real solution was washed with hydrochloric acid, followed by bicarbonate solution and dried over calcium chloride. The solvent was removed and the solid residue recrystallized from ethanol to give 57.5 g. (91%) of *trans*-α,α′-dimethylstilbene (IV), m.p. 105–105.5°.

In a similar manner, a solution of 20.8 g. (0.1 mole) of the 87% *cis* olefin in 125 ml. of dry ether was added to a stirred suspension of 0.025 mole of sodium amide in 500 ml. of liquid ammonia to produce a persistent red color. After adding ammonium chloride, the mixture was worked up essentially as described above to give, on recrystallization of the product from methanol, 6.5 g. (31%) of the *trans* olefin IV, m.p. 104–105°, and on further recrystallization, 12.1 g. (58%) of recovered impure *cis* olefin III, m.p. 54–56° (having the composition of the original mixture).

DURHAM, NORTH CAROLINA

[CONTRIBUTION FROM AVERY LABORATORY, UNIVERSITY OF NEBRASKA]

Cyclopropyl Ketones. I. Synthesis and Spectra of 1-Aroyl-2-arylcyclopropanes[1]

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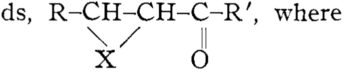
To extend our studies of three-ring carbonyl compounds we have synthesized members of a heretofore unknown class of cyclopropyl ketones. Reaction of α-diazo-4-phenylacetophenone with styrene gave *cis*- and *trans*-1-(4′-phenylbenzoyl)-2-phenylcyclopropanes. The *trans* isomer was also prepared by (a) reaction of di-(4-biphenylyl)-cadmium with 2-phenylcyclopropanecarbonyl chloride, (b) reaction of the new ketone 4-phenylacrylophenone with phenyldiazomethane, and (c) reaction of 4-biphenylylmetallic compounds with the new nitrile 2-phenylcyclopropanecarbonitrile. Four more new cyclopropane carbonyl compounds, 1-benzoyl-2-phenylcyclopropane, 4-phenylbenzoylcyclopropane and the *p*-nitrobenzyl esters of *cis* and *trans* 2-phenylcyclopropanecarboxylic acids, were synthesized. The ultraviolet and infrared spectra of all pertinent compounds were determined and structural assignments, based on spectral results, were made. The results of spectral studies of ethylenimine, ethylene oxide and cyclopropane ketones were compared.

Previous publications from this Laboratory have dealt with studies of the chemistry of *cis* and *trans* forms of analogous series of three-ring carbonyl compounds,



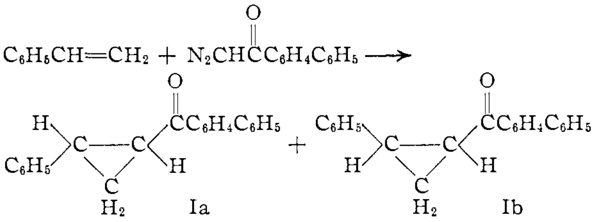
$R\text{–}\underset{\diagdown\;\;\;\diagup}{CH\text{–}CH}\text{–}\underset{\underset{O}{\|}}{C}\text{–}R'$, with X bridging the two CH groups,

where X was N–R″[3] or O.[4] The interrelations between the stereochemistry and absorption spectra of such pairs of isomers have been discussed, and it has been concluded that the geometrical isomer which has its characteristic carbonyl associated absorption band at the lower frequency in both the ultraviolet and infrared ranges of the spectrum possesses the *trans* structure.[3c–e,4] Speculation has been put forth that isomeric pairs of simple arylaroylcyclopropanes might exhibit physical properties analogous to the ethylenimine and ethylene oxide ketones.[3d]

The purpose of the present study was to investigate methods of preparing stereoisomeric pairs of simple 1-carbonyl-2-arylcyclopropanes, particularly stereoisomers in the unknown class of compounds, 1-aroyl-2-arylcyclopropanes, and to study the absorption spectra of such simple cyclopropane carbonyl compounds, free from the effect of other three-ring substituents.

1-(4′-Phenylbenzoyl)-2-phenylcyclopropane (I) was selected as the arylaroylcyclopropane of choice because it would be one of the simplest examples which might exhibit strong carbonyl associated light absorptions (free from the effect of other three-ring substituents) and which might be expected to give rise to solid isomers. Four different methods were employed to prepare 1-(4′-phenylbenzoyl)-2-phenylcyclopropane in yields ranging from poor to fair: (1) reaction of α-diazo-4-phenylacetophenone with styrene, (2) reaction of di-(4-biphenylyl)-cadmium with 2-phenylcyclopropanecarbonyl chloride, (3) reaction of 4-phenylacrylophenone (II) with phenyldiazomethane and (4) reaction of 4-biphenylyl organometallic compounds with 2-phenylcyclopropanecarbonitrile (IV).

α-Diazo-4-phenylacetophenone reacted with a large excess of styrene at 140° to yield a sirupy product from which, after considerable manipulation, a 23% yield of a mixture of *cis*- and *trans*-1-(4′-phenylbenzoyl)-2-phenylcyclopropane was isolated.



A more successful procedure, suggested by D'yakonov's[5] extensive study of the reaction of diazo compounds and olefins, employed copper powder as a catalyst and a lower reaction temperature to give yields of 40% of theoretical of the *trans* isomer Ia. No trace of the *cis* isomer Ib was found. Several runs of the reaction between α-diazo-4-phenylacetophenone and *o*-nitrostyrene (a less easily polymerizable styrene derivative[6]) yielded unreacted *o*-nitrostyrene and intractable polymeric solids.

The reaction of di-(4-biphenylyl)-cadmium with 2-phenylcyclopropanecarbonyl chloride produced satisfactory yields of *trans*-1-(4′-phenylbenzoyl)-2-phenylcyclopropane (Ia), considering the difficulties

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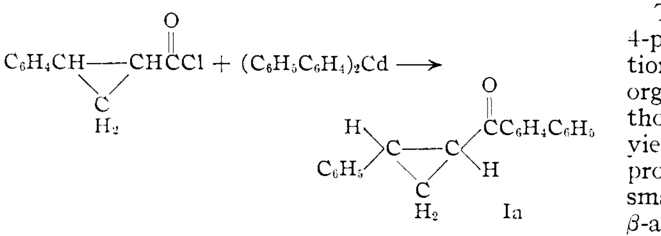
(3) (a) N. H. Cromwell, *et al.*, THIS JOURNAL, **65**, 312 (1943); (b) **71**, 708 (1949); (c) **73**, 1044, 5929 (1951); (d) *J. Org. Chem.*, **17**, 414 (1952); (e) THIS JOURNAL, **75**, 6252 (1953); **77**, 6723 (1955).

