Dissociation and Diels–Alder Reactions of Dicyclopentadienedicarboxylic Esters

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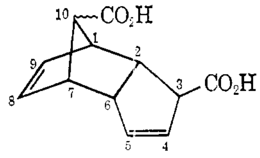
The formation of isomeric dicyclopentadienedicarboxylic acids (**11b** and **12b**) from the carboxylation of cyclopentadienylsodium has been studied. The isomeric dimethyl dicyclopentadienedicarboxylates (**11a** and **12a**) dissociate thermally and redimerize to a mixture of isomers or react with other reagents as dienes or dienophiles. Methyl cyclopentadiene-1-carboxylate (**9a**) has been found to rearrange rapidly and reversibly to the 2 isomer (**10a**), which reacts selectively with dienophiles. The kinetics of the thermal dissociation of 4,9-dicarbomethoxytricyclo[5.2.1.0^{2,6}]deca-3,8-diene (**11a**) have been studied and the ΔH^* and ΔS^* of the dissociation were found to be 25.9 kcal/mole and −13.3 eu, respectively.

In the course of studies of agents for thermally reversible cross links in cotton cellulose, it was necessary to study the chemistry of dicyclopentadienedicarboxylic acid and its esters. Thiele[2] prepared the first acid of this type in 1901 by treating cyclopentadienylpotassium with carbon dioxide. He obtained a dicyclopentadienedicarboxylic acid which yielded a crystalline dimethyl ester and observed dissociation of the latter, upon distillation, to monomeric methyl cyclopentadienecarboxylate. Alder and Stein[3] proposed the structure of 3,10-dicarboxytricyclo[5.2.1.0^{2,6}]deca-4,8-diene (**1**) for Thiele's acid on the basis of the least structural change from the presumed monomeric acid, cyclopentadiene-5-carboxylic acid (**2**).



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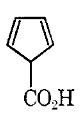

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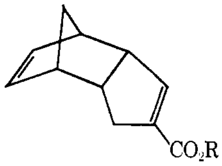
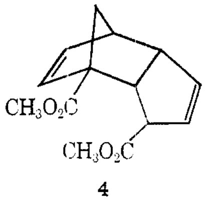


3a, R = CH_3
b, R = H

Alder and coworkers[4] later reported that the monomeric ester reacts with cyclopentadiene to give 4-carbomethoxytricyclo[5.2.1.0^{2,6}]deca-3,8-diene (**3a**). The structure of this adduct was established by chemical degradations to a symmetrical ketone having two α-methylene groups and reduction of the ketone to the known *endo*-tetrahydrodicyclopentadiene. These workers identified the monomeric ester as methyl cyclopentadiene-1-carboxylate (**9**, Scheme I) and suggested structures **4** and **5** for the dimeric ester.



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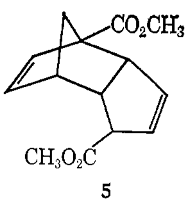

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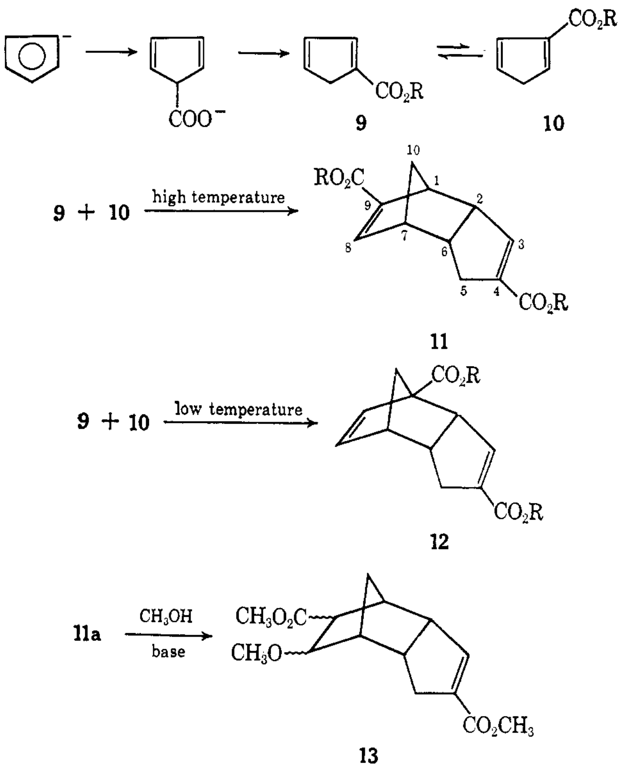
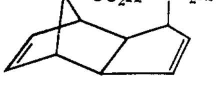
Wiese, in a patent,[5] reported that the carboxylation of cyclopentadienylsodium at −30° produces a second isomeric dicyclopentadienedicarboxylic acid, which forms a liquid dimethyl ester, in addition to the previously known Thiele acid, which forms a solid dimethyl ester. Wiese accepted Alder's original formula (**1**) for the Thiele acid and with no published evidence stated that the new acid is the *exo* isomer (**6**) of the Thiele acid.

Scheme I



a, R = CH_3
b, R = H
c, R = Na
d, R = C_6H_5



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Day[6] reported that both of the carbomethoxy groups of the Thiele diester are conjugated, but could not distinguish the positions of the carbomethoxy groups on the dicyclopentadiene nucleus of the Thiele ester.

Peters[7a] used ultraviolet spectroscopic evidence to show that the monomeric methyl ester is methyl cyclopentadiene-1-carboxylate (**9a**) and contains no signifi-

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[1] One of the laboratories of the Southern Utilization Research and Development Division, Agricultural Research Service, U. S. Department of Agriculture.

[2] J. Thiele, *Ber.*, **34** 68 (1901).

[3] (a) K. Alder and G. Stein, *Ann.*, **514**, 10 (1934); (b) *ibid.*, **515**, 192 (1935).

[4] K. Alder, F. H. Flock, A. Hausweiler, and R. Reeber, *Ber.*, **87**, 1752 (1954).

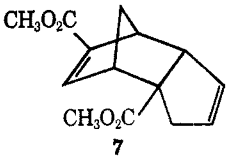
[5] H. K. Wiese, U. S. Patent 2,781,395 (Feb 1957).

