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Syntheses and Spectra of 1-Acetyl-, 1-Benzoyl-, 1-Carbethoxy- and 1-Cyano-1 and/or 2-Methylcyclopropanes. Conjugative and Steric Effects[1]

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The preparation of twelve new cyclopropanes and certain new intermediates is described. The C=O and C≡N stretching frequencies and ultraviolet absorption maxima of a number of cyclopropanes are given. When a 2-methyl group is introduced into an ester or ketone there is a small decrease in the C=O stretching frequency and a bathochromic shift and/or increase in the ultraviolet absorption maximum. In 1-acetyl-2-methylcyclopropane these shifts (-5 cm.$^{-1}$, 3.5 mμ, ϵ/ϵ° 1.47) are believed to indicate electronic interaction between the two substituents through the central cyclopropane ring. The increase in the C=O stretching frequency ($+7$ cm.$^{-1}$) and decrease in ultraviolet absorption intensity (ϵ/ϵ° 0.73) of 1-benzoyl-1-methylcyclopropane indicate some steric hindrance. The additional $+16$ cm.$^{-1}$ shift in the C=O stretching frequency, 9 mμ bathochromic shift and decrease in intensity (ϵ/ϵ° 0.8) of 1-benzoyl-1,2,2-trimethylcyclopropane indicate an indirect steric effect of the 2-methyl groups of a "buttressing" nature.

This study was initiated in 1951 with the objective of determining the ability of the cyclopropane ring to transmit conjugative effects to methyl groups. Since then Smith and Rogier[2] and Eastman[3a] and his students[3b,c] have concluded from ultraviolet studies that the cyclopropane ring cannot transmit conjugative effects.[4] Recently Trachtenberg and Odian have reported[5] that the ρ-values for a series of substituted *trans*-2-phenylcyclopropanecarboxylic acids are close to those of their saturated analogs and conclude that the cyclopropane ring does not transmit conjugative effects in the ground state.

On the other hand, the 1,6-addition of diethyl malonate anion to diethyl vinylcyclopropane-1,1-dicarboxylate[6a] and the ultraviolet spectrum of ethyl 1-acetyl-2-vinylcyclopropane-1-carboxylate[6b] have been considered evidence for electronic interaction between the cyclopropane ring, the double bond and the respective carbonyl groups.[7] More recently Mohrbacher and Cromwell[8] have studied the ultraviolet and infrared spectra of *cis*- and *trans*-1-(4'-phenylbenzoyl)-2-phenylcyclopropanes, the corresponding carboxylic acids and their *p*-nitrobenzyl esters. The occurrence of carbonyl-associated absorption maxima at longer wave lengths and/or higher intensities in their ultraviolet and lower frequencies in their infrared spectra are considered evidence for the transmission of conjugative effects. Thus the ability of the cyclopropane ring to *transmit* conjugative effects is still controversial.

Syntheses.—Twelve new cyclopropanes with methyl groups *alpha* and/or *beta* to an electron-withdrawing group were prepared for this work. The majority were synthesized most conveniently by conventional methods in which a γ-lactone is converted to a γ-chloro acid chloride,[9] ester[10] or ketone.[11] The ring was then closed by treatment with base and the desired acid, acid chloride, ketone, amide and nitrile obtained by conventional reactions. For example, α-methyl-γ-butyrolactone was transformed, by treatment with hydrochloric acid and then thionyl chloride, in 68% yield to the previously unknown α-methyl-γ-chlorobutyryl chloride. Subsequent Friedel–Crafts reaction with benzene yielded crude α-methyl-γ-chlorobutyrophenone. The chloroketone was cyclized in 58% yield to 1-benzoyl-1-methylcyclopropane (XXX) with sodium amide in benzene. Conversion of the chloroketone to the ester followed by cyclization yielded ethyl 2-methylcyclopropanecarboxylate (XXIV).

α,γ-Dimethyl-γ-valerolactone[12] was converted to ethyl γ-chloro-α-methylisocaproate in 86% yield by the method of Cason and co-workers.[13] However, this ester repeatedly gave low chlorine analyses and its infrared spectrum indicated contamination by unreacted starting lactone from which it could not be freed by careful fractionation. The lactone is removed in the ensuing cyclization and ester XXV and subsequent compounds are lactone-free. Ethyl 2-methylcyclopropanecarboxylate (XXI) was obtained from γ-valerolactone in the same manner and subsequently converted to 1-benzoyl-2-methylcyclopropane.

α-Acetyl-γ-valerolactone[14] gave previously un-

(1) Taken from the Ph.D. theses of Popkin Shenian (1955) and Arthur A. Santilli (1958). This research was supported in part by the Office of Ordnance Research, U. S. Army, under contracts No. DA-19-059-ORD-1317 and DA-19-059-ORD-2196.

(2) L. I. Smith and E. R. Rogier, THIS JOURNAL, **73**, 3840 (1951).

(3) (a) R. H. Eastman, *ibid.*, **76**, 4115 (1954); (b) R. H. Eastman and J. C. Selover, *ibid.*, **76**, 4118 (1954); and (c) R. H. Eastman and S. K. Freeman, *ibid.*, **77**, 6642 (1955).

(4) The necessary *cis* fusion of the cyclopropane ring in certain compounds studied by Eastman[3] may be responsible in part for this conclusion. It has been pointed out [N. H. Cromwell and M. A. Graff, *J. Org. Chem.*, **17**, 414 (1952)] that unsaturated groups on both carbon atoms of the cyclopropane ring must be in the *trans* position if maximum overlap with the *bent* bond orbitals of the ring is to occur. It should be noted that the stereochemistry of cyclopropanes XXI, XXVII, XXIX and XXXIII employed in the present study is unknown.

(5) E. N. Trachtenberg and G. Odian, *Chemistry & Industry*, 490 (1958).

(6) (a) R. W. Kierstead, R. P. Linstead and B. C. L. Weedon, *J. Chem. Soc.*, 3616 (1952); (b) 1799 (1953).

(7) However, it is stated [R. W. Kierstead, R. P. Linstead and B. C. L. Weedon, *ibid.*, 3610 (1952)] that the exaltation of molecular refraction is due almost exclusively to interaction of the cyclopropane ring with the vinyl group, and Eastman and Freeman[3c] consider the difference in the spectrum of ethyl 1-acetyl-2-vinylcyclopropane-1-carboxylate and that expected of an unsaturated analog to support their contention that the ring cannot transmit conjugative effects.

(8) R. J. Mohrbacher and N. H. Cromwell, THIS JOURNAL, **79**, 401 (1957).

(9) W. J. Close, *ibid.*, **79**, 145 (1957).

(10) P. A. Levene and T. Mori, *J. Biol. Chem.*, **78**, 1 (1928).

(11) G. W. Cannon, R. E. Ellis and J. R. Leal, *Org. Syntheses*, **31**, 74 (1951).

