.m.r. spectra. The relative yields of III–VI were slightly altered by changes in reaction temperature between 80 and 300° or by changes in the ratio of reactants, but the order *exo*-2-cyano > *endo*-2-cyano > *exo*-3-cyano ⩾ *exo*-2-cyano was unchanged. The isomers did not rearrange under conditions used to prepare them.

As part of a continuing program aimed at producing new chemical intermediates from terpenes, the Diels–Alder adducts of α-terpinene (I), 1-isopropyl-4-methyl-1,3-cyclohexadiene) are of interest. α-Terpinene is obtained by acid isomerization of α-pinene[3] or by dehydration of α-terpineol,[4] both of which are commercially available. Maleic anhydride and quinone adducts of α-terpinene have been described,[5] but there have been no investigations of the stereochemistry of its reaction with unsymmetrically substituted dienophiles. In fact, neither Martin and Hill[6] nor Woodward and Katz[7] give any example of the reaction of a 1- or 4-substituted 1,3-cyclohexadiene with an unsymmetrically substituted dienophile in their extensive reviews of the stereochemistry of the Diels–Alder reaction.

The present investigation was concerned with the adducts of α-terpinene with acrylonitrile (II), fumaronitrile, and tetracyanoethylene. The addition of II to I occurred slowly at reflux temperature but readily at 200° in a closed system. Gas–liquid chromatography of the product using either polar or nonpolar columns gave four major components, designated hereafter as AN-1 to 4 in order of emergence. Elemental analysis and infrared spectra established that these were the expected four isomeric 1:1 adducts.

Fumaronitrile did not add to I readily at room temperature but did when the temperature was raised to about 150°. Gas–liquid chromatography of the product using a 2500-plate column gave only a single peak, but fractional crystallization of the chromatographed or distilled product yielded about 10% of a 1:1 adduct, m.p. 107° (FN-H), and about 30% of the isomeric adduct, m.p. 49–51° (FN-L), still containing a substantial amount of FN-H. Gas–liquid chromatography of the two solids gave a slightly longer retention time (α = 1.03) for FN-H than for FN-L and a 6500-plate column gave sufficient separation of the two isomers for semiquantitative analysis of mixtures. The best sample of FN-L obtained by preparative g.l.c. and fractional crystallization was about 85–90% pure.



III, $R_1 = R_2 = R_4 = H$; $R_3 = CN$
IV, $R_2 = R_3 = R_4 = H$; $R_1 = CN$
V, $R_1 = R_2 = R_3 = H$; $R_4 = CN$
VI, $R_1 = R_3 = R_4 = H$; $R_2 = CN$
VII, $R_2 = R_3 = H$; $R_1 = R_4 = CN$
VIII, $R_1 = R_4 = H$; $R_2 = R_3 = CN$
IX, $R_1 = R_2 = R_3 = R_4 = CN$

The tetracyanoethylene adduct (IX) formed readily at room temperature and was readily purified.

As might be expected, assignment of the proper structures (III–VI) to AN-1 to 4 posed some problems. The epimeric pairings were determined without difficulty. Hydrogenation of AN-1 or 3 yielded a single saturated amine or nitrile (AN-1H), depending on the conditions, while AN-2 or 4 yielded another saturated nitrile (AN-2H) and amine. The similarity in relative emergence times suggested that AN-1 and 2 had one configuration (*exo* or *endo*), while AN-3 and 4 had the opposite configuration. Similarities in the infrared spectra of AN-1 and 2 and of AN-3 and 4 in the 14–15-μ region also supported these pairings. Attempts to establish which pair was *endo* by conversion through the acids to the lactones were unsuccessful. Alkaline hydrogen peroxide converted the nitriles to the corresponding amides but the yields were poor, especially in the case of the solid isomers. More vigorous hydrolysis led to epimerization, as has been observed in other instances.[8] Alder, *et al.*,[9] noted that the acrylonitrile–cyclohexadiene adduct having the higher boiling and melting points also had the higher frequency olefinic hydrogen bending band near 14 μ and assigned the *endo* configuration to this isomer by analogy to the corresponding cyclopentadiene adducts. On this basis, the higher boiling AN-3 and 4 with out-of-plane bending bands at 702 and 705 cm.$^{-1}$, respectively, would be assigned the *endo*-CN configuration and AN-1 and 2 with bands at 690 and 692 cm.$^{-1}$ would be *exo*-CN. However, the significance of this correlation is weakened by the fact that the higher melting, higher boiling fumaronitrile adduct (FN-H), which must contain both *exo* and *endo* cyano groups, also has its out-of-plane bending band at higher frequency than the one in FN-L.

