moval of water for 116 h. The benzene and excess pyrrolidine were removed by distillation, and the residue was fractionally distilled to give 1.40 g (10%) of enamine **33** [bp 112–114 °C (0.7 mm)] which contained 20% of the starting ketone (NMR): IR 1630, 1710 (residual C=O); NMR δ 0.86 (s, 9 H, *tert*-butyl), 1.09 (d, J = 7.1 Hz, CH_3CH), 4.15 (d, J = 1.5 Hz, vinyl H of major isomer), 4.41 (br s, vinyl H of minor isomer).

The lower boiling fractions from the reaction mixture consisted of recovered ketone and mixtures of the ketone and enamine.

11-Methyl-14-noreudesm-4-en-3-one (34). To a solution of 0.469 g (0.0021 mol) of enamine **33** in 1.0 mL of dry methanol, under nitrogen, was added rapidly, with stirring, 0.389 g (0.0056 mol) of MVK. The reaction mixture was heated at reflux for 5 h and then hydrolyzed, and the products were isolated by the procedure described above. The combined crude products from five runs of approximately this scale using a total of 2.44 g (0.012 mol) of enamine were combined and distilled [bp 136–146 °C (air bath; 0.01 mm)] to give 0.426 g (18%) of enone **34** as a yellow oil, contaminated with 18% of the starting cyclohexanone (GLC), which was dissolved in hexanes and chromatographed on silica gel. Elution with hexanes–ether mixtures gave 0.187 g of enone **34** as a white crystalline solid which was homogeneous to GLC. Repeated crystallization from pentane at −15 °C afforded material with the following: mp 78–78.5 °C; IR 1645, 2910; NMR δ 0.90 (s, 9 H, *tert*-butyl), 1.21 (s, 3 H, CH_3), 5.73 (s, 1 H, C=CH); mass spectrum, m/e (relative intensity) 221 (13), 220 (70), 149 (80), 136 (44), 135 (47), 124 (38), 123 (48), 122 (62), 121 (100).

Anal. Calcd for $C_{15}H_{24}O$: C, 81.76; H, 10.98. Found: C, 81.68; H, 10.97.

GLC analysis of the crude reaction mixture indicated that enone **34** and 2-methyl-5-*tert*-butylcyclohexanone were the only volatile substances present.

Acknowledgment. The JEOL FX-90 Q NMR spectrometer was obtained through an NSF Support of Research Equipment grant.

Geminate-Substituted Cyclopentadienes. 1. Synthesis of 5,5-Dialkylcyclopentadienes via 4,4-Dialkylcyclopent-2-en-1-ones[1]

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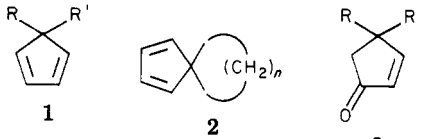
Received September 1, 1981

A synthetic route for the preparation of 5,5-dialkylcyclopentadienes (1) via 4,4-dialkylcyclopent-2-en-1-ones (3) is described. Beginning with ketones (in which the two carbonyl substituents will become the two alkyl groups in the title compounds), the route traverses the Guareschi imides **5**, 3,3-dialkylglutaric acids **4** and their ethyl esters **7**, masked acyloins **8**, cyclopentenones **3**, alcohols **9**, and bromides **10** to reach the dienes **1**. Physical properties of five such derivatives **1** and **3** (dimethyl, methylethyl, diethyl, methyl-*n*-propyl, and methylisopropyl) are presented.

Introduction

It is possible to formulate a number of mechanistic problems which could be addressed if even small quantities of geminate-substituted cyclopentadienes (1) were readily available. Indeed, a few such studies already have been



1 2 3

carried out, using materials synthesized rather laboriously by a number of procedures. For example, Brown et al.[3] needed apobornene and made it by a circuitous method not involving a Diels–Alder reaction of 5,5-dimethylcyclopentadiene since "the synthesis of the diene appeared to offer severe difficulties". Apobornene and apobornadiene were subsequently prepared from 5,5-dimethylcyclopentadiene,[4] available from a route essentially the same as that outlined by us earlier[1] and reported in detail in this paper.

Most of the relevant mechanistic work already described involves the thermal sigmatropic rearrangements of trimethylcyclopentadienes,[5–8] pentamethylcyclopentadiene,[9] 5,5-diphenylcyclopentadiene,[10] and various spirocyclic derivatives **2**,[11–19] some of which can be prepared relatively easily.

(1) Preliminary results were presented as a paper: Holder, R. W.; Daub, J. P.; Baker, W. E.; Gilbert, R. "Abstracts of Papers", 175th National Meeting of the American Chemical Society, Anaheim, CA, March 1978; American Chemical Society, Washington, DC, 1978; ORGN 80.
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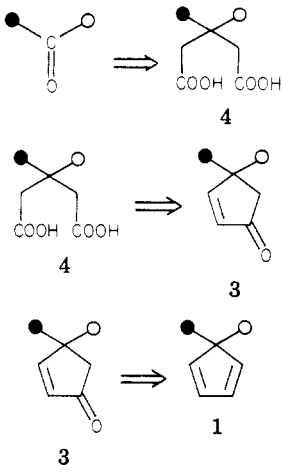
Scheme I



A few Diels–Alder reactions have been described,[13,19–21] but this rich area remains largely untapped. By analogy with recent work involving cycloadditions with cyclopentadiene itself, allyl cations and various 1 should lead to usefully substituted bicyclo[3.2.1] systems,[22–24] ketene cycloadditions would afford bicyclo[3.2.0]hept-2-en-6-ones,[25] and ring expansion of these could lead to interesting bicyclo[3.3.0] systems,[20,22] while solvolyses of reduced derivatives could afford cycloheptatrienes or fulvenes with novel substitution patterns.[28] Clearly, the ready availability of derivatives of 1 would be useful.