[6] R. J. Day, Ph.D. Dissertation, Cornell University, Ithaca, N. Y., 1958; *Dissertation Abstr.*, **19**, 39 (1958).

[7] (a) D. Peters, *J. Chem. Soc.*, 1761 (1959); (b) *ibid.*, 1832 (1960); (c) *ibid.*, 1037 (1961); (d) *ibid.*, 1042 (1961).

cant amount of methyl cyclopentadiene-2-carboxylate (**10a**). The uv spectrum of the Thiele dimeric ester indicated the presence of two α,β-unsaturated carbomethoxy groups. With this evidence, Peters suggested structure **11a** (*endo*-4,9-dicarbomethoxytricyclo[5.2.1.0^{2,6}]deca-3,8-diene) on the basis of the least amount of structural rearrangement of the monomers during the dimerization.

In a subsequent paper,[7d] Peters reports that the dimerization of pure methyl cyclopentadienecarboxylate gives three dimeric esters: 65% of the Thiele ester (**11a**), 10% of a second solid diester (**7**), and 25% of Wiese's liquid diester, to which Peters assigned structure **8**. These structures were assigned on the basis of uv and ir spectra and on the basis of the addition of dimethylamine to **11a** and **7**, in which the norbornene double bonds are conjugated with carbomethoxy groups.



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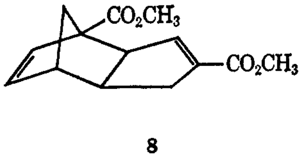

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The Thiele ester was found to have two α,β-unsaturated carbomethoxy groups, while the other two dimeric esters (**7** and **8**) had one α,β-unsaturated carbomethoxy group each. The two solid dimeric esters had conjugated norbornene double bonds, while the liquid dimeric ester had an unconjugated norbornene double bond. The *exo* configuration was assigned to the liquid dimeric ester on the basis of its low melting point and in apparent deference to Wiese's assignment.

The present work was undertaken to study the kinetics of the thermal dissociation of dimethyl dicyclopentadienedicarboxylate and to obtain further clarification of the structures of the dimeric acids and esters.

Results

Dicyclopentadienedicarboxylic Acids and Esters.—Commercial dicyclopentadienedicarboxylic acid, usually prepared by the reaction of carbon dioxide with a suspension of cyclopentadienylsodium in an inert solvent at room temperature or above, was found to consist almost entirely of Thiele acid **11b**. The solid dimethyl ester of the commerical acid, prepared by Thiele's method[2] with methanol and sulfuric acid, was found by thin layer chromatography to be a single isomer.

Attempted esterification of the diacid **11b** with dimethyl sulfate in the presence of sodium carbonate and methanol[8] gave only 8-methoxy-4,9-dicarbomethoxytricyclo[5.2.1.0^{2,6}]dec-3-ene (**13**). This methanol addition product could also be obtained by heating the dimethyl ester **11a** in methanol in the presence of sodium carbonate. The original acid **11b** was regenerated by heating the methoxy derivative in aqueous sodium hydroxide.

Attempted preparation of the Thiele diester **11a** from the acid with trifluoroacetic anhydride and methanol[9] was unsuccessful, but the diphenyl ester **11d** was prepared by this method in good yield.

A second dicyclopentadienedicarboxylic acid was obtained by a modification of Wiese's procedure[5] in which a solution of cyclopentadienylsodium in tetrahydrofuran was added to a slurry of Dry Ice in xylene. The crude dicarboxylic acid was esterified with methanol and sulfuric acid to give a semisolid mixture of esters, which was found to consist of only two isomers by thin layer chromatography and nmr spectra. The ratio of the isomers was variable from reactions conducted under identical conditions. Integration of the vinyl proton regions of the nmr spectra of the esterified products from three apparently identical carboxylations showed them to consist of 21 to 47% of isomer **12a** and 79 to 53% of isomer **11a**. The yields of diesters were 70 to 90%, based on cyclopentadienylsodium.

The nmr spectra of the Thiele diester and the liquid diester are consistent with the structures (**11a** and **8**, respectively) proposed by Peters[7d] for these compounds. The spectrum of the Thiele diester (**11a**) shows a one-proton doublet for H_8 at τ 3.20 with the peaks separated by 3 cps. The spectrum of the liquid diester (**12a** or **8**) shows a two-proton signal for H_8 and H_9 at τ 3.88 as an apparent doublet with a peak separation of 1 cps.

The cyclopentene vinyl proton (H_3) gives a characteristic signal in the τ 3.2 to 3.5 region in the spectra of the Thiele diester (**11a**), the liquid diester (**12a** or **8**), the diphenyl esters of the two dimeric acids (**11d** and **12d**), the methanol addition product of the Thiele diester (**13**), and the adducts of methyl cyclopentadienecarboxylate with cyclopentadiene and hexachlorocyclopentadiene (**3** and **17**, respectively). In each of the spectra the signal appears to be a quartet with a peak height ratio of 1:2.5:2.5:1 and a separation of 2 cps between adjacent peaks. Double resonance experiments on adduct **17** were unsuccessful because of the spacing of the coupling protons at multiples of 60 cps. Since the cyclopentene vinyl proton signals from these compounds are very similar and the structure of one of these compounds (**3**) has been established by chemical reactions,[4,7c] we assume that the cyclopentene carbomethoxy groups in the dimeric esters and in the adducts are all in the 4 position.

Dimeric esters with a carbomethoxy group in the 4 position would arise from reactions of one molecule of **9a** or **10a**, as dienes, with a molecule of **9a**, as the dienophile. Dimeric esters having the carbomethoxy group in the 3 or 5 position are considered much less probable in view of the fact that Peters[7a] found no evidence for the existence of an appreciable amount of **10a** in the monomeric ester and in view of our estimation of the lower reactivity of **10a** than **9a** as a dienophile (*vide infra*).

Table I lists the chemical shifts of the compounds studied.

The bridge (C_{10}) protons appear in the spectrum of **11a** as an AB quartet centered at τ 8.46. This AB pattern with separations of 10–25 cps for the bridge protons has been reported for a number of norbornene derivatives.[10] A similar pattern appears in the spectra

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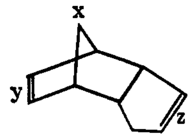
(8) C. G. Young and B. M. Craigs, *J. Am. Oil Chemists' Soc.*, **28**, 521 (1951).

