2.[18] No carbonyl derivatives of **2** could be formed, although attempts in this direction were not exhaustive. All these facts were of assistance in ascribing the structure given to **2**.

Reduction of 2 to Bis(1-phenylcyclopentyl)carbinol (3).—Treatment of **2** with excess lithium aluminum hydride in ether at room temperature in the usual manner led to alcohol **3** in 85% yield: mp 97–98° from aqueous ethanol, mixture melting point with **2** depressed (69–88°); λ^{KBr} 2.92 (O–H), 9.68 and 9.81 (C–O), 3.31, 3.36, 3.45, 3.55, 6.29, 6.72, 7.27, 7.41, 7.60, 7.8–8.1 (broad), 8.32, 9.05, 9.30, 10.0, 10.38, 10.6, 11.3, 13.14, 14.40; $\delta_{TMS}^{CCl_4}$ 7.25 m (sharp, Ar–H), 4.07 s (broad, >CHOH), 1.99 s (broad, lost in D_2O, –OH), 1.83–1.0 m (all cyclopentyl H's).

Anal. Calcd for $C_{23}H_{28}O$: C, 86.20; H, 8.81. Found: C, 85.89; H, 8.80.

Reactions of Other 1-Phenylcycloalkanecarbonitriles with Methyl Grignard Reagent.—The cyclopropyl, cyclobutyl, and cyclohexyl analogs were available from earlier work.[19] Small scale (*ca.* 10 mmol) reaction of these with methylmagnesium iodide in ether under the concentrated reactant conditions described earlier for the cyclopentyl case failed to give products analogous to **2** in workable amounts, although traces of unidentified semisolid or solid material was occasionally obtained. The ketone products were collected by glpc or Hickman still distillation, so boiling points were not determined. The cyclohexyl analog gave **1-phenylcyclohexyl methyl ketone** in 26.5% yield, mp 31–33°, lit.[20] mp 33–35° (λ^{melt} 5.88, 7.40 (–$COCH_3$)), and much recovered nitrile.[21] The cyclobutyl member afforded **1-phenylcyclobutyl methyl ketone** in 31.4% yield (oil, λ^{neat} 5.90, 7.40, (–$COCH_3$), lit.[3] bp 56–57° (0.2 mm)) with some starting nitrile again being recovered. Finally, the cyclopropyl example yielded **1-phenylcyclopropyl methyl ketone** in 29.5% yield (oil, λ^{neat} 5.93, 7.40 (–$COCH_3$), 7.80, 8.70, 9.12, 9.72, 13.17, 14.25; lit.[22] bp 122° (25 mm), lit.[23] λ^{neat} *inter alia* 5.86, 7.79, 8.70, 9.12, 9.72, 13.16, 14.24) and, as usual, some starting nitrile. In this case an unidentified oil was isolated from the aqueous phase. Its properties were much unlike those of **2**, however, and its spectra suggested that it was a ring-opened derivative of the methyl ketone.

Registry No.—1-Phenylcyclopentanecarbonitrile, 77-57-6; methylmagnesium iodide, 917-64-6; **1**, 4046-09-7; **1** 2,4-dinitrophenylhydrazone, 15811-00-4; **1** semicarbazone, 15811-01-5; **2**, 15811-02-6; **3**, 15811-03-7.

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[18] Whereas excellent in some less-hindered cases, this method, as reported,[6] gave only a 9% cleavage of the hindered ketone, camphenilone.

[19] J. W. Wilt and H. Philip, *J. Org. Chem.*, **24**, 616 (1959); J. W. Wilt and D. D. Roberts, *ibid.*, **27**, 3434 (1962).

[20] G. G. Lyle, R. A. Covey, and R. E. Lyle, *J. Amer. Chem. Soc.*, **76**, 2713 (1954).

[21] MacKenzie, *et al.*,[3] reported that this cyclohexyl homolog failed to react with methyl Grignard reagent under the conditions that they used for the cyclopentyl case.

[22] S. C. Bunce and J. B. Cloke, *J. Amer. Chem. Soc.*, **76**, 2244 (1954).

