2,2-Dimethyl-3-isopropylidenecyclopropyl Propionate (1).—1,1-Dibromo-2-methylpropene was prepared by the method of Farrell and Bachman.[13] To 1.95 g (0.083 g-atom) of magnesium turnings in 150 ml of tetrahydrofuran (freshly distilled from lithium aluminum hydride) was added a small amount of a mixture of 15.6 g (0.14 mole) of 2-methyl-1-propenyl propionate and 15.0 g (0.07 mole) of 1,1-dibromo-2-methylpropene. The resulting mixture was heated until reaction started. Heating was then discontinued and the remainder of the enol ester–dibromide mixture was added at a rate sufficient to keep the reaction under control. When addition was complete, the mixture was refluxed for 30 min, cooled, poured into an aqueous ammonium chloride solution, and extracted twice with ether. The combined ether layers were washed twice with water, dried with magnesium sulfate, and filtered. Following removal of solvent by distillation, the residue was distilled. After a fraction consisting of starting materials, there was collected 2.26 g (18%) of the desired product, bp 80–87° (20 mm) [lit.[5a] bp 50–55° (bath) (4 mm)], which contained 15% of impurities by gas chromatography. An analytical sample was purified by preparative gas chromatography.[12]

Anal. Calcd for $C_{11}H_{18}O_2$: C, 72.49; H, 9.96. Found: C, 72.33; H, 9.87.

(13) J. K. Farrell and G. B. Bachman, *J. Am. Chem. Soc.*, **57**, 1282 (1935).

Fused Ring Derivatives of [12]Paracyclophane

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More than 10 years ago Allen and VanAllan[1] described the synthesis of 3,4-diphenyl-2,5-dodecamethylenecyclopentadienone and its use in preparing [12]paracyclophanes. They interpreted the ultraviolet absorption spectra to indicate no distortion of the aromatic ring.

Their synthetic procedure has now been extended to include the preparation of fused ring derivatives of [12]paracyclophane, **1–5** (see Chart I), by utilizing aryne chemistry. We have, in addition, prepared the dipropyl analogs, **1Pr–5Pr**, of each of the [12]paracyclophanes (Table I).

TABLE I
[12]PARACYCLOPHANES AND THEIR DIPROPYL ANALOGS

Compd	Mp or bp (μ), °C	Yield, %	C, % Calcd	C, % Found	H, % Calcd	H, % Found
1	130–132	65	90.8	90.9	9.1	9.2
1Pr	80 (4)	43.5	91.8	91.5	8.3	8.2
2	229.5–231.5	58	91.9	91.6	8.0	8.1
2Pr	272–273	7.4	92.7	92.9	7.3	7.3
3	113–115	63	91.4	91.3	8.6	8.7
3Pr	127–129	69	92.2	91.9	7.7	7.5
4	251.5–253.5	22	91.9	91.6	8.1	8.4
4Pr	161.5–163	39.5	92.7	92.9	7.3	7.0
5	253–257	43	92.2	91.9	7.7	7.8
5Pr	245–247	38	93.0	93.2	6.9	7.0

Comparison of the ultraviolet absorption spectra (Table II) of the dipropyl and dodecamethylene analogs shows them to be essentially identical, indicating a lack of ring distortion, in agreement with the conclusions of Allen and VanAllan.

(1) C. F. H. Allen and J. A. VanAllan, *J. Org. Chem.*, **18**, 882 (1953).

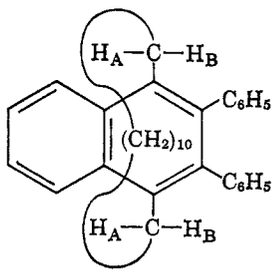

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Figure 1.