(12) J. W. Nemec, Abstracts 124th Meeting of the American Chemical Society, Chicago, Ill., September, 1953, p. 56-O. The authors are indebted to Dr. Nemec, Rohm and Haas Co., for providing the experimental procedure for this method prior to publication and permission to include it in this paper.

(13) J. Cason, C. E. Adams, L. L. Bennett, Jr., and U. D. Register, THIS JOURNAL, **66**, 1764 (1944).

(14) R. M. Adams and C. A. VanderWerf, *ibid.*, **72**, 4368 (1950).

TABLE I

CARBONYL AND NITRILE STRETCHING FREQUENCIES AND ULTRAVIOLET ABSORPTION MAXIMA OF SATURATED AND UNSATURATED ANALOGS[a]

No.	Compound	ν_{max}, cm.$^{-1}$	$\Delta\nu_{max}$, cm.$^{-1}$	λ_{max}, mμ	$\Delta\lambda_{max}$, mμ	ϵ_{max}	ϵ/ϵ^{o}
I	$CH_3CH_2COCH_3$	1720[b]		272[c]		18.2[c]	
II	$CH_3CH_2CH_2COCH_3$	1720[b]	0	274[c]	2	19.7[c]	1.08
III	$CH_3CH_2COOC_2H_5$	1738					
IV	$CH_3CH_2CH_2COOC_2H_5$	1738	0				
V	$CH_3COC_6H_5$	1691					
VI	$CH_3CH_2COC_6H_5$			236.9[d]		11,450[d]	
VII	$CH_3CH_2CH_2COC_6H_5$			237.5[d]	0.6	11,500	1.005
VIII	CH_2=$CHCOOC_2H_5$	1728		208		3,000	
IX	CH_3CH=$CHCOOC_2H_5$	1722	− 6	210	2	12,600	4.2
X	CH_2=$C(CH_3)COOC_2H_5$			208	0	8,575	2.86
XI	CH_2=$CHCOCH_3$	1684[e]		211		6,560	
XII	CH_3CH=$CHCOCH_3$	1676	− 8	221	10	11,500	1.75
XIII	CH_2=$CHCOC_6H_5$			248[f]		11,000[f]	
XIV	CH_3CH=$CHCOC_6H_5$			256	8	17,400[g]	1.58
XV	CH_2=$CHCN$	2230		214–217[h]		50[h]	
XVI	CH_2=$C(CH_3)CN$	2230	0	215		677	13.5
XVII	CH_3CH=$CHCN$ (*trans*)[i]	2223	− 7				
XVIII	CH_3CH=$CHCN$ (*cis*)[i]	2221	− 9				
XIX	$(CH_3)_2C$=$C(CH_3)CN$	2213	−17	216.5	1.5	12,200	18

[a] Infrared spectra determined on carbon tetrachloride and ultraviolet spectra determined on 95% ethanol solutions unless specified otherwise. [b] Ref. 10. [c] Methanol solutions [R. A. Day, Jr., A. E. Robinson, Jr., J. M. Bellis and S. B. Till, THIS JOURNAL, 72, 1379 (1950)]. [d] *n*-Heptane solutions [G. D. Hedden and W. G. Brown, *ibid.*, 75, 3744 (1953)]. [e] Gift of American Cyanamid Co. [f] K. Bowden, E. A. Braude and E. R. H. Jones, *J. Chem. Soc.*, 948 (1946). [g] Ref. 27. [h] Ref. 28. [i] R. E. Kitson and N. E. Griffith, *Anal. Chem.*, 24, 334 (1952). Spectra determined on the pure liquids; private communication, Dr. R. C. Voter.

known 5-chlorohexanone-2 in 25.6% yield on treatment with concentrated hydrochloric acid. Cyclization to 1-acetyl-2-methylcyclopropane (X-XVII) was accomplished in 44% yield with sodium amide.

Infrared Spectra.—The C=O and C≡N stretching frequencies of a number of saturated and unsaturated esters, ketones and nitriles have been redetermined carefully in order to have more precise measurements of their differences resulting from substitution of methyl groups. These values and certain values taken from the literature are collected in Table I.

The C=O stretching frequencies for sixteen aliphatic ketones have been determined within ±1 cm.$^{-1}$.[15] These values show that for simple aliphatic ketones (I and II, Table I) the C=O stretching frequency is 1720 cm.$^{-1}$ and that the shift in the C=O frequency accompanying the introduction of one additional methyl group does not exceed 1 cm.$^{-1}$. The same situation appears to pertain to simple saturated esters (see compounds III and IV). A comparison of the C=O and C≡N frequencies of compounds VIII-XIX shows that the substitution of one methyl group in the β-position of an α,β-unsaturated ester, ketone or nitrile results in shifts of −6, −8 and −7 to −9 cm.$^{-1}$, respectively. It should be noted that the C≡N stretching frequency of methacrylonitrile (XVI) is the same as acrylonitrile (XV), possibly because the methyl group is not at the end of the linear conjugated system.

The C=O and C≡N stretching frequencies of the cyclopropanes are listed in Table II. The precision of these determinations (see Experimental) is better than ±1 cm.$^{-1}$ for each pair of compounds to be compared. A study of the C=O stretching frequencies of compounds XX-XXIX reveals that −2 to −5 cm.$^{-1}$ shifts occur each time a contiguous methyl group is introduced into the cyclopropane ring.[16] The largest shift (−5 cm.$^{-1}$) occurs with 1-acetyl-2-methylcyclopropane (X-XVII). It is not unreasonable that a larger shift is observed for XXVII than for 1-benzoyl-2-methylcyclopropane (XXIX) because in the latter compound the carbonyl group is cross-conjugated with the phenyl group.

A comparison of compounds XXVIII and XXX shows that a +7 cm.$^{-1}$ shift accompanies the insertion of a methyl group at the 1-position of benzoylcyclopropane. This is indicative of a steric factor forcing the cyclopropyl and/or phenyl rings out of coplanarity with the carbonyl group with a resultant decrease in electronic interaction. Previously Jones, Forbes and Mueller[17] have observed a +13 cm.$^{-1}$ shift in the C=O stretching frequency of 2,3,5,6-tetramethylacetophenone relative to acetophenone, and Fuson and House[18] report two carbonyl bands at 1675 and 1700 cm.$^{-1}$ for 1,3-diacetyl-2,4-dimethylbenzene, the higher band presumably being assigned to the more hindered acetyl group. Braude and Timmons[19] report a progressive increase in the C=O stretching

(15) N. Fuson, M. Josien and E. M. Shelton, THIS JOURNAL, 76, 2526 (1954).

(16) These shifts are considerably less than the −11 cm.$^{-1}$ shift resulting from the interaction of a C=O group with a *trans*-methyl group through the ethylenimine ring [N. H. Cromwell and R. J. Mohrbacher, *ibid.*, 75, 6252 (1953)]. This may be rationalized in that the nitrogen atom is better able to support the positive charge resulting from electronic interactions; see Cromwell and Graff, footnote 4.