[23] S. E. Wiberley and S. C. Bunce, *Anal. Chem.*, **24**, 623 (1952).

7,7-Dicarbomethoxycycloheptatriene[1a]

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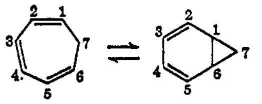
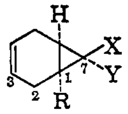
Received October 30, 1967

Although substitution of cyano groups at C-7 shifts the cycloheptatriene (**1**)–norcaradiene (**2**) equilibrium constant in favor of the bicyclic valency tautomer,[2] this structural feature does not seem to be required for the existence of a stable norcaradiene (*cf.* the 2,5,7-triphenyl derivative[3]). As a point on the developing but still incompletely understood plot of substitution pattern *vs.* structure in this series, we record the properties of 7,7-dicarbomethoxycycloheptatriene. The syntheses of this sensitive substance and other tropilidene derivatives are carried out by methods that should be widely applicable to members of this class.



1 **2**

The synthetic approach to the tropilidene ring system is by cyclopropanation of a dihydrobenzene, essentially as in the method so effectively developed by Vogel and his coworkers.[4] However, the oxidation state of the resulting norcarene, which has been adjusted in previous syntheses[4] by addition of bromine to the double bond and dehydrohalogenation with amines or alcoholic alkali, involves procedures that are unsuitable to some of the cases of interest to us. For example, addition of bromine to norcarenes with a *syn*-7-carbomethoxy group leads either to complex mixtures in the case of **3a** or to a bromolactone rather than to the desired dibromide in the case of **3b**. Although a dibromide, mp 136°, can be obtained from the cyano ester **3c** with $C_5H_6N^+Br_3^-$/HOAc, dehydrohalogenation leads again to a complex mixture.



3a, $R = H; X = Y = CO_2CH_3$
b, $R = CH_3; X = Y = CO_2CH_3$
c, $R = H; X = CN; Y = CO_2CH_3$

7,7-Dicarbomethoxynorcar-3-ene (**4**), prepared from the photolysis of methyl diazomalonate in 1,4-cyclohexadiene,[5] when treated with selenium dioxide in aqueous dioxane gives a mixture of the allylic alcohols **5** and **6** in the ratio 86 : 14 as determined by nuclear magnetic resonance (nmr) analysis. The same two alcohols are obtained (17:83 ratio) by oxidation of the isomeric diester **7**, prepared from 1,3-cyclohexadiene (see Scheme I). Although direct acid-catalyzed dehydration of these alcohols fails, conversion into bromides (PBr_3/CCl_4) and treatment with sodium methoxide gives 7,7-dicarbomethoxycycloheptatriene **8**. Dehydrogenation of **7** (with N-bromosuccinimide in CCl_4), or of **4** (with dicyanodichloroquinone in benzene), also gives **8** directly in yields of about 30%, but the substance is accompanied by unreacted starting material and aromatization product (phenylmalonic ester), from which it is difficultly separable. The method of choice in this case involves reaction of the mixture of alcohols **5** and **6** with *p*-bromobenzenesulfonyl chloride in 2,6-lutidine at 0–20°. Isolation by chromatography gives **8**, mp 45–45.5°, in yields of 25–30%. The synthesis of 3,7,7-trimethylcycloheptatriene **10**, which is much less subject than **8** to aro-

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[1] (a) This work was supported in part by the National Science Foundation and the Air Force Office of Scientific Research. (b) National Institutes of Health Postdoctoral Fellow, 1966–1967.