Since the positional isomers are obtained in about a 3:2 ratio it is obvious that there is no strong directive effect due to differences between the methyl and isopropyl groups. Meek and Ragsdale[10] claim that the strong *ortho* orientation in the piperylene–acrylonitrile adducts is due to the polarizations resulting from inductive and hyperconjugative effects in the diene and a mesomeric effect in the acrylonitrile. Since the induc-

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[2] Use of a company or product name by the department does not imply approval or recommendation of the product to the exclusion of others which may also be suitable.

[3] J. L. Simonsen, "The Terpenes," Vol. 1, 2nd Ed., Cambridge University Press, London, 1947, p. 174.

[4] Oil, Paint and Drug Report, Annual Buyer's Directory Issue, Schnell Publishing Co. Inc., New York, N. Y., 1963, pp. 1222, 1575.

[5] See ref., 3 p. 186.

[6] J. G. Martin and R. K. Hill, *Chem. Rev.*, **61**, 537 (1961).

[7] R. B. Woodward and T. J. Katz, *Tetrahedron*, **5**, 70 (1959).

[8] N. J. Halbrook, R. V. Lawrence, R. L. Dressler, R. C. Blackstone, and W. Herz, *J. Org. Chem.*, **29**, 1017 (1964).

[9] K. Alder, K. Heimbach, and R. Reubke, *Ber.*, **91**, 1516 (1958).

[10] J. S. Meek and J. N. Ragsdale, *J. Am. Chem. Soc.*, **70**, 2502 (1948).

tive effect of the isopropyl group is greater than that of the methyl, while the hyperconjugative effect is less,[11] net polarization of the diene is uncertain and the preferred orientation cannot be predicted on this basis.

When the n.m.r. spectra of the four isomeric acrylonitrile adducts were examined, differences in chemical shifts were observed (Table I). The isolated methyl group in the AN-2 and 4 is deshielded relative to the same group in AN-1 and 3. That this deshielding is due to the proximity of the cyano group is established by the observation of similar deshielding in the two fumaronitrile adducts and the even greater deshielding in the tetracyanoethylene adduct. Hydrogenation of the adducts shifts this band to higher field without change in the effect of the cyano group. Hence, AN-2 and 4 have structures with the cyano group *ortho* to the methyl group (*i.e.*, IV or VI). Proximity of the cyano group exerts a similar but smaller effect on both methyls of the isopropyl group in AN-1 but only on one of them in AN-3. Again the deshielding is increased by additional cyano groups, and the difference in shielding persists in the hydrogenated adducts.

TABLE I

CHEMICAL SHIFTS[a] OF SELECTED PROTONS

Compd.	C-2	C-3	C-5, C-6	C-9	C-11, C-12	Structure
AN-1	2.43 q	. . .	6.06	1.18	1.01 d	III
AN-2	. . .	2.2 m	5.94 d, 6.15 d	1.31	0.95 d	IV
AN-3	2.74 q	. . .	6.09 d, 6.16 d	1.15	0.95 d, 1.01 d	V
AN-4	. . .	2.46 m	6.02 d, 6.25 d	1.35	0.96 d	VI
FN-H	2.97 d	2.56 d	6.21	1.37	1.01 d, 1.04 d	VII
FN-L	2.71	2.75	6.22 d, 6.26 d	1.41	1.05 d, 1.09 d	VIII
AN-1H[b]	2.71 m	. . .	. . .	0.84	0.87 d	
AN-2H[b]	. . .	2.46 m	. . .	0.99	0.82 d	
TCNE[c]	. . .	. . .	6.40	1.68	1.19 d, 1.28 d	

[a] Concentration, 10–20% in CCl_4, with tetramethylsilane as the internal standard, $\delta = 0$; d = doublet, q = quadruplet, m = poorly resolved quadruplet; all bands had the proper area. [b] AN-1H = saturated nitrile from AN-1 or 3, AN-2H = saturated nitrile from AN-2 or 4. [c] Tetracyanoethylene adduct of α-terpinene.