The route described below for the preparation of derivatives of 1 passes through cyclopentenones 3. The 3-oxocyclopentene unit is widely found in many biologically active natural products (e.g., *cis*-jasmone, certain prostaglandins, rethrolones, etc.), and methods for the synthesis of this unit have been reviewed.[29] Our derivatives 3 might easily lead to new natural product analogues with interesting properties, as well as spirosteroids,[30] geminal prostanoids,[31] etc.

In addition, cyclopentenones can act as dienophiles in Diels–Alder reactions, either uncatalyzed[32–34] or catalyzed,[35] to form derivatives of the bicyclo[4.3.0]nonane skeleton; this method was recently used to synthesize coronafacic acid.[36] Again, derivatives 3 could afford new compounds of possibly useful biological behavior.

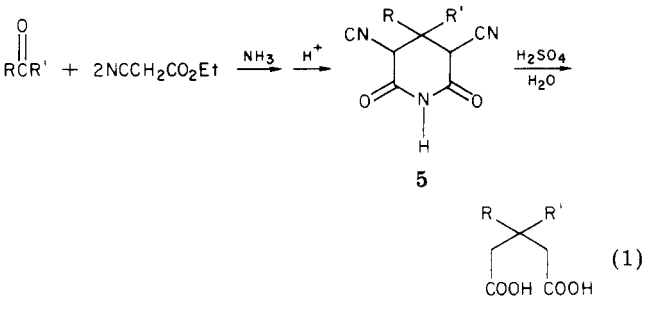
Finally, the base-catalyzed reactions of cyclopentenones[37] and the rich photochemistry of these chromophores[37–40] are well-known. The easy availability of derivatives 3 should facilitate new studies in both areas.

Results and Discussion

Although spirocyclic derivatives 2 (n = 2, 4, 5) can be made in a straightforward manner from cyclopentadiene, 2 equiv of base, and the appropriate 1,2-, 1,4-, or 1,5-dihalide,[20,41,42] this procedure fails for 2 (n = 3)[43] and would be unlikely to work very efficiently for 1. The several special techniques available for the spirocyclic compounds,[12,13,15,44,45] including those used by Semmelhack and his colleagues to prepare all of the possible spirocyclo[4.4]nonapolyenes,[18,46] are also not applicable to syntheses of 1. Indeed, the elusive 2 (n = 3) must be prepared by either a pinacol route[19,47] or by a variation of the method reported below;[48] in only a few cases[10,49,50] have other routes been effective in preparing molecules of type 1.

We report herein the preparation and physical properties of five compounds of type 1 (**a**, R = R′ = CH_3; **b**, R = CH_3, R′ = CH_2CH_3; **c**, R = R′ = CH_2CH_3; **d**, R = CH_3, R′ = $CH_2CH_2CH_3$; **e**, R = CH_3, R′ = $CH(CH_3)_2$) by the three-phase approach outlined in Scheme I. Commercially available ketones are transformed to 3,3-dialkylglutaric acids (4), these are cyclized to the cyclopentenones 3, and the ketone functionality of 3 is utilized to introduce the second double bond to form 1.

In the first step, 3,3-dialkylglutaric acids **4a**[51]–**4c** are prepared from the corresponding ketones via hydrolysis of the Guareschi imides **5**, which in turn are obtained by the Guareschi reaction, discovered by Guareschi,[52,53] and explored more fully by Thorpe[54] and by Vogel[55] (eq 1).



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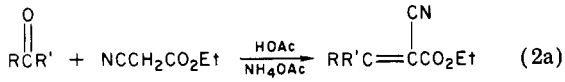
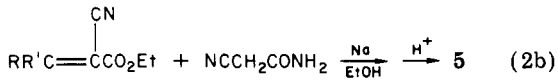
The imide hydrolysis is very sensitive to reaction conditions: if an incorrect ratio of acid to water is used, or if this solution is added too rapidly, an acid-insoluble diimide may be formed, which is difficult to handle further. Although the yields of **5a** (65%) and **5b** (75%) are acceptable, **5c** is obtained in only 33% and it seemed likely the convenient Guareschi one-pot procedure might not work well with more complex ketones.[56] Thus, we apply an alternative two-step procedure (eq 2a and 2b) via the cyano esters **6** as relay compounds to obtain the remaining imides **5c–5e**. The first condensation was discovered by Cope,[57]



(2a)

6

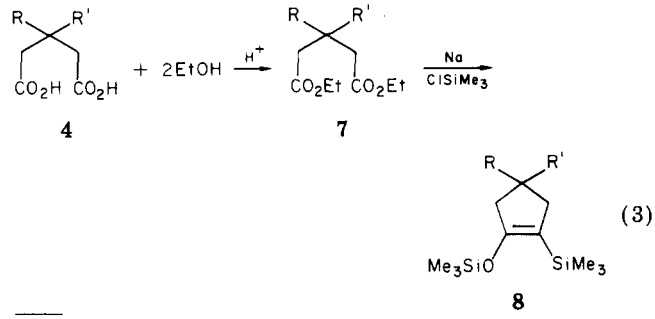


(2b)

6

who also noted that branching in the ketone alkyls retards the reaction to some extent. The second step utilizes the conjugate base of cyanoacetamide to add the second unit and close to the imide. This procedure seems to have been used first by McElvain and Clemens,[58] and later by Bruice and Bradbury.[59] We obtain **5c** (77%), **5d** (44%), and **5e** (56%) in fair yields in this manner.