TABLE II
ULTRAVIOLET ABSORPTION DATA

Substance	λmax, mμ	Log ε	Substance	λmax, mμ	Log ε
1[a]	214	4.57	**1Pr**[a,b]	214	4.58
	227 sh	4.48		227 sh	4.49
2[a]	218	4.67	**2Pr**[a,b]	218	4.63
	232 sh	4.65		234	4.64
3[a]	241	4.79	**3Pr**[a]	238	4.80
	278 sh	3.73		275 sh	3.77
	289	3.85		286	3.88
	300	3.90		296	3.94
	312 sh	3.73		307 sh	3.76
4[c]	273	4.92	**4Pr**[b,c]	272	4.95
	360	3.70		359	3.71
	377	3.82		377	3.87
	399	3.75		398	3.78
5[a]	212	4.76	**5Pr**[a]	217	4.74
	236 sh	4.66		235 sh	4.68
	262	3.91		262	3.89
	271 sh	3.73		271 sh	3.73
	279	3.64		280	3.65

[a] Solvent cyclohexane. [b] T. H. Regan and J. B. Miller, *J. Org. Chem.*, in press. [c] Solvent chloroform.

The nmr spectra (Table III), of **3**, **4**, and **5**, when compared with those of **3Pr**, **4Pr**, and **5Pr**, respectively, confirm what molecular models imply, namely, that the α-methylene portions of the propyl groups are free to rotate[2] unlike those same portions of the dodecamethylene chains. Thus, in **3Pr**, **4Pr**, and **5Pr** the protons of any α-methylene group are identical ($\delta_{H_A} = \delta_{H_B}$), whereas in **3**, **4**, and **5** these protons are magnetically nonequivalent ($\delta_{H_A} - \delta_{H_B} = 0.5$–$0.7$ ppm; see Figure 1).

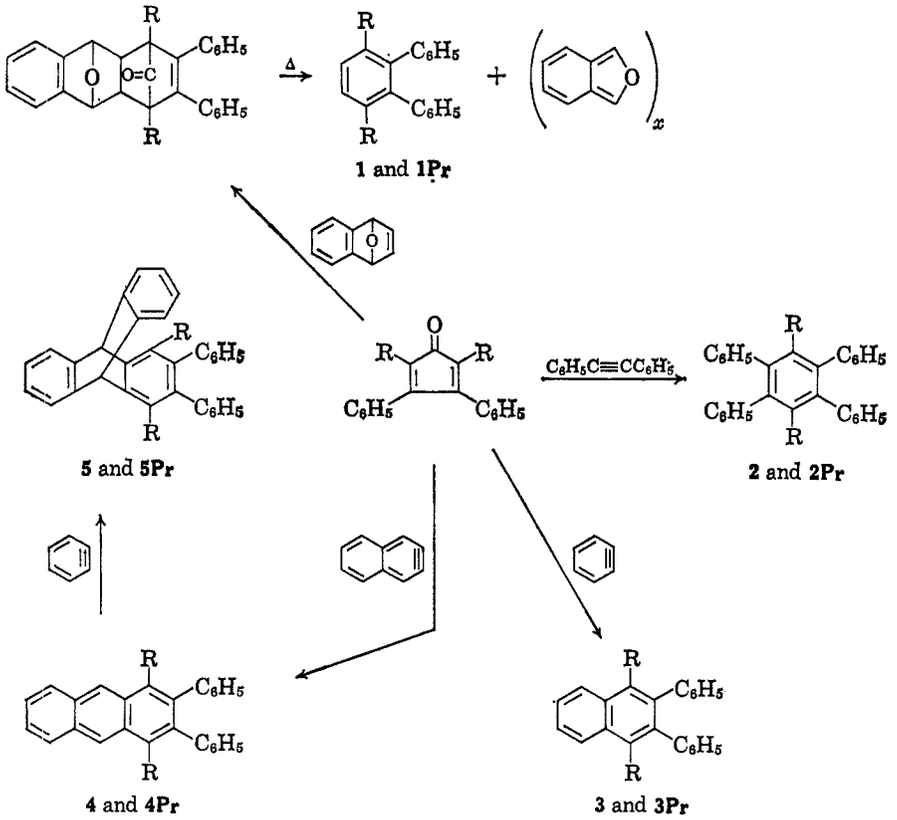
TABLE III
NUCLEAR MAGNETIC RESONANCE DATA