(9) R. C. Parish and L. M. Stock, *Tetrahedron Letters*, No. 20, 1285 (1964).

(10) (a) J. C. Davis, Jr., and T. V. Van Auken, *J. Am. Chem. Soc.*, **87**, 3900 (1965); (b) P. M. Subramanian, M. T. Emerson, and N. A. LeBel, *J. Org. Chem.*, **30**, 2624 (1965); (c) K. Tori, Y. Hata, R. Muneyuki, Y. Takano, T. Tsuji, and H. Tanida, *Can. J. Chem.*, **42**, 926 (1964); (d) P. Laszlo and P. von R. Schleyer, *J. Am. Chem. Soc.*, **86**, 1171 (1964).

TABLE I
NUCLEAR MAGNETIC RESONANCE SPECTRA



Compd	Chemical shifts in τ units		
	H_x	H_y	H_z
3b	8.52 (8, 14)[a]	3.93 (2 H, m)[b]	3.26 (q?)
11a	8.46 (7.5, 13.5)	3.20 (d)	3.53 (q?)
11d	8.38 (9, 18)	2.8[c]	3.29 (q?)
12a	8.25 (—, 1.5)	3.88 (2 H, d)	3.44 (q?)
12d	8.12 (—, 3)	3.74 (2 H, m)	3.22 (q?)
13	8.41 (10, 19.5)		3.42 (q?)
14a[d]	7.74 (12, 21)	2.50 (spl d)	
14b[d]	7.68 (11, 21)	2.3[c]	
15	8.18 (8.5, 14)	2.95[c]	
16	8.01 (—, 1)	3.59 (2 H, q)	
17			3.42 (q?)

[a] The numbers in parentheses give the values of the coupling constants, *J*, and the separation in cps for the AB pattern of the bridge protons. [b] The abbreviations are as follows: 2 H, integration shows two protons; d, doublet; q, quartet; m, multiplet; spl d, split doublet. [c] These vinyl proton signals were partially obscured by the phenyl proton absorptions and the values are approximate. [d] Spectra were run in dimethyl sulfoxide-d_6.

of **3b**, **13**, and the Diels–Alder adducts derived from cyclopentadiene-2-carboxylate esters **14** and **15**.

The bridge protons of **12a** appear as a poorly resolved doublet at τ 8.25, *i.e.*, at approximately the same chemical shift as the downfield proton of the AB quartet in the spectrum of the Thiele diester. A similar doublet for the bridge protons appears in the spectrum of the corresponding diphenyl ester (**12d**) and the N-phenylmaleimide adduct from methyl cyclopentadiene-1-carboxylate (**16**). The reason for the shift in the signal of only one bridge proton is obscure, although it is apparently not caused by a preferred conformation of the carbomethoxy group on C_1, as the signal from the bridge protons of adduct **16** in tetrachloroethane was identical at 35 and 120°.

The remaining protons of the diesters gave complex, overlapping patterns between τ 6.5 and 8.0, which were not further analyzed.

The nmr data give no evidence as to the position of the cyclopentene double bond at C_3 or at C_4. However, molecular models show that an allylic hydrogen at C_3 of the 4,8-diene would be much closer to the carbomethoxy group at C_9 or C_1 than would be the vinyl hydrogen of the corresponding 3,8-dienes. The less-crowded transition states leading to the 3,8-diene structures would appear to be favored. Until further evidence is available, we prefer the 4,9-dicarbomethoxy-3,8-diene structure (**11a**) for the Thiele diester and the 1,4-dicarbomethoxy-3,8-diene structure (**12a** or **8**) for the liquid diester as arising from the less crowded transition states. Although it is possible that Woodward–Katz rearrangements are involved in the formation of the dimeric acids and esters, we believe these rearrangements to be unlikely at the low temperatures at which the dimerizations occur.

There is at present no evidence to permit the firm assignment of an *endo* or an *exo* configuration to either of the dimeric esters. Alder[4] and Peters[7d] prefer the *endo* configuration (**11a**) for the Thiele diester by analogy with other Diels–Alder reactions. Wiese[5] assigned an *exo* configuration (**6**) to the liquid diester on the basis of incorrect assumptions regarding the structures of the two dimeric esters. He presents no evidence to support this *exo* configuration other than the fact that the Thiele diester and the liquid diester are not the same compound. Day[6] apparently accepts the *exo* configuration of the liquid diester and the corresponding acid, but states that it is unusual to obtain an *exo* isomer at low temperature and an *endo* isomer at a higher temperature. Although Peters[7d] revised the structure of the liquid diester (**8**), he continued to accept the *exo* configuration of Wiese. The only evidence he cites in proof of this configuration is the fact that the diester is a liquid. The dimerizations of the monoesters **9a** and **10a** and of the salts **9c** and **10c** are analogous to the many cases in which the Alder *endo* rule is followed.[11] Since the diesters and the diacids dissociate only at temperatures much higher than their temperatures of formation, these dimerizations are not analogous to the reported exceptions to the Alder *endo* rule. We therefore prefer the *endo* configuration (**12a**) for the liquid diester rather than the *exo* configuration (**8**) until definite evidence is at hand to confirm one of these configurations.

The difference in product composition between the two carboxylation–dimerization reactions is ascribed to a difference in the relative rates of isomerization and dimerization of the intermediate cyclopentadienecarboxylates **9c** and **10c** at the different reaction temperatures. Since no products from cyclopentadiene-5-carboxylate have been found in this series, the 5-carboxylate isomer must rearrange immediately upon formation to **9c**.

The reaction of **9c** with **10c** to form the dimer **11c** is expected to be favored at all temperatures over the dimerization of **9c** to form **12c** because of the greater separation of the carboxylate group of **10c** from the site of reaction. Under the conditions of the reaction, it is expected that **9c** and **10c** would be in an equilibrium with each other if they were not being consumed by the dimerizations and that **9c**, because of more effective conjugation of the carboxylate group with the diene system, will be the major component of the equilibrium.[7a] The reported exclusive formation of **11b** at or above room temperature[2–4,7] indicates that **10c** is amply available for reaction with **9c** to the practical exclusion of the formation of **12c** by the dimerization of **9c**. Such a condition can occur only if the rearrangement from **9c** to **10c** occurs more rapidly than the dimerization of **9c** to **12c**.