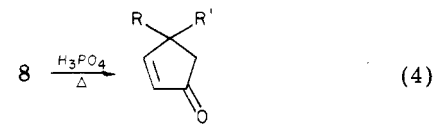
In the second phase of this route, we esterify the diacids **4** in 81–92% yield by a standard procedure[60] and then carry out the acyloin condensation using the very useful modification of Schräpler and Rühlmann[61–63] (eq 3).



4 **7** **8**

(3)

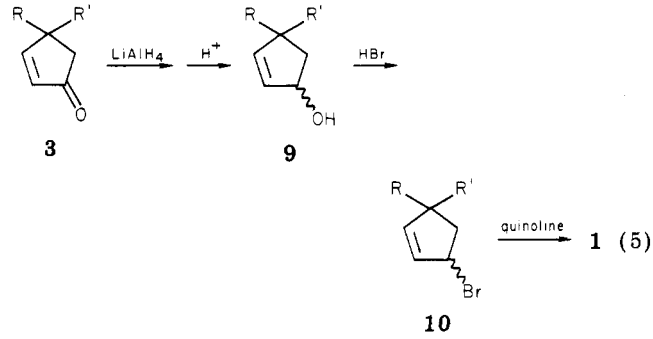
Yields of the masked acyloins (**7**) were 64–74%. These were subsequently hydrolyzed to the acyloins and dehydrated in one pot in yields of 55–86% (eq 4). This technique avoids rearrangements noted in other methods of acyloin dehydration.[38] Table I presents the pertinent physical and spectral properties of the important ketones **3**. The acyloin condensation has proved convenient before in preparing similar cyclopentyl derivatives from diethyl glutarates.[64,65]



(4)

3

In the last phase of the synthesis, we reduce the ketone function using $LiAlH_4$ (75–95%), form the crude allylic bromide with HBr (73–95%), and dehydrobrominate by distillation from pure quinoline (58–95%) to obtain cyclopentadienes **1** (eq 5). This procedure, used first by



3 **9** **10**

1 (5)

Rouse and Tyler[66] and later by Russell et al.,[67] is convenient for us because we wish to prepare **1a–1e** with specifically sited deuterium, but pilot experiments involving treatment of the tosylhydrazone of **3a** with methyllithium have given essentially equivalent yields of **1a**. Jefford et al.[4] have dehydrated **9a** directly in 90% yield using methyltriphenoxyphosphonium iodide in HMPT.

The physical and spectral properties of **1a–1e** are presented in Table II, together with the literature data for other geminate-substituted cyclopentadienes. Beyond noting exceptional stability to Diels–Alder dimerizations, we have not yet initiated our planned extensive studies of the chemistry of these dienes.

Experimental Section

Elemental analyses were performed by Ruby Ju of the University of New Mexico. Melting points were obtained with a Thomas-Hoover capillary apparatus and are uncorrected. All reported boiling points are uncorrected. Infrared (IR) spectra were recorded as thin films between NaCl places (liquids) or as KBr disks (solids) on Perkin-Elmer 237 or 337 spectrophotometers; all recorded absorptions were corrected by reference to polystyrene bands in the appropriate spectral regions. Proton nuclear magnetic resonance (^1H NMR) spectra were obtained on Varian A-60 or FT-80A instruments; carbon-13 nuclear magnetic resonance (^{13}C NMR) spectra were measured on the Varian FT-80A instrument. Ultraviolet (UV) measurements were made on a Cary-14RI spectrophotometer. Preparative gas–liquid chromatographic (GLC) separations were obtained with a Varian Aerograph Model 920 instrument equipped with a thermal conductivity detector with helium as the carrier gas. Analytical GLC determinations were measured with a Hewlett-Packard Model 5750 gas chromatograph equipped with a flame-ionization detector and with nitrogen as the carrier gas.

For an example of the typical procedures used for the preparation of the 5,5-dialkylcyclopentadienes, the complete synthesis of 5,5-diethylcyclopentadiene (**1c**) is described below. Tables I and II summarize the yields, physical data, and spectral characteristics of the cyclopentadienes and their cyclopentenone precursors. Satisfactory elemental analyses were obtained for all these new compounds and were submitted to the editor and the referees. The starting ketones were all obtained commercially and used without special purification.

2,4-Dicyano-3,3-diethylpentanimide (5c). In a 500-mL, round-bottom flask were combined 34.45 g (0.41 mol) of 3-pentanone, 66.31 g (0.59 mol) of ethyl cyanoacetate, 8.51 g (0.11 mol)