Fraser[12] and Ayer, *et al.*,[13] have pointed out the utility of the difference in shielding of *exo* and *endo* protons in assigning configurations in the bicyclo[2.2.2]octene system, provided such protons can be observed and identified in the spectra. In the present case, well-resolved quadruplets of one proton area typical of the B portion of an intermediately coupled A_2B spectrum[14] occur in the spectra of AN-3 and 4. This band is assigned to methine proton on the carbon bearing the cyano groups on the basis of its low-field position. This assignment is confirmed by the higher field position of the band in AN-4 than in AN-3 due to the shielding by the proximate methyl group. In the spectra of AN-1 and AN-2 the band due to the lowest field nonolefinic proton is not well resolved; so the assignment of this band to the methine proton on the bridge is somewhat arbitrary and the position is only approximate. However, there is no doubt that the methine proton on the bridge appears at higher field in AN-1 and 2 than in AN-3 and 4 and therefore has the *endo* configuration. This assignment is also supported by the shifts in the methine proton absorption on hydrogenation of the double bond. Shielding of the proton decreases in AN-1 and AN-2 and increases in AN-3 and AN-4. It should be noted that the magnitude of the shift is much greater for the *endo* protons, in contrast to the greater shift for the *exo* protons observed by Fraser[12] in the bicyclo[2.2.1]heptenes. Hence, AN-1 to AN-4 have structures III–VI, respectively. The slight deshielding of the olefinic protons in the *endo* cyano isomers relative to their *exo* epimers also confirms these assignments.

Structural assignment is quite straightforward in the case of the two fumaronitrile adducts. Structure VII has methine protons at the same positions as IV and V while in VIII they correspond to those in III and VI. The relative shielding in the four positions should remain the same although the splitting pattern will be changed from A_2B to AB and there will be a general downfield shift due to the added cyano group in VII and VIII. Hence, one of the two methine protons in VII should appear as a well-resolved doublet at relatively low field while the two in VIII should appear close together at higher field. As shown in Table II, FN-H has a single proton doublet at δ 2.97 and a second less well-resolved one at 2.56 and hence has structure VII. In the n.m.r. spectrum of FN-L, the corresponding protons give two closely spaced doublets at intermediate field as expected for structure VIII.

TABLE II

VARIATION OF COMPOSITION OF α-TERPINENE (I) ACRYLONITRILE (II) ADDUCTS WITH REACTION CONDITIONS

	Composition of isomer, %[a]											
	III			IV			V			VI		
Temp.,	I–II ratio[b]			I–II ratio			I–II ratio			I–II ratio		
°C.	0.1	1	10	0.1	1	10	0.1	1	10	0.1	1	10
80[c]	34	35	38	13	14	16	31	30	27	22	21	19
200[d]	33	34	36	16	17	18	30	28	27	22	21	19
300[e]	32	33	34	18	19	19	29	28	27	21	20	20

[a] By g.l.c. with normalization of the peak areas for the four isomers. [b] Molar ratio. [c] 92 hr., single run. [d] 30–60 min., average of three runs; standard deviations: III, 0.8; IV, 0.2; V, 0.5; VI, 0.3. [e] 30 sec., average of two runs; standard deviations: III, 0.2; IV, 0.1; V, 0.3; VI, 0.3.

In the case of the acrylonitrile adducts the assignments based on n.m.r. are in accord with those derived from other physical properties. It should be noted that the *endo* epimer predominates slightly at C-3, as expected, while the *exo* epimer predominates at C-2. Predominance of the *exo*-2 isomer is attributed to the steric effect of the isopropyl group. In the preferred conformation of α-terpinene, the two methyl groups will bracket the double bond and tend to repel the entering *endo* cyano group. These steric influences are even more pronounced in the fumaronitrile adducts with the *exo*-2-*endo*-3-dicyano isomer predominating by a 2:1 ratio.[15]

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(11) J. W. Baker, "Electronic Theory of Organic Chemistry," Oxford University Press, London, 1958, p. 58.