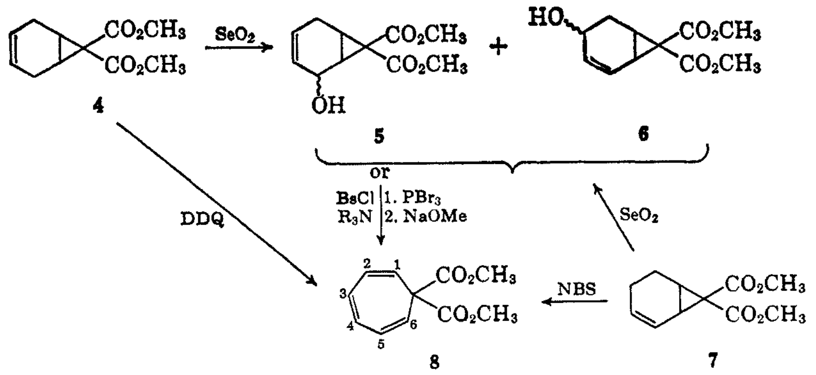
[2] E. Ciganek, *J. Amer. Chem. Soc.*, **89**, 1454 (1967).

[3] T. Mukai, H. Kubota, T. Toda, *Tetrahedron Lett.*, 3581 (1967).

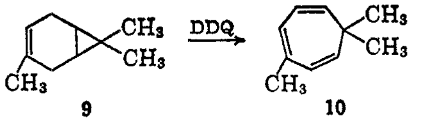
[4] E. Vogel, W. Wiedemann, H. Kiefer, and V. F. Harrison, *ibid.*, 673 (1963), and subsequent papers.

[5] For the corresponding diethyl ester, see H. Musso and U. Biethan, *Chem. Ber.*, **97**, 2282 (1964).

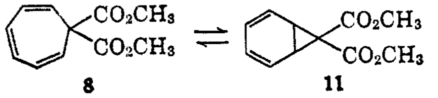
SCHEME I



matization, is accomplished in about 60% yield by the direct dicyanodichloroquinone dehydrogenation of 3-carene (**9**).



The ultraviolet spectrum [λ_{max}^{EtOH} 258 mμ (ε 3120)], of compound **8** corresponds to that of a cycloheptatriene[6] rather than a norcaradiene, for which absorptions in the regions near 235 and 275 mμ are expected.[2,7] The nmr spectrum at +35° in $CDCl_3$ shows absorptions of the C-2, C-3, C-4, and C-5 protons as a multiplet between τ 3.44 and 3.95, those of the C-1 and C-6 protons as a multiplet (broadened doublet) between 4.9 and 5.3, and those of the methoxyl protons as a singlet ($w_{1/2}$ = *ca.* 1 cps). At −35°, the methoxyl absorption remains sharp, but the separation between it and the center of gravity of the C-1–C-6 absorption decreases by about 0.2 ppm. If it is assumed that **8** and its norcaradiene valency tautomer **11** have methoxyl resonances with fortuitously close chemical shifts, the upfield movement of the C-1–C-6 absorption at low temperature could be compatible with a small change in the composition of a rapidly interconverting equilibrium mixture of the two isomers. The possibility that the temperature effect has some other origin is the subject of a more thorough nmr study. It is already clear from the present data, however, that the substance exists largely as the cycloheptatriene **8**.[7a]



At or above 100° in $CDCl_3$ solution, **8** aromatizes to dimethyl phenylmalonate (98% yield) in a few hours. Since the most plausible mechanism for aromatization involves preliminary cycloheptatriene → norcaradiene isomerization,[6-8] the facility of aromatization of **8** compared with that of cycloheptatriene (which aromatizes very slowly below 300°) is consistent with a smaller energy difference between the norcaradiene and the cycloheptatriene forms in the dicarbomethoxy series ($\mathbf{8} \rightleftharpoons \mathbf{11}$) than in the unsubstituted ($\mathbf{1} \rightleftharpoons \mathbf{2}$) case.

Experimental Section[9]

7,7-Dicarbomethoxybicyclo[4.1.0]hept-3-ene (4).—A mixture of 17.2 g (0.109 mol) of dimethyldiazomalonate[10] and 50 g of 1,4-cyclohexadiene was diluted to 200 ml with benzene and irradiated through a Pyrex filter with a 450-W Hanovia ultraviolet lamp for 23 hr. Chromatography on neutral alumina gave 21 g of crude product which after recrystallization from pentane gave 16.5 g of material of mp 66–67°. The nmr spectrum showed absorptions for vinyl protons (2 H) at τ 4.66 (broad singlet), *exo-* and *endo*-carbomethoxy protons (6 H) as sharp singlets at 6.35 and 6.45, respectively, methylene protons at 7.55 (broad singlet), and bridgehead protons at 8.13 (broad singlet).