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Table I. Properties of Cyclopentenones 3

compd[c]	bp, °C/mm	% yield	IR, cm^{-1}	UV (95% EtOH), nm (ϵ)	^1H NMR ($CDCl_3$) δ	^{13}C NMR ($CDCl_3$) δ
3a	65-68/35	87	1680, 1590, 800	220 (9200)	7.52 (d, J = 5.5 Hz, 1 H), 5.95 (d, J = 5.5 Hz, 1 H), 2.22 (s, 2 H), 1.27 (s, 6 H)	208.96, 173.09 130.69, 49.58, 41.02, 27.62
3b	79-82/17	69	1700, 1590, 810	221 (11 600)	7.43 (d, J = 5.6 Hz, 1 H), 6.03 (d, J = 5.6 Hz, 1 H), 2.36 and 2.00 (AB q $\|J\|$ = 18.6 Hz, 2 H), 1.55 (asym q, J = 7.2 Hz, 2 H), 1.21 (s, 3 H), 0.86 (t, J = 7.3 Hz, 3 H)	209.00, 172.06, 131.51, 47.07, 44.81, 32.71, 25.40, 8.70
3c	97-107/25	70	1711, 1595, 810	223 (10 400)	7.39 (d, J = 5.7 Hz, 1 H), 6.07 (d, J = 5.7 Hz, 1 H), 2.14 (s, 2 H), 1.55 (asym q, J = 7.0 Hz, 4 H), 0.83 (t, J = 7.1 Hz, 6 H)	209.21, 171.03, 132.56, 48.75, 44.56, 30.53, 8.42
3d	101-102/22	53	1715, 1585, 795	222 (11 700)	7.43 (d, J = 5.7 Hz, 1 H), 6.01 (d, J = 5.7 Hz, 1 H), 2.11 and 2.29 (AB q, $\|J\|$ = 18.6 Hz, 2 H), 1.19 (s, 3 H), 0.6-1.6 (m, 7 H)	209.32, 172.50, 131.42, 47.78, 44.77, 42.46, 25.98, 18.03, 14.32
3e	not distilled[a]		1715, 1585, 800	223 (7 800)	7.51 (d, J = 5.7 Hz, 1 H), 6.00 (d, J = 5.7 Hz, 1 H), 1.73 and 1.37 (AB q, $\|J\|$ = 18.9 Hz, 2 H), 1.18 (s, 3 H), 0.90[b] (d, J = 5.0 Hz, 3 H), 0.85[b] (d, J = 4.7 Hz, 3 H)	209.71, 172.43, 131.34, 48.13, 45.26, 35.07, 23.55, 18.06,[b] 17.62[b]

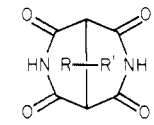
[a] Spectral data obtained on samples purified by preparative GC. [b] Note the two methyls of the isopropyl group are nonequivalent. [c] Satisfactory analytical data (±0.3% for C and H) were submitted for review.

of ammonium acetate, 28.40 g (0.47 mol) of glacial acetic acid, and 105 mL of benzene. The flask was equipped with a Dean–Stark tube fitted to an efficient condenser attached to a $CaCl_2$ drying tube. The solution was refluxed for 45 h, while 17.5 mL (>100%) of water was separated.

The cooled benzene solution was washed thrice with 75-mL portions of water, dried over $CaCl_2$, filtered, and concentrated by rotary evaporation to an orange-red oil. Distillation through a 10-cm Vigreux column afforded 60.51 g (84%) of **6c**.

To a 500-mL, three-necked, round-bottom flask equipped with overhead stirrer, water-cooled reflux condenser fitted with a $CaCl_2$ tube, and dropping funnel were added 180 mL of absolute ethanol and 10.29 g (0.45 mol) of clean sodium. After the sodium had reacted, 84.08 g (0.45 mol) of cyanoacetamide was added and the resulting slurry refluxed 15 min while another 20 mL of ethanol was added. The mixture was cooled and a solution of 40.54 g (0.224 mol) of **6c** in 40 mL of ethanol added as a thin stream. The reaction mixture, which was very thick, turned yellow-orange and was mildly exothermic. Stirring was continued overnight, and then the slurry was poured into 950 mL of water, forming a homogeneous orange solution. With cooling, 47 mL of concentrated hydrochloric acid was added, forcing out a heavy precipitate. After cooling thoroughly in an ice/water bath, the solid was collected by suction filtration, washed with cold water, air-dried for 12 h, and further dried at 100 °C for 2 h to afford **5c** (44.96 g) as a white fluffy solid. Data for the five Guareschi imides **5a–5e** are summarized in Table III.

3,3-Diethylpentanedioic Acid (4c). In a 2-L Erlenmeyer flask were placed 66.0 g (0.32 mol) of powdered Guareschi imide **5c** and 155 mL of concentrated H_2SO_4. The flask was equipped with a magnetic stir bar and a constant-pressure dropping funnel. With stirring, 50 mL of water was added dropwise over a 45-min period. Sometimes solids emerged and then redissolved during this procedure. The dropping funnel was replaced with a reflux condenser, and the stirred reaction mixture was heated slowly on a hot plate. When the temperature approached reflux, gas was evolved vigorously, causing appreciable frothing (thus, the large flask). After ca. 1 h this moderated, and a clear yellow-brown solution was evident. Heating was discontinued, and after 10 min, 60 mL of water was added dropwise over a 35-min period to the still hot solution. Then heating was resumed, and the reaction mixture was brought to reflux and maintained there for 24 h. We emphasize the importance of following the above procedure; adding the water too quickly or using more water usually leads to formation of the relatively intractable Guareschi diimides **11**. These can be acid hydrolyzed to diacids **4** only with difficulty.



11

After the cooling period, a dark supernatant solid was separated by suction filtration through sintered glass. This was triturated 3 times with generous portions of ether, and the combined decantates were dried over $MgSO_4$. A scoopula of Norit was added, and, after an hour, the solids were removed by gravity filtration. The clear, colorless filtrate was subjected to rotary evaporation to afford a colorless oil which quickly began to form white crystals of **4c**. When air-dried, these weighed 53.95 g. Some data for the five diacids prepared are given in Table IV.