(4) N. H. Cromwell and R. A. Setterquist, *ibid.*, **76**, 5752 (1954).

(5) I. A. D'yakonov, *et al.*, *J. Gen. Chem.*, *U.S.S.R.*, **23**, 66 (1953).

(6) R. H. Wiley and N. R. Smith, THIS JOURNAL, **72**, 5198 (1950).

to be expected in the preparation of the intermediate 4-biphenyllithium.[7]



Ia

Although method 3, involving reaction of 4-phenylacrylophenone (II) with phenyldiazomethane (Fig. 1), was the least successful method of preparing 1-(4'-phenylbenzoyl)-2-phenylcyclopropane (I), the chemistry of the intermediates was interesting.

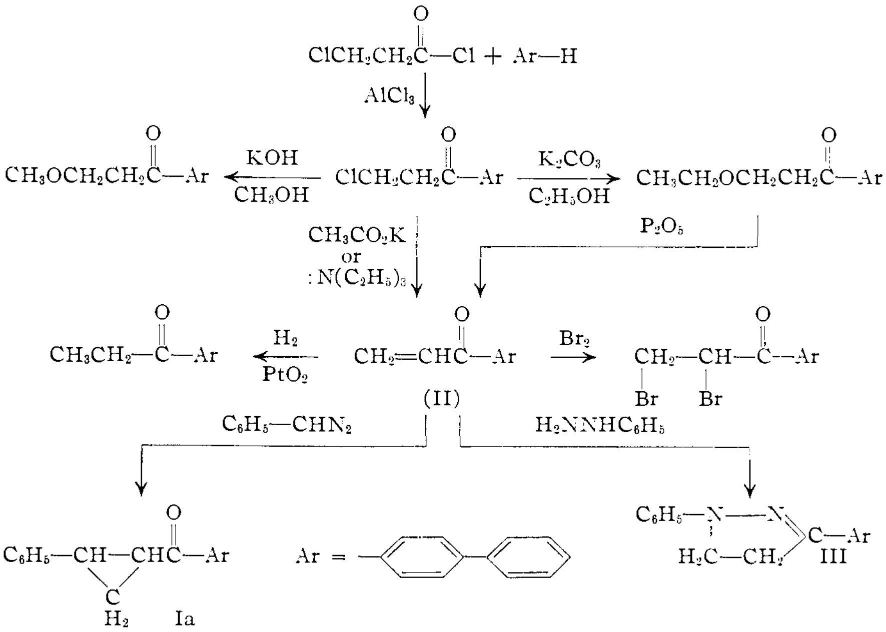


Fig. 1.—Schematic representation of experiments with 4-phenylacrylophenone (II).

The preparation of β-chloro-4-phenylpropiophenone by Friedel–Crafts acylation of biphenyl proceeded smoothly in good yield. A survey of the literature disclosed that two workers[8] had previously carried out the reaction of β-chloropropionyl chloride with biphenyl and obtained compounds which may have been β-chloro-4-phenylpropiophenone. As illustrated in Fig. 1, our product (m.p. 120.5°) was indirectly converted to the known 4-phenylpropiophenone[9] and the known α,β-dibromo-4-phenylpropiophenone.[3c] From the evidence reported here it is most probable that the pure product (m.p. 120.5°) from the Friedel–Crafts reaction of β-chloropropionyl chloride and biphenyl possesses the structure of β-chloro-4-phenylpropiophenone.

The difficulty encountered in the preparation of 4-phenylacrylophenone (II) by dehydrochlorination of β-chloro-4-phenylpropiophenone using inorganic bases was somewhat anticipated. Although Allen[10a] prepared acrylophenone in 75% yield by reaction of sodium acetate with β-chloropropiophenone in alcohol, von Auwers[10b] obtained a small amount of acrylophenone and a high yield of β-acetoxypropiophenone by reaction of sodium or potassium acetate with β-chloropropiophenone in acetic acid. The mechanism of formation of the β-alkoxy derivatives in our study is not apparent. Two possible mechanisms are (a) the nucleophilic substitution of the β-chlorine atom by an alkoxide group or, (b) the addition of alcohol to the double bond of 4-phenylacrylophenone formed *in situ*. Mechanism a generally takes place between an active chlorine compound and an alkali alkoxide, such as sodium ethoxide. The concentration of potassium ethoxide would be expected to be very low in a 95% ethanolic mixture of potassium carbonate. Mechanism b is the more probable since there are numerous examples of the addition of alcohols to acrylic esters in the presence of catalytic amounts of potassium hydroxide or sodium methoxide.[11] The low yields of 4-phenylacrylophenone (II) produced by dehydrochlorination with triethylamine were due partly to the ease with which the vinyl ketone polymerized. Traces of triethylamine (difficult to remove) might catalyze such a polymerization.

Because of the unusual spectral results obtained from 4-phenylacrylophenone (II) (Table I and III), it was imperative to provide extensive chemical proof of the structure of this entity. The results mentioned above and illustrated in Fig. 1 are consistent with the assigned structure. The facile formation of a pyrazoline (III) is characteristic of α,β-unsaturated ketones.[12] The de-ethoxylation of β-ethoxy-4-phenylpropiophenone following Weizmann's[13] procedure related the structures of β-ethoxy-4-phenylpropiophenone and II.

The preparation of phenyldiazomethane involved a modification of Staudinger's[14] method of oxidation

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[7] (a) H. Gilman and C. E. Dunn, THIS JOURNAL, **73**, 5077 (1951); (b) E. Muller and T. Töpel, *Ber.*, **72**, 273 (1939); (c) H. Gilman, E. A. Zoellner and W. M. Selby, THIS JOURNAL, **55**, 1252 (1933).

