[Contribution from the Department of Chemistry, Loyola University of Chicago, and Chemical Laboratories of Northwestern University]

ULTRAVIOLET ABSORPTION SPECTRA OF ALICYCLIC COMPOUNDS. IV. 4-PHENYL-1,3-BUTADIENYL CYCLOPROPYL KETONE[1]

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The present work was undertaken to determine the effect of added conjugation in the series $C_6H_5(CH{=}CH)_nCO$-cyclopropyl, where n = 0, 1, and 2. Previous work on compounds where n = 0 and 1, showed the double bond character of the cyclopropyl group (1) to be effectively damped out. In the present work, it was of interest to see if the same effect is evident where n = 2. It was also of interest to compare the cyclopropyl compound with an analogous aliphatic compound, and to further observe the solvent effects noted in the previous series (1).

The butadienyl ketones were prepared by the method of Harries and Bromberger (2) using cinnamaldehyde in place of benzaldehyde. Because of the lesser reactivity of cinnamaldehyde, the yields from this reaction were very low. In every case, approximately 70% of unchanged starting materials were recovered[3] after a reaction period of approximately one month. Stronger bases were not employed to accelerate the reaction since it was felt that such reagents would very much favor self-condensation of the ketone.

In the present series, n = 2, the double-bonded character of the cyclopropyl group (I) is essentially damped out (Fig. 1), as compared to that of the *n*-propyl group (II) but it is observed that the cyclopropyl compound, in each series, has a noticeably higher extinction coefficient than the other members. The cyclopropyl compound in each series absorbed at longer wavelengths when compared to the other homologs, although the differences in positions of the main maxima in isooctane are never more than 1–2 mμ.

As n increases, there is a definite linear increase of the main maxima as well as a linear increase in the intensity of absorption, as can be seen in Fig. 2. Another interesting relationship was noted (Fig. 3) when the extinction coefficients of the main maxima were plotted against the positions of the main maxima. In this case also, a linearity was noted as n increases. Other such linearity relationships have been observed in other series when n is plotted against the *square* of λ_{max} (3).

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[1] Taken in part from the Ph.D. Thesis of R. R. Raube, submitted to the graduate faculty of Northwestern University.

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[3] The amount of recovered methyl ketone was in every case substantially less than that of the cinnamaldehyde. This could indicate that some of the ketone had undergone self-condensation. Since no effort was made to fractionate carefully the colorless forerun, it is impossible to say if any of this condensation product had in fact been formed.

The figures for the various series (n = 0, 1, and 2) are as follows:

POSITION OF MAXIMUM AND INTENSITY OF ABSORPTION

KETONE SERIES	CYCLOPROPYL		n-PROPYL	
	$\lambda_{max.}$ mμ	log ε	$\lambda_{max.}$ mμ	log ε
IN ALCOHOL				
C_6H_5—	244	4.15	242	4.09[a]
C_6H_5CH=CH—	291	4.38	288	4.34
C_6H_5CH=CH—CH=CH—	323	4.47	318	4.37
IN ISOOCTANE				
C_6H_5—	238	4.15	239	4.08[a]
C_6H_5CH=CH—	282	4.37	280	4.33
C_6H_5CH=CH—CH=CH—	314	4.51	313	4.42

[a] Methyl homolog.

It was also noticed, as in the previous series, that as the polarity of the solvent increased, the maxima shifted to longer wavelengths.

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EXPERIMENTAL[4]

4-Phenyl-1,3-butadienyl cyclopropyl ketone. A mixture of 34 g. (0.41 mole) of methyl cyclopropyl ketone, 93 g. (0.70 mole) of freshly distilled cinnamaldehyde, 1.5 ml. of 10% aqueous sodium hydroxide, and 495 ml. of water was shaken intermittently during a 12-day period. A solid slowly precipitated and was filtered. Concentration of the residue produced more crystals, the total yield being 23 g. The yield, based on recovered cinnamaldehyde and methyl ketone, was 38% of material melting at 76–95°. Recrystallization from ethanol produced pale yellow-green plates melting 101.5–102.1°.

Anal. Calc'd for $C_{14}H_{14}O$: C, 84.81; H, 7.12.
Found: C, 84.77; H, 6.85.