Diethyl 3,3-Diethylpentanedioate (7c). In a 250-mL, round-bottom flask were combined 29.63 g (0.16 mol) of **4c**, 100 mL of absolute ethanol, 50 mL of dry toluene, and 10 drops of concentrated H_2SO_4. A Soxhlet apparatus containing a thimble of 65 g of anhydrous potassium carbonate was attached, and the solution was brought to reflux. After 24 h of continuous extraction, the solution was concentrated by rotary evaporation to a slurry, taken up in 250 mL of ether, washed with water and saturated sodium bicarbonate, and dried over $MgSO_4$. Filtration and concentration by rotary evaporation afforded a yellow oil, which was distilled in vacuo to give 31.24 g of **7c** as a clear colorless, sharp-smelling oil. The physical properties of the diesters are recorded below.

7a: bp 128–131 °C (20 mm), 92%; IR 1740 cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.12 (q, J = 7.0 Hz, 4 H), 2.42 (s, 4 H), 1.25 (t, J = 7.5 Hz, 6 H), 1.15 (s, 6 H); ^{13}C NMR ($CDCl_3$) δ 171.53, 59.69, 45.11, 32.36, 27.39, 14.02.

7b: bp 142–145 °C (21 mm), 91%; IR 1733 cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.13 (q, J = 7.0 Hz, 4 H), 2.43 (s, 4 H), 1.37 (q, J = 8.0 Hz, 2 H), 1.27 (t, J = 7.0 Hz, 6 H), 1.10 (s, 3 H), 0.88 (t, J = 8.0 Hz, 3 H); ^{13}C NMR ($CDCl_3$) δ 171.73, 59.73, 42.58, 35.25, 32.29, 24.30, 14.03, 7.81.

7c: bp 147–153 °C (20 mm), 80%; IR 1725 cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.08 (q, J = 7.0 Hz, 4 H), 2.42 (s, 4 H), 1.37 (q, J = 7.5 Hz, 4 H), 1.23 (t, J = 7.0 Hz, 6 H), 0.84 (t, J = 7.5 Hz, 6 H); ^{13}C

Table II. Properties of Geminate Cyclopentadienes 1

compd[e]	bp, °C/mm	% yield	IR, cm^{-1}	UV (95% EtOH), nm (ϵ)	^1H NMR ($CDCl_3$) δ	^{13}C NMR ($CDCl_3$) δ
1a	62–64/634	83	3120, 3090, 3050, 1650, 1460, 740	250 (2800)	6.20 (s, 4 H), 1.18 (s, 6 H)	147.17, 127.61, 52.68, 21.59
1b	98–100/634	78	3115, 3090, 3070, 3050, 1650, 1460, 740	250 (2400)	6.22 (s, 4 H), 1.58 (q, J = 7.5 Hz, 2 H), 1.15 (s, 3 H), 0.80 (t, J = 7.5 Hz, 3 H)	143.60, 128.59, 56.86, 29.00, 19.61, 9.70
1c	127–129/634	58	3111, 3089, 3067, 3056, 1645, 1460, 1375, 730	252 (1950)	6.18 (s, 4 H), 1.60 (q, J = 7.5 Hz, 4 H), 0.76 (t, J = 7.5 Hz, 6 H)	143.95, 129.91, 61.46, 27.33, 9.50
1d	122–124/634	95	3115, 3085, 3065, 3050, 1645, 1450, 1380, 750	251 (1700)	6.25 (s, 4 H), 1.45 (m, 2 H), 1.13 (s, 3 H), 0.6–1.0 (m, 5 H, including s at 0.85)	145.56, 128.31, 56.48, 38.76, 20.16, 18.98, 14.64
1e	122–124/634	69	3120, 3085, 3070, 3060, 1655, 1465, 745	251 (1935)	6.28 (s, 4 H), 1.80 (septet, J = 6.5 Hz, 1 H), 1.13 (s, 3 H), 0.90 (d, J = 6.5 Hz, 6 H)	144.76, 128.77, 60.23, 30.16, 18.99, 17.89
cyclopentadiene	41/772			239 (3400)		133.0, 133.4, 42.2[a]
5,5-diphenyl-cyclopentadiene[b]	mp 45–46	83	1590, 1481, 1440, 730, 690	235 (7280), isooctane	7.23 (s, 10 H), 6.79 (m, 2 H), 6.36 (m, 2 H) (CCl_4)	144.96, 141.88, 129.55, 128.30, 127.67, 126.65, 31.89
spiro[4.3]octa-5,7-diene[c]		$\leq$30	3100, 3080, 3060, 3040, 2970, 2940, 2870, 1630, 1510, 1445, 1370, 1330, 1080, 965, 910, 795, 765 sh, 756, 728, 215 sh	261 (1950)	6.35 (m, 2 H), 6.05 (m, 2 H), 2.33–1.93 (m, 6 H) (CCl_4)	
spiro[4.4]nona-1,3-diene[d]		40			6.32 (t, J = 5 Hz, 2 H), 6.24 (t, J = 5 Hz, 2 H), 1.86 (t, $J \approx$ 5 Hz, 4 H), 1.71 (t, $J \approx$ 5 Hz, 4 H) (CCl_4)	143.81, 127.75, 64.04, 32.29, 25.97

[a] Grishin, Yu. K; Sergeyev, N. M; Ustynyuk, Yu. A *Org. Magn. Reson.* **1972**, *4*, 377. [b] Reference 10. [c] Miller, R. D.; Schneider, M.; Dolce, D. L. *J. Am. Chem. Soc.* **1973**, *95*, 8468. [d] Prepared by us according to the procedure of ref 11, as well as those used by Levina, R. Ya; Tantsyreva, T. I. *Proc. Acad. Sci. U.S.S.R.* **1953**, *89*, 697, and Wilcox, C. F., Jr.; Craig, R. R. *J. Am. Chem. Soc.* **1961**, *83*, 3966, 4258. [e] Satisfactory analytical data (±0.3% for C and H) for compounds 1a–1e were submitted for review.