Anal. Calcd for $C_{11}H_{14}O_4$: C, 62.85; H, 6.71. Found: C, 63.00; H, 6.64.

7,7-Dicarbomethoxybicyclo[4.1.0]hepten-2-ene (7) was prepared in a similar manner from 1,3-cyclohexadiene. It had mp 40–42° (pentane). The nmr spectrum showed absorptions for vinyl protons (2 H) at τ 4.08 to 4.67 (complex quartet), *exo-* and *endo*-carbomethoxy protons as sharp singlets at 6.40 and 6.45 (6 H), and methylene and bridgehead protons at 7.58–8.52 (broad multiplet, 6 H).

Anal. Calcd for $C_{11}H_{14}O_4$: C, 62.85; H, 6.71. Found: C, 62.88; H, 6.74.

7,7-Dicarbomethoxybicyclo[4.1.0]hept-3-en-2-ol (5).—To a solution of 4.00 g (19.0 mmol) of 7,7-dicarbomethoxybicyclo-[4.1.0]hept-3-ene in 40 ml of 50% aqueous dioxane was added dropwise over a period of 90 min a solution of 2.23 g (20.0 mmol) of selenium dioxide in 30 ml of 50% aqueous dioxane. The mixture was stirred at 83° for 20.5 hr, cooled, filtered, diluted with ether, and washed with water. The ether layer was dried over sodium sulfate, and the solvent was removed to give 3.99 g of a viscous yellow oil. Chromatography on 120 g of Woelm basic alumina (activity IV) gave 1.45 g of a mixture of allylic alcohols (40% yield based on 600 mg of starting material recovered) which nmr analysis showed to consist of 14% 7,7-dicarbomethoxybicyclo[4.1.0]hept-2-en-4-ol (**6**) and 86% of 7,7-dicarbomethoxybicyclo[4.1.0]hept-3-en-2-ol (**5**). Repeated chromatography on alumina separated the two isomers, the Δ^2-alcohol (**6**) emerging first.

The Δ^3-alcohol **5** (probably a mixture of C-2 epimers), after bulb-to-bulb distillation at 135° (0.2 mm), showed nmr absorptions for vinyl protons (2 H) at τ 4.44 (broad singlet), α-hydroxyl proton (1 H) at 5.57, *exo-* and *endo*-carbomethoxy protons (6 H) at 6.31 and 6.42 (sharp singlets), methylene protons (2 H) at 7.43, and bridgehead protons (2 H) at 8.00.

Anal. Calcd for $C_{11}H_{14}O_5$: C, 58.40; H, 6.24. Found: C, 58.31; H, 6.36.

7,7-Dicarbomethoxybicyclo[4.1.0]-hept-2-en-4-ol (6) was prepared in a similar manner from **7**. The mixed allylic alcohols

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(6) *Cf.* J. A. Berson and M. R. Willcott, III, *J. Amer. Chem. Soc.*, **88**, 2494 (1966), and references cited there.

(7) J. A. Berson, P. W. Grubb, R. A. Clark, D. R. Hartter, and M. R. Willcott, III, *ibid.*, **89**, 4076 (1967).

(7a) NOTE ADDED IN PROOF.—H. Günther and M. Görlitz, University of Cologne, have carried out a low-temperature study of the nmr spectrum which permits direct observation of both isomers. At −139°, the interconversion is slow enough to prevent averaging of the chemical shifts. Details will be given in a separate paper by these authors, to whom we are indebted for advance information.

(8) W. G. Woods, *J. Org. Chem.*, **23**, 110 (1958).

