TABLE I

CARBAMOYLPHOSPHINES AND THEIR OXIDES

Product	M.p., °C.	Solvent	Yield, %	Calcd., %				Found, %			
				C	H	N	P	C	H	N	P
$(C_6H_{11})_2PCONH_2$	121–124	Crude[a]	80	64.48	10.03			64.07	9.93		
$(C_6H_{11})_2P(O)CONH_2$	177–179	C_6H_{14}–MeOH	. . .	60.68	9.40	5.44	12.04	60.36	9.61	5.55	12.19
$(C_6H_5)_2PCONH_2$	115–116	C_6H_{14}–C_6H_6	26[b]	68.12	5.28	6.11	13.52	68.04	5.59	5.9	13.45
$(C_6H_5)_2P(O)CONH_2$	190–191	C_6H_{14}–C_6H_6	15[b]	63.67	4.93	5.71		63.32	5.48	5.76	
$(NCCH_2CH_2)_2P(O)CONH_2$	179–180	MeOH	34	42.21	5.06	21.10	15.55	42.52	4.92	20.81	15.85
$(n\text{-}C_4H_9)_2P(O)CONH_2$	177–178	C_6H_6	34[c]	52.67	9.82	6.82		52.46	9.86	6.86	
$C_6H_5P(CONH_2)_2$	159–161	MeOH	14			14.28	15.78			14.47	15.75
$C_6H_{11}P(H)CONH_2$	Oil	Crude[a]	57[b]								
$C_6H_{11}P(H)(O)CONH_2$	157–159	*i*-PrOH	23[b]	47.99	8.06		17.68	47.79	8.03		17.30

[a] Characterized as the oxide. [b] The oxide and the phosphine were both isolated. [c] Nonaqueous addition.

in situ has been found to react similarly with primary and secondary phosphines (but not with phosphine itself) to form unsubstituted mono- and dicarbamoylphosphines (**2**). Reactivity of the carbamoylphosphines toward atmospheric oxygen varied with the

$$R_xPH_{3-x} + (3 - x)R'NCO \longrightarrow \underset{\mathbf{1}}{R_xP(CONHR')_{3-x}}$$

$$x = 0, 1, 2$$

$$R_xPH_{3-x} + (3 - x)HOCN \longrightarrow \underset{\mathbf{2}}{R_xP(CONH_2)_{3-x}} \xrightarrow{[O]} \underset{\mathbf{3}}{R_xP(O)(CONH_2)_{3-x}}$$

$$x = 1, 2$$

substituent: alkyl > aryl ⩾ alicyclic. Alkyl derivatives, such as butyl and 2-cyanoethyl, were isolable only as oxides (**3**), while cyclohexyl and phenyl derivatives formed oxides upon attempted recrystallization or prolonged exposure to air.

Experimental Section

The liberation of cyanic acid from potassium cyanate can be conveniently effected in an aqueous or nonaqueous medium, as required by the water solubility of the phosphine product. In a typical preparation, a concentrated aqueous solution of 5.6 g. (0.07 mole) of potassium cyanate was added in 10 min. under nitrogen to a stirred solution of 7.0 g. (0.035 mole) of dicyclohexylphosphine in 40 g. (0.67 mole) of glacial acetic acid at 70–80°. Heating at reflux was continued until the evolution of cyanic acid ceased, after which the cooled mixture was poured into water to precipitate 6.7 g. (80%) of carbamoyldicyclohexylphosphine. (Additional product in the form of the oxide could be obtained by methanol extraction of the concentrated filtrate, after conversion of the acetate salts present to sulfates with sulfuric acid.) Infrared and elemental analyses of the crude material were satisfactory, but attempted recrystallization from hexane–methanol converted it to the oxide. Reverse addition of excess acetic acid to an acetonitrile slurry of a phosphine and freshly ground potassium cyanate was substituted when the product was appreciably water soluble, as was carbamoyldi-*n*-butylphosphine (Table I).