[8] (a) F. Mayer and P. Muller, *Ber.*, **60**, 2278 (1927), reported no analysis or subsequent reaction of their product (m.p. 120°); (b) C. F. H. Allen, H. W. Cressman and A. C. Bell, *Can. J. Research*, **8**, 440 (1933), reported an estimate of the chlorine content and the oxidation of their product (m.p. 112°) to 4-phenylbenzoic acid.

[9] N. R. Campbell and F. W. Chattaway, *Proc. Roy. Soc., London*, **130B**, 435 (1942); S. Machlis and K. C. Blanchard, THIS JOURNAL, **57**, 176 (1935).

[10] (a) C. F. H. Allen, A. C. Bell, A. Bell and J. Van Allan, THIS JOURNAL, **62**, 663 (1940); (b) K. von Auwers and H. Muller, *J. prakt. Chem.*, **137**, 102 (1933).

[11] R. B. Wagner and H. D. Zook, "Synthetic Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1953, p. 233.

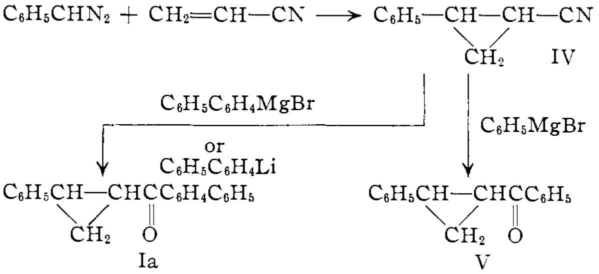
[12] L. C. Raiford and W. J. Peterson, *J. Org. Chem.*, **1**, 544 (1937).

[13] Ch. Weizmann, M. Sulzbacher and E. Bergmann, THIS JOURNAL, **70**, 1153 (1948).

[14] H. Staudinger and A. Gaule, *Ber.*, **49**, 1897 (1916).

of benzalhydrazine. The use of silver oxide,[15] instead of mercuric oxide, as oxidizing agent results in a faster reaction with comparable yields. The reaction of 4-phenylacrylophenone (II) with phenyldiazomethane to give a small amount of 1-(4′-phenylbenzoyl)-2-phenylcyclopropane (Ia) appears to be the first reported isolation of a cyclopropyl carbonyl compound from the reaction of a diazohydrocarbon, other than diazomethane, with an α,β-unsaturated carbonyl compound. The major portion of the reaction product was a mixture which could not be purified by recrystallization methods. Chromatographic separation yielded ambiguous results, perhaps due to further reaction of the organic material on the column. Further work, to ascertain the feasibility of reaction of diazohydrocarbons with α,β-unsaturated ketones to prepare cyclopropyl ketones, is contemplated.

The fourth, and most successful, method of preparing 1-(4′-phenylbenzoyl)-2-arylcyclopropanes involved the new compound, 2-phenylcyclopropanecarbonitrile (IV).



2-Phenylcyclopropanecarbonitrile (IV) was prepared in good yield by a method similar to Walborsky's[16] method of preparing 2,2-diphenylcyclopropanecarbonitrile. Hydrolysis of a sample of IV to *trans*-2-phenylcyclopropanecarboxylic acid[17] established the structure of the nitrile as that of 2-phenylcyclopropanecarbonitrile. It cannot be certain that the nitrile has the *trans* structure because such vigorous hydrolytic conditions could cause isomerization.

The method employed for the reaction of 2-phenylcyclopropanecarbonitrile and cyclopropyl cyanide with organometallic compounds was similar to that of Humphlett.[18] The yields of 1-(4′-phenylbenzoyl)-2-phenylcyclopropane (Ia) and 4-phenylbenzoylcyclopropane (VI), respectively, were good considering the low yields of 4-biphenylyl organometallic compounds available.[7] The reaction of phenylmagnesium bromide with 2-phenylcyclopropanecarbonitrile gave a good yield of 1-benzoyl-2-phenylcyclopropane (V), but subsequent distillation of the semi-solid at high pot temperatures caused some decomposition of the cyclopropyl ketone.

The preparation of the first pair of solid stereoisomeric esters (*p*-nitrobenzyl) of *cis*- and *trans*-2-phenylcyclopropanecarboxylic acids employed mild conditions, which have frequently been used to prepare esters of acids which isomerize during direct esterification.[19]

Discussion of Absorption Spectra.—The ultraviolet and infrared absorption spectra of all pertinent compounds prepared in this study are listed in Table III. Anomalous results were obtained in both the ultraviolet and infrared ranges of the spectrum for 4-phenylacrylophenone (II). On comparison of the ultraviolet spectra of the three related phenyl ketones (A,B,C) listed in Table I, the expected shift in the aroyl band maxima is observed.

TABLE I

ULTRAVIOLET ABSORPTION SPECTRA OF RELATED KETONES

Ar = –*p*-C_6H_4–R	R = H		R = C_6H_5	
	λ_{max}, mμ	$\epsilon \times 10^{-3}$	λ_{max}, mμ	$\epsilon \times 10^{-3}$
$CH_3CH_2\overset{\overset{O}{\Vert}}{C}—Ar$	(A) 238	11.5[a]	(D) 276	23.4[e]
$CH_2{=}CH\overset{\overset{O}{\Vert}}{C}—Ar$	(B) 247.5	10.5[b]	(II) 291	22.2[e]
$CH_3CH{=}CH\overset{\overset{O}{\Vert}}{C}—Ar$	(C) 250	17.5[c]	(E) 287	23.9[d]

[a] Ref. 20a. [b] Ref. 20b. [c] Ref. 20c. [d] Ref. 3e. [e] See footnote *h*, Table III.

The aroyl band maxima are shifted to longer wave lengths as a double bond is introduced into the α,β-position (A → B) and upon alkyl substitution of the carbon–carbon double bond (B → C) (Woodward's rule).[21] However, comparison of the absorption maxima of the 4-phenyl substituted series shows that the 4-phenylbenzoyl-vinyl maximum of 4-phenylacrylophenone (II) occurred at a *longer* wave length than did the corresponding band of 4-phenylcrotonophenone (E). This is a direct contradiction of the well-substantiated Woodward's rule,[21] which appears not to apply to some cross-conjugated systems.