(12) R. R. Fraser, *Can. J. Chem.*, **40**, 78 (1962).

(13) W. A. Ayer, C. E. McDonald, and J. B. Stothers, *ibid.*, **41**, 1113 (1963).

(14) P. L. Corio, *Chem. Rev.*, **60**, 363 (1960).

(15) If the Diels–Alder reaction proceeds by a two-step mechanism, a possible explanation of the greater selectivity with fumaronitrile lies in the fact that two different first steps are possible for each isomeric adduct. In the case of acrylonitrile, one of these always involves the unsubstituted carbon. From steric considerations one would expect this possibility to account for nearly all of V, most of III, over half of IV, and perhaps half of VI. No strong *exo* or *endo* directing influences would be expected in these reactions. The alternate initial steps, involving asymmetry at both reacting centers, would be subject to directive effects and the portion of the total product formed by these four reactions would have a quite different (more selective) isomeric distribution than the whole product. In the case of fumaronitrile, only the second, more selective set of initial steps is possible. When the second, intramolecular step involves two unsymmetrical centers, it will also be subject to similar but weaker steric effects. FN-L has the more favorable configuration at both positions.

Since increased reaction temperature has been widely reported to increase the *exo–endo* isomeric ratio,[5,9] it was of interest to see whether the ratio of III–V could be increased in this way. As shown in Table II, the ratio of IV–VI increased normally with temperature, but the ratio of III–V remained constant or decreased slightly, presumably because the steric effect of the isopropyl group is reduced at higher temperatures. The individual isomers did not undergo detectible isomerization when they were heated for several hours at 200° or several minutes at 300°, indicating that the observed temperature effects were not due to isomerization. When the reaction time at 300° was extended to 18 hr., the product distribution was drastically altered (III–IV–V–VI = 14:36:10:40) and several unidentified peaks appeared in the gas chromatogram. Similarly, heating of the individual isomers for 2 hr. at 300° led to isomerization, hydrocarbon formation, and other side reactions. Qualitatively, III was least stable followed by V, IV, and VI.

As indicated in Table II, the molar ratio of reactants was also varied and found to influence the product distribution. The *exo–endo* ratio at both positions was increased by increasing proportions of the diene, but the ratio of structural isomers was not affected. No satisfactory explanation of this effect can be offered at this time. Further work with other systems will be required to establish its generality.[16]

Experimental[17,18]

Preparation of α-Terpinene–Acrylonitrile Adducts. A. Preparative Scale.—A bomb containing 105 ml. of α-terpinene (86.7 g., 0.64 mole) and 45 ml. of acrylonitrile (36.1 g., 0.68 mole) was heated to 200° and maintained at that temperature for 2 hr. The cooled reaction mixture was poured into 300 ml. of hexane. Insoluble polymeric material was filtered off, and the adducts were isolated by fractional distillation. Gas-liquid chromatography of the crude product (96 g., 79% yield) gave four major peaks having normalized areas of 34, 17, 28, and 21 in order of emergence. As shown in Table III, various substrates gave similar relative emergence times for the four isomers.

B. Micro Scale.—In a typical experiment, 16 μl. of α-terpinine and 6.6 μl. of acrylonitrile (0.1 mmole each) were delivered to a capillary melting point tube with micro syringes and the capillary was sealed. After thorough mixing of the contents, the tube was inserted in the injection port of a gas chromatograph preheated to 300°, allowed 10 sec. to reach temperature, and heated for an additional 30 sec. The tube was removed and quenched in cold water, and the contents were analyzed by g.l.c. Runs with 9 *M* excess of each reactant were made in the same way. Reactions at 80 and 200° were run in the oven of the gas chromatograph, with the three concentrations being run simultaneously. Since the variations in composition were small, the experiments at 300 and 200° were repeated. Yields for the equimolar runs were estimated from the g.l.c. sample size and total peak areas using pure adduct as the standard: 80° = 20%, 200° = 65%, 300° = 40%. Under the same conditions, use of a large excess of I or II gave a nearly quantitative yield at 200° based on the limiting reagent and about doubled the yields at the other temperatures.

