Formation and Reactions of Dihydrophthalic Acids

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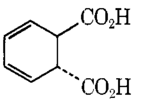
Electrochemical reduction of phthalic acid gave *trans-* and *cis*-1,2-dihydrophthalic acid isomers, ~6:1. Diels-Alder adducts formed from tetracyanoethylene with *cis*-1,2-dihydrophthalic acid, anhydride, and dimethyl ester. 1,2-Dihydrophthalic anhydride dimerized to dicyclohexadiene dianhydride; an isomeric adduct was obtained from 1,2- and 1,4-dihydrophthalic anhydride. A catalyst system of bis(triphenylphosphine)cobalt dibromide plus boron trifluoride etherate inhibited dimerization of 1,2-dihydrophthalic anhydride, isomerized 1,2-dihydrophthalic anhydride to the 1,4 isomer, and catalyzed cycloaddition of 1,2- to 1,4-dihydrophthalic anhydride. Palladium on carbon catalyzed the stereospecific disproportionation of dimethyl dihydro- and tetrahydrophthalates to phthalate and hexahydrophthalates and effected partial decarboxylation of dihydrophthalic acids to benzoic acid. Hydrogen transfer reactions were first order in palladium and zero order in olefin and proceeded mainly by 1,2 addition of hydrogen.

trans-1,2-Dihydrophthalic acid (1) was first prepared by Baeyer in 1892 by Na(Hg) reduction of phthalic acid.[1] Baeyer also prepared *cis*-1,2-dihydrophthalic anhydride (6), *cis*-1,2-dihydrophthalic acid (2), 3,6-dihydrophthalic acid (3), 2,3-dihydrophthalic acid (4), and 1,4-dihydrophthalic acid (5) from 1. 1,2-Dihydrophthalic acid can now be made in high yields on a large scale by electrochemical reduction of phthalic acid, but the dihydrophthalic acid so produced is an unspecified mixture of isomers.[2-5]



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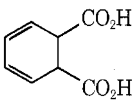

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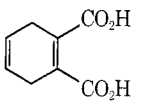

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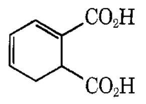

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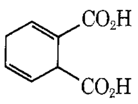

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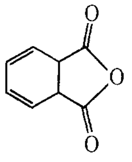

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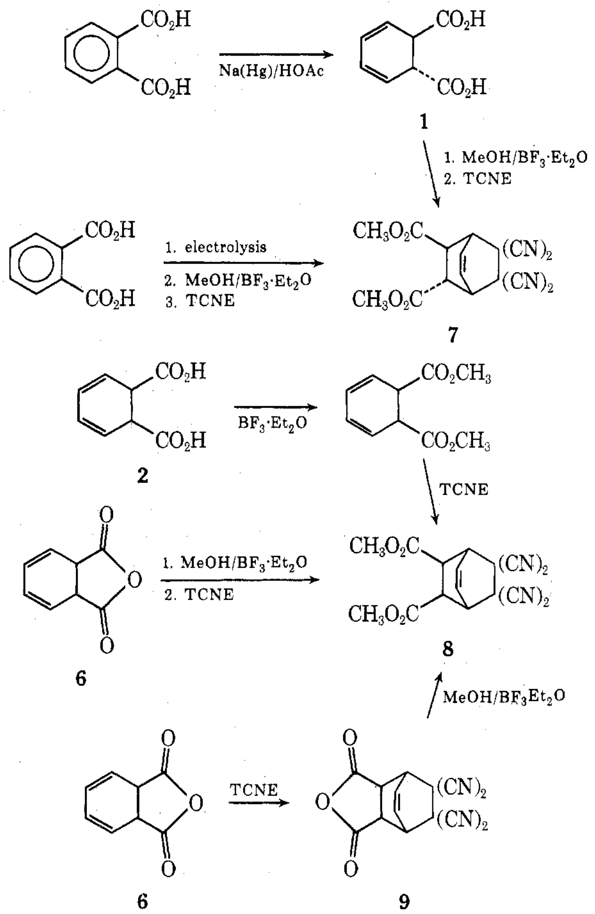
Dihydrophthalic acids are of interest as chemical intermediates, being both dienes and dibasic acids. However, the chemistry of these dienes has hitherto been relatively unexplored. In this work, we have developed methods for analysis and characterization of the electrochemically reduced phthalic acids, prepared several new Diels-Alder adducts, and studied the transition metal catalyzed disproportionation reactions of dihydrophthalic acids and derivatives.

Results and Discussion

Characterization of the Electrochemical Reduction Products of Phthalic Acid. Each of the dihydrophthalic acid isomers has a characteristic nmr spectrum,[6,7] but mixtures of *cis-* and *trans*-1,2-dihydrophthalic acid cannot be analyzed, as their nmr spectra are nearly superimposable, differing only in the shape of the multiplet due to the olefinic protons. The dihydrophthalic acid isomers can be separated and analyzed by esterification gas chromatography (egc).

