(*p*-cyanophenyl)phenylphosphine oxide, no adduct precipitated, and removal of solvent left an oil that failed to crystallize.

Attempted Distillation of Diphenylphosphine Oxide.—Two grams of diphenylphosphine oxide was subjected to distillation at 10^{-3} mm. A distillate (0.9 g.) was received over the range 115–121°. Solid residue remained in the still. The analysis for the distillate suggested it to be impure diphenylphosphine, and not diphenylphosphine oxide.

Anal. Calcd. for $C_{12}H_{11}P$: C, 77.41; H, 5.96; P, 16.64. Found: C, 76.23; H, 5.74; P, 16.23.

Preparation of Diarylphosphine Oxides.—The ether extract of a hydrolysis mixture prepared as described in the chloral adduct reaction was extracted with two 30-ml. portions of 5% sodium bicarbonate. Small amounts of phosphinic acid generally precipitated on acidification of the aqueous layer. The ether layer was washed once with 20 ml. of water and then dried with magnesium sulfate for 30 min. Removal of ether on a rotary evaporator left an oil, which was then further freed of volatiles by evacuation at 1 mm. overnight. Compounds IVA–C (see Table III) solidified completely in 1–2 days, and were recrystallized from pentane by slow cooling of a saturated solution to about −50°. Compound IVD on one occasion crystallized on similar treatment of the oil, but later attempts to repeat this crystallization failed. Compounds IVE–G could not be made to crystallize, and were analyzed without purification. The oxides were quite hygroscopic. Yield and analytical data for all compounds appear in Table III. The infrared spectra for compounds IVA–C were taken on potassium bromide pellets; other spectra were taken on the oils. All showed peaks at 2265–2300 cm.$^{-1}$ (weak, sharp) for P–H and at 1190–1205 cm.$^{-1}$ (strong) for $P \rightarrow O$. Since compounds IVE–F could not be crystallized, further details on prominent features of their spectra are offered.[28]

IVE, 2990(w), 2300(w), 2200(m), 1430(m), 1380(m), 1200(s), 1120(s), 945(s), 830(m), 750(m), 708(m), 693(m); IVF, 2990(w), 2285(w), 1430(m, shoulder 1410), 1320(s), 1195(s, shoulder 1165), 1120(s), 1070(m), 945(m), 805(m), 745(m), 695(m); IVG, 3000(w), 2290(w), 1575(m, shoulder 1555), 1475(m, shoulder 1460), 1395(m, shoulder 1380), 1190(s), 1140(s), 1085(s), 943(m), 820(m), 790(m), 750(s), 683(m).

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[28] Longer wave numbers are accurate to no more than about ±5 cm.$^{-1}$; spectra were taken with a Perkin-Elmer Model 137 spectrophotometer. Abbreviations: w, weak; m, medium; s, strong.

Diene Structure and Diels–Alder Reactivity

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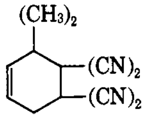
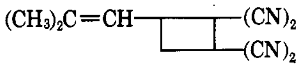
Adducts from tetracyanoethylene and a variety of dienes, including several *cis*-pentadienes, have been prepared and relative reactivities examined.

Diels–Alder reactions between maleic anhydride and dienes which contain a *cis*-methyl substituent on the terminal carbon of the diene system have been reported in a number of instances,[1-3] but in general such reactions are limited due to low reactivity and the enhancement of side reactions such as polymerization.[4] The current investigation was undertaken to determine the usefulness of the more potent dienophile, tetracyanoethylene[5] (TCNE), toward these less reactive dienes. A preliminary communication[6] has reported the simultaneous formation from 4-methyl-1,3-pentadiene of the Diels–Alder adduct, 3,3-dimethyl-4,4,5,5-tetracyanocyclohexene (I), and the four-membered ring adduct, 3-(2-methyl-1-propenyl)-1,1,2,2-tetracyanocyclobutane (II).