Pure samples of 4-phenylacrylophenone (II) and 4-phenylcrotonophenone (E) (obtained from supplies in this Laboratory) were examined on the spectrophotometer on the same day, under identical conditions, by the same operator. The absorption values of 4-phenylcrotonophenone (E) found in this latest measurement were identical with those reported previously,[3e] within the reproducibility of the instrument. Previously, we had hydrogenated 4-phenylcrotonophenone (E) to 4-phenylbutyrophenone,[3e] and we wish to report here that we have oxidized a sample of the saturated derivative to the known 4-phenylbenzoic acid, thus proving that the 4-biphenylyl assignment was correct.

This spectral anomaly extends itself into the infrared region of the spectrum. The absorption band characteristic of the carbonyl bond stretching vibration appears at a lower frequency for 4-phenylacrylophenone (II) (1666 cm.$^{-1}$ in carbon tetrachloride, 1660 cm.$^{-1}$ in Nujol) than does the comparable band for 4-phenylcrotonophenone (E)[3e] (1671 cm.$^{-1}$ in carbon tetrachloride; 1666 cm.$^{-1}$ in Nujol). Although the effects of β-substituents on

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[15] W. Schroeder and L. Katz, *J. Org. Chem.*, **19**, 718 (1955).

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

[17] A. Burger and W. L. Yost, *ibid.*, **70**, 2198 (1948).

[18] W. J. Humphlett, M. J. Weiss and C. R. Hauser, *ibid.*, **70**, 4020 (1948).

[19] See ref. 11, p. 484.

[20] (a) G. D. Hedden and W. G. Brown, THIS JOURNAL, **75**, 3744 (1953); (b) K. Bowden, E. A. Braude and E. R. H. Jones, *J. Chem. Soc.*, 948 (1946); (c) N. H. Cromwell and W. R. Watson, *J. Org. Chem.*, **14**, 411 (1949).

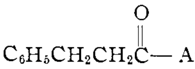
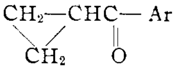
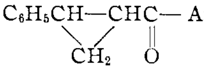
[21] R. B. Woodward, THIS JOURNAL, **64**, 76 (1942).

α,β-unsaturated ketones should be less in the infrared spectrum than in the ultraviolet, one might expect the carbonyl group of 4-phenylcrotonophenone (E) to have more single bond character in the ground state resonance hybrid than that of 4-phenylacrylophenone (II). However, from the infrared spectra of II one must conclude that in the ground state the carbonyl group of 4-phenylacrylophenone (II) possesses a bit more single bond character than that of 4-phenylcrotonophenone (E). Further work is presently being carried out to elucidate this anomaly.

There has been considerable evidence gathered in this Laboratory[3c—e] which has led to the conclusion that in β-substituted three-ring carbonyl compounds there is an electrical interaction, especially in the excited state, of the β-substituent with the carbonyl group through the three-ring. Comparison of the ultraviolet absorption spectra of 1-(4′-phenylbenzoyl)-2-phenylcyclopropane (I) (Table III) with that of 4-phenylbenzoylcyclopropane (VI) shows that the β-phenyl derivative I absorb ultraviolet light at a slightly longer wave length than does the unsubstituted derivative VI.

TABLE II

ULTRAVIOLET ABSORPTION SPECTRA OF RELATED KETONES

	R = H		R = C_6H_5	
Ar = -*p*-C_6H_4-R	λ_{max}, mμ	$\epsilon \times 10^{-3}$	λ_{max}, mμ	$\epsilon \times 10^{-3}$
 $C_6H_5CH_2CH_2\overset{O}{\overset{\Vert}{C}}—Ar$	(F) 238[a]	12.4	(H) 276[c]	25.2
	(G) 238[b]	14.4	(VI) 276	26.0
	(V) 242	18.2	(I) 280	23.0 (*cis*) 28.0 (*trans*)

[a] Ref. 20c. [b] Ref. 22. [c] Ref. 3e.

Comparison of the aroyl maxima of the propiophenone compounds (A, D) listed in Table I with the aroyl maxima of the analogous β-phenylpropiophenones (F, H) (Table II) shows that substitution of the phenyl group on the β-position of the alkyl moiety has no effect upon the position of the aroyl band maxima. However, substitution of a phenyl group into the β-position of the cyclopropane ring (V, I) causes a small bathochromic shift in the wave length of maximum absorption compared to the unsubstituted cyclopropyl ketones (G, VI). This effect can be attributed to a transmission of the phenyl ring unsaturation through the cyclopropane ring into the aroyl chromophore, causing a smaller energy difference between the ground and excited electronic states of the 2-phenylcyclopropyl ketones as compared to the analogous energy difference in the unsubstituted cyclopropyl ketones.

It is interesting to contrast the above results and conclusions with those of Eastman,[23a,b] who suggested that the cyclopropane ring lacks the ability of transmitting conjugative effects between contiguous unsaturated groups. We agree that the effects are small[23b] but believe they are definitely present.

Eastman's conclusions were based on studies of substituted acetylvinylcyclopropane[23b] and derivatives of the bicyclic umbellulone.[23a] In molecules containing a bicyclic arrangement of the cyclopropane ring one might not expect to detect a significant transmission of conjugative effects through the three ring. Evidence of the effect of steric restriction in bicyclic three-ring carbonyl compounds (ethylenimines and ethylene oxides) has been presented previously.[24] It was suggested that for the unsaturated group in the position beta to the carbonyl to manifest maximal effect, the β-substituent and the carbonyl group must have some freedom of orientation about their respective bonds to the three ring. Evidence for an electronic interaction between a vinyl group, cyclopropane ring and a carbonyl group has been claimed by others[23c] for the 1-acetyl-1-carboethoxy-2-vinylcyclopropane. Our results confirm the findings of Corey and Burke[23d] that cross-conjugation of carbon-to-carbon unsaturation and a cyclopropane ring to a carbonyl group has little effect on the carbonyl associated chromophore in the excited state (compare values G and VI in Table II with A and D in Table I or with values F and H in Table II). However, in the ground state the interaction of the cyclopropane ring makes a significant contribution to the single bond character of the carbonyl group in such cross conjugated systems (compare the infrared carbonyl bands for 4-phenylbenzoylcyclopropane, Table III, with those for *p*-phenylbutyrophenone,[3e] 1680 cm.$^{-1}$ (Nujol), 1687 cm.$^{-1}$ (CCl_4)). Because of the basic simplicity of the cyclopropyl ketones (G, VI, V and I, discussed in the present study, these results seem to present unambiguous evidence that a cyclopropane ring can transmit conjugative effects, especially in the excited state.