Compd	δ, ppm H_A[a]	δ, ppm H_B[a]	δ, ppm C_6H_5
1	2.5	2.5	7.05
1Pr	2.3	2.3	7.00
2	2.3	2.3	7.1[a]
2Pr	2.1	2.1	7.10
3	3.2	2.7	7.0[a]
3Pr	2.8	2.8	7.08
4	3.5	2.8	7.2[a]
4Pr	2.9	2.9	7.03
5	3.0	2.5	7.0[a,b]
5Pr	2.6	2.6	7.0[a,b]

[a] Visually estimated center of a multiplet. [b] Multiplicity owing at least in part to the superposition of the high-field portion of the A_2B_2 resonance of the benzo moiety on the phenyl resonance.

(2) As indicated in Table III, these protons appear as a multiplet similar to the published spectrum of hexapropylbenzene. This deviation from the expected triplet appearance has been attributed to some restricted rotation: H. Hopff and A. Gati, *Helv. Chim. Acta*, **48**, 509 (1965).

CHART I



1–5 R—R ≡ $(CH_2)_{12}$
1Pr–5Pr, R ≡ n-C_3H_7

This restricted rotation further manifests itself in the absorption of the pendant phenyl groups which is a very narrow band (2.0–2.5-cps width at half-height) for the dipropyl cases, **2Pr–4Pr**, but is a complex multiplet (30-cps total band width) in the dodecamethylene cases, **2–4**. Since these pendant phenyl groups are perpendicular to the central ring, the presence of the macrocyclic ring makes, for example, the two *ortho* protons of any given phenyl ring decidedly different from each other.

The nmr spectrum of **1** is interesting since $\delta_{H_A} = \delta_{H_B}$. This could mean that restricted rotation is necessary but not sufficient to make $\delta_{H_A} \neq \delta_{H_B}$ without further factors influencing H_A preferentially (a fused ring, for example). However, the pendant phenyl absorption in **1** is a sharp band (2.5 cps width at half-height) and were rotation restricted we would expect complex absorption for these phenyl groups. Therefore, we interpret the spectrum of **1** to indicate a sufficient degree of rotation of the dodecamethylene chain in its entirety to permit magnetic equivalence of H_A and H_B as well as of the protons of the pendant phenyl groups. The ability of a dodecamethylene chain to rotate around the edge of the benzene ring has been predicted by Smith.[3]

The highest field absorption observed in these compounds was with **5** (δ = 0.5 ppm) which implies that some of the methylene protons lie between the wings of the triptycene structure in a strongly shielded region. The bridgehead protons of **5** and **5Pr** fall at 5.82 and 5.75 ppm, respectively, and thus show a large shift to low field when compared with triptycene (5.36 ppm). This is related to compressional factors as was found for 1,4-dimethyltriptycene (5.62 ppm).[4]

(3) B. H. Smith, "Bridged Aromatic Compounds," Academic Press Inc., New York, N. Y., 1964, p 348.

Experimental Section

2,3-Diphenyl-1,4-dodecamethylenebenzene (1).—A solution of 3.98 g (0.01 mole) of 3,4-diphenyl-2,5-dodecamethylenecyclopentadienone and 1.58 g (0.011 mole) of 1,4-dihydronaphthalene 1,4-oxide in benzene was refluxed for 2.5 hr. The solvent was removed under vacuum; the residue was filtered and washed with methanol. The resulting solid, 2,3-diphenyl-1,4-dodecamethylene-9,10-epoxy-11-keto-1,4-methano-1,4,4a,9,10,10a-hexahydroanthracene, was refluxed overnight in diglyme. Water was added and the solution was extracted three times with chloroform. The chloroform layer was dried with sodium sulfate and the solvent was removed under vacuum. The residue was dissolved in a minimum of benzene, and the polymer which precipitated with the addition of ligroin (bp 30–60°) was removed by filtration. The benzene–ligroin solution was concentrated under vacuum. Two recrystallizations from ethanol–benzene provided 2.58 g of an analytical sample.