(17) R. N. Jones, W. F. Forbes and W. A. Mueller, *Can. J. Chem.*, 35, 504 (1957).

(18) R. C. Fuson and H. O. House, *J. Org. Chem.*, 18, 496 (1954).

(19) E. A. Braude and C. J. Timmons, *J. Chem. Soc.*, 3766 (1955).

TABLE II

CARBONYL AND NITRILE STRETCHING FREQUENCIES AND ULTRAVIOLET ABSORPTION MAXIMA OF CYCLOPROPANES[a]

No.	Compound	ν_{max}, cm.$^{-1}$[b]	$\Delta\nu_{max}$, cm.$^{-1}$	λ_{max}, mμ	$\Delta\lambda_{max}$, mμ	ϵ_{max}	$\epsilon/\epsilon^{\circ}$
XX	$C_3H_5COOC_2H_5$	1730 (1030)		208		75.6	
XXI	2-$CH_3C_3H_4COOC_2H_5$[c]	1728 (1037)	− 2	208	0	128	1.7
XXII	$C_3H_4(COOC_2H_5)_2$	1731 (1027)		208		198	
XXIII	2-$CH_3C_3H_3(COOC_2H_5)_2$	1728 (1026)	− 3	208	0	292	1.47
XXIV	1-$CH_3C_3H_4COOC_2H_5$	1725 (1031)		215.5	7.5	604	8
XXV	1,2,2-$(CH_3)_3C_3H_2COOC_2H_5$	1722 (1026)	− 3	205	−10.5(?)	935	1.55
XXVI	$C_3H_5COCH_3$	1704 (1026)		206		1,310	
				270[d]		21.3	
XXVII	2-$CH_3C_3H_4COCH_3$[c]	1699 (1037 or 1020)	− 5	209.5	3.5	1,930	1.47
				243[d]	−27	153	7.2
XXVIII	$C_3H_5COC_6H_5$	1673 (1021)		243		13,520	
XXIX	2-$CH_3C_3H_4COC_6H_5$[c]	1671 (1026)	− 2	243	0	14,100	1.04
XXX	1-$CH_3C_3H_4COC_6H_5$	1680 (1022)	+ 7	240.5	− 2.5	9,900	0.73
XXXI	1,2,2-$(CH_3)_3C_3H_2COC_6H_5$	1696 (1012)	+16	249.5	9	7,900	.8
XXXII	C_3H_5CN	2245 (1046)		208		6.6	
XXXIII	2-$CH_3C_3H_4CN$[c]	2245 (1046)	0	208	0	7.4	
XXXIV	1,2,2-$(CH_3)_3C_3H_2CN$	2234 (1038)	−11	208.5	0.5	12.4	

[a] All infrared spectra determined on carbon tetrachloride and ultraviolet spectra on 95% ethanol solutions. [b] The values given for the C=O or C≡N stretching frequencies are the average of ten determinations; see Experimental. The value given in parentheses is assigned to the cyclopropane ring; see Discussion. [c] Stereochemistry unknown. [d] R-band absorption.

frequencies of 1-acetylcyclohexene, 1-acetyl-2-methylcyclohexene, *t*-butyl 2-methylcyclohexenyl ketone and 1-acetyl-2,6,6-trimethylcyclohexene from 1665 to 1693 cm.$^{-1}$ as steric hindrance increases.

In the case of 1-benzoyl-1,2,2-trimethylcyclopropane (XXXI) comparison with XXX, XXVIII and V shows a +16 cm.$^{-1}$ shift with the introduction of the β-methyl groups and +23 and +5 cm.$^{-1}$ shifts from the C=O frequencies of benzoylcyclopropane (XXVIII) and acetophenone (V), respectively. These shifts clearly indicate an increase in the double bond character of the carbonyl group of XXXI resulting from further steric inhibition of conjugation. This effect may be due to the 2-methyl groups exerting an indirect steric effect by "buttressing" the substituents in the 1-positions.[20] Although integrated absorption intensities were not determined, it was readily apparent from visual observation of the spectrum of XXXI that the intensity of the C=O stretching band was considerably weaker than those of any of the other compounds studied. In a qualitative way C=O band intensities are related to the resonance energy of conjugation.[21] Thus the low intensity of the C=O band further supports the belief that large steric factors are operative in XXXI. Since it is not known to what extent electronic interaction in the ground state between the C=O and the phenyl groups is inhibited, it is impossible to reach any conclusions regarding transmission of conjugative effects in XXXI.[22]

The C≡N stretching frequencies of the nitriles XXXII and XXXIII provide no evidence for transmission of conjugative effects in the ground state in XXXIII. There is, however, the experimentally significant −11 cm.$^{-1}$ shift in the C≡N frequency of 1-cyano-1,2,2-trimethylcyclopropane (XXXIV). Unfortunately, 1-cyano-1-methylcyclopropane was not available for comparison and the significance of this shift cannot be assessed at this time.

Finally, attention is called to the band assigned to the cyclopropane ring. At various times bands at 1000–1020, 866 and 3012 and 3096 cm.$^{-1}$ have been assigned to the cyclopropane ring.[23] However, the 866 cm.$^{-1}$ band does not occur consistently[24] and it has been concluded[23] that neither the 1000–1020 nor the 3012 and 3096 cm.$^{-1}$ regions afford a clear indication of the presence or absence of the cyclopropyl group. The absorption bands assigned to the cyclopropane ring in the compounds employed in this study occur at 1012–1046 cm.$^{-1}$.[25] For the majority the band is at frequencies higher than 1020 cm.$^{-1}$, the upper limit of the range cited by Bellamy,[26] but within the range observed by Slabey.[27] The spectra of thirty-four compounds obtained by Slabey[27] show that the presence of two substituents or an acyl group on a cyclopropane ring raises the characteristic frequency. Similarly the spectra of 1-cyano-2,2-dialkylcyclopropanes and related compounds have absorption bands at 1024–1037 cm.$^{-1}$.[28] Thus there is qualitative evidence that for polysubstituted and negatively substituted cyclopro-

(20) See W. F. Forbes and W. A. Mueller, THIS JOURNAL, **79**, 6495 (1957), for evidence of a "buttressing effect" in the electronic spectra of *m*-substituted benzene derivatives.

(21) Reference 17 and references cited there.

(22) However, it might be noted that if all C=O phenyl interaction were inhibited, the −8 cm.$^{-1}$ shift in the C=O frequency of XXXI from that of acetylcyclopropane could be interpreted as indicating some transmission of conjugative effects by the cyclopropane ring to the β-methyl groups.

(23) C. F. H. Allen, T. J. Davis, W. J. Humphlett and D. W Stewart, *J. Org. Chem.*, **22**, 1291 (1957), and references cited there.