Completeness of the reaction could be determined by following the reduction or elimination of the P-H absorption and the corresponding appearance of P–CO–NH_2 bands in the infrared spectrum of the products. (Aliphatic and aromatic primary and secondary phosphines absorb at 2320–2275 cm.$^{-1}$.) The P–CO–NH_2 group has infrared bands similar to those of the group C–CO–NH_2, with absorption at 3400–3150 (usually a doublet), NH_2 stretch; 1670–1630, C=O stretch; and 1615–1590 cm.$^{-1}$, NH_2 deformation, when run as a Nujol mull.[4]

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[4] We are grateful to Mr. N. B. Colthup for the spectral assignments.

1,4- and 3,4-Cycloaddition Reactions of 1,1-Diphenyl-1,3-butadiene with Tetracyanoethylene

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Current interest in organometallic additions to conjugated dienes and in the allylic rearrangements of the resulting organometallic systems has prompted us to examine the behavior of 1,1-diphenyl-1,3-butadiene (II) toward other electrophilic addends as well. The finding that diisobutylaluminum hydride adds to II in a 3,4 fashion and that the resulting adduct then rearranges to a 1,4 adduct[2] suggested that other electrophiles might show a similar behavior. In the present study the interaction of 1,1-diphenyl-1,3-butadiene with the potent electrophile, tetracyanoethylene (TCNE), was investigated.

From the experience of other workers, one might expect TCNE to add to II in a 1,2[3] or 3,4 fashion,[4] a 1,4 Diels–Alder fashion,[5] or possibly a Diels–Alder reaction involving the *ortho* positions of the phenyl groups and the 1,2-olefinic linkage.[6] Furthermore, a recent report published during the course of this study reveals that with 4-methyl-1,3-pentadiene 1,2 and 1,4 additions of TCNE can result concurrently.[7] Despite subsequent examination of more than a dozen other dienes, only the normal 1,4 addition of TCNE was observed.[8] Such competing 1,2 and 1,4 additions to dienes are of potential interest in elucidating the detailed mechanism of the Diels–Alder reaction.[8] Of additional value would be a diene system which

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[1] Inquiries should be directed to this author at The Catholic University of America.

[2] J. J. Eisch and G. R. Husk, *J. Organometal. Chem.*, **4**, 415 (1965).

[3] J. K. Williams, D. W. Wiley, and B. C. McKusick, *J. Am. Chem. Soc.*, **84**, 2210 (1962).

[4] A. T. Blomquist and Y. C. Meinwald, *ibid.*, **81**, 667 (1959).

[5] W. J. Middleton, R. E. Heckert, E. L. Little, and C. G. Krespan, *ibid.*, **80**, 2783 (1958).

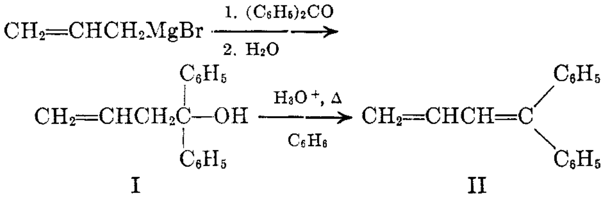
[6] T. Wagner-Jauregg, *Ann.*, **491**, 1 (1931); W. J. Middleton, *J. Org. Chem.*, **30**, 1390 (1965).

[7] C. A. Stewart, Jr., *J. Am. Chem. Soc.*, **84**, 117 (1962).

[8] C. A. Stewart, Jr., *J. Org. Chem.*, **28**, 3320 (1963).

not only underwent both types of addition, but which yielded adducts able to undergo thermal isomerization without decomposition.[9] This paper reports the observation of such competing additions with 1,1-diphenyl-1,3-butadiene (II) and presents preliminary qualitative evidence for the thermal isomerization of the TCNE adducts.