The major product from electrochemical reduction of phthalic acid was the trans isomer 1 by comparison of the nmr spectrum of its tetracyanoethylene (TCNE) adduct 7 with a reported spectrum of this Diels-Alder adduct.[6]



A minor electrochemical reduction product was identified as the cis isomer 2 by these results: esterification gave a compound with the same egc retention time as the product from esterification of 6; the TCNE adduct 8 isolated from a mixture enriched (80%) in the dimethyl ester of this isomer was different from 7 and was identical with the adduct obtained from reaction of TCNE with the dimethyl ester prepared by esterification of 6; and 8 was identical with the esterification product of the TCNE adduct 9. The compositions of the TCNE Diels-Alder adducts 8 and 9 were shown by their elemental analyses and molecular weights (mass spectra). Both were characterized as cis,endo stereoisomers on the basis of their symmetrical nmr spectra: 9 (acetone-d_6), δ 7.02 (multiplet, 2 H, olefinic), 4.80 (multiplet, 2 H, bridgehead), and 4.18 (singlet, 2 **H**, exo tertiary); 8 (acetone-d_6), δ 6.70 (multiplet, 2 H olefinic), 4.30 (multiplet, 2 H, bridgehead), 3.74 (singlet, 2 H, exo tertiary), and 3.66 (singlet, 6 H, endo methyl groups). For comparison, the nmr spectra of the trans adduct 7 in acetone-d_6 showed the olefinic protons as two multiplets at δ 6.94 (1 H) and 6.66 (1 H), the bridgehead protons at 4.43 (multiplet, 2 H), two multiplets for

Table I
Electrochemical Reduction Products of Phthalic Acid (PA)

	Electrolysis conditions— Solvent	Temp, °C	Products, % 1	2	4	5	PA
A	5% H_2SO_4	90	70.2	2.7	1.1	16.2	10.0
B	50% THF/50% 5% H_2SO_4	40	73.6	10.0	0.2	6.4	9.8
C[a]			76.6	4.0	0.3	9.3	9.8

[a] The product distribution in C was obtained by heating the products B in 5% sulfuric acid at 90° for 2 hr.

the tertiary protons at 3.80 (exo, 1 H) and 3.38 (endo, 1 H), and two singlets due to the carbomethoxy groups at 3.83 (exo, 3 H) and 3.76 (endo, 3 H). The single peaks for the methyl groups and the tertiary protons and the similarity of the nmr spectra of **8** and **9** (derived from cis anhydride **6**) is evidence that the carbomethoxy groups in **8** are cis. That the substituents are endo is shown by the chemical shifts of the exo tertiary protons in **8** and **9**, which are at approximately the same chemical shift as the proton assigned[6] to the exo tertiary position in **7**, and are at lower field than the endo proton in **7**, shielded by the anisotropy of the adjacent double bond.[8]

1,4-Dihydrophthalic acid (**5**) was identified by comparison of its nmr and egc spectra with those of an authentic sample prepared by thermal isomerization of **1** in water.[9]

Electrochemical reduction of phthalic acid in an experimental batch cell[4,5,10] at 90° gave dihydrophthalic acids containing 10–20% **5** and 1–5% **2**; reduction at 40° gave 2–7% **5** and 10–18% **2**. Typical analyses are shown in Table I. When the products from low-temperature electrolysis (B) were heated in 5% sulfuric acid at 90° for 2 hr, 60% of **2** was isomerized to **1** and **5** (C). Therefore, *trans*- and *cis*-1,2-dihydrophthalic acids (**1** and **2**) are formed in a ratio of about 6:1 by electrochemical reduction of phthalic acid; **4** and **5** are secondary products due to thermal isomerization of **1** and **2** in the solvent system.

Diels–Alder Reactions of 1,2-Dihydrophthalic Acid. Prior to this work, the only known Diels–Alder adduct of 1,2-dihydrophthalic anhydride (**6**) was its maleic anhydride adduct.[9] *trans*-1,2-Dihydrophthalic acid (**1**) was reported not to undergo Diels–Alder reactions, although several adducts of the corresponding dimethyl ester have been prepared.[6] Anhydride **6**, prepared *in situ* from **1** in acetic anhydride, reacted with TCNE to give an 86% yield of adduct **9**, which sublimed and partially decomposed to **6** and TCNE at 300°. Hydrolysis of **9** gave diacid **10**, isolated in 70% yield as a tetrahydrate on recrystallization from water. Anhydrous **10** was obtained by recrystallization from acetone and benzene. When **10** was heated at 60° under vacuum a new product was obtained, which was identified as the dihydroxy lactone **11** on the basis of its characteristic infrared spectral bands at 3300, 1750, and 1150 cm^{-1} and elemental analysis. Both **10** and **11** gave **9** in acetic anhydride or at 200–220°. In water or acetone **11** was converted to **10**.

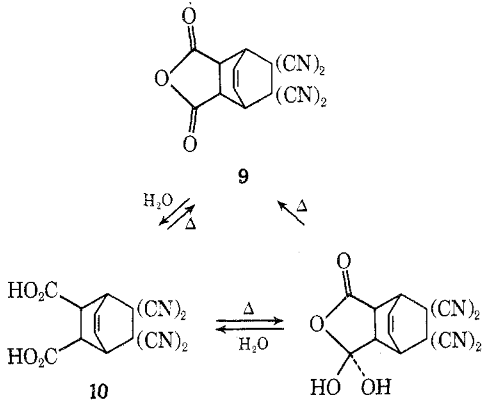


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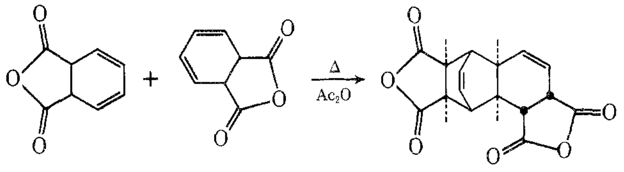
Table II
Dimerization of Dihydrophthalic Acid in Refluxing Acetic Anhydride

1, mmol	5 mmol	$CoBr_2\cdot PPh_3$, mmol	$BF_3\cdot Et_2O$, mmol	Time, hr	Yield, % 12	13
1000.0				15	62	
1000.0				66	70	
11.0		0.27	0.82	15		28
6.0	6.0			15		17
6.0	6.5	0.27	0.82	15		36
7.0	8.4	0.27	0.82	15		22
6.0	6.5	0.33	0.33	15		
6.0	6.0		0.82	15		7
6.0	6.0	0.27		15		
	6.0			16		
	6.0	0.27	0.82	15		