TABLE III

Substrate	AN-1[a]	AN-2[b]	AN-3[b]	AN-4		
Craig[c]	4	1.17	1.55	1.77[b]	1.14[d]	1.51[e]
MPE[f]	4	1.12	1.26	1.38	1.10	1.23
Vers[g]	7	1.23	1.54	1.84	1.19	1.50
20M[h]	18	1.16	1.39	1.58	1.14	1.36
Cast[i]	7	1.19	1.45	1.67	1.15	1.40

[a] Retention time, min. [b] Relative retention time, AN-1 = 1. [c] Butanediol succinate, 20%, 10 ft., 175°. [d] AN-2 = 1. [e] AN-3 = 1. [f] Polymetaphenyl ether, 20%, 10 ft., 275°. [g] Versamide-900, 2%, 10 ft., 120°. [h] Carbowax 20M, 30%, 15 ft., 200°. [i] Castorwax, 2%, 10 ft., 130°.

Separation of the Isomers.—Neither fractional distillation nor crystallization alone gave adequate separation of the four isomers. Separation was achieved by fractional distillation through a 3-ft. column packed with protruded metal packing, boiling range 65–85° (0.05 mm.), followed by partial freezing of the fractions in Dry Ice and filtration. In this manner, each isomer could be obtained in about 90% purity.

1-Isopropyl-*exo*-2-cyano-4-methylbicyclo[2.2.2]-5-octene (III).—Several recrystallizations of AN-1 from hexane and from acetone gave dense crystals: m.p. 40°; b.p. 82° (1 mm.); infrared ν_{max} 690 vs, 715 w, 2230 s cm.$^{-1}$.

Anal. Calcd. for $C_{13}H_{19}N$: C, 82.48; H, 10.12; N, 7.40. Found: C, 82.65; H, 10.18; N, 7.36.

1-Isopropyl-*exo*-3-cyano-4-methylbicyclo[2.2.2]-5-octene (IV).—Preparative-scale g.l.c. of AN-2 using a 20 ft. × $^{3}/_{8}$ in. butanediol succinate (20%) column gave IV substantially free from other isomers but slightly discolored by column bleed off. Simple vacuum distillation gave a colorless mobile liquid: b.p. 85° (1 mm.); d^{20}_{4} 0.940; n^{20}_{D} 1.4880; infrared ν_{max} 690 vs, 720 w, 2230 s cm.$^{-1}$.

Anal. Found: C, 82.62; H. 10.19; N, 7.61.

1-Isopropyl-*endo*-2-cyano-4-methylbicyclo[2.2.2]-5-octene (V).—Recrystallization of AN-3 in the same way as AN-1 yielded needles: m.p. 57°; b.p. 90° (1 mm.); infrared ν_{max} 700 vs, 733 s, 2230 s cm.$^{-1}$.

Anal. Found: C, 82.30; H, 9.97; N, 7.30.

1-Isopropyl-*endo*-3-cyano-4-methylbicyclo[2.2.2]-5-octene (VI).—Purification of AN-4 in the same manner as AN-2 yielded a colorless mobile liquid: b.p. 92° (1 mm.), d^{20}_{4} 0.9525, n^{20}_{D} 1.4889, infrared ν_{max} 698 vs, 738 s, 2230 s cm.$^{-1}$.

Anal. Found: C, 82.65; H, 10.18; N, 7.36.

Hydrogenation of III–VI. A. In Acetic Acid.—Catalytic reduction of 0.01-mole samples (1.89 g.) of the four isomers in 10 ml. of glacial acetic acid with 0.1 g. of PtO_2 resulted in the absorption of 0.03 mole of hydrogen in each case. Most of the acetic acid was distilled, and the residue was dissolved in ether. The amines were freed by aqueous alkali and taken up in ether; the amine hydrochlorides were precipitated by adding concentrated HCl dropwise. Infrared spectra showed that the two solid isomers gave one amine and the two liquid isomers gave another. Recrystallized from ethanol, the salts did not melt but decomposed slowly at about 225 and 210° for the salts from solid and liquid isomers, respectively, with slight decomposition starting in all the salts at or near 150°.

B. In Ethyl Acetate.—Reduction of the four isomers was repeated as above except that 10 ml. of ethyl acetate replaced the acetic acid as solvent and only slightly more than 1 mole of hydrogen/mole of nitrile was absorbed. Gas-liquid chromatographic analysis of the products after removal of amines with HCl showed a large and a very small peak in each case. The small peaks resulted from the use of starting materials having traces of other isomers present.