Table III

compd	method	% yield	mp, °C
5a	Guareschi[55]	90	214–216 (lit.[56] 214–215)
5b	Guareschi[55]	75	191–193 (lit.[56] 192–193)
5c	described above	77	207–209 (lit.[56] 204–206)
5d	like 5c	56	204–206 (lit.[56] 202–203)
5e	like 5c	44	237–238 (lit.[56] 234–236)

Table IV

compd	% yield	mp, °C
4a	97	100–102 (lit.[55] 101)
4b	95	82–84 (lit.[55] 85)
4c	91	94–95 (lit.[55] 106)
4d	77	91–92 (lit.[55] 92–93)
4e	80	95–98 (lit.[59] 109–110)

Table V

compd	% yield	bp, °C/mm	IR, cm^{-1}
8a	79	70–74/2.4	1265
8b	84	92–94/3.7	1255
8c	70	102–107/2.9	1255
8d	64	100–103/2.5	1252
8e	71	not distilled	1253

NMR ($CDCl_3$) δ 171.69, 59.59, 39.80, 28.45, 13.94, 7.31.

7d: bp 103–104 °C (0.4 mm), 91%; IR 1728 cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.15 (q, J = 7.0 Hz, 4 H), 2.43 (s, 4 H), 1.26 (t, J = 7.0 Hz, 6 H), 1.10 (s, 3 H), 0.95–1.50 (m, 4 H), 0.90 (br t, 3 H); ^{13}C NMR δ 171.67, 59.69, 43.01, 43.32, 35.21, 24.85, 16.68, 14.39, 14.03.

7e: bp 124–125 °C (2.3 mm), 81%; IR 1735 cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.15 (q, J = 7.0 Hz, 4 H), 2.48 (s, 4 H), 1.9 (septet, J = 7.8 Hz, 1 H), 1.24 (t, J = 7.0 Hz, 6 H), 1.05 (s, 3 H), 0.88 (d, J = 6.8 Hz, 6 H); ^{13}C NMR δ 172.07, 59.70, 40.73, 37.73, 34.26, 21.20, 16.99, 14.01.

4,4-Diethyl-1,2-bis(trimethylsiloxy)cyclopentene (8c). A three-necked, 1-L, round-bottom flask fitted with dropping funnel, reflux condenser, and high-speed stirrer (Lab-Line Stir-o-Vac) was flame-dried under a flow of nitrogen. All subsequent operations were carried out in the nitrogen atmosphere. A mixture of 15.43 g (0.67 mol) of sodium and 400 mL of dry toluene was brought to reflux by means of a heating mantle. When the sodium was melted, it was dispersed into fine sand by high-speed stirring for ca. 1 min. The stirrer was stopped and the mantle was removed, and the temperature was allowed to cool naturally; this procedure resulted in an excellent dispersion of Na, with a minimum of recombination.

The high-speed stirrer was replaced with a regular overhead stirrer, and the dispersion was heated again and held just below reflux while a solution of 38.12 g (0.16 mol) of **7c**, 50 mL of dry toluene, and 90 mL of dry chlorotrimethylsilane was added dropwise over a 2-h period. At the end of this addition, a further portion of 50 mL of toluene was added in order to rinse the funnel. The color changed from light tan to dark purple during the addition. Stirring and heating were continued for 28 h, and additional 25-mL portions of chlorotrimethylsilane were added at t = 4 h and 24 h to replace evaporative losses [total chlorotrimethylsilane added was 119.8 g (1.10 mol)]. At the end of this period GLC (Carbowax 20M) showed no remaining **7c**, and the reaction mixture was allowed to cool to room temperature. Solids were removed by suction filtration and the filtrate concentrated by rotary evaporation to a yellow oil which was distilled in vacuo to afford 32.82 g of **8c** as a clear, colorless oil. The bis(trimethylsiloxy)cyclopentenes were not extensively purified or investigated, but some properties are summarized in Table V.

4,4-Diethylcyclopent-2-en-1-one (3c). Into a 100-mL, round-bottom flask containing 38.78 g of **8c** and a magnetic stir bar was poured 35 mL of 85% phosphoric acid. After the contents were mixed, the flask was fitted with a short-path condenser cooled with ice–water via a copper coil and an ice-cooled 100-mL receiving flask. The reaction flask was plunged into an oil bath preheated to 100 °C, and the pressure was reduced, using an aspirator, to 40 mm over a 10-min period. The initially vigorous distillation became slower after ca. 15 min, and the bath temperature was raised to 170 °C. After 40 min, when distillation again became slow, the pressure was lowered to 20 mm. After a 30-min period of slow distillation, the reaction was terminated.