1 refluxed in acetic anhydride for several minutes was reported to give 84% of anhydride **6**.[1,9] We found that refluxing **1** for several hours in acetic anhydride resulted in formation of a Diels–Alder dimer **12** in 70 mol % yield. **12** was also obtained when **6** was heated in acetic anhydride or acetic acid. A mixture of **1** and **5** in acetic anhydride gave an isomeric adduct **13** in 17% yield by [4 + 2] cycloaddition of **6** to the isolated double bond of the anhydride of **5**. The proposed endo,endo stereochemistries are assumed based on rules of Diels–Alder additions and the most favorable geometries of the transition states.[11]



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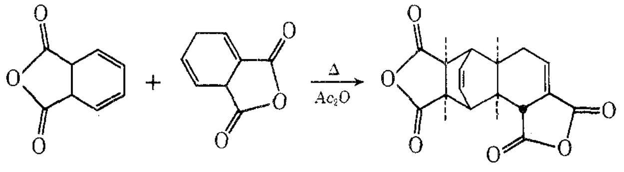

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Transition metal compounds are known to catalyze symmetry-forbidden [2 + 2] and [4 + 4] cycloaddition reactions.[12-15] An attempt to effect dimerization of **1** or **6** using $CoBr_2\cdot 2PPh_3$ and $BF_3\cdot Et_2O$, a catalyst system that dimerizes norbornadiene to Binor-S,[14] gave no new products. Instead, we obtained a 30% yield of **13**. Dimer **12**, obtained in 70% yield in the absence of catalyst, was not observed. The possibility that **12** was the initial product and was catalytically isomerized to **13** was ruled out, as **12** was recovered unchanged when heated under these conditions. **1** and **5** in acetic anhydride with $CoBr_2\cdot 2PPh_3$ and $BF_3\cdot Et_2O$ gave the cross dimer **13** in yields twice that of the uncatalyzed reaction. **5** alone gave no dimers in acetic anhydride in the presence or absence of catalyst. The catalyst system inhibited self-dimerization of **1**, partially isomerized **1** to **5** (or their anhydrides), and catalyzed the [4 + 2] cycloaddition to **13**.

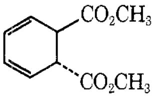
Both $CoBr_2\cdot 2PPh_3$ and $BF_3\cdot Et_2O$ were necessary for catalysis; the optimum mole ratio of cobalt to boron was 1:3. No dimers were formed when $BF_3\cdot Et_2O$ was omitted, and yields of **13**, compared to the uncatalyzed system, were lower in the absence of $CoBr_2\cdot 2PPh_3$, as shown in Table II.

Table III
Palladium-Catalyzed Disproportionation Reactions[a]

Starting material	Pd/C, mol % Pd	Solvent	Time	Yield, % 16	17	18	19 + 21	20
14	2.65	PhH	7 hr	50.5			49.3	0.2
14	4.06	HOAc	2 hr	66.0	29.2	1.0		2.8
19 + 21[b]	2.65	PhH	9 days	66.5	27.0		1.3	5.2
19 + 21[b]	2.65	PhH	12 days	68.2	28.8	1.8	0.7	0.5
15	2.73	PhH	1 hr	52.2	0.9	3.5		43.4
15	4.60	HOAc	2 hr	64.7	0.7	3.3		30.2
20	2.73	PhH	5 days	76.0	3.7	17.7		2.6
20	4.60	HOAc	16 hr	84.4	4.2	11.4		

[a] All reactions were at the boiling points of the solvents indicated. [b] Products 19 and 21 were present in a ratio of 65:35.

Palladium-Catalyzed Reactions of Dihydrophthalic Acids. Palladium compounds are known to dimerize acyclic conjugated dienes such as butadiene,[16] and to effect isomerization and disproportionation of cyclic dienes such as cyclohexadiene.[17] We found that palladium supported on carbon catalyzed the disproportionation of the cyclohexadiene derivatives dimethyl *trans*-1,2-dihydrophthalate (14) and 1,4-dihydrophthalate (15) to approximately a 2:1 mixture of dimethyl phthalate (16) and hexahydrophthalate. The reactions were stereospecific: hexahydrophthalate obtained from 14 was 94% *trans*-hexahydrophthalate (17) and 6% *cis*-hexahydrophthalate (18); hexahydrophthalate from 15 was 83% 18, 17% 17. The reduction products from palladium-catalyzed disproportionation have the same stereochemistry as from palladium-catalyzed hydrogenation: 14 was hydrogenated to give 100% 17; 15 was hydrogenated to give 97% 18 and 3% 17. No dimers were obtained. Palladium-catalyzed dimerizations of cyclohexadienes evidently do not compete with hydrogen-transfer reactions leading to disproportionation.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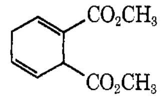
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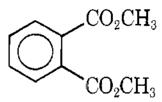
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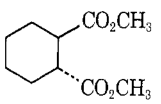
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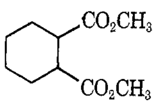
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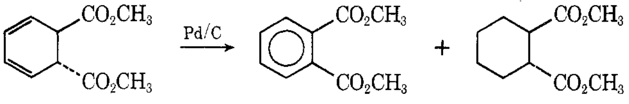
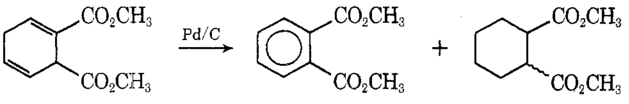
Hydrogen-transfer reactions catalyzed by transition metal compounds proceed *via* metal hydride intermediates.[18-20] The observed ratios of phthalate to hexahydrophthalate, which were higher than the theoretical 2:1 ratio, are attributed to dehydrogenation by formation and loss of hydrogen, in competition with disproportionation by hydrogen transfer from metal hydride intermediates.