The requisite diene II was synthesized conveniently by the acid-catalyzed dehydration of allyldiphenylcarbinol (I), itself readily obtained from the interaction of benzophenone with allylmagnesium bromide.

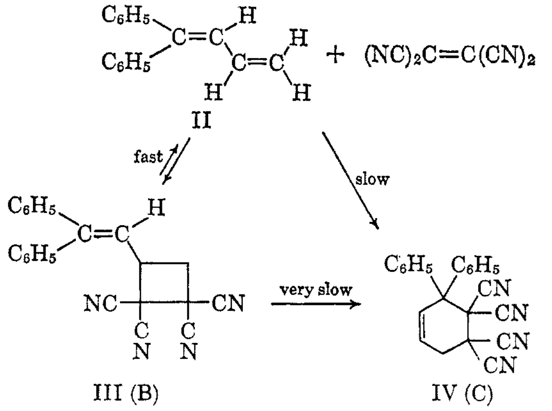


$$CH_2{=}CHCH_2MgBr \xrightarrow[2.\ H_2O]{1.\ (C_6H_5)_2CO} CH_2{=}CHCH_2C(C_6H_5)_2{-}OH \xrightarrow[C_6H_6]{H_3O^+,\ \Delta} CH_2{=}CHCH{=}C(C_6H_5)_2 \qquad (1)$$

I II

Although the preparation of II by the dehydration of propenyldiphenylcarbinol has been reported, the resulting product is an oil at 17.5°.[10] On the other hand, this study showed II to be a solid (m.p. 39°). Spectral and analytical data are in complete accord with this structural assignment.[11] In comparison with other suggested preparations of this diene (II),[10,11] the present method seems to be the one of choice, both as to convenience and yield of pure product. 1,1-Diphenyl-1,3-butadiene proved to be unstable in air at ambient temperatures; over a period of several weeks, it gradually turns into a viscous, orange, apparently polymeric material.

In the treatment of the diene with TCNE in hot benzene solution, smooth adduction occurred to yield both a major (III, m.p. 155°) and a minor (IV, m.p. 200°) product. As demonstrated by elemental analyses and molecular weight estimation, both products proved to be 1:1 adducts of the reactants. Possible structures for these adducts which must be considered are the following: (a) 1,2 addition, leading to 2-allyl-1,1-diphenyl-3,3,4,4-tetracyanocyclobutane (A); (b) 3,4 addition, leading to 1-(2,2-diphenylvinyl)-3,3,4,4-tetracyanocyclobutane (B); (c) 1,4 addition, yielding 5,5-diphenyl-3,3,4,4-tetracyanocyclohexene (C); and (d) Diels–Alder addition involving the *ortho* position and 1,2-ethylenic linkage, yielding 2-allyl-1-phenyl-3,3,4,4-tetracyano-1,2,3,4-tetrahydronaphthalene (D). Structures A and D can be eliminated from consideration, since neither the infrared nor the n.m.r. spectra of III and IV exhibit bands characteristic of the terminal vinyl group (infrared: 910, 990, and 1650 cm.$^{-1}$; n.m.r.: multiplets between δ 4.9 and 5.2). Since III absorbs strongly at 268 mμ in the ultraviolet region and possesses infrared bands characteristic of a phenyl-conjugated C=C stretch (1580 and 1630 cm.$^{-1}$), it appeared to have structure B. In contrast, isomer IV has only end ultraviolet absorption above 230 mμ and only a typical phenyl C=C stretch at 1600 cm.$^{-1}$ in the infrared spectrum. Hence, IV is assigned structure C. Complete corroboration of both these structure assignments was secured by an analysis of the n.m.r. spectra of III and IV obtained in perdeuterioacetone. The spin–spin coupling patterns and the relative proton count are uniquely interpretable in terms of III having structure B and of IV having structure C. The course of the TCNE adduction, therefore, is as shown in eq. 2.