1,4-Dodecamethylene-2,3,5,6-tetraphenylbenzene (2).—A solution of 1.99 g (0.005 mole) of 3,4-diphenyl-2,5-dodecamethylenecyclopentadienone and 3.56 g (0.02 mole) of diphenylacetylene was refluxed until the color faded. Cooling and diluting with methanol gave 2.16 g (79%) of product, mp 225–229°. Recrystallization from acetic acid provided an analytical sample.

2,3-Diphenyl-1,4-dodecamethylenenaphthalene (3).—A solution of 3.98 g (0.01 mole) of 3,4-diphenyl-2,5-dodecamethylenecyclopentadienone in 20 ml of 1,2-dimethoxyethane was refluxed. Solutions of 1.65 g (0.012 mole) of anthranilic acid in 20 ml of 1,2-dimethoxyethane and 1.52 g (0.013 mole) of isoamyl nitrite in 20 ml of the same solvent were added simultaneously over 15 min. The mixture was refluxed for a total of 1.25 hr, cooled, made basic with 5% sodium hydroxide solution, diluted with water, and extracted with chloroform. The chloroform extract was dried and concentrated under vacuum to a yellow oil which

(4) T. H. Regan and J. B. Miller, unpublished results.

crystallized on trituration with methanol. Recrystallization from ethanol–methanol gave 2.80 g of pure material.

2,3-Diphenyl-1,4-dipropylnaphthalene (3Pr).—By using 3.16 g (0.01 mole) of 3,4-diphenyl-2,5-dipropylcyclopentadienone and the procedure given for **3**, 2.51 g of pure material was obtained after recrystallization from methanol–water.

2,3-Diphenyl-1,4-dodecamethyleneanthracene (4).—To a refluxing solution of 15.9 g (0.04 mole) of 3,4-diphenyl-2,5-dodecamethylenecyclopentadienone in 100 ml of 1,2-dimethoxyethane were added, dropwise, solutions of 7.48 g (0.04 mole) of 3-amino-2-naphthoic acid in 80 ml of 1,2-dimethoxyethane and 12 ml of isoamyl nitrite in 80 ml of the same solvent. The mixture was refluxed for 2 hr, cooled, and made basic with 5% sodium hydroxide solution. The resulting scarlet solid was stirred in benzene and filtered to remove insoluble residue. After drying, the benzene solution was chromatographed on alumina. The effluent was stripped to yield an orange solid. Washing with methanol gave 6.83 g of yellow solid, mp 244–249°. Two recrystallizations from acetic acid provided an analytical sample as yellow needles.

The **tetracyanoethylene derivative** was prepared by reaction in tetrahydrofuran at room temperature overnight. After the solvent had been stripped, the residual solid was recrystallized from benzene–ligroin (bp 30–60°), mp 274–278°.

Anal. Calcd for $C_{44}H_{40}N_4$: C, 84.5; H, 6.4; N, 8.9. Found: C, 84.2; H, 6.4; N, 9.2.

2,3-Diphenyl-1,4-dodecamethylenetriptycene (5).—A solution of 4.0 g (0.008 mole) of 2,3-diphenyl-1,4-dodecamethyleneanthracene in 50 ml of 1,2-dimethoxyethane was refluxed. Solutions of 1.11 g (0.008 mole) of anthranilic acid in 50 ml of 1,2-dimethoxyethane and 0.92 g (0.008 mole) of isoamyl nitrite in 50 ml of the same solvent were added simultaneously over 0.5 hr. The mixture was refluxed a total of 1.5 hr, cooled, made basic with 5% sodium hydroxide solution, diluted with water, and refrigerated, and the solid was collected and dried. To remove anthracene, the solid was dissolved in tetrahydrofuran and treated with tetracyanoethylene in tetrahydrofuran. The solvent was then removed under vacuum and the residue was dissolved in benzene. The benzene solution was chromatographed on alumina; the benzene effluent was concentrated under vacuum. Two recrystallizations from acetic acid provided 2.0 g of an analytical sample.

