154°; λ_{max}^{EtOH} 220 mμ (ε 4510), 243 (s) (17,400), 248 (20,300), 286 (s) (5580), 294 (7140), 301 (s) (6200), 349 (8160); $\lambda_{max}^{CCl_4}$ 3.43, 3.58, 5.89, 6.20, 6.78, 6.90, 7.15, 7.41, 7.80, 7.95, 9.51, 11.62, 12.05 μ.

Anal. Calcd for $C_{13}H_{10}ClNO_2$: C, 63.0; H, 4.1; N, 5.7. Found: C, 63.3; H, 4.2; N, 5.6.

A New Synthesis of 2,2-Dimethyl-3-isopropylidenecyclopropyl Propionate

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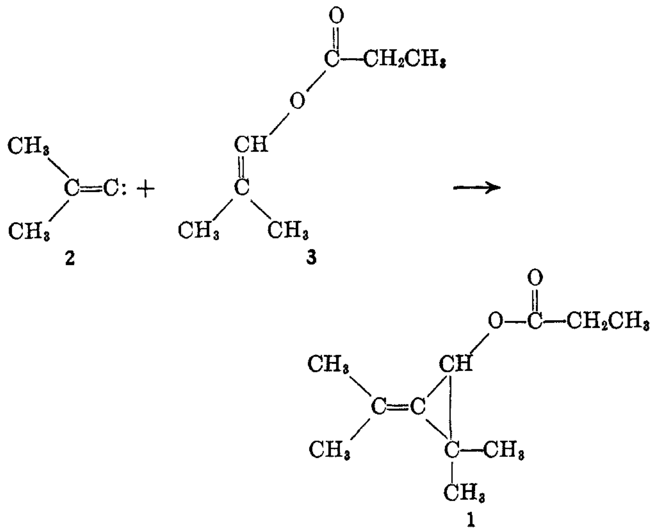
The title compound (**1**) was proposed as the sex attractant of the virgin female American cockroach, *Periplaneta americana* (L), by members of this laboratory.[1] Widespread interest in this compound was evidenced by reports of unsuccessful attempts to synthesize it,[2-4] but a successful synthesis by Day and Whiting[5] showed that **1** did not have biological activity. Our findings corroborate this.[6]

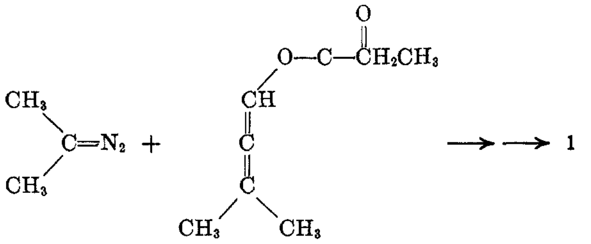
We wish to report a new synthesis of this compound. The general approach was to generate the vinylidenecarbene (**2**) or an entity behaving similarly which could than be made to react with the appropriate enol ester (**3**).



2-Methyl-1-propenyl propionate (**3**) was prepared from isobutyraldehyde, priopionic anhydride, and a catalytic amount of *p*-toluenesulfonic acid.

Tanabe and Walsh have reported that **2** could be generated from the reaction of either 1-chloro-2-methylpropene or 3-chloro-2-methylpropene with potassium *t*-butoxide in tetrahydrofuran.[7] When olefin **3** was used as the carbene acceptor, however, the reaction was unsuccessful.[8] The reaction of 1,1-dibromo-2-methylpropene with methyllithium in the presence of cyclohexene did form an isopropylidenecyclopropane.[9] As the latter method was obviously inapplicable when the olefin was an enol ester, a suitable modification was sought.

1,1-Dibromo-2-methylpropene reacted exothermically with magnesium in dry tetrahydrofuran in the presence of cyclohexene. Only a trace of the adduct, 7-isopropylidenenorcarane, was detected by gas chromatography. When enol ester **3** was used in place of cyclohexene, the desired product (**1**) was obtained in 18% yield. No other products were obtained in more than 1.5% yield and these were not studied further. It had identical glpc retention time and infrared and nmr spectra as the product obtained by Day and Whiting[5b,10] from different fragments, as shown, thus confirming the structure of **1**.