I



II

Results

Good yields of adducts have indeed been obtained from the dienes examined with the exception of *cis*-1,3-pentadiene by allowing excess diene to react with TCNE in tetrahydrofuran solution at room temperature. As with the more reactive *trans* isomers, a deep brown to red-brown color is developed immediately when the *cis* dienes are added to the reagent and adducts may be isolated in high yield by evaporation of the solution when the color has faded (Table I). In the case of 1,3-cyclohexadiene, the reaction is over within minutes, as is the case with the *trans* dienes examined. For 4-methyl-1,3-pentadiene, 3-methyl-*cis*-1,3-pentadiene, and *cis,trans*-2,4-hexadiene, two to three days at room temperature are required before color fading is complete. In the case of *cis*-1,3-pentadiene, significant color fading did not occur even on prolonged heating, and unreacted TCNE was recovered, although occasionally an apparently polymeric material having the right composition for a 1:1 adduct was obtained. Spectral properties of the adducts were consistent with the structures expected for a normal Diels–Alder reaction (analogous to I) in all cases except 4-methyl-1,3-pentadiene.[6] Attempts to favor cyclobutane formation for other dienes by use of the more polar solvent, nitromethane, led only to the same products obtained in tetrahydrofuran.

Relative reactivity toward TCNE was determined for these dienes and for a selection of more reactive compounds in an attempt to gain more insight into the nature of the process. Semiquantitative values were obtained from visual estimates of the rate of disappearance of the characteristic color and more precise values for dienes of comparable reactivity by competition experiments. Calculated second-order rate constants are listed in Table I. In view of the strong tendency for complex formation, it is possible that significant absolute error is involved in the assumption of second-order kinetics,[7,8] but relatively little relative error is expected from this source. For comparison,

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[1] D. Craig, *J. Am. Chem. Soc.*, **72**, 1678 (1950).

[2] N. L. Goldman, thesis, Columbia University, 1959.

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

[4] G. B. Bachman and C. G. Goebel, *J. Am. Chem. Soc.*, **64**, 787 (1942).

[5] W. J. Middleton, R. E. Heckert, and E. L. Little, C. G. Crespan, *ibid.*, **83**, 2199 (1961).

[6] C. A. Stewart, *ibid.*, **84**, 117 (1962).

[7] L. J. Andrews and R. M. Keefer, *ibid.*, **77**, 6284 (1955).

[8] J. A. Berson and W. A. Mueller, *ibid.*, **83**, 4940 (1961).

TABLE I

TETRACYANOCYCLOHEXENES FROM TCNE AND SUBSTITUTED BUTADIENES

1,3-Diene	Yield, %	M.p., °C.	% Nitrogen		Fade time,[a] min.	k_2, 1/mole hr.	
			Found	Calcd.		TCNE[b]	Maleic anhydride[c]
2-Methyl-*trans*-penta-	98[d]	62–63	26.6	26.6	<1	1000	
3-Methyl-*trans*-penta-	89[d]	83.5–84.5	26.2	26.6	<1	570	
2,3-Dimethylbuta-	100	136–137[e]			<1	240	2.0
trans,trans-2,4-Hexa-	91[d]	126.5–127.5[f]	26.8	26.6	<1	200	
trans-Penta	91[d]	79.5–80.5	29.2	28.6	~1	27	0.92
Cyclohexa-	100	214–216	27.2	26.9	~1	> 20	0.55
2-Methylbuta-	98	114–116	28.5	28.6	4	15	0.57
2-Chloro-3-methylbuta-	100	133–135	23.8[g]	24.3	40	~ 1.5	0.12
4-Methylpenta-	11[h]				(350)	25×10^{-3}[h]	
cis, trans-2,4-Hexa-	80[d]	123.5–124.5[f]	26.8	26.6	2000[i]	18×10^{-3}	
3-Methyl-*cis*-penta-	96	80–84[j]			2000	9×10^{-3}	
2-Chlorobuta-	97	135–138[k]			3000	$\sim 2 \times 10^{-3}$	19×10^{-3}
2,3-Dichlorobuta-	59	183	22.0[l]	22.0	390 at 62°		0.9×10^{-3}
cis-Penta	0					$<2 \times 10^{-4}$	

[a] See Experimental for conditions. [b] From competitive reactions where available. [c] Data of Craig, ref. 9. [d] Prepared from mixtures containing less reactive dienes. [e] Lit. 136–137°. [f] Mixture melting points of isomers, 88–102°. [g] Calcd. for Cl, 15.4. Found, 15.4. [h] Refers to cyclohexene adduct only, see ref. 6. [i] 660 min. at 25° in nitromethane solution. [j] Mixture melting point with adduct from *trans* isomer, 82–84°. [k] Reported 134–135°. [l] Calcd. for Cl, 28.3. Found, 28.4.

reactivities of these dienes toward maleic anhydride are listed from the data of Craig, *et al.*[9]

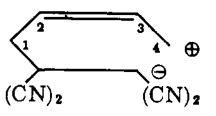
Discussion

In spite of a reactivity difference of nearly 10^5, the substituted *cis*-pentadienes appear to show the same characteristics as their *trans* isomers in reaction with TCNE: a similar degree of complexing is observed; highly selective *cis* addition occurs as demonstrated by the clean formation of isomeric adducts from both *trans,trans*- and *cis,trans*-2,4-hexadienes; and, as will be discussed further, the relative reactivities appear to require comparable substituent effects.