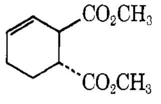


Refluxed in acetic acid	74%	24%
benzene	67%	31%



Refluxed in acetic acid	84%	16%
benzene	73%	22%

Disproportionations catalyzed by palladium on carbon proceeded stepwise through tetrahydrophthalate intermediates. The rate of disproportionation of dihydrophthalate was about 100 times faster than the disproportionation of tetrahydrophthalate so that the reactions could be stopped easily at the intermediate stage, and 1:1 mixtures of phthalate and tetrahydrophthalates were isolated.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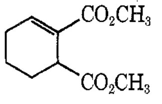
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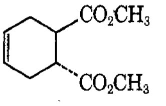
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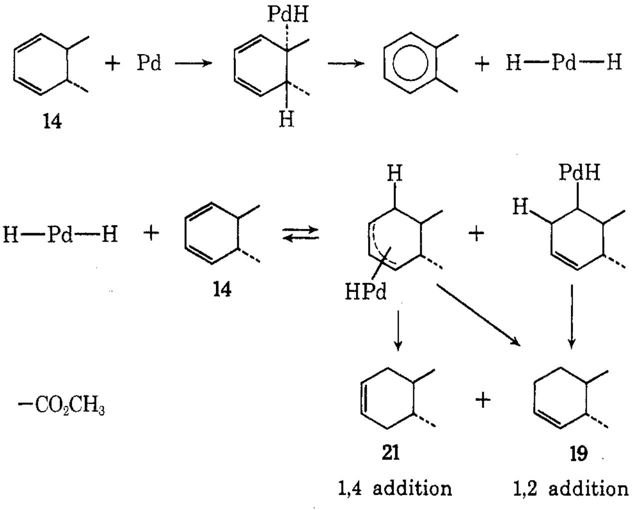
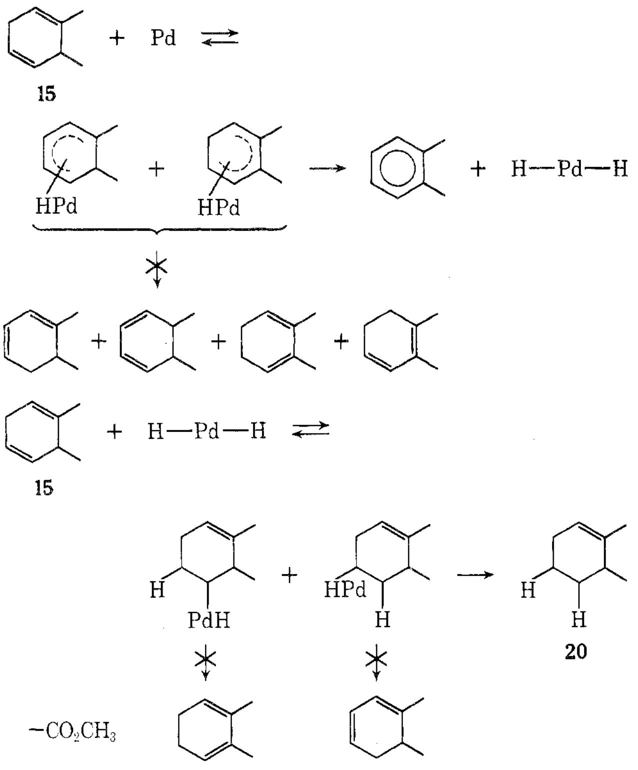
Transition metal compounds are known to catalyze hydrogen transfer reactions of 1,3-cyclohexadienes predominantly by 1,4 addition of hydrogen and to disproportionate 1,4-cyclohexadienes by prior isomerization to the conjugated 1,3 isomers.[19,20] We found that *trans*-1,2-dihydrophthalate (14) disproportionated mainly by 1,2 addition of hydrogen. The tetrahydrophthalates consisted of 65% *trans*-1,2,3,4- (19, 1,2-addition product) and 35% *trans*-1,2,3,6-tetrahydrophthalate (21, 1,4-addition product). Tetrahydrophthalate isomers were identified by their nmr spectra. Their stereochemistries are trans, as continued reaction in the presence of palladium gave *trans*-hexahydrophthalate (17), which was 95% isomerically pure.

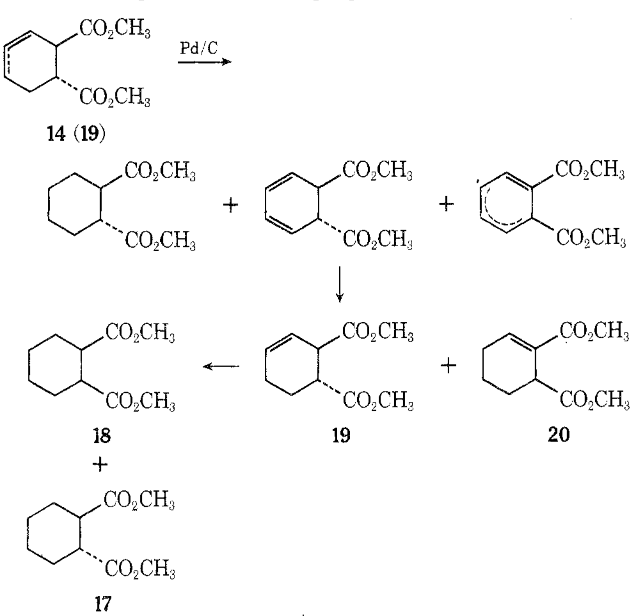


Disproportionation of 1,4-dihydrophthalate (15) gave a 1:1 mixture of phthalate and 2,3,4,5-tetrahydrophthalate (20) as the only tetrahydro isomer. It formed exclusively by 1,2 addition of hydrogen to the isolated double bond. 15 did not isomerize to a conjugated diene by addition–elimination of palladium or a palladium hydride species, as this would have given dienes and subsequently olefins that were not observed. 15 was not isomerized to a conjugated diene because of its greater thermodynamic stability compared to 14;[9] the steric interactions in the almost planar 14 are relieved on going to 15 and one of the double bonds becomes conjugated with a carboxy group.