Thus far, attempts to extend the scope of this novel reaction have failed. No adducts were formed when ethyl vinyl ether, 1-cyclohexenyl acetate, or isopropenyl acetate were used. The reaction of 1,1-dibromo-2-methylpropene with enol ester **3** using zinc–copper couple[11] in tetrahydrofuran or 1,2-dimethoxyethane likewise failed.

The nature of the carbenoid species is unknown. When 1,1-dibromo-2-methylpropene was treated with magnesium in tetrahydrofuran and subsequently either **3** or Dry Ice was added neither **1** nor 2-bromo-3-methylcrotonic acid was formed. This would indicate that 1-bromo-2-methylpropenylmagnesium bromide, which is presumably the first intermediate, decomposes rapidly under the reaction conditions. However, this sheds no light on the actual species involved in the addition.

Experimental Section[12]

2-Methyl-1-propenyl Propionate (3).—A mixture of isobutyraldehyde (115 g, 1.6 moles), propionic anhydride (415 g, 3.2 moles), and *p*-toluenesulfonic acid monohydrate (3.8 g, 0.02 mole) was refluxed for 3 hr. After cooling, the mixture was poured into aqueous sodium carbonate, and additional sodium carbonate was added, keeping the temperature below 40° by the addition of ice, until carbon dioxide was no longer evolved. Two 250-ml portions of ether were used for extraction, after which the ether was washed with 50-ml portions of water and dried with magnesium sulfate. The solution was filtered and freed of solvent and the residue was distilled to give 100 g (55%) of 2-methyl-1-propenyl propionate, bp 145–147° (lit.[2] bp 140°).

Anal. Calcd for $C_7H_{12}O_2$: C, 65.60; H, 9.44. Found: C, 65.37; H, 9.62.

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[1] M. Jacobson, M. Beroza, and R. T. Yamamoto, *Science*, **139**, 48 (1963).

[2] J. Meinwald, J. W. Wheeler, A. A. Nimetz, and J. S. Liu, *J. Org. Chem.*, **30**, 1038 (1965).

[3] B. Singh, *ibid.*, **31**, 181 (1966).

[4] J. R. Chapman, *Tetrahedron Letters*, 113 (1966).

[5] (a) A. C. Day and M. C. Whiting, *Proc. Chem. Soc.*, 368 (1964); (b) A. C. Day and M. C. Whiting, *J. Chem. Soc.*, 464 (1966).

[6] M. Jacobson and M. Beroza, *Science*, **147**, 748 (1965).

[7] M. Tanabe and R. A. Walsh, *J. Am. Chem. Soc.*, **85**, 3522 (1963).

[8] Meinwald[2] has since described this reaction.

[9] H. D. Hartzler [*J. Am. Chem. Soc.*, **86**, 526 (1964)] has since described this reaction.

[10] We wish to thank Professor Day for carrying out this comparison.

[11] E. LeGoff, *J. Org. Chem.*, **29**, 2648 (1964).

[12] Boiling points are uncorrected. Analysis for compound **3** was performed by Galbraith Laboratories, Knoxville, Tenn., and for compound **1** by Chemco, Inc., Washington, D. C. Preparative chromatography was run on an Aerograph Autoprep with a 6.1 m × 9.5 mm column of SE-30 on Chromosorb W at 165°, retention time 10 min.

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.

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[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.

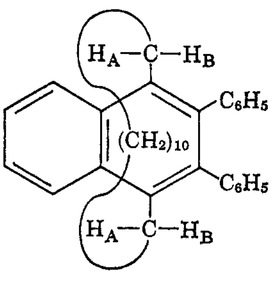

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Figure 1.

TABLE II
ULTRAVIOLET ABSORPTION DATA

Substance	λ_{max}, mμ	$\log \epsilon$	Substance	λ_{max}, mμ	$\log \epsilon$
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]	H_B[a]	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.

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

[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).