2,4-Dinitrophenylhydrazone, m.p. 211–212°.

Anal. Calc'd for $C_{20}H_{18}N_4O_4$: N, 14.8. Found: N, 14.8.

p-Nitrophenylhydrazone, m.p. 148°.

Anal. Calc'd for $C_{20}H_{19}N_3O_2$: N, 12.6. Found: N, 12.4.

Hexabromo derivative: m.p.147°.

Anal. Calc'd for $C_{14}H_{14}Br_6O$: C, 24.80; H, 2.08.
Found: C, 24.55; H, 2.07.

The *tetrabromo* derivative was a viscous oil which resisted all attempts at crystallization and purification.

4-Phenyl-1,3-butadienyl n-propyl ketone. A mixture of 26 g. (0.30 mole) of methyl *n*-propyl ketone, 56 g. (0.42 mole) of cinnamaldehyde, and proportionate amounts of the other reagents, produced in a period of 34 days, 76 g. of a dark colored residue. Fractionation gave 26 g. of yellow-green liquid boiling at 150–158° at 0.9 mm. Based on recovered starting

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[4] Microanalyses by Misses Sorensen and Brauer.

materials this represents a 60% yield. The material remained liquid after 24 hours at −5°. Purified material boiled at 128–132° at 0.70 mm., n_D^{25} 1.6258.

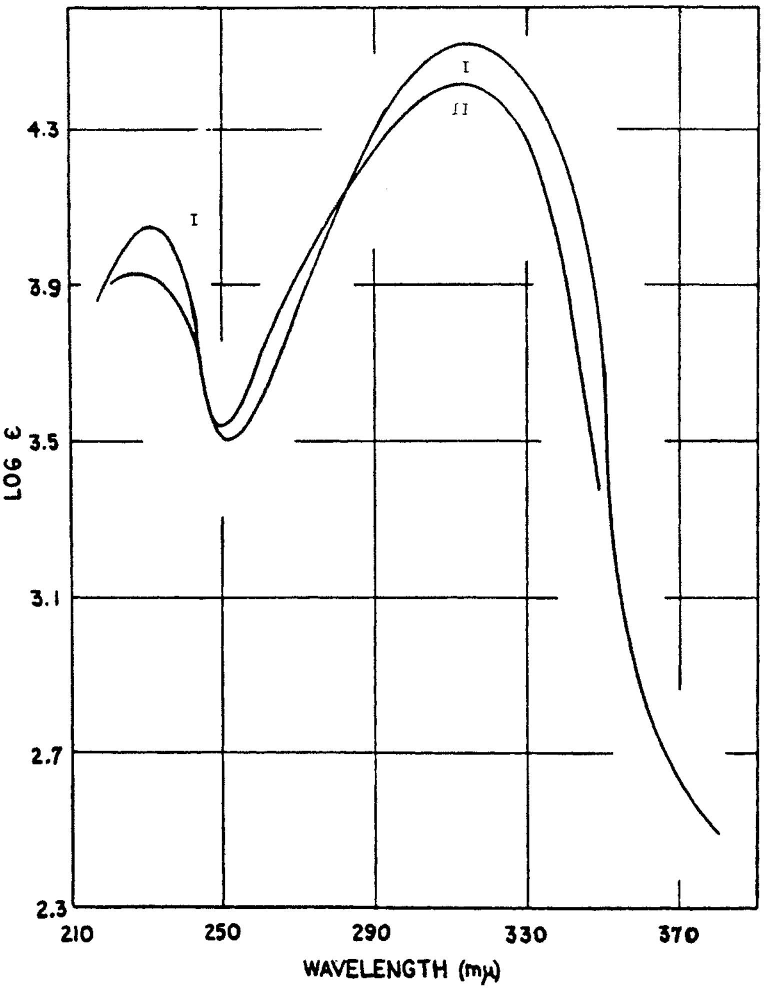

FIG. 1. ULTRAVIOLET ABSORPTION SPECTRA OF 4-PHENYL-1,3-BUTADIENYL CYCLOPROPYL (I) AND *n*-PROPYL (II) KETONES IN ISOOCTANE.

2,4-Dinitrophenylhydrazone, m.p. 194°.