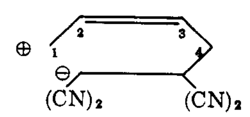
The large inhibition resulting from a *cis*-methyl substituent—corresponding to about 6-kcal. difference in free energy of activation compared to corresponding *trans* compounds—has been attributed to steric interference between the methyl group and the alternate terminus of the diene in the cisoid conformation,[1,9] which is considered to be a necessary intermediate in the Diels–Alder reaction.[10,11] This energy difference is significantly greater than the resonance benefit of coplanarity in butadiene.[12] On this basis, one would expect that dienes in which a comparable degree of strain is present in the transoid conformation should be noncoplanar and exhibit little of the characteristic stability of diene systems. Such is the case for 2-methyl-*cis*-1,3-pentadiene or 2,4-dimethyl-1,3-pentadiene. The former compound is absent in preparations of its isomers and only recently has been prepared as a transient product in the thermal isomerization of 4-methyl-1,3-pentadiene to 2-methyl-*trans*-1,3-pentadiene.[13] The dimethylpentadiene shows an abnormally low ultraviolet extinction[14] and is readily converted to the isomeric tetramethylallene.[15]

Since 1,3-cyclohexadiene, which is of necessity cisoid in conformation, and the *cis*-pentadienes, which are almost exclusively transoid in view of the strain energy involved, both form complexes with TCNE immediately and with apparently comparable ease, it appears either that TCNE may enter into complexes with both conformations of the diene or else that only a portion of the diene system is involved, the complexes being similar to those of TCNE with electron-rich monoolefins.[16] Whichever the case may be, it appears that there are complexes unrelated to the path of the Diels–Alder reaction and no light is shed on the problem of whether a similar discrete complex of the appropriate conformation is necessary as an intermediate in the reaction.[7,8,17]

The substituent effects observed are most easily explained in terms of electrophilic attack predominantly at one end of the diene system, as may be expressed in resonance terminology by assigning a significant contribution of a dipolar ion, IIIa, as one resonance form of the transition state. Numbering positions on the diene system so that C-1 is the terminus most susceptible to electrophilic attack, it is obvious that the accelerating effect of a methyl substituent increases in the order 1 < 3 < 2 < 4. If a corresponding structure, IIIb, made an equivalent contribution to the transition state—that is, if the transition state were fully symmetrical with respect to bond formation at each terminus—then at least one of the symmetrical dienes, *trans, trans*-2,4-hexadiene or 2,3-dimethylbutadiene, should be more reactive than the unsymmetrical 2-methyl- and 3-methyl-1,3-pentadienes, but, in fact,



IIIa



IIIb

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these compounds are found to be the most reactive dienes examined.[18]

One exception is shown to the substituent effect as described in that *cis,trans*-2,4-hexadiene is slightly more reactive than 3-methyl-*cis*-1,3-pentadiene, while the converse is true for the *trans* isomers. This may be explained in terms of the higher initial-state energy of the *cis* double bond. If the reaction is unsymmetrical as postulated, some difference may be due also to greater relief of steric strain in the transition state for the *cis,trans*-2,4-hexadiene if preferential reaction occurs at the *cis*-substituted terminus, polar factors being relatively comparable. A likely geometry for the transition state is a helix, more open at the dipolar end of the system than at the end at which bonding is progressing to the greatest extent. Such an array seems adequate for the resonance pictured and is intermediate in position between the parallel orientation postulated prior to reaction[10] and a boat form of the adduct.

Comparing the reactivities toward TCNE and maleic anhydride, it appears that the accelerating effect of a methyl substituent and the decelerating effect of a chlorine substituent are both greater in the case of the more electrophilic TCNE. The chlorinated dienes, further, show a qualitative difference in that the solutions show the green color characteristic of TCNE in the solvent rather than the brown color of the complexes present with the hydrocarbon dienes.