At the lower temperature of reaction reported here, the dimerization of two molecules of **9c** competes successfully with the reaction of **9c** with **10c**. This would be the expected result if the rate of the rearrangement of **9c** to **10c** was decreased to a greater extent by lowering the temperature than were the rates of the dimerizations. This explanation is supported by the only reported activation energies of analogous reactions. The energy of activation of the dimerization of **9a** is reported to be 14.7 kcal/mole,[7d] while the energy of activation of the rearrangement of 5-methylcyclopentadiene to the 1-methyl isomer is 20.4 kcal/mole.[12]

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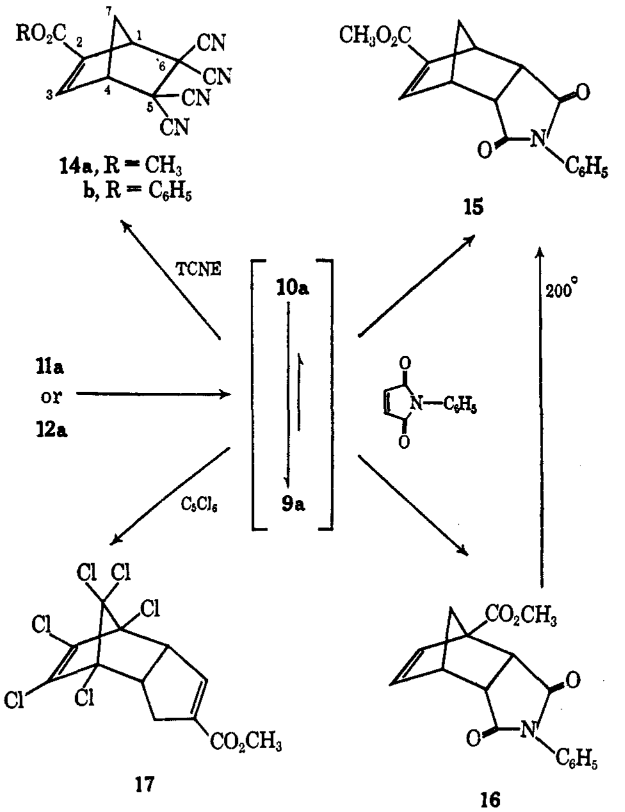
(11) A recent review of the validity and exceptions to the Alder *endo* rule appears in J. Sauer, *Angew. Chem. Intern. Ed. Engl.*, **6**, 16 (1967).

(12) S. McLean and P. Haynes, *Tetrahedron*, **21**, 2329 (1965).

Dissociation Diels–Alder Reactions.—The reports[2-4,7] on the dissociation of **11a** state only that the monomeric ester distils at a good rate when the dimeric ester is heated at 160° under vacuum. It seemed likely that the dissociation was occurring at temperatures below 160°, but that the monomer was not escaping at the lower temperatures. In order to investigate this possibility, the dimeric esters **11a** and **12a** were heated at temperatures of 100 to 145° in the presence of reactive dienophiles in inert solvents.

Tetracyanoethylene (TCNE) has been reported[13] to be a very reactive dienophile; it therefore appeared that TCNE might be a suitable trapping agent for studying the thermal dissociations of **11a** and **12a**. When either **11a** or **12a** was heated with TCNE at 100–145° (see Scheme II) only one adduct was formed, in isolated yields of 75–82%. The nmr spectrum of this adduct showed one vinyl proton and a widely spaced AB pattern (21 cps) for the bridge (C_7) protons. The TCNE adduct is therefore, 5,5,6,6-tetracyano-2-carbomethoxy-2-norbornene (**14a**), the adduct from TCNE and **10a**. The diphenyl esters **11d** and **12d** also gave 70–80% yields of the analogous TCNE adduct **14b**. Adducts **14a** and **14b** were found by thin layer chromatography to be pure as they crystallized from the reaction solution, and no trace of any other TCNE adduct from either the methyl or phenyl diester was found. There may have been traces of another adduct in the reaction mixture, but it did not crystallize from the reaction solution with the main product and was not separated from the excess TCNE.

SCHEME II



When either dimethyl ester **11a** or **12a** was heated with N-phenylmaleimide under the same conditions employed for the TCNE reactions, a mixture of a solid adduct and a liquid adduct was formed. The solid adduct was assigned the 1-carbomethoxy-5,6-(N-phenyldicarbimido)-2-norbornene (**16**) structure on the basis of its nmr spectrum, which showed two vinyl protons and a very close doublet (a cps) for the bridge (C_7) protons. The oily adduct was not completely separated from the solid, but the nmr spectrum of the partially purified oil showed six protons (one vinyl and five aromatic) between τ 2.3 and 3.1 and the characteristic AB pattern (14 cps) of the bridge protons at τ 8.18. The liquid adduct was therefore assigned the structure of 2-carbomethoxy-5,6-(N-phenyldicarbimido)-2-norbornene (**15**). The nmr spectrum of the liquid adduct showed no signals which could not be attributed to either **15** or **16**. Fractional crystallization of the products from the reactions of both **11a** and **12a** with N-phenylmaleimide gave the same yields of **16**.

When adduct **16** was heated at 200° for 2 hr, it was converted to adduct **15** in 90% yield, as measured by the nmr spectrum of the crude isomerization mixture.

Gas–liquid partition chromatography (glpc) was used to determine the ratio of **15** to **16** formed in the action of **11a** with excess N-phenylmaleimide in refluxing dioxane. Because adducts **15** and **16** dissociate thermally at temperatures below those required for gas chromatography, it was necessary to hydrogenate the reaction mixture before separating it by glpc. The observed ratio of adducts was 66% of the solid adduct **16** and 34% of the liquid adduct **15**. The only peaks observed on the gas chromatograph were those from the hydrogenated N-phenylmaleimide and the hydrogenated adducts **16** and **15**.