(2)

Two further observations are noteworthy. First, after repeated purification of isomer III, this adduct still developed a distinct yellow color when redissolved in hot benzene. This suggests some redissociation of III into TCNE and the diene.[12] Second, the foregoing observation prompted a test of the thermal isomerization of III into IV by the prolonged heating of III in benzene solution (eq. 2, III → II → IV). Indeed, such treatment did produce some of isomer IV. Future work will attempt to obtain quantitative rate data on the formation and isomerization of 1,1-diarylbutadiene–TCNE adducts. In addition, an attempt will be made to distinguish between the isomerization pathway proposed in eq. 2 and an intramolecular rearrangement of III directly to IV.

Experimental Section

Allyldiphenylcarbinol (I).—Allylmagnesium bromide was prepared in 73% yield (determined by titration of a hydrolyzed aliquot with standard acid) from 73.8 g. (0.61 mole) of allyl bromide and 89.0 g. (3.66 g.-atoms) of magnesium turnings in 160 ml. of anhydrous ether.[13] A solution of 69.0 g. (0.38 mole) of benzophenone in 200 ml. of anhydrous ether was added to the allyl Grignard solution over a period of 30 min. The clear dark solution changed to a cloudy white suspension with the evolution of heat. Stirring was continued for 8 hr., whereupon the reaction mixture was hydrolyzed with a saturated, aqueous ammonium chloride solution. The separated organic layer was dried over anhydrous calcium sulfate. Solvent removal and distillation of the residue through a 25-cm. Vigreux column at reduced pressure afforded 64.8 g. (77%) of the colorless carbinol, b.p. 126–128° (1 mm.), n^{25}D 1.5825 [lit.[14] b.p. 150–155° (3 mm.), b.p. 135–138° (0.5 mm.)]. Characteristic infrared absorptions appeared at 912, 990 ($CH{=}CH_2$), 1650 (C=C), 3500, and 3600 cm.$^{-1}$ (OH). Other prominent bands occurred at 670, 695, 725, 750, 780, 890, 1035, 1050, 1170, 1355, 1455, 1500, 2950, and

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[9] Attempts to interconvert the cyclobutane and cyclohexene adducts of 4-methyl-1,3-pentadiene with TCNE were blocked because of the thermal sensitivity of the former adduct.[7]

[10] H. Normant and P. Maitte, *Bull. Soc. Chim. France*, 951 (1956).

[11] After this synthetic work had been completed (1959), Professor Georg Wittig, Heidelberg, informed us of his preparation of this diene, either by treatment of β-phenylcinnamaldehyde with triphenylphosphine methylene or by the dehydration of the carbinol resulting from β-phenylcinnamaldehyde and methylmagnesium iodide. More recently, this diene has been prepared from benzophenone and γ-dimethylaminopropylmagnesium chloride in a four-step sequence: T. Holm, *Acta Chem. Scand.*, **18**, 2437 (1963).

[12] R. E. Merrifield and W. D. Phillips [*J. Am. Chem. Soc.*, **80**, 2778 (1958)] reported that the yellow charge-transfer complex between TCNE and benzene absorbs at 384 mμ (K = 2.00).

[13] H. Gilman and J. H. McGlumphy, *Bull. Soc. Chim. France*, **43**, 1325 (1928).

[14] (a) M. S. Kharasch and S. Weinhouse, *J. Org. Chem.*, **1**, 227 (1936); (b) J. F. Vozza, *ibid.*, **24**, 720 (1959).

3000 cm.$^{-1}$. The n.m.r. spectrum displayed a sharp singlet at δ 2.47, doublet at δ 2.96, vinyl multiplet between δ 4.8 and 5.8, and aromatic multiplet between δ 7.1 and 7.55.