The present examples represent only one extreme in the spectrum of Diels–Alder reactions which range from highly electrophilic dienophiles and nucleophilic dienes through relatively neutral materials to what might be called "inverse" Diels–Alder reactions such as the condensations of acrolein or hexachlorocyclopentadiene,[19,20] where the polarities of the "diene" and dienophile (and the effect of polar substituents) are reversed. It seems likely, however, that the indicated asymmetry of bond formation and the retention of the general characteristics of the reaction in the presence of the high strain of the *cis*-pentadienes should be generally applicable to the extent that a qualitatively single mechanism can be applied to such a varied assortment of reagents.

Experimental

Reagents used were commercially available products except as indicated. Melting points were determined using a Fisher-Johns block at a heating rate of 2–5°/min. Diene mixtures were examined by vapor phase chromatography, using a 5-m. column of tricresyl phosphate at various temperatures (25–100°) as needed for resolution. Infrared spectra of adducts were determined from mulls in Primol D hydrocarbon oil.

1,3-Pentadienes.—Commercial piperylene (62% *trans*-1,3-pentadiene by v.p.c.) was added to excess maleic anhydride in acetone at reflux and the mixture steam distilled to yield essentially pure *cis*-1,3-pentadiene after extraction with water and drying with sodium sulfate.

3-Methyl-1,3-pentadienes.—Distillation of 3-methyl-1-pentene-3-ol[21] from *p*-toluenesulfonic acid afforded a 79% yield of mixed dienes estimated by v.p.c. to contain 28% 2-ethylbutadiene, 28% 3-methyl-*cis*-pentadiene, and 41% 3-methyl-*trans*-pentadiene. Ethylbutadiene was identified from a low-boiling distillation fraction by its maleic anhydride adduct, m.p. 68–69° lit.[22] 67–69°. A TCNE adduct prepared from the same fraction had m.p. 96–99°. A distillation fraction used for subsequent reactions contained 58% *trans* isomer and 40% *cis* isomer, b.p. 77–78.5°, $n^{25}\mathrm{D}$ 1.4498. Treatment of this material with excess maleic anhydride gave pure 3-methyl-*cis*-1,3-pentadiene, $n^{25}\mathrm{D}$ 1.4469. Infrared bands at 9.1, 12.2, and 13.5 μ for the *cis* isomer and 9.3, 12.0, and 13.2 μ for the *trans* served to differentiate the two. Structure of the *trans* isomer (maleic anhydride adduct, m.p. 67.5–68°) was established by the synthesis of Farmer and Warren.[23]

2,4-Hexadienes.—2,4-Hexadiene was obtained as a carefully redistilled sample, 82–82.5°, $n^{25}\mathrm{D}$ 1.4501, available from other work in these laboratories, estimated composition (v.p.c.) 59% *trans,trans*, 37% *cis,trans*, and 4% minor component believed to be the *cis,cis* isomer.[24] Maleic anhydride treatment gave a mixture containing 88% *cis,trans* isomer and 12% *cis,cis* isomer, $n^{25}\mathrm{D}$ 1.4527.

2- and 4-Methylpentadienes.—Mixed dienes were prepared by dehydration of 2-methyl-2,5-pentanediol catalyzed by aniline and iodine. Distillation of the crude product through a precision still and careful examination of fractions by infrared and v.p.c. revealed no significant impurities boiling between isobutylene (< 10°) and methylpentenols (74–76° at 100 mm). 4-Methyl-1,3-pentadiene, obtained by maleic anhydride removal of the isomer,[4] showed no indication of vinylidene unsaturation (11.3 μ) which should be present if the product were contaminated with either *cis*- or *trans*-2-methyl isomer. The ratio of 2-methylpentadiene to 4-methylpentadiene obtained in the dehydration was estimated to be about 3 to 1. Dehydration of dimethylallylcarbinol[25] over toluenesulfonic acid gave a nearly theoretical yield of dienes estimated to contain approximately equal amounts of 2-methyl-1,4-pentadiene, 4-methyl-1,3-pentadiene, and 2-methyl-*trans*-1,3-pentadiene. As in the foregoing, fractionation and examination of fractions gave no indication of the 2-methyl-*cis*-pentadiene isomer. A distillation fraction estimated to contain 64% 2-methyl- and 36% 4-methyl-1,3-pentadienes, b.p. 76.0°, $n^{25}\mathrm{D}$ 1.4468, was employed for preparation of adducts of 2-methylpentadiene.