(9) Nmr spectra were taken in CCl_4 or $CDCl_3$ solutions with the Varian A-60-A or HA-100 instruments. Chemical shifts are relative to internal tetramethylsilane at τ 10.00. Microanalyses are by Spang Microanalytical Laboratories.

(10) M. Regitz, *Chem. Ber.*, **99**, 3128 (1966).

(24% yield based on recovered starting material) consisted of a 17:83 mixture of **5** and **6** from which **6** was isolated by chromatography. Its nmr spectrum showed absorption for vinyl protons at τ 3.92–4.57 (2 H) as an AB quartet, α-hydroxy proton (1 H) at 6.2, carbomethoxy protons at 6.32 and 6.37 (6 H) as sharp singlets, and methylene and bridgehead protons as a broad multiplet from 7.1 to 8.5.

Anal. Calcd for $C_{11}H_{14}O_5$: C, 58.40; H, 6.24. Found: C, 58.55; H, 6.36.

7,7-Dicarbomethoxycycloheptatriene (8).—To a mixture of the allylic alcohols (1.34 g, 5.90 mmol, 80% **5** and 20% **6**) dissolved in 20 ml of dry 2,6-lutidine was added dropwise at 0° a solution of 4.50 g (17.7 mmol) of *p*-bromobenzenesulfonyl chloride in 5 ml of 2,6-lutidine. After 20 hr at room temperature, the mixture was treated with 20 ml of water and extracted with ether. The extract was washed successively with 10% hydrochloric acid, water, and sodium bicarbonate solution, dried over sodium sulfate, and evaporated to give 692 mg of a viscous yellow oil. Chromatography on 20 g of Woelm basic alumina (activity IV) gave a total of 387 mg of partially crystalline material which consisted mainly of **8** contaminated with a few per cent of dimethyl phenylmalonate. Recrystallization from pentane–ether gave 322 mg of colorless prisms, mp 45–45.5°. The yield based on starting material (112 mg recovered) was 28%.

Anal. Calcd for $C_{11}H_{12}O_4$: C, 63.45; H, 5.81. Found: C, 63.54; H, 5.87.

The 60-Mc nmr spectrum in CCl_4 showed the C-2, C-3, C-4, and C-5 protons as a multiplet from τ 3.44 to 3.95, the C-1 and C-6 protons as an unresolved doublet from 4.90 to 5.30, and the six carbomethoxy protons as a sharp singlet at 6.37. The spectrum at −35° is described in the discussion section.

3,7,7-Trimethylcycloheptatriene was formed when 1.3 g (9.9 mmol) of 3-carene was added to a solution of 2.27 g (10 mmol) of dichlorodicyanoquinone in 10 ml of dry ether, and the mixture was heated at reflux for 30 min. Ether was removed on a rotary evaporator. Pentane was added to the residue, the precipitated solid was filtered off and extracted with pentane in a soxhlet, and the filtrate was evaporated to give 0.83 g of material which nmr analysis showed to be about 90% 3,7,7-trimethylcycloheptatriene **10** contaminated with some 3-carene. Vapor chromatographic isolation gave pure **10**, which had an infrared spectrum identical with that of an authentic sample.[6]

Registry No.—**4**, 15833-41-7; **5**, 15833-42-8; **6**, 15833-43-9; **7**, 15833-44-0; **8**, 15833-45-1.

β,γ-Unsaturated Acids and Esters by Photochemical Isomerization of α,β Congeners[1,2]

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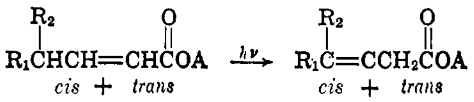
Received August 24, 1967

β,γ-Unsaturated acids and esters have been less readily available than their α,β-unsaturated relatives, for which several convenient methods of synthesis are available.[5,6] Although it is well known that β,γ isomers can be brought into equilibrium with their α,β congeners by catalysis with acid or base,[7] this method is based on thermodynamic control and suffers as a general synthetic method from wide variability with structure of the maximum attainable yield.