The two-phase distillate was taken up in 30 mL of ether and separated, and the aqueous portion was extracted with two 30-mL portions of ether. The combined ether extracts were dried over $MgSO_4$. After filtration, the ether was removed by rotary evaporation to leave a pale-yellow oil, which was distilled in vacuo to afford 12.48 g of **3c** as a clear, colorless, sharp-smelling mobile liquid. Table I summarizes the properties of the conjugated cyclopentenones **3**.

4,4-Diethylcyclopent-2-en-1-ol (9c). In a dry, N_2-flushed, 250-mL, round-bottom, three-necked flask equipped with a magnetic stir bar, constant-pressure addition funnel, and condenser were placed 2.60 g (68.5 mmol) of lithium aluminum hydride and 90 mL of anhydrous ether. With stirring, a solution of 13.82 g (100 mmol) of **3c** in 35 mL of ether was added dropwise at a rate sufficient to maintain gentle reflux. The stirred reaction mixture was then refluxed gently for 22 h.

After the mixture was stirred for 2 h, a scoopula of anhydrous Na_2SO_4 was added, and after 1 h of additional stirring, the white, granular solids were removed by gravity filtration and washed with 35 mL of anhydrous ether. The ether was removed from the crude alcohol by rotary evaporation. Distillation in vacuo provided 13.04 g of pure **9c** as a clear, colorless oil.

Alcohols **9b**, **9d**, and **9e** were each obtained as a pair of diastereomers. These could be resolved by GLC (120 °C, Carbowax 20M) but were not collected individually for spectrscopic analysis. Accordingly, no ^{13}C NMR spectra were recorded, and the ^1H NMR and IR spectra described below are for the mixtures in these cases.

9a: bp 67–69 °C (20 mm), 79%; IR 3350 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.68 (m, 2 H, H_2, H_3), 4.87 (m, 1 H, H_1), 3.38 (s, 1 H, OH), 2.10 (1 H, H_5 cis), 1.52 (1 H, H_5 trans), 1.19 (s, 3 H, methyl cis), 1.07 (s, 3 H, methyl trans). Protons H_5 and H_1 constitute an AMX system, and the two H_5 signals are well resolved. Spin simulation on the Varian simulation program in "FT-80A Software, Edition II" matches these signals for the given chemical shifts and J_{AX} = 7.0 Hz, $J_{AM} = \mp$ 13.0 Hz, J_{MX} = 4.5 Hz.

9b: bp 84–86 °C (17 mm), 74%; IR 3370 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.78 (m, 2 H, H_2, H_3), 4.8 (br s, 2 H, H_1, OH), 0.7–2.2 [complex m; 0.98 (t, J = 7.5 Hz, 10 H)].

9c: bp 101–103 °C (20 mm), 93%; IR 3370 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.72 (br s, 2 H, H_2, H_3), 4.87 (m, 1 H, H_1), 2.18 (s, 1 H, OH), 2.12 (m, 1 H, H_5 cis), 1–1.7 (m, 5 H, H_5 trans, methylenes of ethyls), 0.7–1.0 (two overlapping triplets, 6 H, methyls of ethyls).

9d: bp 96–97 °C (16 mm), 85%; IR 3345 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.71 (br s, 2 H, H_2, H_3), 4.89 (m, 1 H, H_1), 3.13 (s, 1 H, OH), 0.7–2.4 [complex m, 1.00 (t, J = 7.0 Hz, 12 H, H_5, H_5, methyl, n-propyl)].

9e: not distilled, 95% crude; IR 3340 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.75 (br s, 2 H, H_2, H_3), 4.95 (m, 1 H, H_1), 3.30 (s, 1 H, OH), 0.7–2.4 (complex m, 12 H, H_5, H_5, methyl, isopropyl).

5-Bromo-3,3-diethylcyclopentene (10c). In a 250-mL, N_2-flushed, round-bottom flask equipped with a magnetic stir bar was placed 86 mL of cold 48% hydrobromic acid. With swirling and cooling, 10 mL of concentrated sulfuric acid was added. The mixture was removed from the ice bath, and, with stirring, 14.02 g (100 mmol) of **9c** was added in a thin stream. The flask was fitted with a stopper and the mixture was stirred at 25 °C for 2 days.

The opaque, blue-green mixture was poured into 100 mL of cold water, and the resulting solution was extracted with four 35-mL portions of pentane. The combined organic portions were dried over anhydrous magnesium sulfate. After filtration, the pentane was removed by rotary evaporation at 25 °C, with the apparatus opened to a N_2 line instead of to the atmosphere when the pentane had been removed. The dark-blue crude product weighed 16.87 g.

The bromides **10**, obtained crude in yields of 73–95%, decompose unless carefully purified by repeated vacuum distillation. Accordingly, they were immediately subjected to the last step of the synthetic sequence without purification or spectral analysis.

5,5-Diethylcyclopentadiene (1c). In a 100-mL, round-bottom flask equipped with a N_2 ebulator extending to the bottom were combined 21.01 g of **10c** and 55 mL of dry [from BaO, 81 °C (2.8)] quinoline. The flask was attached to a simple distilling head, an ice–water cooled condenser, and an ice–water cooled receiver. The flask was immersed in an oil bath preheated to 150 °C. With a gentle flow of nitrogen, a clear liquid began to distill immediately. After 15 min when the distillation became quite slow, the oil bath temperature was raised to 195 °C. The reaction was stopped when the distillation became extremely slow.

Redistillation of the product at atmospheric pressure (not 760 mm in Albuquerque, NM) afforded 7.25 g of **1c** as a clear, mobile, colorless oil. The properties of the cyclopentadienes are summarized in Table II.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research.