(24) J. M. Derfer, E. E. Pickett and C. E. Boord, THIS JOURNAL, **71**, 2482 (1949).

(25) Since the completion of this work W. H. Washburn and M. J. Mahoney, *ibid.*, **80**, 504 (1958), have assigned bands at 6135–6061 and 4405–4505 cm.$^{-1}$ to the cyclopropane ring. Unfortunately, the spectra obtained in the present study do not cover the near-infrared region.

(26) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1954, pp. 27–28.

(27) V. A. Slabey, THIS JOURNAL, **76**, 3604 (1954).

(28) E. R. Nelson, N. Maienthal, L. A. Lane and A. A. Benderly, *ibid.*, **79**, 3467 (1957).

panes this band is shifted to frequencies higher than the 1000–1020 cm.$^{-1}$ region originally cited.[29]

Ultraviolet Spectra.—The ultraviolet absorption maxima of the cyclopropanes studied are given in Table II and those for a number of saturated and unsaturated analogs along with previously reported values are listed in Table I. An examination of the saturated ketones and esters in Table I and other examples given by Gillam and Stern[30] show that the addition of one methyl group to a saturated ester or ketone usually results in a bathochromic shift of 2 mμ or less and a negligible change in the extinction coefficient. The remainder of the values in Table I show that bathochromic shifts of 10 mμ for α,β-unsaturated ketones (as expected),[31] 2 mμ for α,β-unsaturated esters and *ca.* 1 mμ for α,β-unsaturated nitriles result when one β-methyl group is added. Even in the cases of α,β-unsaturated esters and nitriles, where the bathochromic shift is at best small, a large increase in the extinction coefficient accompanies the introduction of a β-methyl group. It appears that electronic interactions of cyano and carbethoxyl groups through the cyclopropane ring would not be manifested by appreciable bathochromic shifts but could be expected to result in increased absorption intensities.

The values listed in Table II show that in the case of cyclopropane esters, as expected, no bathochromic shift has resulted from the introduction of a 2-methyl group. A small but experimentally significant increase in the extinction coefficient does occur, although it is of a different order of magnitude than that observed in the case of unsaturated esters.

Mariella and Raube[32] report that the spectra of acetophenone and a number of cycloalkyl phenyl ketones are essentially the same. This is ascribed to the fact that interaction of the phenyl and carbonyl groups is so great that the crossconjugation effects of various cycloalkyl groups are "damped out." If this is so, any further electronic interaction with the methyl group could not be expected to manifest itself in the spectrum of 1-benzoyl-2-methylcyclopropane (XXIX). Such is the case although a small increase in intensity is observed. The nitriles XXXIII and XXXIV exhibit neither bathochromic shifts nor increases in absorption intensities.

The maximum for XXIV was rechecked a number of times, but appears anomalous since it occurs at longer wave lengths even than the maxima of α,β-unsaturated esters. Consequently the effect of the 2-methyl groups in XXV is uncertain and comment concerning the significance of the apparent hysochromic shift is impossible.

A comparison of the maxima of XXVI and XXVII shows a 3.5 mμ bathochromic shift and approximately 50% increase in absorption intensity. Although this shift is only one-third that expected for the corresponding α,β-unsaturated ketone, both it and the intensity increase are significantly greater than that observed with the addition of a methyl group to an alkyl methyl ketone. This we consider evidence for a small but real interaction between the methyl group and the carbonyl group through the central cyclopropane ring. The large hypsochromic shift in the R-band maximum of XXVII may seem anomalous, but a similar though smaller hypsochromic shift in the R-band maximum of acetylcyclopropane has been observed by Rogers,[33] and verified by Mariella and Raube[32] and the present study.

1-Benzoyl-1-methylcyclopropane (XXX) shows a small hypsochromic shift of 2.5 mμ and a reduction in the absorption intensity relative to benzoylcyclopropane (XXVIII). This decrease in absorption intensity without an appreciable change in maximal wave length is indicative of a weak steric hindrance (designated by Braude and Sondheimer[34] as a Type I steric effect) resulting in electronic transitions between a non-planar ground state and near-planar excited electronic state.[35] For example, acetophenone, *o*-methylacetophenone and *t*-butyl phenyl ketone have the same absorption maximum (242 mμ), but their extinction coefficients are 13,200,[34] 8,700[34] and 9,100,[19] respectively.

A comparison of the values for 1-benzoyl-1-methylcyclopropane (XXX) and 1-benzoyl-1,2,2-trimethylcyclopropane (XXXI) shows a 9 mμ bathochromic shift and a further decrease in intensity. This further decrease in intensity indicates an additional increase in steric hindrance apparently because of the previously mentioned "buttressing effect" of the 2-methyl groups. In fact the situation is similar to that found in 1-acetyl-2-methylcyclohexene (λ_{max} 245 mμ, ε 6,500)[19] whose extinction coefficient is halved relative to 1-acetylcyclohexene (λ_{max} 232 mμ, ε 12,500)[19] but whose absorption maximum shows the expected bathochromic shift. Similar effects are observed in the case of 2,6-dimethylacetophenone (λ_{max} 251 mμ, ε 5,600) relative to 2-methylacetophenone (λ_{max} 242 mμ, ε 8,700).[34] The 9 mμ bathochromic shift tentatively may be accounted for by assuming that the increased steric factors affect the conjugation between the phenyl and carbonyl groups so that absorption effects due to cross-conjugation with the cyclopropyl group are not "damped out." Since it is as large as the bathochromic effect of the α,β-double bond in vinyl phenyl ketone and the methyl group in propenyl phenyl ketone, it further suggests that there is in fact some electronic interaction through the ring with the methyl group.

Experimental[36]

α,γ-Dimethyl-γ-valerolactone.—The product was prepared essentially according to the unpublished procedure of Nemec.[12] A mixture of 687 g. (3.64 moles) of methyl α-

(29) The authors do not dispute the point made by Allen, *et al.*,[31] that this band is of questionable value for determining either the absence or presence of a cyclopropane ring because "between one-third and one-half of all organic compounds might be expected to have one or more bands in this region . . ."

(30) A. E. Gillam and E. S. Stern, "Electron Absorption Spectroscopy," Edward Arnold, Ltd., London, Eng., 1954, pp. 50–51.

(31) R. B. Woodward, THIS JOURNAL, **64**, 76 (1942).

(32) R. P. Mariella and R. R. Raube, *ibid.*, **74**, 521 (1952).

(33) M. T. Rogers, *ibid.*, **69**, 2544 (1947).

(34) E. A. Braude and F. Sondheimer, *J. Chem. Soc.*, 3754 (1955).

(35) For an alternative hypothesis to account for this type of steric effect see W. F. Forbes and W. A. Mueller, *Can. J. Chem.*, **34**, 1347 (1956).