Small amounts of 20 were observed in the disproportionation of 14 and 19, Table III. We attribute this to the formation of dienes containing a Δ^2 double bond in the conversion of tetrahydrophthalate to phthalate and hexahydrophthalate. Subsequent disproportionation of the isom-



erized olefins may be responsible for the lack of total stereospecificity observed in the formation of hexahydrophthalates. **20** may also be formed by isomerization of **14** to **15**, in competition with disproportionation.



The kinetics of these palladium-catalyzed reactions were studied in an attempt to elucidate the mechanism(s). Each reaction was found to be first order in catalyst and zero order in olefin. Observation of pseudo-zero-order kinetics in heterogeneous catalysis is not uncommon.[21] This indicates that the catalyst is saturated with substrate and the concentration of substrate on the surface of the catalyst is effectively constant over the course of the reaction. Unfortunately, no insight into the molecularity of the hydrogen transfer reactions can be deduced in such cases.

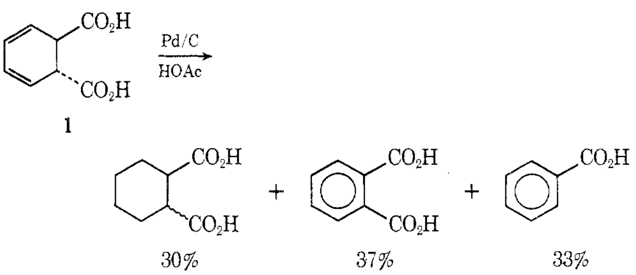
Palladium was the most effective catalyst we found for disproportionations of **14**. The rhodium-catalyzed reaction of **14** stopped at the tetrahydrophthalate stage. A comparison of several transition metal catalyzed reactions of **14** is shown in Table IV.

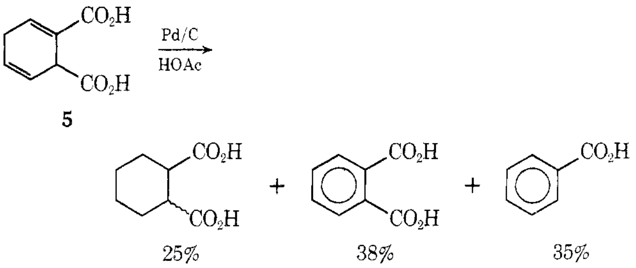
Table IV
Reactions of Dimethyl *trans*-1,2-Dihydrophthalate (14) Catalyzed by Transition Metals

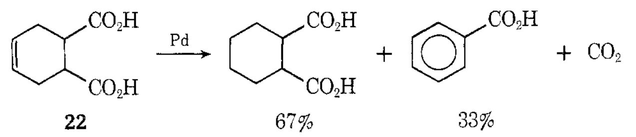
Catalyst	Mol % catalyst	Product distribution, %				
		14	**16**	**17**	**19 + 21**	**20**
10% Pd/C[a]	2.4		66.2	30.9		2.9
5% Rh/C[a]	2.4		51.9		43.5	4.6
5% Ru/C[a]	2.5	72.6	7.8		2.0	6.2
5% Pt/C[a]	1.2	49.9	23.9		17.1	4.6
Pd(OAc)$_2$[b]	5.7		65.0		35.0	

[a] In acetic acid at reflux for 2.0 hr. [b] In acetic acid at room temperature for 4 days; Pd(OAc)$_2$ is rapidly reduced to Pd metal.

In the palladium-catalyzed reactions of dihydrophthalic acids, we found a considerable amount of decarboxylation to benzoic acid in addition to the disproportionation products. When an acetic acid solution of diacid **1** was refluxed in the presence of palladium on carbon for 20 hr, benzoic acid (33%), hexahydrophthalic acid (30%), and phthalic acid (37%) were obtained. Similarly, reaction of diacid **5** gave 35% benzoic acid, 25% hexahydrophthalic acid, and 38% phthalic acid. The palladium-catalyzed reactions gave tetrahydrophthalic acids (19% from **1**, 41% from **5**) together with phthalic acid (35%) and benzoic acid (20%) after 1 hr in refluxing acetic acid. Benzoic acid was formed by loss of carbon dioxide and hydrogen from dihydro- and tetrahydrophthalic acids. Mass spectral analysis of gas samples during the reactions showed carbon dioxide, but no hydrogen. From the relative amounts of phthalic and hexahydrophthalic acids formed, we conclude that the hydrogen produced on formation of benzoic acid was bound to the catalyst and subsequently transferred to olefin parallel to the formation of hexahydrophthalic and benzoic acids by decarboxylation in the palladium-catalyzed reaction of 1,2,3,6-tetrahydrophthalic acid (**22**).[22]







Experimental Section

Nmr spectra were recorded on a Jeol H-100 spectrometer using tetramethylsilane as an internal standard. Infrared spectra were recorded on a Perkin-Elmer 237B spectrophotometer. All new compounds gave satisfactory elemental analyses (±0.3%). Melting points and boiling points are uncorrected.