To study the reactions of diesters **11a** and **12a** with another type of trapping agent, the diesters were heated with the reactive diene, hexachlorocyclopentadiene. Only one mixed adduct was isolated, but in a low yield (37%), because of the difficulty of removing the excess hexachlorocyclopentadiene. The nmr spectrum of this adduct showed no bridge protons and one vinyl proton as an apparent quartet at τ 3.42; therefore, the structure of 4-carbomethoxy-1,7,8,9,10,10-hexachlorotricyclo-$[5.2.1.0^{2,6}]$deca-3,8-diene (**17**) was assigned to the adduct.

Kinetics.—In our study of the course of the dissociation reaction, the kinetics of the reaction of **3a** with TCNE were measured by analyzing aliquots from the reaction for TCNE after specified times. The rates of the reaction in refluxing dioxane, in tetraglyme at 130°, and in diglyme at six temperatures between 120 and 140° were measured. The reaction was found to follow first-order kinetics with respect to the diester throughout at least three half-lives and was independent of the concentration of TCNE. The rate constants are listed in Table II. From the rate constants of the reactions in diglyme solution, the following activation parameters were calculated:[14] $\Delta H^* = 24.3$ kcal/mole, and $\Delta S^* = -13.3$ eu. These values are in the general range found for other reverse Diels–Alder reactions.[15]

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(13) W. J. Middleton, R. E. Heckert, E. L. Little, and C. G. Krespan, *J. Am. Chem. Soc.*, **80**, 2783 (1958).

(14) S. Glasstone, K. J. Laidler, and H. Eyring, "The Theory of Rate Processes," McGraw-Hill Book Co., Inc., New York, N. Y., 1941, p 199.

(15) Recent reviews of the kinetics of the Diels–Alder reaction are found in (a) A. S. Onishchenko, "Diene Synthesis," Daniel Davey and Co., Inc., New York, N. Y., 1964, p 60 ff, and (b) A. Wasserman, "Diels–Alder Reactions," American Elsevier Publishing Co., Inc., New York, N. Y., 1965.

TABLE II
RATE CONSTANTS AND CONDITIONS OF REACTION OF **11a** WITH TCNE

Run no.	Solvent	Temp, °C	$k \times 10^4$ sec^{-1}	Initial concentrations, moles of **11a**/mole of TCNE[a]
1	Dioxane	101 (reflux)	2.18	0.30
2	Diglyme	120.1	3.21	0.30
3	Diglyme	125.0	4.77	0.375
4	Diglyme	126.8	6.11	0.375
5	Diglyme	132.0	8.37	0.375
6	Diglyme	140.0	15.4	0.30
7	Tetraglyme	130.0	8.88	0.375

[a] Initial concentration of TCNE in runs 2–7 was 0.20 *M*; in run 1 it was 0.40 *M*.

Combination of the expression found in this study for the rate constant of the dissociation of **11a** with the values of E_a and log *A* reported by Peters[7d] for the dimerization of **9a** permits the calculation of equilibrium constants for the dissociation of **11a**. The expression for the equilibrium constant of the dissociation of **11a** is given in eq 1. Thus, at 150° a 1 *M* solution

$$\log K_{eq} = 3.1 - \frac{10{,}400}{2.3RT} \tag{1}$$

of **3a** will be 7% dissociated. These values can be regarded only as approximations, since the reported[7d] kinetic data for the dimerization reaction refer to the sum of three simultaneous dimerizations to give **11a**, **12a**, and **7**. Investigations into the validity of this equation are under way.

Discussion

The kinetic data on the reaction of **11a** with TCNE show that the dissociation of **11a** by the reverse Diels–Alder reaction is the rate-determining step and that the dissociation is irreversible under the reaction conditions. On dissociation by the reverse Diels–Alder reaction, diester **12a** should give two molecules of **9a** while **11a** should give one molecule of **9a** and one of **10a**. In all of the observed dissociation-trapping reactions, the structure and isomer distribution of the adducts are independent of the structure of the starting dimer **11a** or **12a** (or the corresponding phenyl esters), but depend on the trapping agent and the conditions of the reaction. To yield the observed products, monomers **9a** and **10a** must be rapidly interconverted at the temperature of the dissociations. The products of these reactions are consistent with and explained by the ratio of isomers **9a** and **10a** in the monomeric ester, the reactivities of the isomers, and the stabilities of the adducts from the two isomers.

Adduct **17** is the expected product when the trapping agent, hexachlorocyclopentadiene, reacts as a diene. Because of the end conjugation of the carbomethoxy group with the diene system, monomer **9a** is more reactive as a dienophile than is **10a**, in which the carbomethoxy group is cross conjugated with the diene system. As is observed, the Diels–Alder reaction would be expected to occur on the C_3 double bond, which has fewer bulky substituents than the C_1 double bond. A similar result was reported in the reaction of **9a** (isolated as a pure liquid) with cyclopentadiene to give **3a**.[4,7c]

When N-phenylmaleimide was used as the trapping agent, adducts from **9a** and **10a** were formed. The major product, **16**, is that derived from **9a**, which is the predominant isomer in the monomeric ester.[7a] The high ratio of **16** to **15** formed in boiling dioxane may be said to be the result of kinetic control in the sense that monoester **9a** is more plentifully available for reaction and thus the rate of formation of **16** exceeds that of **15**.

It is to be expected that adduct **15** is more easily formed and more stable than adduct **16** because of the greater distance between the carbomethoxy and carbimido carbonyl groups in **15**. The almost complete conversion of adduct **16** to adduct **15** at 200° confirms this assumption. The relatively large amount (34%) adduct **15** formed at 100° may arise from either partial thermodynamic control or from a rapid rearrangement of **9a** to **10a** followed by a greatly favored reaction of **10a** with N-phenylmaleimide.

When TCNE was used as the trapping agent, only the adduct (**14a**) from monoester **10a** was observed, although **10a** is a very minor component in the equilibrium of the isomeric monoesters.[7a] It is to be expected that the observed adduct, **14a**, is much more easily formed and more stable than the unobserved adduct from **9a** and TCNE because of the close proximity of the carbomethoxy group of the unobserved adduct to the two cyano groups on the adjacent carbon atom. The product of this reaction may result either from a fast rearrangement of **9a** to **10a** followed by a rapid reaction of **10a** with TCNE (*i.e.*, competing effectively with the reaction of **9a** with TCNE) or from rearrangement of an initial unstable adduct to **14a**.