As a partial solution to the problem of synthesizing β,γ-unsaturated acids, we offer the photochemical isomerization of *acyclic* α,β-unsaturated acids or esters. This method is analogous to the related isomerization of α,β-unsaturated ketones and aldehydes.[8–12] The work also finds close parallels in the photochemical studies on the ionones[11] and in studies of the photochemical behavior of certain conjugated esters by Jorgenson.[13]

The conjugated acids and esters shown in Scheme I were irradiated as 2–5% solutions in saturated hydrocarbons, methanol, or in ethyl acetate with an unfiltered 450-W Hanovia Type L lamp. Although the maximum absorption of the conjugated derivatives lies about 210 nm, there is still adequate absorption at 253.7 nm mercury line to permit the isomerization. With a Pyrex filter, which absorbs irradiation below 300 nm, there is no isomerization. Typical results are shown in Table I.

Scheme I



$$\underset{cis\ +\ trans}{R_1\overset{R_2}{\overset{|}{C}}HCH{=}CH\overset{O}{\overset{\|}{C}}OA} \xrightarrow{h\nu} \underset{cis\ +\ trans}{R_1\overset{R_2}{\overset{|}{C}}{=}CCH_2\overset{O}{\overset{\|}{C}}OA}$$

Compound	R_1	R_2	A
1	CH_3	CH_3	C_2H_5
2	CH_3	H	CH_3
3	H	H	CH_3
4	*n*-C_6H_{13}	H	H
5	*n*-C_7H_{15}	H	H
6	*n*-$C_{12}H_{25}$	H	H

Table I

Irradiation of α,β-Unsaturated Acids and Esters

Compd	Reacn time, hr	Solvent	*cis/trans*	% yield[a]
1	5	Pentane		85
2	5	Pentane	*b*	85
3	12	Pentane		20[c]
4	18	Pentane	0.5	94
5	18	Hexane	0.5	95[d]
6	18	Hexane	0.5	95[d,e]

[a] Based on starting material (% conversion). [b] Not determined. [c] Remaining material isolated as 50% methyl crotonate and 30% methyl isocrotonate. [d] Also carried out in methanol with similar results. [e] This experiment was conducted by Dr. S. Safe and is included here with his generous permission.

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(1) Taken in part from the dissertation of R. R. Rando submitted in partial fulfillment of the requirements for the Ph.D. Degree, Yale University, Dec 1966.

(2) This work was supported in part by Research Grant GP-0959 to Yale University by the National Science Foundation.

(3) R. R. Rando expresses his gratitude to the National Institutes of Health for the award of a predoctoral fellowship, 1963–1966, and a postdoctoral fellowship (Harvard University), 1966–1967.

(4) Where inquiries should be addressed.

(5) E. H. Rodd, Ed., "Chemistry of Carbon Compounds," Vol. 1, Elsevier Publishing Co., Amsterdam, 1951, pp 624–626; W. S. Johnson, *Org. Reactions*, **1**, 252 (1942).

(6) W. S. Wadsworth and W. D. Emmons, *J. Amer. Chem. Soc.*, **83**, 1733 (1961).

(7) See, for example, E. Boorman and R. P. Linstead, *J. Chem. Soc.*, 258 (1935), and earlier references, or G. Kon, R. P. Linstead, and G. Maclennen, *ibid.*, 2454 (1932).

(8) N. C. Yang and M. J. Jorgenson, *Tetrahedron Lett.*, 1203 (1964).

(9) H. Wehrli, R. Wenger, K. Schaffner, and O. Jeger, *Helv. Chim. Acta*, **46**, 678 (1963).

(10) C. A. McDowell and S. S. Sifniades, *J. Amer. Chem. Soc.*, **84**, 4606 (1962).

(11) M. Mousseron-Canet, M. Mousseron, and P. Legendre, *Bull. Soc. Chim. Fr.*, 1509 (1961).

(12) K. J. Crowley, R. A. Schneider, and J. Meinwald, *J. Chem. Soc., Sect. C*, 571 (1966).

(13) M. J. Jorgenson, *Chem. Commun.*, 137 (1965).