It has been shown that in a given pair of β-substituted ethylenimine[3c—e] or ethylene oxide ketone[4,25] stereoisomers, the isomer possessing the *trans* structure exhibits a carbonyl associated ultraviolet absorption maximum at longer wave lengths and with greater intensity than does the *cis* isomer. This comparison has now been extended to cyclopropane carbonyl compounds. The difference in light absorptions is small in the cyclopropane compounds, but in the three pairs of stereoisomers reported in this study (Ia and Ib, *trans*- and *cis*-2-phenylcyclopropanecarbonylcarboxylic acids, *trans*- and *cis*-*p*-nitrobenzyl 2-phenylcyclopropanecarboxylates), the isomer which exhibits a carbonyl associated absorption maximum at an equal or lower frequency and greater intensity in both the ultraviolet and infrared ranges of the spectrum is the one to which the *trans* configuration is assigned, also based on other considerations; see Table III.

The stereochemical configuration of the *cis* and *trans* isomers of 2-phenylcyclopropanecarboxylic acids has been elucidated by the excellent chemical evidence of Burger and Yost.[17] The *p*-nitrobenzyl esters exhibit the expected spectral differences

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(22) R. P. Mariella and R. R. Raube, THIS JOURNAL, **74**, 521 (1952).

(23) (a) R. H. Eastman, *et al.*, *ibid.*, **76**, 4115, 4118 (1954); (b) **77**, 6642 (1955); (c) R. W. Kierstead, R. P. Linstead and B. C. L. Weedon, *J. Chem. Soc.*, 1799 (1953); (d) E. J. Corey and H. J. Burke, THIS JOURNAL, **76**, 5258 (1954).

(24) N. H. Cromwell and G. V. Hudson, *ibid.*, **75**, 872 (1953).

(25) H. H. Wasserman and N. E. Aubrey, *ibid.*, **77**, 590 (1955).

Table III

Ultraviolet and Infrared Absorption Spectra of Cyclopropanecarbonyl Compounds and Precursors

	Ultraviolet max.[a]		Infrared bands cm.$^{-1}$		Approx. % abs.[b]
	λ, mμ	ε × 10^{-3}	Band	CCl_4	Nujol mull
β-Ethoxy-4-phenylpropiophenone	278	22.9	C=O	1678/76	1671/21
			Phenyl	1600/62	1600/9
			$-CH_2OCH_2-$	1112/76	1110/16
β-Methoxy-4-phenylpropiophenone	277	23.6	C=O	.....	1668/58
			Phenyl	.....	1598/40
			$-CH_2OCH_2-$	.....	1121/49
4-Phenylacrylophenone (II)	291	22.2	C=O	1666/74	1660/43
			Phenyl	1601/71	1604/43
1-Phenyl-3-(4'-biphenylyl)-pyrazoline	267	16.5		.....	.....
	375	19.3			
2-Phenylcyclopropanecarbonitrile (IV)	..	..	C≡N	2250/87	2250/80[c]
			Phenyl	1608/61	1608/70
			Cyclopropane		1029/34
2-Phenyl-1-benzoylcyclopropane (V)	242	18.2	C=O	1669/89	1668/77[c]
			Phenyl	1600/63	1603/46
			Cyclopropane		1025/54
4-Phenylbenzoylcyclopropane (VI)	276	26.0	C=O	1671/97	1664/56
			Phenyl	1608/78	1605/50
			Cyclopropane	1041/71	1035/31
trans-1-(4'-Phenylbenzoyl)-2-phenylcyclopropane (Ia)[d]	280	28.0	C=O	1667/92	1655/51
			Phenyl	1605/77	1605/29
			Cyclopropane	1034/70	1036/49
cis-1-(4'-Phenylbenzoyl)-2-phenylcyclopropane (Ib)[d]	280	23.0	C=O	1670/92	1664/66
			Phenyl	1605/77	1605/19
			Cyclopropane	1028/40	1027/13
trans-2-Phenylcyclopropanecarboxylic acid (m.p. 93°)	232	2.92	C=O	1688/59	1685/69
	267	0.033	Phenyl	1607/9	1602/31
			Cyclopropane		1025/28
cis-2-Phenylcyclopropanecarboxylic acid (m.p. 107°)	227	2.83	C=O	1694/67	1689/69
	261	0.018	Phenyl	1601/11	1608/29
			Cyclopropane		1024/15
trans-p-Nitrobenzyl 2-phenylcyclopropanecarboxylate (m.p. 65°)	258	12.2	C=O	1731/65	1712/45
			Phenyl	1608/28	1601/24
			Cyclopropane		1033/21
cis-p-Nitrobenzyl 2-phenylcyclopropanecarboxylate (m.p. 74°)	260	10.6	C=O	1737/56	1725/49
			Phenyl	1608/24	1602/25
			Cyclopropane		1030/15

[a] Ultraviolet determinations were made at about 25° at 1 × 10^{-4} molar (except *trans*- and -*cis*-2-phenylcyclopropanecarboxylic acids 1 × 10^{-3} molar) concentrations of 2,2,4-trimethylpentane solutions. 1-Phenyl-3-(4'-biphenylyl)-pyrazoline was examined in pure chloroform solution. The spectra were determined with a Cary recording spectrophotometer using 1-cm. fused silica cells. [b] Infrared spectra determinations were made with a Perkin–Elmer recording instrument model 21 using the solvent as blank. The compounds were examined in Nujol mulls and/or carbon tetrachloride solutions (concentrations 20 mg./ml.) using 1.0-mm. matched NaCl cells between 650 and 4000 cm.$^{-1}$. [c] The infrared spectra of these compounds were obtained by applying a thin film of the compound on the sodium chloride plate of the cell. [d] These results were obtained by Dr. Hudson, see ref. 26.

(Table III) and this constitutes further evidence for their structural assignment.

On the basis of (a) the lower melting isomer being formed exclusively in three and predominantly in a fourth method of synthesis, (b) the greater intensity of absorption in the ultraviolet of the low melting isomer and (c) the lower frequency carbonyl band absorption in the infrared, we assign the *trans* configuration to the lower melting isomer of 1-(4'-phenylbenzoyl)-2-phenylcyclopropane (Ia).