TCNE Reactions, Preparative.—Adducts were prepared by adding 0.5 to 2 g. of TCNE to excess diene in tetrahydrofuran solution (adducts of *trans*-pentadienes were prepared from isomer mixtures described previously). A dark brown to red-brown color developed immediately with each of the hydrocarbon dienes, green or blue-green color with the chlorinated dienes. In the case of the more reactive dienes, color was seen only at the edges of the dissolving solid and faded faster than it could be mixed into the solution. When the solution became colorless, the product was obtained by evaporation of diene and solvent and recrystallization from benzene and cyclohexane.

In the case of 2,3-dichlorobutadiene, the reaction was worked up before completion and the crude product was extracted with sodium bisulfite solution to remove residual TCNE. Unchanged TCNE (81%) was recovered after heating with *cis*-1,3-pentadiene in tetrahydrofuran for 6 hr. at 100° in a sealed vial. More drastic conditions led to brown solids which were insoluble in boiling *o*-dichlorobenzene and infusible in a flame. Preparation and separation of 3,3-dimethyl-4,4,5,5-tetracyanocyclohexene-1 and 3-(2-methyl-1-propenyl)-1,1,2,2-tetracyanocyclobutane have been described previously.[6]

Spectra of Adducts.—Infrared spectra of all the adducts showed expected weak to moderate absorptions at 4.45 (CN) and 6.0 (C═C) and several strong peaks in the 10–15-μ region. An intense band was invariably found between 11.7 and 12.3 μ and all derivatives having an unsubstituted cyclohexene double bond showed absorption at 13.7–14.1 μ. Where possible cyclobutane structures could not be eliminated by absence of absorptions at 10.1 and 11.1, 10.3, or 11.3 μ for vinyl, *trans*-internal, or vinylidene unsaturation,[26] n.m.r. spectra were determined to verify the proposed structure. Additional evidence in favor of the proposed structures is the identity of 3-methylpentadiene adducts

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[18] Statistical correction for symmetry will only increase the effects noted. The suggested structure is intended to represent an aspect of the transition state, whether or not a discrete intermediate of such type is formed.

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[26] L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1958, p. 34.

and the nonidentity of 2,4-hexadiene adducts. The sharp crystallization and ready sublimation of the adducts eliminated polymeric materials from consideration.

The n.m.r. spectrum (60 Mc., deuterioacetone solution, TMS internal standard) of the cyclobutane adduct II from 4-methylpentadiene showed peaks at 326 (doublet, $J = 8$), 269 and 200 (apparent ABX pattern), and −110 (singlet) in the expected ratio (1:1:2:6) for vinylic, ring, and allylic methyl protons. The spectrum of the cyclohexene adduct I showed singlet peaks at 351, 201, and 97. The isomeric adducts from 2,4-hexadienes gave identical spectra, 355, 209, 97, with a splitting constant of 7 c.p.s. for CHCH$_3$. Adducts from other dienes were examined in CDCl$_3$ solution and the following shifts were observed: *trans*-pentadiene, 345, 185, 93; 2-chlorobutadiene, 360, 192; 2,3-dichlorobutadiene, 205. The adduct from cyclohexadiene proved to be too insoluble to obtain an adequate spectrum in suitable solvents.

Rate and Competition Experiments.—Competitive reactions and fade time observations were made by adding 0.64 g. (0.005 mole) of powdered TCNE to a solution of 0.10 mole of diene, or of each of two dienes, in 5 ml. tetrahydrofuran. "Fade time" was noted by visual comparison to an arbitrary standard corresponding to an estimated two-thirds reaction. When the solution was colorless, solvent and diene were evaporated. The observed yield in each case was essentially quantitative. Assumed second-order rate constants were calculated from fade times by the relation $k = 1/T_F$ for the concentrations employed. Relative rates were determined by infrared comparison of the crude products (Primol mull) with synthetic mixtures and calculation assuming the reactions to be first order in diene, $k_A/k_B = (\log A_0/A_0 - X_A)/(\log B_0/B_0 - X_B)$, where X_A and X_B are the fractions of the respective adducts found. Observed results are shown in Table II.[27] Absolute rates, Table I, were calculated from relative rates, where available and the fade time observations with isoprene and with 4-methylpentadiene as time standards for the fast and slow series, respectively.