Experimental Section

Nuclear magnetic resonance spectra were determined in deuteriochloroform (or deuteriodimethyl sulfoxide where specified) with tetramethylsilane as internal standard using a Varian Model A-60A spectrometer[16] at a probe temperature of 35°. Thin layer chromatography was carried out on Eastman Chromagram silica gel sheets;[16] the solvents used were petroleum ether (bp 30–60°) or petroleum ether–ether (9:1, v/v). The infrared spectra were determined from KBr disks or thin films of pure liquids on a Perkin-Elmer Model 21 spectrophotometer.[16] Practical grade diglyme and tetraglyme were heated over sodium metal and distilled in a nitrogen atmosphere before use. Cyclopentadienylsodium was obtained in the form of an 18% solution in tetrahydrofuran from Distillation Products Industries.[16]

Dicyclopentadienedicarboxylic acid (obtained from K & K Laboratories)[16] was crystallized from ethanol to give a white solid (**11b**), mp 209–211° (lit.[2] 210°). Esterification of this diacid by Thiele's method[2] with methanol and sulfuric acid gave diester **11a**, mp 84–85° (lit.[2] 85°).

4,9-Dicarbomethoxy-8-methoxytricyclo[5.2.1.0^{2,6}]dec-3-ene (13).—Attempted esterification of **11b** with dimethyl sulfate and excess potassium carbonate in methanol gave a 33% yield of the methanol addition product **13** as the only neutral product.

A solution of 400 mg (1.6 mmoles) of diester **11a** in 10 ml of methanol was refluxed over 1.3 g (10 mmoles) of solid potassium carbonate for 90 min.

Chloroform and water were added to the reaction mixture, and the chloroform layer was dried and evaporated. Recrystallization of the residue from petroleum ether gave 240 mg (53%) of the methanol addition product **13**, mp 110.5–111.5° (lit.[7d] 110°), which had infrared absorption peaks at 9.17, 9.23, 9.70, 13.36, and 13.87 μ, as reported.[7d]

The methanol addition compound **13** (248 mg, 0.9 mmole) was refluxed with a solution of 130 mg (3.5 mmoles) of sodium hydroxide in 10 ml of 50% aqueous methanol for 1 hr. Water was

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(16) Mention of a company and/or product by the U. S. Department of Agriculture does not imply approval of recommendation of the product to the exclusion of others which may be suitable.

added and the solution was acidified. The solid acid was recrystallized from methanol–water to give 133 mg (61%) of diacid; the melting point and mixture melting point with **11b** was 208–210°.

Treatment of diacid **11b** with trifluoroacetic anhydride and methanol in benzene[9] gave only recovered starting material.

4,9-Dicarbophenoxytricyclo[5.2.1.0^{2,6}]deca-3,8-diene (11d).—Diacid **11b** (2.20 g, 10 mmoles) was suspended in 50 ml of benzene and 10 ml (15 g, 70 mmoles) of trifluoroacetic anhydride was added. The suspension was stirred until complete solution occurred, then 4.4 g (23 mmoles) of phenol in 25 ml of benzene was added. The solution was stirred at room temperature for 90 min, then washed with 5% sodium bicarbonate, with 5% sodium hydroxide, and with water. The benzene solution was dried and evaporated. The residual oil was crystallized from petroleum ether–ether, then from methanol to give 3.03 g (82%) of diphenyl ester **11d**, mp 92–94°.

Anal. Calcd for $C_{24}H_{20}O_4$: C, 77.40; H, 5.41. Found: C, 77.33; H, 5.45.

1,4-Dicarbomethoxytricyclo[5.2.1.0^{2,6}]deca-3,8-diene (12a).—The acid (**12b**) was prepared by a variation of Wiese's method.[5] Dry Ice (100 g) was added to 200 ml of xylene and the slurry was stirred vigorously as 100 ml of an 18% solution of cyclopentadienylsodium (0.2 mole) in tetrahydrofuran was added. The mixture was allowed to warm to room temperature and water was added to dissolve the precipitated salts. The water layer was extracted with chloroform and acidified. The solid product was filtered and dried to give 22.5 g (97%) of a mixture of diacids **11b** and **12b** as a light tan powder, mp 199–202°. Recrystallization from methanol removed the color but did not raise the melting point. Fractional crystallization from methanol or methanol–water did not separate the isomers.

The crude diacid mixture was esterified according to Thiele's[2] directions to give a liquid mixture of diesters **11a** and **12a**. The color could be partially removed by dissolving the amber mixture in dichloromethane, treating with Darco, and evaporating the solvent. This process was not usually necessary and did not change the composition of the mixture. Tlc showed only two components in the mixture. A portion of the mixture was dissociated to the monomer by distillation at 160–180° (7 mm) and allowed to redimerize. Tlc showed the presence of the same two constituents in the semicrystalline redimerized mixture and an indication of a third constituent.[7d]

The esterification products from a number of preparations of **12a** were analyzed by comparing the integrated vinyl proton signals at τ 3.00 to 3.25 (**11a**, 1 H) in the nmr spectrum of the mixture with the signals at τ 3.80 to 4.00 (**12a**, 2 H). The fraction of **12a** in the diester mixtures varied from 21 to 56% in apparently identical runs of the carboxylation–esterification, all of which gave 75 to 85% yields of diesters based on cyclopentadienylsodium. Treatment of the esterification product with diethylamine or with morpholine[7a] did not remove the 4,9 diester **11a**. Attempted fractional crystallization from ethanol of the diester mixture[5] failed to give any solid diester. The mixture was separated by column chromatography on silicic acid from petroleum ether.[7d] Pure diester **12a** had infrared absorptions at 9.1, 9.5, 13.2, 13.6, and 14.2 μ, as reported.[7d]

1,4-Dicarbophenoxytricyclo[5.2.1.0^{2,6}]deca-3,8-diene (12d).—Because of the difficulty in obtaining pure diacid **12b** by esterification, chromatography, and saponification, and because of the instability of **12a** to air oxidation over long periods of storage, the mixture of **12b** and **11b** was recrystallized and used without separation. The diacid mixture was treated with trifluoroacetic anhydride and phenol in benzene as above and gave a 60% yield of the mixed diphenyl esters. The nmr spectrum of the oily product showed only signals which could be attributed to either **12d** or **11d**. Integration of the C_{10} proton portion of the spectrum (τ 7.9 to 8.7) showed that the product consisted of 64% of **12d** and 36% of **11d**.