(36) Previously described compounds omitted from this section were prepared by reliable methods reported in the literature. Their physical constants were in close agreement with literature values.

methyl-γ-nitroisocaproate[37] and 1020 ml. of concentrated hydrochloric acid was refluxed for 75 hours. After cooling the mixture in an ice-bath, a yellow crystalline material separated weighing 213 g., m.p. 49–50°. The mother liquor was refluxed for another 24 hours. On cooling in ice an additional 104 g. (total weight 317 g. (68%)) of the ester was obtained.

Ethyl α,γ-Dimethyl-γ-chlorovalerate.—The following procedure is based on the method of Cason and co-workers.[13] To a solution of 40 g. (0.31 mole) of α,γ-dimethyl-γ-valerolactone in 60 ml. of dry benzene there was added slowly 110.6 g. (0.93 mole) of thionyl chloride and the mixture was refluxed with stirring for 4 hours. A saturated solution (at 0°) of dry hydrogen chloride in 200 ml. of commercial absolute ethanol was added slowly with ice-bath cooling to the above reaction mixture. The mixture was allowed to stand overnight at room temperature. Hydrogen chloride and ethanol were removed *in vacuo*. Fractionation of the residue gave 60 g. (86%) of colorless product, b.p. 69° (5.5 mm.), $n^{25}D$ 1.4292. Analyses of this compound were always satisfactory. Its infrared spectrum indicated that it contained unreacted starting lactone which was not removed by careful fractionation in a Todd column.

Anal. Calcd. for $C_9H_{17}O_2Cl$: C, 56.10; H, 8.89; Cl, 18.40. Found: C, 58.24; H, 9.45; Cl, 13.98.

Ethyl 1,2,2-Trimethylcyclopropane-1-carboxylate (XXV).—To a stirred suspension of 30 g. (0.77 mole) of powdered sodium amide in 350 ml. of dry ether there was added dropwise 115 g. (0.6 mole) of ethyl α,γ-dimethyl-γ-chlorovalerate over a period of 2 hours. The mixture was stirred for 4 days. The reaction mixture became quite pasty and it frequently was necessary to add additional dry ether. A total of 100 ml. of water was added dropwise with caution and the two layers were separated. The aqueous layer was extracted with 50 ml. of ether. The combined ether solutions were washed with water and dried over sodium sulfate. Fractionation yielded 67.2 g. (71.5%) of product, b.p. 51–52° (8.5 mm.), $n^{25}D$ 1.4265.

Anal. Calcd. for $C_9H_{16}O_2$: C, 69.19; H, 10.45. Found: C, 69.51; H, 10.47.

1,2,2-Trimethylcyclopropane-1-carboxylic acid was obtained using a hydrolysis method described by Rupe and Busolt.[38] A solution of 59 g. (0.38 mole) of XXV in 300 ml. of methanol containing 100 g. (1.79 moles) of potassium hydroxide was refluxed for 24 hours. The mixture was cooled and 330 ml. of water was added. The mixture was made neutral to litmus with hydrochloric acid and then made slightly basic by the addition of solid sodium hydroxide. Methyl alcohol and water were distilled until the vapor temperature reached 95°. The cooled mixture was neutralized with acid (congo red). It was then extracted continuously for 24 hours with ether and the ether extract dried in two stages with calcium chloride. Distillation yielded 44 g. (91%) of the acid, b.p. 70–72° (1 mm.), $n^{25}D$ 1.4444.

Anal. Calcd. for $C_7H_{12}O_2$: C, 65.59; H, 9.44. Found: C, 65.31; H, 9.56.

1,2,2-Trimethylcyclopropane-1-carbonyl Chloride.—To 70 g. (0.59 mole) of thionyl chloride there was added cautiously 50 g. (0.39 mole) of the acid. The mixture was allowed to stand for 1 hour at room temperature and then heated in an oil-bath maintained at 50–60° for 2 hours. The excess thionyl chloride was removed *in vacuo*, and on fractionation there was obtained 47 g. (83%) of product, b.p. 53–55° (18 mm.), $n^{25}D$ 1.4496.

Anal. Calcd. for $C_7H_{11}OCl$: C, 57.34; H, 7.58. Found: C, 57.78; H, 7.56.

1,2,2-Trimethylcyclopropane-1-carboxamide.—Gaseous ammonia was passed into a solution of 13 g. (0.089 mole) of 1,2,2-trimethylcyclopropane-1-carbonyl chloride in 100 ml. of dry ether until a sample of the supernatant reaction mixture no longer gave a precipitate when ammonia was passed into it. The precipitate of ammonium chloride and amide was placed in a Soxhlet extractor and extracted with chloroform for 48 hours. On cooling the chloroform extract in ice there was obtained 11 g. (97.5%) of the amide, m.p. 163–164°.

Anal. Calcd. for $C_7H_{13}NO$: C, 65.87; H, 10.07. Found: C, 66.02; H, 10.30.

1-Cyano-1,2,2-trimethylcyclopropane (XXXIV).—The method of Walborsky and Hornyak[39] was used. A mixture of 12.7 g. (0.1 mole) of the above amide, 50 ml. of dry triethylamine, 36 g. (0.25 mole) of phosphorus pentoxide and 100 ml. of dry thiophene-free benzene was refluxed for 45 min. and allowed to stand overnight at room temperature. The benzene layer was decanted and enough water was added to dissolve the solid. The aqueous layer was extracted with ether. The combined extracts were dried over magnesium sulfate and fractionated. There was obtained 7.3 g. (62%) of nitrile, b.p. 66.5° (29.5 mm.), $n^{25}D$ 1.4282.

Anal. Calcd. for $C_7H_{11}N$: C, 77.01; H, 10.16. Found: C, 76.93; H, 10.17.

1-Benzoyl-1,2,2-trimethylcyclopropane (XXXI).—An adaptation of Cason's procedure[40] was used. A solution of phenylmagnesium bromide was prepared from 27 g. (0.17 mole) of bromobenzene, 4 g. (0.17 mole) of magnesium and 300 ml. of dry ether. After cooling the Grignard solution to about 0°, 29 g. (0.16 mole) of anhydrous cadmium chloride was added in small portions over a period of 0.5 hour and the reaction mixture was allowed to come to room temperature (2 hours). To the stirred mixture there was added dropwise 20 g. (0.14 mole) of 1,2,2-trimethylcyclopropane-1-carbonyl chloride over a period of 1 hour after which it was refluxed for 5 hours. Then 100 g. of water was added followed by 50 ml. of 10% hydrochloric acid. The layers were separated and the aqueous phase was extracted with 25 ml. of ether. The ethereal solutions were combined and washed with 50-ml. portions of water, saturated sodium bicarbonate solution and finally water. After drying over sodium sulfate, distillation yielded 13 g. (49%) of crude XXXI, b.p. 118–125° (5 mm.). After careful fractionation through the Todd column it had b.p. 96.5° (2 mm.), $n^{25}D$ 1.5325.