Anal. Calc'd for $C_{20}H_{20}N_4O_4$: N, 14.8. Found: N, 15.0.

p-Nitrophenylhydrazone, m.p. 141°.

Anal. Calc'd for $C_{20}H_{21}N_3O_2$: N, 12.5. Found: N, 12.4.

The *tetrabromo* derivative was a viscous oil which resisted all efforts at crystallization and purification.

Other ketones. Attempts were made to prepare the cyclobutyl and cyclohexyl members of this series, however, the extreme unreactivity of cinnamaldehyde and the apparent sensitivity of the products combined to make their preparation impractical.

Methyl cyclohexyl ketone (11 g., 0.09 mole), when treated with 24 g. (0.20 mole) of cinnamaldehyde and suitable quantities of the other reagents, led to the formation of 0.70 g. of

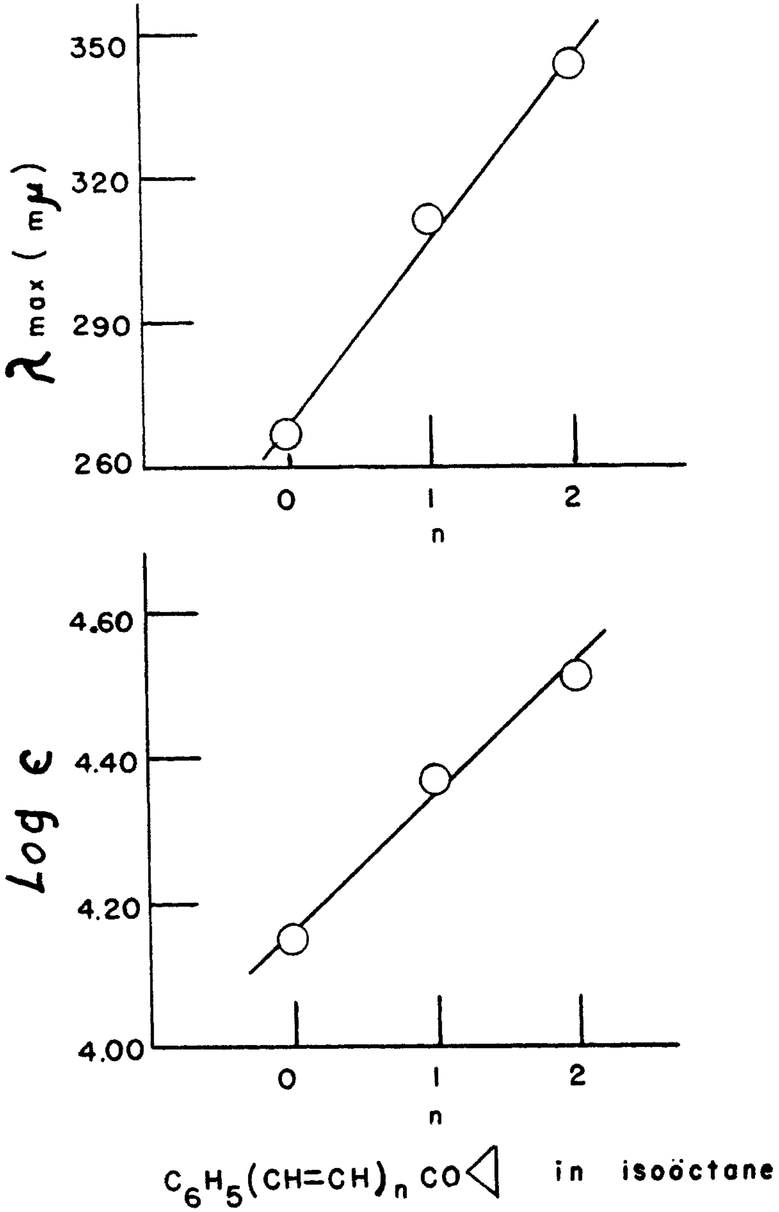

FIG. 2. PLOTS OF n *vs.* Log ε AND n *vs.* $\lambda_{\max}$

material boiling at 149–149.5° at 1.5 mm., n_D^{25} 1.6342. The spectrum of this compound was quite similar to that of cinnamaldehyde and the 2,4-dinitrophenylhydrazone gave analytical figures consistent with this latter compound.