Anal. Calcd for $C_{24}H_{20}O_4$: C, 77.40; H, 5.41. Found: C, 77.58; H, 5.57.

2-Carbomethoxy-5,5,6,6-tetracyano-2-norbornene (14a).—Diester **11a** (500 mg, 2 mmoles) and TCNE (512 mg, 4 mmoles) were dissolved in 10 ml of diglyme and the solution was heated at 160° for 20 min. After cooling, the solid product was filtered and benzene added to the filtrate to precipitate a small second crop of the product. The combined product was recrystallized from tetrahydrofuran to give 810 mg (80%) of the TCNE adduct **14a**, mp 239° dec. Tlc and nmr showed this to be a single compound.

Anal. Calcd for $C_{13}H_8O_2N_4$: C, 61.90; H, 3.20; N, 22.21. Found: C, 62.09; H, 3.40; N, 22.06.

Treatment of 1.00 g of a mixture of 56% of **12a** and 44% of **11a** with 1.02 g of TCNE in diglyme as above gave 1.40 g (70%) of the adduct, which was identical to **14a** by ir, tlc, and mixture melting point.

2-Carbophenoxy-5,5,6,6-tetracyano-2-norbornene (14b).—A solution of 750 mg (2 mmoles) of diphenyl ester **11d** and 512 mg (4 mmoles) of TCNE in 20 ml of diglyme was heated at 160° for 15 min and cooled. Petroleum ether (100 ml) was added to the solution. The solid product was filtered and recrystallized from tetrahydrofuran to give 1.01 g (80%) of adduct **14b**, mp 204–205° dec.

Anal. Calcd for $C_{18}H_{10}O_2N_4$: C, 68.78; H, 3.21; N, 17.83. Found: C, 68.49; H, 3.12; N, 17.70.

Diphenyl ester **12d** (as a mixture with 36% of **11d**) was treated in the same manner with TCNE in diglyme to give a 70% yield of adduct, which was identical with **14b** by ir and mixture melting point.

1-Carbomethoxy-5,6-(N-phenyldicarbimido)-2-norbornene (16).—A solution of 1.00 g (4 mmoles) of diester **11a** and 1.40 g (8 mmoles) of N-phenylmaleimide in 16 ml of diglyme was heated at 160° for 10 min and cooled. The solid product (0.66 g, 27%) was filtered and recrystallized from methanol to give white plates of **16**, mp 177.5–178°.

Anal. Calcd for $C_{17}H_{15}NO_4$: C, 68.67; H, 5.09; N, 4.71. Found: C, 68.52; H, 4.91; N, 4.69.

2-Carbomethoxy-5,6-(N-phenyldicarbimido)-2-norbornene (15).—The oily adduct was obtained by reducing the volume of the filtrate from the preparation of **16**, and oiling out **16** and part of the liquid adduct **15** by adding water. Integration of the C_7 portion (τ 7.7 to 8.5) of the nmr spectrum of the last fraction of oil showed that it contained 88% of **15** and 12% of **16**. Only signals which could be assigned to either **15** or **16** were found.

Treatment of a mixture of 56% of **12a** and 44% of **11a** with N-phenylmaleimide in diglyme as above gave a 28% crude yield of the solid adduct and the oily mixture of adducts as above. Similar yields of **15** and **16** were obtained from diester **12a** and N-phenylmaleimide in dioxane at 100° (18 hr).

A 400-mg sample of **16** was heated in a metal bath at 200° for 2 hr. An nmr spectrum of the resulting unpurified, light brown oil showed that it containd 90% of **15** and 10% of **16**.

2,5- (or 6-) Dicarboxy-6- (or 5-) carbanilido-2-norbornene.—The oily adduct (**15**) from the previous preparation (0.94 g) was heated at reflux with 12 ml of 5% sodium hydroxide until complete solution occurred and then for 5 min. The solution was cooled and extracted with dichloromethane, then acidified. An oil separated and solidified. Recrystallization of the solid from methanol–water gave 0.64 g (66%) of the dicarboxy amide, mp 231–232°.

Anal. Calcd for $C_{16}H_{15}NO_5$: C, 63.77; H, 5.03; N, 4.65. Found: C, 63.74; H, 5.10; N, 4.69.

1-Carboxy-5,6-(N-phenyldicarbimido)-2-norbornene.—The solid adduct **16** (500 mg, 1.6 mmoles) was heated at reflux in a solution of 0.5 ml of methanol and 7 ml of 5% aqueous sodium hydroxide until all the solid dissolved. The solution was cooled and acidified and the product salted out with sodium sulfate. The crude product was treated with Darco and crystallized from methanol to give 150 mg (33%) of the imido acid, mp 231–232°. Mixture melting point with the dicarboxy amide (above) was 199–214°.

Anal. Calcd for $C_{16}H_{13}NO_4$: C, 67.84; H, 4.62; N, 4.95. Found: C, 67.87; H, 4.58; N, 5.08.

1-Carbomethoxy-2,3-(N-phenyldicarbimido)norbornane.—The solid adduct **16** (370 mg, 1.25 mmoles) was hydrogenated for 1 hr at 40 psi in 75 ml of ethanol with 50 mg of 10% palladium-on-carbon catalyst. The catalyst was filtered off and the solution was evaporated to give 300 mg (80%) of colorless needles, mp 165.5–167°.

Anal. Calcd for $C_{17}H_{17}NO_4$: C, 68.21; H, 5.73; N, 4.68. Found: C, 68.38; H, 5.81; N, 4.75.

The ratio of adducts **16** and **15** formed from **11a** and N-phenylmaleimide in dioxane at 100° was determined by evaporating the dioxane, hydrogenating the nonvolatile material in ethanol (31 psi, 2 hr), and analyzing the hydrogenated material by gas chromatography (19.8% SE-52 on Chromosorb W, 3-ft column, 260°). The hydrogenation was necessary because of the thermal dissociation of the adducts below the temperature necessary for gas chromatography. A very small N-phenylsuccinimide peak and two adduct peaks were found, but no peak corresponding to a hydrogenated diester. The areas of the adduct peaks were used to calculate the ratio of adducts in the reaction, which was found to be 62:38 **16**:**15**.