Egc Analyses. A Hewlett-Packard Model 5750 gas chromatograph attached to a Varian Aerograph Model 477 digital integrator was used for gc analyses. Methyl ester samples were prepared from the corresponding acids with diazomethane in ether or with boron trifluoride etherate in methanol according to standard procedures. Dimethyl esters of phthalic acid and dihydrophthalic acid isomers elute in the following order: on a 15 ft × 0.125 in. column packed with 10% OV 210 (methyl silicone with 50% trifluoropropyl groups) on Chromsorb W (80/100), *cis*- and *trans*-1,2-dihydrophthalate (same retention times), 2,3-dihydrophthalate, 1,4-dihydrophthalate, phthalate; on a 15 ft × 0.125 in. column packed with 10% OV 17 (methyl silicone with 50% phenyl groups) on Chromsorb W (80/100), *trans*-1,2-dihydrophthalate, *cis*-1,2-hydrophthalate, 2,3-dihydrophthalate, phthalate and 1,4-dihydrophthalate (same retention times).

Dimethyl *trans*-1,2-Dihydrophthalate (14). A mixture of 50.0 g of **1** (95%) and phthalic acid (5%) with 500 ml of methanol and 40 ml of $BF_3 \cdot Et_2O$ was refluxed for 24 hr. The reaction mixture was diluted with water and the products were extracted with benzene. The extract was dried, the solvent was removed on a rotary evaporator, and the products were distilled through a Vigreux column to yield a center-cut fraction of 47.5 g (85%), bp 82–85° (1.0 mm), consisting of 95% **14**, 2.5% dimethyl *cis*-1,2-dihydrophthalate, 1.0% **15**, and 1.5% **16**.

Dimethyl 1,4-Dihydrophthalate (15). 1,4-Dihydrophthalic acid (**5**) was prepared by isomerization of **1** in water,[9] mp 226–228°. Esterification of **5** (5.74 g) in 100 ml of methanol with 7 ml of $BF_3 \cdot Et_2O$ as above gave 6.24 g of distillate, bp 83–85° (0.2mm), consisting of 96% **15**, 1.5% **14**, 0.1% **16**, and 2.4% dimethyl 2,3-dihydrophthalate.

Dimethyl 2,2,3,3-Tetracyanobicyclo[2.2.2]oct-5-ene-*trans*-7,8-dicarboxylate (7). Adduct **7** was prepared in 93% yield by heating an equimolar mixture of **14** and TCNE on a steam bath for 20 hr, mp 172–174° (lit.[6] mp 172–173°), identical nmr spectra as reported for **7**.[6]

Dimethyl 2,2,3,3-Tetracyanobicyclo[2.2.2]oct-5-ene-*cis*-*endo*-7,8-dicarboxylate (8). *cis*-1,2-Dihydrophthalic anhydride (**6**), obtained by refluxing **1** in acetic anhydride,[4] was esterified with $BF_3 \cdot Et_2O$ in methanol. The ester was heated with a 50% excess of TCNE under nitrogen on a steam bath for 16 hr to give an 82% yield of **8** after recrystallization from benzene, mp 183–185°, ir (Nujol) 1740 cm^{-1}.

2,2,3,3-Tetracyanobicyclo[2.2.2]oct-5-ene-*endo*-7,8-dicarboxylic Anhydride (9). Ten grams of a mixture of **1** (93.2%, 55.5 mmol) and phthalic acid (6.8%) was refluxed in 25 ml of acetic anhydride for 30 min. TCNE (6.55 g, 51.1 mmol) was added to the cooled solution and the resulting mixture was heated at 50° for 5 days. White crystals precipitated during the course of the reaction. The solid was filtered and washed with benzene: yield 12.43 g (88% based on TCNE); mp 300° dec; ir (Nujol) 1880, 1775 cm^{-1}. The mass spectrum shows no parent ion, but contains a strong M + 1 peak at 279, M − CO_2 at 234.

Anal. Calcd for $C_{14}H_6N_4O_3$: C, 60.4; H, 2.2. Found: C, 60.5; H, 2.3.

Adduct 8 Prepared from Anhydride 9. A solution of **9** (2.00 g) in 25 ml of methanol and 2 ml of $BF_3 \cdot Et_2O$ refluxed for 16 hr produced 2.37 g after recrystallization from benzene. Sublimation at 150° (0.02 mm) and recrystallization from benzene gave 2.04 g (88%) of **8**, mp 181–183°, identical by ir and nmr with the sample prepared above.

Hydrolysis of 9. **9** (3.00 g) was refluxed in 50 ml of water until all solids were in solution (45 min). The solution was cooled to 0° and filtered to give a 70% yield of **10** tetrahydrate, mp 295° dec, ir (Nujol) 3625, 3540, 3360, 1725 cm. When **10** tetrahydrate is heated at 60° *in vacuo* overnight, **11** dihydrate is formed, mp 295° dec, ir (Nujol) 3320, 1750, 1725 (shoulder), 1150 cm^{-1}. Recrystallization of **10** tetrahydrate from acetone–benzene (~1:1) gave an anhydrous sample of **10**, mp 295–300° dec, ir (Nujol) 1735, 1725 cm^{-1}. Heating anhydrous **10** at 60° *in vacuo* overnight gave anhydrous **11**, mp 295° dec, ir (Nujol) 3325, 1750, 1740, 1725 (shoulder), 1150 cm^{-1}. Nmr spectrum of **10** (acetone-d_6): δ 9.92 (singlet, 2 H, acidic protons), 6.80 (multiplet, 2 H, olefinic), 4.32 (multiplet, 2 H, bridgehead), and 3.76 (singlet, 2 H, exo tertiary).