It is of interest to compare in a semi-quantitative manner the differences in carbonyl associated ultraviolet and infrared absorption maxima of the stereoisomeric pairs of three-ring carbonyl compounds which have been prepared in these interrelated studies (Table IV).

In all 11 pairs of isomers listed in Table IV the *trans* isomer exhibited a carbonyl associated absorption maximum in the ultraviolet region at a longer wave length[27] and/or higher intensity than the *cis* isomer. Wasserman,[25] from his chemical and spectral study of several pairs of stereoisomeric ethylene

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(26) G. V. Hudson, research assistant to N. H. Cromwell, May, 1953, University of Nebraska.

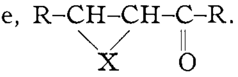
(27) The ultraviolet absorption spectra of *cis*- and *trans-p*-nitrobenzyl 2-phenylcyclopropanecarboxylates were very similar. The anomalous order of the wave lengths of the maxima was not borne out by the absorption intensities in the ultraviolet nor by the carbonyl maxima wave numbers in the infrared spectra. Moreover, the powerful chromophoric activity of the $p-NO_2C_6H_4-$ group may mask the effect of the carbonyl associated absorptions.

TABLE IV

SPECTRAL DIFFERENCES[a] IN THREE-RING CARBONYL COMPOUNDS

Ethylenimine	Ultraviolet $\Delta\lambda_{max}$, mμ	Ultraviolet $\Delta e \times 10^{-3}$	Infrared Δwave no. cm.$^{-1}$ Nujol mull	Infrared Δwave no. cm.$^{-1}$ CCl_4 or $CHCl_3$
1-Benzyl 2-phenyl-3-benzoyl[b]	5	1.8	17	15
1-Benzyl-2-phenyl-3-*p*-toluyl[b]	8	2.0	20	..
1-Cyclohexyl-2-phenyl-3-benzoyl[b]	2	5.1	18	..
1-Cyclohexyl-2-phenyl-3-*p*-toluyl[b]	5	2.8	32	19
1-Cyclohexyl-2-phenyl-3-(4′-phenylbenzoyl)[c]	6	6.3	29	..
1-Methyl-2-phenyl-3-(4′-phenylbenzoyl)[c]	7	6.1	21	..
1-Cyclohexyl-2-methyl-3-(4′-phenylbenzoyl)[d]	5	2.8	17	21
Ethylene oxide				
1-(*o*-Nitrophenyl-2-benzoyl[e]	1	1.4	..	0
Cyclopropane				
1-(4′-Phenylbenzoyl)-2-phenyl	0	5.0	9	3
1-Carboxyl-2-phenyl	5	0.9	4	6
	6	0.015		
2-Phenyl-1-carbo-*p*-nitrobenzyloxy	−2	1.6	13	6

[a] All the increments listed were calculated by subtracting the respective spectral constants for the *cis* isomer from those of the *trans* isomer. [b] Ref. 3c. [c] Ref. 3d. [d] Ref. 3e. [e] Ref. 4.

oxide ketones, reported the same phenomena. The characteristic carbonyl band maxima in the infrared range occurred at a lower frequency for the *trans* isomer in the cases studied (Table IV), except for the isomeric 1-*o*-nitrophenyl-2-benzoylethylene oxides where the *cis* and *trans* forms have identical carbonyl band frequencies.[4] Therefore, as suggested previously,[3d] spectral methods may be used to assign the configurations to *cis* and *trans* three-ring compounds of the type,  $R-\underset{\diagdown\, X\,\diagup}{CH-CH}-\underset{\overset{\|}{O}}{C}-R$. It was also suggested previously[3d] that in the *trans* forms of aryl-aroyl-ethylenimines, ethylene oxides and cyclopropanes the π-orbitals of the formally unsaturated groups (carbonyl, phenyl) can be arranged to provide for maximum overlap with the *bent* bond orbitals of the three-ring. This *trans* arrangement provides for a more extensive polycentric molecular orbital than is possible with the more sterically hindered *cis* isomer. These theoretical hypotheses have been well supported by the spectral studies which have been made to date.

Slabey,[28] from a study of 34 cyclopropane derivatives, concluded that a moderately strong absorption band in the 1000 to 1050 cm.$^{-1}$ region of the infrared could be used to determine the presence of the cyclopropane ring. It is interesting to note that in the infrared spectra of all the cyclopropyl compounds reported in this present study, there is strong absorption in the 1000 to 1050 cm.$^{-1}$ region (Nujol mull) with a moderately strong absorption band centered in the 1024 to 1036 cm.$^{-1}$ region. In general the infrared spectra in Nujol of the *trans* isomers have more fine structure in the 1000 to 1400 cm.$^{-1}$ region than do the corresponding *cis* isomers.

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Experimental[29]

Reaction of α-Diazo-4-phenylacetophenone with Styrene.—The preparation of 4-phenylbenzoic acid by a modification of the method of Cason and Rapoport[30] employing hypohalite oxidation of 4-phenylacetophenone was used. If an excess of potassium hydroxide, 31% greater than the amount recommended,[30] was used, yields of 89–98% of theoretical were obtained. Addition of small portions of dioxane during the addition of the hypohalite solution aided in maintaining a homogeneous liquid phase. 4-Phenylbenzoic acid was converted to the acid chloride[31] in 94% yield.

Ten grams of α-diazo-4-phenylacetophenone (prepared in 69% yield by the method of Erickson[32] from 4-phenylbenzoyl chloride) was dissolved in 100 ml. of styrene and added over a 2–5 hour period to 50 ml. of styrene. The reaction mixture was held at 140° during the addition and nitrogen was evolved. Excess styrene was removed by vacuum distillation and the sirupy residue mixed with chloroform and methanol to precipitate large amounts of polymerized styrene. Evaporation of the solvent left a sirupy residue. This was crystallized from methanol to give 4.0 g. of solid product. A 2-g. sample of this material was chromatographed on activated alumina to give 0.7 g. of a compound melting at 127–128°, 0.1 g. of material melting at 139–141°, and 0.8 g. melting at 111–130°. The total yield represented 23% of the theoretical amount of 1-(4′-phenylbenzoyl)-2-phenylcyclopropane (I).[25] Attempts to repeat the chromatographic separation on another sample of the crude material from the reaction was unsuccessful. The two sharp-melting solids from the chromatogram were recrystallized from methanol to give compounds melting at 129–130° (Ia) and 144–145° (Ib), respectively. A mixture of Ia and Ib melted at 113–126°.