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[16] It should be noted that the differences in activation energies for the transition states leading to the various isomeric products are all considerably less than 1 kcal/mole.[5] Hence, the observed changes in isomeric ratios due to reaction conditions require only extremely small changes in these differences.

[17] The α-terpinene used in this work was supplied through the courtesy of Newport Industries, Pensacola, Fla., and The Glidden Co., Jacksonville, Fla. It was used without purification for the preparative-scale reactions but was purified by preparative-scale g.l.c. through Carbowax 20M[2] and stabilized with ditertiary butylhydroquinone for use in the small-scale studies of the effects of reaction conditions. The acrylonitrile was purified and stabilized in the same way for the small-scale runs but used as received for the preparative-scale work. Fumaronitrile and tetracyanoethylene were used as received.

[18] All temperature readings given are uncorrected. Melting points were taken in an open capillary in a Thomas-Hoover apparatus. Microanalyses were performed by Galbraith Laboratories. Infrared spectra were recorded on a Perkin-Elmer Model 21 spectrophotometer with NaCl optics; solids were run as mulls in mineral oil. G.l.c. analyses were carried out on a Wilkens Model 600 gas chromatograph using a 15 ft. × $^{1}/_{8}$ in. Carbowax 20M (30%) column at a column temperature of 200° for the acrylonitrile adducts and a 25 ft. × $^{1}/_{4}$ in. butanediol succinate (2%) column for the fumaronitrile adducts. Preparative separations were made on an F and M Model 500 or Wilkens Autoprep. Chromosorb W, 60–80 mesh, was the support in all cases. N.m.r. spectra were determined with a Varian Associates A-60 spectrometer using 10–20% solutions in carbon tetrachloride with tetramethylsilane as an internal standard.

Pure samples of the saturated nitriles were obtained by collecting the respective chromatographic peaks, then distilling at reduced pressure. The isomer AN-1H, $d^{24}{}_4$ 0.9544, $n^{20}{}_D$ 1.4842, produced by the reduction of the original 1 and 3 isomers preceded the other AN-2H, $d^{24}{}_4$ 0.9506, $n^{20}{}_D$ 1.4825, from the chromatograph. Both isomers were liquids which did not solidify in Dry Ice.

Anal. Calcd. for $C_{13}H_{21}N$: C, 81.60; H, 11.06; N, 7.32. Found for AN-1H: C, 81.44; H, 10.86; N, 7.52. Found for AN-2H: C, 81.82; H, 11.14; N, 7.60.

Hydrolysis of III–VI. A. With Base.—A solution of 3.8 g. of III and 20 g. of KOH in 30 ml. of diethylene glycol was refluxed for several days. The cooled solution was poured into 200 ml. of water, extracted with ether, acidified, and re-extracted with ether. The acidic extracts yielded 1.4 g. of acid, m.p. 106–110°. After removal of ether the neutral product was extracted with cold hexane to remove unreacted III leaving 1.1 g. of amide, m.p. 106–125°. Similar treatment gave a low yield of acid, m.p. 106–110°, from V and low yields of solid amides and liquid acids from IV and VI. The broad melting ranges and the infrared spectra of the products indicate that they were all mixtures.

The products obtained in very low yields under milder conditions, *e.g.*, refluxing with aqueous or ethanolic base, also appeared to be mixtures.

B. Attempted Hydrolysis with Acids.—All attempts to hydrolyze the adducts with acid were unsuccessful.

C. With Alkaline Hydrogen Peroxide.—The four isomeric amides were successfully prepared by stirring 1.89 g. (0.1 mole) of each nitrile with a solution of 0.8 g. of KOH and 10 ml. of 50% H_2O_2 in 50 ml. of ethanol for several hours, adding 10 ml. more H_2O_2 and stirring for 3 days. The insoluble amides were filtered off, washed with cold hexane to remove adhering nitrile, and recrystallized from hexane. Yields and melting points were for III, trace, 146–147°; IV, 31%, 106–108°; V, trace, 102–104°; VI, 34%, 113–115°. Only traces of acids were obtained by treatment of the amides with nitrous acid.