Anal. Calcd. for $C_{13}H_{16}O$: C, 83.93; H, 8.56. Found: C, 83.39; H, 8.27.

The 2,4-dinitrophenylhydrazone was prepared using the procedure of Brady.[41] On recrystallization from ethyl alcohol orange crystals, m.p. 93–94°, were obtained.

Anal. Calcd. for $C_{19}H_{20}O_4N_4$: C, 61.93; H, 5.47. Found: C, 62.17; H, 5.54.

Ethyl γ-Chlorovalerate.—The following modification of the procedure of Levene and Mori[10] gave 51.5–79% yields.

Dry hydrogen chloride was passed into a solution of 400 g. (4.0 moles) of γ-valerolactone in 1500 ml. of absolute ethanol. The addition was stopped when the reaction temperature (65–70°) began dropping (8–12 hours). There was obtained 518 g. (79%) of product, b.p. 90–91° (22 mm.), $n^{25}D$ 1.4319.

Ethyl 2-Methylcyclopropane-1-carboxylate (XXI). (A) From Ethyl γ-Chlorovalerate.[42]—To a stirred suspension of 39 g. (1 mole) of sodium amide in 500 ml. of dry ether there was added dropwise 164 g. (1 mole) of anhydrous ethyl γ-chlorovalerate over a period of 3 hours. The mixture was allowed to stand with stirring for 24 hours and an additional 60–80 hours with occasional stirring. The unreacted sodium amide was decomposed by cautiously adding 300 ml. of water. After separating the ether layer, the aqueous phase was washed with 50-ml. portions of ether, and the combined ether solutions dried over sodium sulfate. Fractionation through a 60-cm. column gave 109 g. (85.1%) of

Most of the fractional distillations were done in a fractionating unit consisting of a helices packed column (2 cm. in diameter and either 30 or 50 cm. in length) fitted with a total condensation variable reflux ratio distilling head. All compounds were fractionated through a Todd 0.5 × 90 cm. column rated at 60 theoretical plates before their spectra were determined. Melting points were determined with a Fisher–Johns apparatus. Boiling points and melting points are uncorrected. The analyses were done by Geller Analytical Laboratories, Hackensack, N. J., and Drs. Weiler and Strauss, Oxford, England.

(37) M. C. Kloetzel, THIS JOURNAL, **70**, 3571 (1948), who reports a 35% yield. A 69.5% yield was obtained using Nemec's unpublished modifications[13] in which equivalent quantities of methyl methacrylate and 2-nitropropane are employed and Triton-B is used as the base.

(38) H. Rupe and E. Busolt, *Ber.*, **40**, 4538 (1907).

(39) H. M. Walborsky and F. M. Hornyak, THIS JOURNAL, **77**, 6026 (1955).

(40) J. Cason, *ibid.*, **68**, 2078 (1946).

(41) O. L. Brady, *J. Chem. Soc.*, 756 (1931).

(42) Since the completion of this work, the preparation of this ester by cyclization using sodium hydride in benzene has been reported by L. R. Sweet, Abstracts 133rd Meeting of the American Chemical Society, San Francisco, Calif., April, 1958, p. 20-M.

XXI, b.p. 77° (68.5 mm.), $n^{25}D$ 1.4203. This sample of ester contained traces of chlorine assumed to result from contamination by ethyl γ-chlorovalerate.

Anal. Calcd. for $C_7H_{12}O_2$: C, 65.58; H, 9.44. Found: C, 65.34; H, 9.30.

B. From 2-Methylcyclopropane-1-carbonyl Chloride.—Thirty grams (0.253 mole) of 2-methylcyclopropane-1-carbonyl chloride was added cautiously to a solution of 20 g. of pyridine in 50 ml. of absolute ethanol. The mixture was refluxed for 2 hours and then fractionated. The distillate weighed 21 g. (66.1%), b.p. 58–59° (27 mm.), $n^{25}D$ 1.4215 and was chlorine-free.

2-Methylcyclopropane-1-carbonyl Chloride.—The directions reported by Smith and McKenzie[43] for the preparation of cyclopropanecarbonyl chloride were used. From 43 g. (0.43 mole) of 2-methylcyclopropanecarboxylic acid (obtained in 77% yield by alkaline hydrolysis of XXI) and 29.2 g. (0.212 mole) of phosphorus trichloride there was obtained 41 g. (80.5%) of the acid chloride, b.p. 50–52° (30 mm.), $n^{25}D$ 1.4494 (lit.[44] b.p. 39.5° (15 mm.)).

1-Benzoyl-2-methylcyclopropane was obtained in 43% yield by the procedure employed in the preparation of XXXI. It had b.p. 95–97° (6 mm.), $n^{25}D$ 1.5408 (lit.[45] b.p. 240–245°).

The 2,4-dinitrophenylhydrazone was obtained by the usual method[46] as orange crystals, m.p. 160–161°, after recrystallization from ethyl acetate.

Anal. Calcd. for $C_{17}H_{16}N_4O_4$: C, 59.99; H, 4.75. Found: C, 59.57; H, 4.94.

5-Chlorohexanone-2.—A mixture of 80 ml. of concentrated hydrochloric acid, 88 ml. of water and 119 g. (0.92 mole) of α-acetyl-γ-valerolactone[14] was heated in a 1-l. distilling flask. The evolution of carbon dioxide was rapid at the beginning and slowed up as the reaction proceeded. The reaction mixture stood at room temperature overnight and was then distilled with a Dean–Stark water separator, the aqueous layer being returned to the distilling flask. The organic distillate was dried over sodium sulfate and fractionated. There was obtained 31.5 g. (25.6%) of product, b.p. 73–74° (14 mm.), $n^{20}D$ 1.4373.

Anal. Calcd. for $C_6H_{11}OCl$: C, 53.53; H, 8.24. Found: C, 53.99; H, 8.50.

1-Acetyl-2-methylcyclopropane (XXVII).—Thirty-one grams (0.23 mole) of 5-chlorohexanone-2 was added dropwise to a suspension of 9 g. (0.23 mole) of powdered sodium amide in 100 ml. of dry ether. The reaction mixture was stirred for 3 hours at room temperature. Then 50 ml. of water was added cautiously. The water layer was separated and extracted with 50 ml. of ether. The combined ether solutions were dried over sodium sulfate. Fractionation gave 10.0 g. (44.5%) of product, b.p. 64–68° (91 mm.), $n^{25}D$ 1.4241.

Anal. Calcd. for $C_6H_{10}O$: C, 73.43; H, 10.04. Found: C, 73.47; H, 10.20.

The 2,4-dinitrophenylhydrazone was prepared[41] and the yellow crystals were recrystallized from ethanol, m.p. 93–95°.

Anal. Calcd. for $C_{12}H_{14}N_4O_4$: C, 51.79; H, 5.07. Found: C, 51.77; H, 4.68.