The foregoing procedure was executed several times with resulting yields of the carbinol in the range 65–75%. A considerable amount of higher boiling residue was always observed. Fractional redistillation of such residues gave a forerun of allyldiphenylcarbinol and a colorless fraction, b.p. 155–160° (0.5 mm.). This latter fraction has been identified as 1,1-diphenyl-6-hepten-1-ol.[15]

1,1-Diphenyl-1,3-butadiene (II).—Since this diene undergoes resinification easily, the dehydration of the carbinol and the purification of the diene should be done over as short a period as is feasible. Once the diene has crystallized, it should be stored under nitrogen in a refrigerator. Discoloration and liquefaction indicate the onset of decomposition.

A solution of 22.4 g. (0.10 mole) of allyldiphenylcarbinol in 100 ml. of benzene was heated for 2 hr. under reflux in the presence of *ca.* 50 mg. of *p*-toluenesulfonic acid and 25 mg. of hydroquinone. During this time the theoretical quantity of water, 1.8 ml., was collected in the attached Dean-Stark trap. The benzene solution was washed with 5% sodium carbonate solution and then with water. The organic layer was dried over anhydrous calcium sulfate, and the solvent was thereupon removed with a rotary film evaporator. Distillation of the crude product at reduced pressure through a 25-cm. Vigreux column gave 15.9 g. (77%) of the colorless, piquant-smelling diene, b.p. 93–94° (0.3 mm.). Upon standing this product crystallized to a colorless solid. Recrystallization from ethanol or, at −30°, from *n*-heptane, produced colorless prisms, m.p. 38–39°.[16]

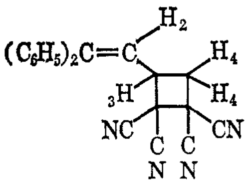
Anal. Calcd. for $C_{16}H_{14}$: C, 93.16; H, 6.84. Found: C, 93.16; H, 6.70.

Characteristic infrared absorptions were displayed at 1625, 1610, 1595 (C=C conjugated with phenyl), 905, 995 (CH=CH$_2$), 695, 760 (monosubstituted benzene), 775, 730, 640 cm.$^{-1}$. The ultraviolet spectrum in cyclohexane displayed a peak at 297 mμ (log ϵ 4.26) and a shoulder at 236 mμ (log ϵ 3.71). The n.m.r. spectrum exhibited only a phenyl doublet (δ 7.22 and 7.24, 10 protons) and vinyl proton resonances (multiplets at δ 4.98–5.60, 2 protons, and δ 6.14–6.8, 2 protons).

Adduction of 1,1-Diphenyl-1,3-butadiene with Tetracyanoethylene. Lower Melting Isomer (III, **B**).—A solution of 4.37 g. (0.0212 mole) of freshly purified 1,1-diphenyl-1,3-butadiene and 2.72 g. (0.0212 mole) of tetracyanoethylene in 50 ml. of dry benzene was heated at reflux for 5 hr. The initial dark green solution changed to dark amber during this time. The majority of the benzene was distilled off and 50 ml. of heptane was added to the semisolid residue. The resulting cream-colored solid was filtered and washed with heptane to yield 6.51 g. (92%) of crude product, melting at 150–153°, resolidifying, and finally remelting to a dark red liquid between 178 and 186°. Recrystallization from benzene gave 4.71 g. (66%) of almost colorless prisms, m.p. 153–155°, red melt, with no solidification upon further heating. Repeated recrystallization produced a colorless solid of the same melting point. However, the benzene solution invariably turned intensely yellow upon heating. This strongly suggests a dissociation of the adduct, leading to free tetracyanoethylene, which then forms a complex with the solvent.

Anal. Calcd. for $C_{22}H_{14}N_4$: C, 79.02; H, 4.22; N, 16.76; mol. wt., 334.3. Found: C, 78.76; H, 4.15; N, 16.92; mol. wt., 390 (Rast, orange melt formed in camphor).