Anal. Calcd for $C_{14}H_8N_4O_4$: C, 56.8; H, 2.7. Found (**10**): C, 56.5; H, 3.1. Found (**11**): C, 56.6; H, 2.7.

Dehydration of 10 and 11 to 9. A sample of **11** was heated at 200–220° *in vacuo* for 30 min. The infrared spectrum of the residue was identical with that of anhydride **9**. When **10** was heated at 200° for 30 min, it was converted to **9** plus small amounts of **11**.

A solution of **11** (0.30 g) in 20 ml of acetic anhydride at room temperature for 16 hr gave, after removal of solvent, a solid with an infrared spectrum identical with that of **9**. Similarly, **10** in acetic anhydride gave a mixture of **9** and unreached **10**.

Dimerization of 1 to Tricyclo[6.2.2.0^{2,7}]dodeca-3,9-diene-5,6,11,12-tetracarboxylic Dianhydride (12). Dihydrophthalic acid (175 g), containing 96% **1** and 4% phthalic acid, was refluxed in 200 ml of acetic anhydride for 66 hr. White crystals formed. The mixture was cooled to room temperature; the solid was filtered and washed thoroughly with benzene. Yield of **12** was 104 g (70%): mp 238–240° dec; ir (Nujol) 1860, 1775 cm^{-1}; mol wt (mass spectrum) 300; nmr (DMSO-d_6) multiplets centered at δ 6.48 (2 H), 6.00 (2 H), 3.75 (4 H), 3.29 (2 H), and 2.86 (2 H).

Anal. Calcd for $C_{16}H_{12}O_6$: C, 64.0; H, 4.0. Found: C, 64.3; H, 4.0.

Tricyclo[6.2.2.0^{2,7}]dodeca-4,9-diene-5,6-11,12-tetracarboxylic Dianhydride (13) by Reaction of 1 and 5. A mixture of **1** (1.01 g), **5** (0.99 g), and 5 ml of acetic anhydride was refluxed for 15 hr. The solid was filtered and washed with ethanol. The yield of **13** was 0.30 g (17%): mp 268–270° dec; ir (Nujol) 1840, 1780, 1665 cm^{-1}; mol wt (mass spectrum) 300; nmr (DMSO-d_6) multiplets centered at δ 7.28 (1 H), 6.48 (2 H), 3.60 (2 H), 3.45 (2 H), 2.70 (1 H), and 2.20–1.60 ppm (4 H).

Anal. Calcd for $C_{16}H_{12}O_6$: C, 64.0; H, 4.0. Found: C, 63.8; H, 4.2.

13 by Catalyzed Reaction of 1. A mixture of **1** (1.87 g, 11.0 mmol), $CoBr_2 \cdot 2PPh_3$ (0.20 g, 0.27 mmol), $BF_3 \cdot Et_2O$ (10 drops, 0.82 mmol), and 5 ml of acetic anhydride was refluxed for 15 hr; the yield of **13** was 0.46 g (28%), mp 267–269° dec.

13 by Catalyzed Reaction of 1 and 5. A mixture of 1.01 g (6.0 mmol) of **1**, 1.09 g (6.5 mmol) of **5**, 0.20 g (0.27 mmol) of $CoBr_2 \cdot 2PPh_3$, 10 drops (0.82 mmol) of $BF_3 \cdot Et_2O$, and 5 ml of acetic anhydride was refluxed for 15 hr; the yield of **13** was 0.69 g (36%), mp 268–270° dec.

Palladium-Catalyzed Disproportionation of Dimethyl Dihydro- and Tetrahydrophthalates. A mixture of dimethyl dihydrophthalate, palladium on carbon, and solvent was stirred at reflux. Products were analyzed by vpc, after filtration of the catalyst and concentration of the filtrate on a rotary evaporator. For the kinetic studies aliquots of the reaction mixture were analyzed at given intervals. Reaction conditions and product analyses are in Table III. Results of reactions of **14** catalyzed by other transition metal compounds are shown in Table IV.

Tetrahydrophthalates **19**, **20**, and **21** were characterized by their nmr spectra (CCl_4): for **19**, multiplets at δ 5.63 (2 H), 3.40 (1 H), 2.80 (1 H), and 2.4–1.8 (4 H), singlet at 3.63 (6 H); for **20**, multiplets at δ 6.99 (1 H), 3.28 (1 H), 2.10 (2 H), 1.80 (2 H), and 1.52 (2 H), singlets at 3.65 (3 H) and 3.60 (3 H); for **21**, multiplets at δ 5.58 (2 H), 2.70 (2 H), and 2.20 (4 H), singlet at 3.58 (6 H).

Dimethyl *cis*-1,2,3,6-tetrahydrophthalate and 3,4,5,6-tetrahydrophthalate were prepared by esterification of their corresponding anhydrides. Absence of these isomers in the palladium-catalyzed reactions of **14**, **15**, **19**, **20**, or **21** was demonstrated by comparisons of nmr spectra and gas chromatographic retention times.

Palladium-Catalyzed Disproportionation Reactions of 1 and 5. A mixture of 2.0 g (11.8 mmol) of dihydrophthalic acids (91.4% **1**, 2.6% **2**, 0.1% **4**, 2.8% **5**, and 3.1% phthalic acid), 0.50 g (0.38 mmol) of 5% Pd/C, and 15 ml of acetic acid was refluxed for 1 hr under argon. The products were esterified with 20 ml of methanol and 2 ml of $BF_3 \cdot Et_2O$ at reflux for 6 hr. Analysis (mass spectrum) of the gases evolved showed carbon dioxide, in addition to argon and air; analysis of the methyl esters by vpc showed methyl benzoate (17%), **17** (28%), **20** (5%), **19** + **21** (14%), and **16** (36%). When the disproportionation reaction was allowed to proceed for 20 hr at reflux, the product distribution was 33% methyl benzoate, 30% **17** and **18**, and 37% **16**.