α-Methyl-γ-chlorobutyryl Chloride.—The method of Close[9] for the preparation of γ-chlorobutyryl chloride was employed. From 32.1 g. (0.32 mole) of α-methyl-γ-butyrolactone,[47] 14 g. (0.38 mole) of anhydrous hydrogen chloride and 41.5 g. (0.35 mole) of thionyl chloride there was obtained after fractionation 33.4 g. (68%) of a lachrymatory, colorless liquid, b.p. 86–91° (33 mm.).

Anal. Calcd. for $C_5H_8OCl_2$: C, 38.74; H, 5.20. Found: C, 38.33; H, 5.79.

α-Methyl-γ-chlorobutyrophenone.—A suspension of 16 g. (0.12 mole) of anhydrous aluminum chloride in 70 ml. of dry benzene was allowed to react with 16.9 g. (0.11 mole) of the above acid chloride according to the directions of Close.[9] The crude product weighed 19.7 g. (91.3%). This material was not distilled since in a previous run attempted distillation had resulted in decomposition of the product.

The 2,4-dinitrophenylhydrazone was prepared[41] and the yellow crystals were recrystallized from ethanol, m.p. 135–136°.

Anal. Calcd. for $C_{17}H_{17}N_4O_4Cl$: C, 54.18; H, 4.55. Found: C, 54.08; H, 4.20.

When the reaction mixture was allowed to stand overnight before work-up, 13.1 g. of material, b.p. 166–169° (2.1 mm.), was obtained. On refractionation through a semi-micro Vigreux column it had b.p. 169° (2 mm.), $n^{25}D$ 1.5610. It is believed to be **α-methyl-γ-phenylbutyrophenone**.

Anal. Calcd. for $C_{17}H_{18}O$: C, 85.69; H, 7.61. Found: C, 86.18; H, 7.35.

The 2,4-dinitrophenylhydrazone was prepared[41] using butanol as the solvent. It was recrystallized from petroleum ether (b.p. 30–60°), m.p. 90–91°.

Anal. Calcd. for $C_{23}H_{22}N_4O_4$: C, 66.01; H, 5.30. Found: C, 66.09; H, 5.33.

1-Benzoyl-1-methylcyclopropane (XXX).—Nineteen grams (0.096 mole) of α-methyl-γ-chlorobutyrophenone was dissolved in 150 ml. of dry benzene, 3.9 g. (0.1 mole) of powdered sodium amide was added and the mixture was refluxed with stirring for 15 hours. The mixture was allowed to cool to room temperature and 20 ml. of water was added dropwise. After extracting the water layer with 20 ml. of benzene, the combined benzene layers were dried over sodium sulfate and distilled. There was obtained 9 g. (58.6%) of product, b.p. 93–97° (2.5 mm.), $n^{25}D$ 1.5304.

Anal. Calcd. for $C_{11}H_{12}O$: C, 82.40; H, 7.55. Found: C, 82.25; H, 7.64.

The 2,4-dinitrophenylhydrazone was prepared[41] and recrystallized from ethanol, m.p. 195–196°.

Anal. Calcd. for $C_{17}H_{16}N_4O_4$: C, 59.99; H, 4.39. Found: C, 60.09; H, 4.45.

Ethyl α-Methyl-γ-chlorobutyrate.—To 27 g. (0.17 mole) of α-methyl-γ-chlorobutyryl chloride 16 g. (0.35 mole) of commercial absolute ethanol was added dropwise with intermittent shaking. The solution was heated under reflux for 20 min. and distilled. There was obtained 24 g. (84%) of product, b.p. 56–57° (2.3 mm.). The infrared spectrum indicated contamination by a lactone. It was carefully refractionated through a Todd column. The fractions shown by their infrared spectra to be lactone-free weighed 12.5 g., b.p. 54.5° (3.0 mm.).

Anal. Calcd. for $C_7H_{13}OCl$: C, 51.11; H, 7.96. Found: C, 51.21; H, 8.03.

Ethyl 1-Methylcyclopropane-1-carboxylate (XXIV). A. From Ethyl α-Methyl-γ-chlorobutyrate.—The procedure employed for preparing 1-benzoyl-1-methylcyclopropane was used. From 24 g. (0.14 mole) of ethyl α-methyl-γ-chlorobutyrate and 6 g. (0.15 mole) of sodium amide in 100 ml. of dry benzene there was obtained 8.5 g. (47.6%) of product, b.p. 71° (66.5 mm.), $n^{25}D$ 1.4184.

Anal. Calcd. for $C_7H_{12}O_2$: C, 65.58; H, 9.44. Found: C, 65.66; H, 9.50.

B. From Ethyl Methacrylate.—The method of Siegel and Bergstrom[48] was used to decompose 22 g. (0.15 mole) of ethyl 5-methyl-Δ^1-pyrazoline-5-carboxylate.[49] Eight grams (44.4%), b.p. 136–138°, $n^{25}D$ 1.4185, of ester was obtained after fractionation.[50]

1-Methylcyclopropane-1-carboxamide.—In a 250-ml. pressure bottle was placed 4.5 g. (0.035 mole) of ethyl 1-methylcyclopropane-1-carboxylate dissolved in 100 ml. of dry methanol. The solution was saturated with ammonia at ice-bath temperature. The flask was capped and kept at room temperature for seven days. The methanol was

(43) L. I. Smith and S. McKenzie, *J. Org. Chem.*, **15**, 77 (1950).

(44) H. Wohlgemuth, *Ann. chim.*, **3**, 141 (1915); *C. A.*, **9**, 2057 (1915).

(45) W. H. Perkin and J. Stenhouse, *J. Chem. Soc.*, **61**, 86 (1892).

(46) R. L. Shriner and R. C. Fuson, "The Systematic Identification of Organic Compounds," 3rd ed., John Wiley and Sons, Inc., New York, N. Y., 1948, p. 171.

(47) L. Ya. Bryusova, E. Simanovskaya and A. Ul'yanova, *Sintezy Dushistykh Veshchestv, Sbornik Statei*, 165 (1939); *C. A.*, **36**, 3784 (1942).

(48) S. Siegel and C. G. Bergstrom, THIS JOURNAL, **72**, 3815 (1950).

(49) K. v. Auwers and F. Konig, *Ann.*, **496**, 27 (1932).

(50) K. v. Auwers and F. Konig [*ibid.*, **496**, 252 (1932)] reported on the basis of bromine titration that decomposition of the pyrazoline yielded a mixture of 37% ethyl 1-methylcyclopropanecarboxylate and 63% ethyl tiglate. The infrared spectra of our samples of XXIV obtained from the pyrazoline and from ethyl α-methyl-γ-chlorobutyrate were identical and did not exhibit any C=C stretching absorption.

removed *in vacuo*. One gram (28.9%) of product was obtained which was purified by sublimation, m.p. 147–148°.