Table II

Competitive Reactions of Dienes with TCNE

1,3-Dienes A	B	Fade time,[a] min.	Adduct composition, X_A
3-Methyl-*trans*-penta-	2-Methyl-*trans*-penta-	< 1	0.40 ± 0.05
trans,trans-2,4-Hexa-	2-Methyl-*trans*-penta-	< 1	0.20 ± 0.04
2,3-Dimethylbuta-	3-Methyl-*trans*-penta-	< 1	0.32 ± 0.02
2-Methylbuta-	*trans,trans*-2,4-hexa	< 1	0.09 ± 0.02
2-Methylbuta-	*trans*-Penta-	1	0.40 ± 0.02
4-Methylpenta-	2-Methylbuta-	4	< 0.05[b]
cis,trans-2,4-Hexa-	4-Methylpenta-	960	0.11 ± 0.04[b]
3-Methyl-*cis*-penta-	*cis,trans*-2,4-Hexa-	4000	0.33 ± 0.06
cis-Penta-	*cis,trans*-2,4-Hexa-	360/57°	< 0.05

[a] See Experimental for definition and conditions. [b] Composition including both adducts from 4-methylpentadiene, see ref. 27.

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(27) Reaction products for 4-methylpentadiene were analyzed for cyclobutane adduct and corrected for cyclohexene adduct on the basis of data given in ref. 6.

Dihydrophthalic Acid Derivatives as Diels–Alder Dienes[1,2]

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The conversion of phthalic and terephthalic acids and/or esters to dienes suitable for use in the Diels–Alder reaction has been reexamined and a number of such reactions have been carried out. In two instances tetracyanoethylene (TCNE) affords relatively stable π-complexes but no true adducts. Conversion of a number of the adducts to amides and nitriles also is reported.

We have described elsewhere exploratory work[1] involving the Diels–Alder reaction, using cyclic conjugated dienes bearing electron-withdrawing substituents (*e.g.*, nitrile, ester). Whereas the nitrile group proved too deactivating for the usual type of Diels–Alder reaction, the ester group proved to be more tractable. The present paper reports similar work with cyclic conjugated dienes bearing two ester groups, both conjugated with the dieneic system and isolated from it. Three principal conjugated dienes, dimethyl cyclohexa-3,5-diene-*trans*-1,2-dicarboxylate (I), dimethyl cyclohexa-2,6-diene-1,2-dicarboxylate (II), and dimethyl cyclohexa-1,3-diene-1,4-dicarboxylate (III) were investigated; and in addition the compound (IV) previously assigned the structure[3] dimethyl cyclohexa-1,4-diene-1,4-dicarboxylate but shown in the sequel to be the isomeric conjugated 1,5-diene also was found to enter into the Diels–Alder reaction by isomerization to III.

Preparation of the Dienes.—Compound I was prepared by esterification (diazomethane) of the free dibasic acid (Ia) obtained by 3% sodium amalgam reduction of phthalic acid[4,5]; and compound IIa was prepared by the thermal isomerization of Ia.[6] The ester, II, was prepared from IIa by acid-catalyzed reaction with methanol.

In view of the structural problem encountered with III and IV, physical examination of the acid and esters Ia, IIa, I, and II was undertaken in order to confirm the structures assigned.[4,5] The infrared and ultraviolet spectra are entirely consistent, I having an unconjugated ester (1750 cm.$^{-1}$) and II a conjugated ester (1730 cm.$^{-1}$) in the infrared spectrum while Ia exhibits an ultraviolet spectrum almost identical with that of cyclohexa-1,3-diene and IIa shows absorption at a longer wave length. The n.m.r. spectra likewise are consistent, Ia showing four vinyl protons and two tertiary α-protons. A nearly identical spectrum was obtained for the corresponding ester I, with the addition of the methoxyl line.

The structure of I is further confirmed by the n.m.r. spectra of its adducts with various dienophiles, all of which show two vinyl protons and complete absence of

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(1) Previous paper in this series, P. Scheiner, K. K. Schmiegel, G. Smith and W. R. Vaughan, *J. Org. Chem.*, **28**, 2960 (1963).

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(3) A. von Baeyer, *Ann.*, **251**, 276 (1889).

(4) A. von Baeyer, *ibid.*, **269**, 189 (1892).

(5) A. Neville, *J. Chem. Soc.*, **89**, 1745 (1906), has resolved this acid in order to confirm the structure.

(6) A. von Baeyer, *Ann.*, **269**, 190 (1892).