A mixture of 1.04 g (6.2 mmol) of dihydrophthalic acids (1.5% **1**, 1.4% **4**, 96.5% **5**, and 0.5% phthalic acid) and 0.25 g (0.19 mmol) of 5% Pd/C was refluxed in 8 ml of acetic acid and the products were esterified. The mass spectrum of a gas sample showed carbon dioxide, argon, and air. Vpc analysis of the methyl esters from a 1-hr reaction showed 20.0% methyl benzoate, 2.7% **17**, 6.0% **19** + **21**, 2.0% **18**, 35.3% **20**, and 34.0% **16**; analysis of products after 20 hr at reflux in acetic acid showed 35% methyl benzoate, 5.3% **17**, 19.7% **18**, 2.0% **20**, and 38% **16**.

Palladium-Catalyzed Hydrogenation of 14 and 15. A mixture of 1.31 g of **14** [93.5% pure, containing the methyl esters of **2** (2.4%), **4** (0.1%), **5** (2.1%), and phthalic acid (1.9%)], 0.26 g of 5% Pd/C, and 100 ml of benzene was hydrogenated in a 300-ml capacity rocking autoclave bomb at 500 psi at room temperature for 1.5 hr. Vpc analysis of the products showed 95.1% **17**, 2.5% **18**, 0.7% **20**, and 1.7% **16**.

Hydrogenation of **15** [90% pure, containing the methyl esters of **1** (0.5%), **4** (7.0%), and phthalic acid (2.5%)] under the same conditions as above gave 1.3% **17**, 34.9% **18**, 60.9% **20**, and 2.9% **16**.

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Registry No.—**1**, 5675-13-8; **5**, 1515-23-7; **6**, 1515-19-1; **8**, 50388-57-3; **9**, 50388-58-4; **10**, 50388-59-5; **11**, 50388-60-8; **12**, 50388-61-9; **13**, 50388-62-0; **14**, 26549-64-4; **15**, 38201-52-4; **19**, 50388-65-3; **20**, 41902-36-7; **21**, 17673-68-6; phthalic acid, 88-99-3.

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Nuclear Magnetic Resonance Studies of the Geometrical Isomers of α,α'-Disubstituted Succinosuccinic Esters

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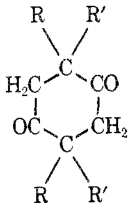
Investigation of the nmr spectra of a series of α,α'-disubstituted succinosuccinic esters, all except one existing as cis and trans isomers, has shown that every pair of these isomers gave nmr spectra which differed from each other in the spacings between the doublets for the four methylene protons in the cyclohexane ring. By association of the nmr spectral data with conformational analysis of the isomeric esters under investigation, it is possible to make plausible assignment of configuration to these isomers. This has found support from nmr spectroscopy of α,α'-dimethylsuccinosuccinic esters at very low temperatures and preliminary results from X-ray analysis of one of the isomers of di-*p*-bromobenzylsuccinosuccinic ester. The difference in the temperature effect on the nmr spectra of the geometrical isomers is discussed. Of the substituted succinosuccinic esters investigated in the present work, those which were previously unknown have been characterized.

While using nmr spectroscopy in the characterization of α,α'-disubstituted succinosuccinic esters, each existing as cis and trans isomers, it was found that, for each pair of such isomers, the nmr spectrum of the one differed from that of the other in the spacing between the doublets for the four methylene protons in the cyclohexane ring. This has led to the attempt at the feasibility of assigning the configurations of these isomers according to their nmr spectra.

The story began when the present authors were reinvestigating the reaction between disodiosuccinosuccinic ester and a benzyl halide, which was first investigated by Nef[1] more than 80 years ago. This latter author regarded the key products that resulted from the reaction as two isomers of diethyl 2,5-dibenzoxy-3,6-dihydroterephthalate, on account of their sluggishness to the action of carbonyl reagents, their resistance to ketonic cleavage by the action of dilute sulfuric acid, and their crystallographic resemblance to the product obtained by reducing diethyl 2,5-dibenzoxyterephthalate.[1] Being curious about the occurrence of the isomerism of the dienolic ethers, Chan[2] repeated Nef's experiment, and isolated exactly the same products as those obtained by Nef. She found, however, that they did react with hydroxylamine to give the corresponding dioximes, showing the presence of two carbonyl groups. Her investigation was not carried any further owing to the failure of the products to undergo ketonic cleavage. Nor did she seem to have obtained pure samples of the dioximes.

Following the discovery of the cleavage of β-keto esters by the action of metal iodides,[3] the present authors again made a study of the reaction between disodiosuccinosuccinic ester and benzyl iodide and of the isomeric products, with a view to elucidating their structure and, should they exist as geometrical isomers, determining their configuration. As those described by Nef, the two crystalline substances that resulted from the reaction melted at 140.5 (Ia) and 148.5° (Ib). Both of them reacted with hydroxylamine, giving the corresponding dioximes, mp 221° dec and 252° dec, respectively. On refluxing for 48 hr with dilute sulfuric acid, Ib was converted into a product of unknown structure, melting at 272°, which had the same percentage



I, R = COOEt; R' = CH_2Ph
II, R = H; R' = CH_2Ph
III, R = COOEt; R' = CH_2COOEt
IV, R = COOEt; R' = CH_3
V, R = H; R' = CH_3
VI, R = COOEt; R' = $CH_2C_6H_4Br$
VII, R = COOEt; R' = $CHPh_2$