Anal. Calcd. for C_6H_9ON: C, 60.58; H, 9.15. Found: C, 60.40; H, 9.16.

Attempted Preparation of 2-Methylcyclopropane-1,1-dicarboxamide.—The procedure recommended[51] for diesters was used. From 500 ml. of methanol, 0.23 g. (0.01 g. atom) of sodium and 20 g. (0.10 mole) of diethyl 2-methylcyclopropane-1,1-dicarboxylate[52] there was obtained, after removal of ammonia and methanol *in vacuo*, 15 g. of water-soluble material. Recrystallization from benzene gave 12 g. (76%) of white crystals, m.p. 72–73°, whose elemental composition suggests that the compound may be **methyl 2-methylcyclopropane-1-carboxamide-1-carboxylate**.

Anal. Calcd. for $C_7H_{11}NO_3$: C, 53.49; H, 7.05; N, 8.91. Found: C, 53.01; H, 6.95; N, 10.13.

2-Methylcyclopropane-1,1-dicarbonyl Chloride.—A mixture of 45 g. (0.31 mole) of 2-methylcyclopropane-1,1-dicarboxylic acid[52] and 60 g. (0.5 mole) of thionyl chloride was stirred at room temperature for 1 hour and then heated at 65–80° for 2 hours. After standing overnight, distillation yielded 23 g. (40%) of a light yellow oil, b.p. 76–82° (15 mm.).

Anal. Calcd. for $C_6H_6O_2Cl_2$: Cl, 39.17. Found: Cl, 38.79.

1,1-Dibenzoylethylene.—A mixture of 12.7 g. (0.05 mole) of dibenzoylmethane, 20 ml. of diethylamine and 35 ml. of ether was cooled in an ice-bath. To the mixture there was added 8 g. (0.1 mole) of 37.3% formalin solution. After standing overnight, the white solid which had crystallized from the reaction mixture was collected, weight 11.6 g. (98%). It was recrystallized from ethanol, m.p. 178–179°. It had infrared bands at 1692 (C=O) and 1667 cm.$^{-1}$ (C=C).

Anal. Calcd. for $C_{16}H_{12}O_2$: C, 81.34; H, 5.12. Found: C, 81.33; H, 5.56.

1-Acetyl-2-nitro-2,3,3-trimethylcyclopropane 2,4-dinitrophenylhydrazone was reported by Smith and Kohlhase[53] with a molecule of methanol of crystallization. The 2,4-dinitrophenylhydrazone prepared in the present work by the procedure of Brady[41] melted at 161–162° after recrystallization from ethanol. Its analysis indicates the absence of solvent of crystallization.

Anal. Calcd. for $C_{14}H_{17}N_5O_6$: C, 47.86; H, 4.88. Found: C, 48.05; H, 4.45.

Infrared spectra were obtained with a Perkin–Elmer model 21 spectrophotometer equipped with sodium chloride optics and a linear wave length scale. All spectra were determined on carbon tetrachloride solutions (3–6%). Since the precision required to obtain significant determinations of the shifts in the C=O and C≡N stretching frequencies is greater than that required by the instrument manufacturer's specifications, the following procedure was used to test the instrument's precision and is typical of that used for each pair of compounds to be compared.

The instrument was allowed to warm up for two hours and the scale expanded by a factor of 8 by changing gears. The spectrum of a solution of one of the cyclopropane compounds was then determined from 5.700 to 6.000 μ on blank paper ten consecutive times. A line was drawn through each of the C=O bands at that point which visually appeared to bisect the band. The positions of the peaks were then determined by measuring the distance from the 5.700 μ (by counter) line to the line bisecting the C=O band. The average value obtained from the ten C=O bands was 5.944 ± 0.0006 μ. The 5.700–6.000 μ region of the spectrum of a second cyclopropane compound to be compared with the first was then determined five times in the same way. The C=O band of the first compound was redetermined at this point and its value was within the limits of the values of the first ten determinations. The last five determinations for the second compound were then made. The average value for the C=O band of the second compound was 5.936 ± 0.0004 μ. Similar reproducibilities of better than ±1 cm.$^{-1}$ were obtained with each pair of compounds.

The instrument was calibrated periodically in the region of the C=O band against water vapor and in the region of the C≡N band against a polystyrene film. After applying these corrections the average values were converted to frequency values.

Ultraviolet spectra were determined with a Beckman model DU spectrophotometer using 95% ethanol solutions. Readings were taken at 0.5-mμ intervals in the regions of the maxima. Maxima below *ca.* 215 mμ were obtained with the selector switch set at the 0.1 position.

AMHERST, MASS.

(51) P. B. Russell, THIS JOURNAL, **72**, 1853 (1950).

(52) R. Marburg, *Ann.*, **294**, 111 (1896).

(53) L. I. Smith and W. L. Kohlhase, *J. Org. Chem.*, **21**, 816 (1956). Prior to publication of this paper we had independently carried out the same reaction sequence in an attempt to prepare 1-nitro-1,2,2-trimethylcyclopropane. Attempts to cleave 1-acetyl-2-nitro-2,3,3-trimethylcyclopropane by the haloform reaction and the method of L. C. King [THIS JOURNAL, **66**, 894 (1944)] failed.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF WISCONSIN]

The Structure of Photosantonic Acid[1]

BY EUGENE E. VAN TAMELEN, STEPHEN H. LEVIN,[2] GERALD BRENNER, JOSEPH WOLINSKY AND PAUL E. ALDRICH

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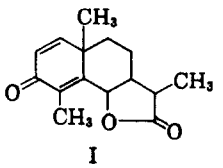
Chemical and physico-chemical findings are presented which define the structure (VIII) of photosantonic acid, the well-known irradiation product of the sesquiterpene santonin. Various chemical transformations and the mechanism of formation of photosantonic acid are discussed in terms of the developed structure.

Of the major constitutional problems which substances derived from santonin (I) have posed in past years, only the structure of photosantonic acid has remained unsolved, despite the fact that this irradiation product has been known since the dawn of structural organic chemistry.[3]



I

Photosantonic acid, an optically active solid of melting point 154–155°, can be prepared by irradiating a solution of santonin with ultraviolet light, or, as was the practice of the early Italian workers, exposing the solution to sunlight for some weeks.

(1) First reported in a Communication to the Editor, THIS JOURNAL, **80**, 501 (1958).

(2) Allied Chemical and Dye Corporation, Nitrogen Division, Fellow.

(3) For reviews and references to the early Italian work on photosantonic acid, see (a) "Elsevier's Encyclopedia of Organic Chemistry," edited by F. Radt, Elsevier, Amsterdam, 1953, Series III, Vol. 12B, p. 3733, and (b) J. Simonsen and D. H. R. Barton, "The Terpenes," University Press, Cambridge, 1952, Vol. III, 2nd Edition, p. 249.