2,3-Diphenyl-1,4-dipropyltriptycene (5Pr).—By using 1.98 g (0.0048 mole) of 2,3-diphenyl-1,4-dipropylanthracene (**4Pr**) and the procedure given for **5**, 0.78 g of pure material was obtained.

Nmr Spectra.—The nmr spectra were determined on a Varian A-60 spectrometer with the probe at the ambient operating temperature (~35°). Spectra were determined in deuteriochloroform solution at concentrations ranging from 1 to 10% (w/v).

Acknowledgment.—We are indebted to Dr. T. H. Regan and Mr. R. L. Young, of these laboratories, for determining and interpreting the nmr spectra.

Acid- and Base-Catalyzed Hydrogen–Deuterium Exchange between Deuterium Oxide and Simple Ketones

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Recent communications by Warkentin and Tee[1] and by Rappe[2] prompt us to report the results of some measurements using proton nmr on the rate of acid- ($KDSO_4$) and base-catalyzed (NaOAc) enolization in D_2O solutions of acetone, methyl ethyl ketone, diethyl ketone, and methoxyacetone. These studies were made in order to explore the feasibility of measuring separately the rate of enolization into the two branches of an unsymmetrical ketone. While the matter of rate of enolization has been the subject of much theoretical discussion,[3-9] experimental investigations have been hampered by the difficulties and uncertainties in the experimental methods employed.[6-14]

The results of our measurements are displayed in Tables I (catalysis by sodium acetate) and II (catalysis by potassium bisulfate). In view of the uncertainties in the rates (±20%), detailed analysis is not warranted, but several interesting points can be made from the qualitative behavior exhibited. (1) The results of Warkentin and Tee[1] are supported. (2) Alkyl or methoxyl substitution affects the rate of enolization in *both branches* quite strongly. (3) The methoxyl substituent accelerates base-catalyzed and retards acid-catalyzed enolization in both branches. (4) Diethyl ketone enolizes more slowly then acetone both in acid and base, in accord with earlier reports[15] that alkyl substitution *retards* acid-catalyzed enolization. (5) The variations in relative rates with temperature are sufficiently great that conclusions drawn on the basis of observations at one temperature may easily be reversed by observations of data at other temperatures.

We agree with Warkentin and Tee[1] that "...the polar effect of an alkyl group on rate of base-promoted enolization in aqueous medium has been overemphasized or even misinterpreted...," and suggest that this statement is equally true of acid-catalyzed enolization.

Experimental Section

Materials.—Reagent grade ketones were used, except for methoxyacetone, which was obtained from K & K Chemical Co. This material was purified by glpc using a 6 ft × 0.25 in. column packed with 20% Carbowax 20 M on Teflon 6, at 65–125° (2.9°/min) with a helium flow of 56 ml/min. The product collected was rechromatographed and had an indicated purity of 97–98%, as judged from peak areas.

Sample Preparation.—Stock solutions of sodium acetate and potassium bisulfate in D_2O were made up gravimetrically. The final solutions were made by pipetting together suitable quantities (9–9.75 ml) of stock acid or base and (0.25–1.00 ml) ketone. After thorough mixing, aliquots were sealed into 5-mm nmr sample cells, which had previously been steamed out and dried. The sample cells were immersed in a thermostat and removed periodically for measurement, at which time they were cooled in ice. Reaction time was accumulated only during the time the tube was in the thermostated bath. Control samples, kept at ice temperature, showed no measurable exchange in 24 hr, in which time the kinetic runs were usually complete.

Measurement.—Measurements were performed on a Varian A-60 spectrometer. Peak integrations were recorded, sweeping the field three times in each direction, for all visible peaks. Dur-

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