Anal. Calcd. for $C_{22}H_{18}O$: C, 88.56; H, 6.08. Found (C) for (Ia): C, 88.66; H, 6.23. Found (C) for (Ib): C, 88.81; H, 6.30.

A **2,4-dinitrophenylhydrazone** derivative of the low melting isomer Ia was prepared and recrystallized from ethyl acetate, m.p. 206–207°.

Anal. Calcd. for $C_{28}H_{22}N_4O_4$: C, 70.28; H, 4.64; N, 11.71. Found (C): C, 70.66; H, 4.80; N, 11.38.

A typical experiment in the reaction of α-diazo-4-phenylacetophenone with styrene in the presence of copper powder was as follows: a mixture of 0.1 g. of purified copper powder and 2.5 g. of styrene (stabilized) was heated to 100° with stirring. A cooled solution of 1 g. (0.0045 mole) of α-diazo-4-phenylacetophenone in 15 g. of styrene (total amount of styrene used was 0.17 mole) was added to the mixture over a period of 75 minutes. The mixture was stirred for 30 minutes, cooled, and diluted with methanol. An amount of slimy polymeric material was removed by filtration and the solvents removed by evaporation *in vacuo*. The semi-solid residue was boiled with methanol, an amount of tan resinous material removed by filtration, and the solution decolorized with charcoal. Cooling yielded 0.5 g. (40% of theory) of solid melting at 116–130°. The crude product was recrystallized from 95% ethanol or benzene and petroleum ether (b.p. 30–60°) to give only the low melting isomer (129–130°) of 1-(4′-phenylbenzoyl)-2-phenylcyclopropane (Ia). In an experiment employing freshly distilled styrene, *without* the commercial stabilizer *t*-butylcatechol, a 44% yield of Ia was obtained.

Several experiments were attempted using a similar procedure in which α-diazo-4-phenylacetophenone (0.02 mole) reacted with *o*-nitrostyrene[6] (0.04 mole) in the presence of copper powder. Upon steam distillation of the reaction mixture 63% of the original amount of *o*-nitrostyrene was recovered. During reaction, 85% of the theoretical amount

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

(29) The microanalyses were carried out by either the Clark Microanalytical Laboratory (C), Urbana, Ill., or Micro-tech Laboratories (M), Skokie, Ill. The melting points are uncorrected.

(30) J. Cason and H. Rapoport, "Laboratory Text in Organic Chemistry," Prentice–Hall, Inc., New York, N. Y., 1950, p. 351.

(31) A. F. Thompson and N. H. Cromwell, THIS JOURNAL, **61**, 1374 (1939).

(32) J. L. E. Erickson, J. M. Dechary and M. R. Kesling, *ibid.*, **73**, 5302 (1951).

of nitrogen was evolved, but only polymeric solids with high (*ca.* 200°), indefinite melting points could be isolated.

Reaction between Di-(4-biphenylyl)-cadmium and 2-Phenylcyclopropanecarbonyl Chloride.—The procedure for the preparation of the intermediate 4-biphenylyllithium was similar to that of Gilman.[7c] A 1.2-g. (0.17 gram atom) portion of freshly scraped lithium was cut into *ca.* 250 pieces and dropped, through a stream of dry nitrogen, into 25 ml. of absolute ether in a dry flask fitted with a sealed ball-joint stirrer, condenser, and dropping funnel. The entire system was flushed with nitrogen previous to the addition of the reagents, and the reaction was run under nitrogen at *ca.* 2–4 mm. pressure. A solution of 18.3 g. (0.08 mole) of 4-bromobiphenyl in 75 ml. of absolute ether was added to the stirred mixture over a period of 35 minutes. The mixture was heated under reflux during the addition and for 1.8 hours at the end of the addition. The gray mixture was cooled, and 7.8 g. (0.042 mole) of anhydrous cadmium chloride[33] was added, in an anhydrous manner, over a period of 5–10 minutes. The black mixture was heated under reflux with stirring for 4 hours, allowed to stand overnight, and refluxed for an additional 6 hours. Gilman tests[33] for biphenylyllithium, taken periodically, were strongly positive. The ether was removed by distillation (until the slurry became very viscous) and 18 ml. of dry benzene was added. A solution of 11 g. (0.06 mole) of 2-phenylcyclopropanecarbonyl chloride[17] in 11 ml. of dry benzene was added to the mixture over a period of 10 minutes. A barely perceptible spontaneous reflux rate was noted during the addition. The reaction mixture, cooled to 5°, was poured onto a mixture of crushed ice and water followed by sufficient 20% sulfuric acid to give two phases. The benzene layer was washed successively with water, 5% sodium carbonate solution, and saturated sodium chloride solution, dried over anhyd. sodium sulfate, and evaporated somewhat. Petroleum ether (30–60°) was added, a small amount of polymeric material removed by filtration, and the solution evaporated and cooled further to yield crude solid material and a tan oil. Extraction of these crude materials with hot methanol and cooling gave 3.7 g. (20% of theory based on the acid chloride) of solid melting from 85–130°. A sample of this product was subjected to chromatographic separation on activated alumina using dry benzene to place the material on the column. A 1–100 absolute alcohol–benzene solution was used as developer and eluent. The material was further eluted from the column with 2–100 absolute alcohol–benzene solution. Only biphenyl and the low melting isomer of 1-(4′-phenylbenzoyl)-2-phenylcyclopropane (Ia) (mixed m.p. experiment) were found in the eluate.

Two attempts to acylate biphenyl with 2-phenylcyclopropanecarbonyl chloride employing the Friedel–Crafts method were unsuccessful. One run, employing carbon disulfide as solvent, and following the procedure of Fuson and Baumgartner,[34] yielded only tan oil. Another run, employing *sym*-tetrachloroethane as solvent,[3e] also produced only a tan oil.