Registry No. **1a**, 4125-18-2; **1b**, 72807-72-8; **1c**, 61111-73-7; **1d**, 80721-08-0; **1e**, 80721-09-1; **3a**, 22748-16-9; **3b**, 72807-68-2; **3c**, 72807-67-1; **3d**, 80721-10-4; **3e**, 80721-11-5; **4a**, 4839-46-7; **4b**, 5345-

01-7; **4c**, 4160-95-6; **4d**, 80721-12-6; **4e**, 4160-99-0; **5a**, 61193-04-2; **5b**, 1135-62-2; **5c**, 80721-13-7; **5d**, 64635-91-2; **5e**, 4161-05-1; **6c**, 868-04-2; **6d**, 759-54-6; **6e**, 868-00-8; **7a**, 17804-59-0; **7b**, 80721-14-8; **7c**, 51111-06-9; **7d**, 80721-15-9; **7e**, 80721-16-0; **8a**, 54851-48-8; **8b**, 72826-61-0; **8c**, 72807-62-6; **8d**, 80721-17-1; **8e**, 80721-18-2; **9a**, 68757-99-3; **9b**, 72807-70-6; **9c**, 72807-69-3; **9d**, 80721-19-3; **9e**, 80721-20-6; **10a**, 80721-21-7; **10b**, 80721-22-8; **10c**, 80721-23-9; **10d**, 80721-24-0; **10e**, 80721-25-1; cyclopentadiene, 542-92-7; 5,5-diphenylcyclopentadiene, 71516-78-4; spiro[4.3]octa-5,7-diene, 15439-15-3; spiro[4.4]nona-1,3-diene, 766-29-0.

(Carbomethoxy)maleic Anhydride, a Highly Reactive New Dienophile and Comonomer

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Received November 6, 1981

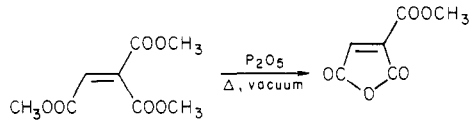
(Carbomethoxy)maleic anhydride (CMA), is an extremely reactive dienophile in [4 + 2] cycloadditions with butadiene, isoprene, and chloroprene. The second-order rate constants prove it to be more reactive than tetracyanoethylene. Diels–Alder reaction with anthracene gives the normal addition product. With cyclopentadiene, the endo adduct is obtained and with furan the exo adduct. With *p*-methoxystyrene, anethole, and diphenylethylene, the 2:1 Wagner-Jauregg-type adducts are obtained, while with styrene both the Wagner-Jauregg and the Diels–Alder ene adduct are formed. Copolymers form in certain conditions. With isobutyl and phenyl vinyl ether, an inverse-electron-demand Diels–Alder reaction with CMA yields 2-isobutoxy- or 2-phenoxy-6-methoxy-3,4-dihydro-2*H*-pyran-3,4-dicarboxylic anhydride. These labile dihydropyrans revert to copolymers.

Introduction

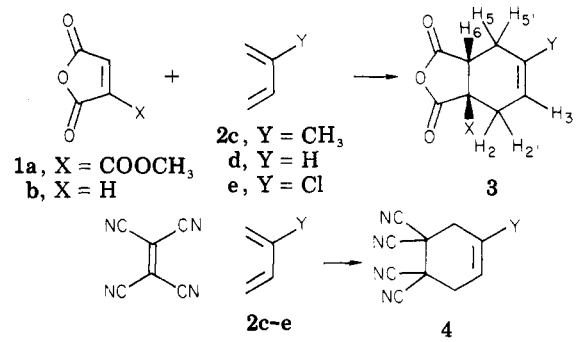
Maleic anhydride takes part in a variety of cycloaddition and copolymerization reactions not readily undergone by 1,2-disubstituted ethylenes due to the minimization of the steric effect by confining the two substituents into a ring and to the planar structure which permits effective resonance stabilization of radical or anionic intermediates. These cycloadditions have been recently reviewed by Sauer and Sustmann.[1]

Our work on electrophilic trisubstituted ethylenes such as trimethyl ethylenetricarboxylate has shown that they are also much more reactive than their 1,2-disubstituted counterparts in cycloaddition and copolymerization reactions.[2-8] Here the reason is that two α-substituents stabilize reactive intermediates much more effectively than one.

Accordingly, a maleic anhydride carrying an electrophilic carbon function should be especially reactive in these reactions. The literature did not offer such a compound. We recently[9] synthesized (carbomethoxy)maleic anhydride (CMA) by a little-used demethoxylation–cyclization reaction:[10]



Scheme I



In the present paper we report a study of the reactions of CMA with electron-rich 1,3-dienes, styrenes, and vinyl ethers.

Results

Reactions with 1,3-Dienes. CMA reacted far more rapidly than maleic anhydride (MAnh) with isoprene, butadiene, and chloroprene. It was even more reactive than tetracyanoethylene (TCNE). The products were the expected Diels–Alder cycloadducts (Scheme I). The structure of adduct **3ac** obtained in the reaction of CMA with isoprene was analyzed by 250-MHz ^{1}H NMR spectroscopy. The details are listed in the Experimental Section. Second-order rate plots are shown in Figure 1. The rate constants for these reactions are reported in Table I.

In chloroform solution at room temperature, CMA reacted with anthracene within a few minutes, as did TCNE.[1,11] MAnh still showed a mixture of adduct and

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