Methyl cyclobutyl ketone (27 g., 0.28 mole) and 53 g. (0.40 mole) of cinnamaldehyde gave 17 g. of material boiling 125–158° at 1.4 mm. Refractionation of this material failed to produce any product boiling higher than 127° at 1.2 mm. Apparently the heat necessary to distill the compound polymerized any butadienyl ketone present since the residue was a clear red glass-like material.

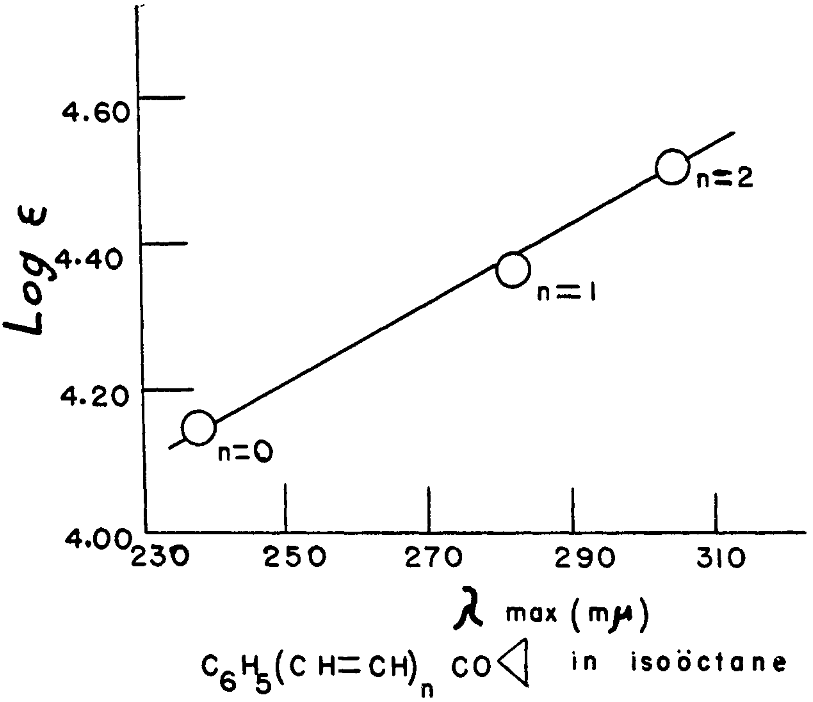

FIG. 3. PLOT OF EXTINCTION COEFFICIENTS OF THE MAIN MAXIMA *vs.* λ_{max} IN mμ

Spectra. All spectra were determined in a Beckman Model DU Spectrophotometer. Both 95% ethanol and isooctane were spectra grade. Using the butadienyl ketones a 2×10^{-5} molar concentration was necessary to give a convenient reading on the spectrophotometer.

POSITION AND INTENSITY OF ABSORPTION OF SOME 4-PHENYL-1,3-BUTADIENYL KETONES

	λ_{max}, mμ	LOG ε	λ_{max}, mμ	LOG ε
		ALCOHOL		
Cyclopropyl	235	4.09	323	4.47
n-Propyl	229	3.99	322	4.26
		ISOOCTANE		
Cyclopropyl	230	4.03	314	4.51
n-Propyl	224	3.93	313	4.42

SUMMARY

4-Phenyl-1,3-butadienyl cyclopropyl and *n*-propyl ketones and derivatives were prepared. Their ultraviolet absorption spectra show that the double-bonded character of the cyclopropyl group is effectively damped out. As the polarity of the solvent is increased the main maxima shift to longer wavelengths. In the series $C_6H_5(CH{=}CH)_nCO$-cyclopropyl, as n increases, there is a definite shift of the main maxima as well as an increase in the intensity of absorption of the maxima.

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REFERENCES

(1) Mariella and Raube, *J. Am. Chem. Soc.*, **74**, 521 (1952).

(2) Harries and Bromberger, *Ber.*, **35**, 3088 (1902).

(3) See Ferguson, *Chem. Revs.*, **43**, 406–412 (1948) for an interesting discussion of this effect.