Preparation of α-Terpinene–Fumaronitrile Adducts. A.—A solution of 7.8 g. (0.1 mole) of fumaronitrile in 32 ml. (0.2 mole) of α-terpinene was refluxed for 2 hr. After removal of the excess terpinene at 5 mm. the product was distilled to yield 17.9 g. (83%) of colorless liquid, b.p. 95–112° (0.03 mm.). Crystallization from ethanol at Dry Ice temperature yielded a series of fractions which were recrystallized from ether, also at Dry Ice temperature. The least soluble major fraction (1.7 g.), m.p. 100–103°, was recrystallized from hexane to yield VII, m.p. 107°, infrared ν_{max} 711 vs and 2230 s cm.$^{-1}$.

Anal. Calcd. for $C_{14}H_{18}N_2$: C, 78.46; H, 8.46; N, 13.07. Found: C, 78.68; H, 8.46; N, 13.13.

The two largest fractions (6 g. total) were chiefly the other isomer VIII, m.p. 49–51°, infrared ν_{max} 706 vs and 2230 s cm.$^{-1}$. Infrared and n.m.r. spectra indicated that VII was still present, but recrystallization and chromatography using columns effective for III–VI failed to improve the melting point.

B.—Equimolar amounts (0.06 mole) of α-terpinene, purified by g.l.c., and fumaronitrile were heated to reflux for about 30 sec., during which time the temperature rose to about 225°, all the fumaronitrile dissolved, and the mixture colored slightly. The reaction mixture was cooled and analyzed by g.l.c.[18] Although the column had an efficiency of 6400 plates (calculated for pure VII, retention time, *ca.* 1 hr.), the peaks overlapped badly (α for VII–VIII = 1.03).[19] Estimation of the peaks by triangulation, assuming equal peak widths, indicated the presence of 67% VIII. The crude product was freed of starting materials and impurities by chromatographing through a 10 ft. × $^3/_8$ in. butanediol succinate (20%) column. No apparent separation of VII and VIII occurred but the first one-third of the peak was collected separately. Each cut was diluted with hexane and allowed to stand at room temperature. The second cut partially solidified overnight, but the first cut yielded only a small amount of solid after several days, indicating that some separation had been achieved. The soluble portions of the two cuts were rechromatographed through a 20 ft. × $^1/_4$ in. column with the same packing. About 0.67 of the peak due to VIII was collected. The peak due to VII appeared as a shoulder. The collected material was freed from bleed-off by passage through a 2-ft. 20% SE-30 column and was then recrystallized from pentane at Dry Ice temperature: m.p. 49–50°, 85% VIII by g.l.c., infrared ν_{max} 706 vs and 2230 s cm.$^{-1}$.

Anal. Calcd. for $C_{14}H_{18}N_2$: C, 78.46; H, 8.47; N, 13.07. Found: C, 78.41; H, 8.58; N, 13.13.

Under magnification, cubic crystals of VIII could be distinguished from needles of VII in the above product. Hand separation yielded a few crystals, m.p. 52–53°.

Preparation of α-Terpinene–Tetracyanoethylene Adduct.—A 5% solution of tetracyanoethylene in methylene chloride was added dropwise at room temperature to 0.3 g. of α-terpinene until it no longer gave a deep blue color. The product was diluted with 10 ml. of isooctane and the methylene chloride was boiled off. On cooling, a pale blue solid, 0.28 g., m.p. 171–174°, separated and was collected. Successive recrystallizations from benzene–isooctane 1:1 and 3:1 yielded a colorless product: m.p. 178–178.5°; infrared ν_{max} 724 s cm.$^{-1}$, with little or no CN stretching band at 2230 cm.$^{-1}$.[20]

Anal. Calcd. for $C_{16}H_{16}N_4$: C, 72.70; H, 6.10; N, 21.20. Found: C, 72.60; H, 6.23; N, 21.22.

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(19) Use of DEGS, MPE, Versamide-900, or silicone gum SE-30 column gave similar low values for α.

(20) J. A. Wells, N. J. Halbrook, R. V. Lawrence, and R. T. O'Connor (*Appl. Spectry.*, in press) have observed the absence of this band in TCNE adduct of levopimaric acid.