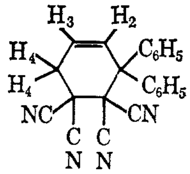
The infrared spectrum displayed important bands at 1630 (C=C), 1610, 1580 (C=C conjugated with phenyl), 1235, 1075, 1030, 945, 925, 880, 765, 725, and 690 cm.$^{-1}$. The ultraviolet spectrum in cyclohexane showed a peak at 268 mμ (ϵ 13,100) and a shoulder at 233 mμ. In acetone-d_6, the n.m.r. spectrum consisted of a complex phenyl multiplet between δ 7.2 and 7.7 (10 protons), a vinyl doublet (H-2) at δ 6.5 (1 proton, $J_{2,3}$ = 9 c.p.s.), a saturated CH triplet (H-3) centered at δ 4.2 (1 proton, $J_{3,2}$ = 9 c.p.s., $J_{3,4}$ = 9 c.p.s.; possible peak at 4.52 obscured by solvent), and a saturated CH doublet (H-4) at δ 3.44 (2 protons, $J_{4,3}$ = 9 c.p.s.).



Higher Melting Isomer (IV, **C**).—Concentration of the mother liquors from which the lower melting adduct (m.p. 153–155°) was obtained yielded 0.45 g. (6%) of colorless rosettes, melting at 196–200° (slight softening at 160°). Recrystallization from benzene (colorless solution, *vide supra*) gave a colorless product, m.p. 199–200° (solid beginning to turn yellow at 186° and red at 198°).

Anal. Calcd. for $C_{22}H_{14}N_4$: C, 79.02; H, 4.22; N, 16.76; mol. wt., 334.3. Found: C, 79.21; H, 4.39; N, 16.78; mol. wt., 320 (Rast, yellow melt in camphor).

The infrared spectrum showed characteristic bands at 1605, 1595, 1265, 1255, 1165, 1135, 1000, 895, 880, 845, 765, 750, 725, 700 and 650 cm.$^{-1}$. The ultraviolet spectrum in cyclohexane consisted of a shoulder at 230 mμ and a weak end absorption in the 240–260-mμ region. In acetone-d_6 the n.m.r. spectrum consisted of an aromatic multiplet between δ 7.3 and 7.5, two vinyl (H-2) triplets centered at δ 6.78 and 6.96 ($J_{2,3}$ = 11 c.p.s., $J_{2,4}$ = 2 c.p.s.), two vinyl triplets (H-3) centered at δ 6.43 and 6.61 ($J_{3,2}$ = 11 c.p.s., $J_{3,4}$ = 4 c.p.s.), and two saturated CH doubets (H-4) centered at δ 3.62 and 3.67 ($J_{4,2}$ = 2 c.p.s., $J_{4,3}$ = 4 c.p.s.). The relative proton count was in the ratio: phenyl:vinyl (H-2 + H-3):alkyl (H-4) 10:2:2.



Isomerization of Isomer Melting at 155° (III → IV).—A 100-mg. sample of the lower melting TCNE adduct in 30 ml. of dry benzene was heated at reflux for 120 hr. Upon initial warming the colorless solution turned distinctly yellow. At the end of the heating period the benzene was evaporated and the residual solid was examined by infrared spectroscopy. Although the bands of the starting isomer still were prominent, new bands characteristic of the higher melting isomer were now evident: 1265, 1000, 895, 845, and 750 cm.$^{-1}$.

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[15] J. J. Eisch and G. R. Husk, *J. Am. Chem. Soc.*, **87**, 4194 (1965).

[16] Previous reports of the properties of 1,1-diphenyl-1,3-butadiene include its description as (a) a liquid, b.p. 109° (0.3 mm.), $n^{17.5}\text{D}$ 1.6412;[10] (b) a solid, m.p. 35–37°;[11] and (c) a solid, m.p. 37–38° (G. Wittig, private communication, 1959).

The Reaction of Δ^2-Cyclohexenone with β-Methylallylmagnesium Chloride and Isobutylmagnesium Chloride. The Effect of Added Cuprous Chloride[1]

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The addition of 1–10 mole % of cuprous chloride has been shown to cause a substantial increase in the pro-

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