4-Carbomethoxy-1,7,8,9,10,10-hexachlorotricyclo[5.2.1.$0^{2,6}$]-deca-3,8-diene (17).—A solution of 1.20 g (4.8 mmoles) of diester **11a** and 2.45 g (9.0 mmoles) of hexachlorocyclopentadiene in 15 ml of dioxane was heated at 100° for 18 hr. The dioxane was evaporated and the residual oil was dissolved in warm petroleum ether. On cooling and further evaporation, a solid product and an oil containing hexachlorocyclopentadiene were formed. The solid (1.00 g, 28%) was recrystallized from dichloromethane–petroleum ether to give large prisms of **17**, mp 142–144°.

Anal. Calcd for $C_{12}H_8Cl_6O_2$: C, 36.31; H, 2.03; Cl, 53.60. Found: C, 36.50; H, 2.10; Cl, 53.35.

Treatment of a mixture of 58% of **12a** and 42% of **11a** with hexachlorocyclopentadiene in dioxane in the same manner gave a 36% yield of **17**.

Kinetics.—Attempts to analyze for TCNE in diglyme solutions by the formation of the blue dye with N,N-dimethylaniline, as applied to the kinetics of dissociation of the cyclopentadiene–maleic anhydride adduct by Berson,[17] gave erratic results with known solutions. Other methods of analysis of TCNE were therefore investigated. The purple π complex of TCNE with naphthalene has been used for a spectrophotometric analysis of TCNE.[18] To avoid interference from the weaker, yellow π complex of TCNE with diglyme, small aliquots of the reaction solution were added to a large excess of a 3.0% solution of naphthalene in chloroform. This method was found to be suitable for determining the concentration of TCNE in dilgyme accurately to better than ±1%.

The apparatus consisted of a 50-ml, three-necked flask equipped with a mechanical stirrer, a rubber septum, and a condenser topped with a drying tube and was mounted on a movable stand for immersion of the flask in a constant temperature (± 0.2°) oil bath. The reactants were weighed into the flask, the solvent was added, and samples were withdrawn for determination of initial concentration. The reaction flask was heated rapidly to the desired temperature in an auxiliary bath maintained at 30 to 50° above the constant-temperature bath. When the contents of the flask had reached the desired temperature (2–6 min), the reaction flask was moved to the constant-temperature bath and 25-μl samples were withdrawn every 2–4 min. The samples were added to 3.00 of a 3% solution of naphthalene in chloroform and the concentration of TCNE in the reaction solution was determined by reading the absorption of the TCNE–naphthalene π complex at 430 or 555 mμ. Standard curves were made from solutions of weighed amounts of TCNE in diglyme.

TCNE was always used in slight excess in the kinetic runs to provide readable values on the spectrophotometer. The concentration of diester **11a** in the reaction solution was calculated from the difference between the observed concentration of TCNE and the concentration of TCNE at infinite time. A plot of the log of the concentration of **11a** against time showed a straight-line decrease from the end of the preliminary heating period through at least three half-lives (20–30 points), where the concentration of **11a** was less than the limit of error in the TCNE determination. A plot of the logarithm of the ratio of the concentrations of **11a** and TCNE against time showed a pronounced upward curvature, indicating that the reaction was not a pseudo-first-order reaction, but was first order with respect to the diester, only. The first-order rate constants were determined from the half-lives. The rate constants and temperatures are given in Table II. A plot of log k against the reciprocal of the temperature for the reactions in diglyme was used to calculate E_a and log A. These empirical values were used to calculate[14] ΔH^* and ΔS^*.

Registry No.—**3b**, 15230-99-6; **11a**, 15275-62-4; **11d**, 15231-00-2; **12a**, 15231-01-3; **12d**, 15231-02-4; **13**, 15231-03-5; **14a**, 15231-04-6; **14b**, 15231-05-7; **15**, 15231-06-8; **16**, 15231-07-9; 1-carboxy-5,6-(N-phenyldicarbimido)-2-norbornene, 15231-08-0; 1-carbomethoxy-2,3-(N-phenyldicarbimido)norbornane, 15231-09-1; **17**, 15275-63-5.

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Phosphonic Acids and Esters. XIX. Syntheses of Substituted Phenyl- and Arylphosphonates by the Photoinitiated Arylation of Trialkyl Phosphites[1]

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The syntheses of a variety of nuclear substituted (methyl, ethyl, methoxy, hydroxy, amino, formyl) phenylphosphonates **3** and other aryl- (1-naphthyl-, 2-thienyl-, 2-furyl-) phosphonates have been carried out by the low-temperature ultraviolet photolyses of the corresponding aryl iodides in excess trialkyl (methyl or ethyl) phosphite **1**. The process constitutes an experimentally simple one-step procedure for the synthesis of these compounds in good yield. The nitroiodobenzenes are the only class of compounds examined which failed to yield the corresponding **3**; photolyses of these compounds in the presence of **1** resulted in deoxygenation to yield the corresponding phosphate and, presumably, an electron-deficient nitrogen intermediate. Infrared and proton magnetic resonance data are presented for certain **3**, particularly *para*-substituted compounds and those structures capable of exhibiting intra- or intermolecular hydrogen bonds.

In a preceding study,[2] it was shown that the photolysis of iodobenzene in the presence of trialkyl phosphites **1** results in the formation of dialkyl phenylphosphonates **2** (eq 1). This reaction effectively constitutes a photolytic modification of the Michaelis–Arbuzov

$$C_6H_5I + \underset{\mathbf{1}}{P(OR)_3} \longrightarrow \underset{\mathbf{2}}{C_6H_5P(O)(OR)_2} + RI \qquad (1)$$

reaction;[3] high yields of **2** can be realized by carrying out the reaction at low temperatures in the presence of a large excess of **1**. Thus, the irradiation of iodobenzene for 24 hr at 0° in a three- to fivefold excess of trimethyl phosphite results in the formation of dimethyl phenylphosphonate (**2**, R = CH_3) in quantitative yield.[2]

The high yields of **2** obtained by this reaction and the experimental simplicity of the process suggested

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