β-Chloro-4-phenylpropiophenone.—A 10-g. (0.079 mole) sample of β-chloropropionyl chloride and 15.9 g. (0.103 mole) of biphenyl were dissolved in 40 ml. of pure carbon disulfide and the solution cooled to 5°. A 13.7-g. (0.103 mole) sample of anhydrous aluminum chloride was added over a period of one hour to the cooled stirred solution. The green colored mixture was stirred for 10 minutes at 5° and for 30 minutes while it was warmed to 35°. A 25-ml. portion of carbon disulfide was added during the reaction. The reaction mixture was poured onto a mixture of ice and concd. hydrochloric acid, benzene was added until the solid dissolved. The organic layer was dried (sodium sulfate) and petroleum ether (30–60°) was added. On cooling 16.2 g. (84% of theory) of solid material, m.p. 115–120°, was obtained. Recrystallization from benzene and petroleum ether[35] gave white planks, m.p. 120.5–121.5°.

Anal. Calcd. for $C_{15}H_{13}OCl$: C, 73.60; H, 5.35. Found (M): C, 73.66; H, 5.44.

4-Phenylacrylophenone (II). (a).—A 10-g. (0.041 mole) sample of β-chloro-4-phenylpropiophenone was dissolved in 350 ml. of 95% ethanol and 4.4 g. (0.045 mole) of anhydrous potassium acetate was added. The mixture was refluxed for 3.5 hours, cooled and filtered. The white, water-soluble solid represented an 82% yield of potassium chloride. The filtrate was evaporated (nitrogen ebullition) and cooled to give 5.8 g. (68%) of material melting at 83–86°. Recrystallization from benzene and petroleum ether, then methanol, gave slightly cream colored plates, m.p. 89.5–90.5°.

Anal. Calcd. for $C_{15}H_{12}O$: C, 86.51; H, 5.81. Found (M): C, 86.52; H, 5.92.

(b).—To 20 g. (0.081 mole) of β-chloro-4-phenylpropiophenone in 720 ml. of 95% ethanol was added 6.2 g. (0.045 mole) of anhydrous potassium carbonate. The mixture was refluxed for 2 hours, cooled and filtered. The white, water-soluble solid represented a 94% yield of potassium chloride. Evaporation and cooling of the filtrate and recrystallization of the crude product from petroleum ether gave 7.3 g. (43%) of 4-phenylacrylophenone (II). In four similar experiments two runs yielded mixtures from which 4-phenylacrylophenone could not be isolated easily; one run yielded only a rubber-like polymer, and another, employing mechanical stirring, gave a 95% yield of β-ethoxy-4-phenylpropiophenone, m.p. 62–63°.

Anal. Calcd. for $C_{17}H_{18}O_2$: C, 80.28; H, 7.13. Found (M): C, 80.37; H, 7.26.

(c).—A methanolic solution of 1.0 g. (0.004 mole) of β-chloro-4-phenylpropiophenone and 0.25 g. (0.0045 mole) of potassium hydroxide was refluxed for 2 hours. After cooling and removal of the potassium chloride, 0.49 g. of solid melting at 69–70° was collected. Recrystallization from benzene and petroleum ether gave white needles of β-methoxy-4-phenylpropiophenone, m.p. 69–70°.

Anal. Calcd. for $C_{16}H_{16}O_2$: C, 79.97; H, 6.71. Found (M): C, 80.13; H, 6.85.

Attempts to prepare 4-phenylacrylophenone by dehydrochlorination of β-chloro-4-phenylpropiophenone employing potassium carbonate in isopropyl alcohol, absolute ethanol, 60% aqueous ethanol or dioxane failed to yield the desired product.

(d).—A 5-g. (0.025 mole) sample of β-chloro-4-phenylpropiophenone was added to 36.5 g. (0.36 mole) of stirred triethylamine at 60° over a period of 10 minutes. A flocculent solid separated upon addition of the chloroketone to the triethylamine. The mixture was stirred for 15 minutes at 60°, cooled to 5°, and filtered. The solid triethylamine hydrochloride was washed with absolute ether (25 ml.) and found to weigh 2.6 g. (93%). The filtrate and ether washings were added to 40 ml. of cold water with stirring. The organic layer was washed successively, three times with cold 20% acetic acid, once with cold 0.5 *M* hydrochloric acid, once with cold 20% acetic acid, and twice with cold water. The contact time of the two phases was as short as possible. The ether layer was dried for 45 minutes over magnesium sulfate; an amount of calcium chloride was added, and the mixture allowed to stand for 1 hour. After filtration the solvent was completely removed *in vacuo* with gentle heating (40°). The yellow solid was recrystallized from benzene and petroleum ether to give 1.8 g. (41%) of 4-phenylacrylophenone.

The following experiments were done to establish the structure of 4-phenylacrylophenone (II): (i) A strong positive Baeyer potassium permanganate test for olefinic double bonds was obtained.

(ii) The dibromide of 4-phenylacrylophenone was prepared by addition of bromine in carbon tetrachloride to a carbon tetrachloride solution of II. The product melted at 92–94° after one recrystallization. In a previous publication[3c] the melting point of α,β-dibromo-4-phenylpropiophenone was reported to be 85–86°. A sample of this compound was obtained from supplies in this Laboratory and, after several recrystallizations from ethanol, melted at 94–95°. A mixed melting point experiment of the product from the bromination reaction of 4-phenylacrylophenone with a pure sample of α,β-dibromo-4-phenylpropiophenone (m.p. 94–95°) showed no depression.

(iii) A 1.0-g. sample of 4-phenylacrylophenone was hydrogenated to give 0.8 g. (79%) of 4-phenylpropiophenone.[9] A platinum oxide catalyst in absolute ethanol with 45 lb. pressure of hydrogen was used. Recrystallization from 95% ethanol gave white plates melting at 98–99°.

(iv) To a warm solution of 1.3 g. (0.006 mole) of 4-phenylacrylophenone in 5 ml. of glacial acetic acid was added 0.65 g. (0.006 mole) of phenylhydrazine with shaking. The

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[33] J. Cason and F. S. Prout, "Organic Syntheses," Coll. Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1955, p. 601.

[34] R. C. Fuson and F. N. Baumgartner, THIS JOURNAL, **70**, 3255 (1948).

[35] Skellysolve B, b.p. 60–68°.

mixture was heated on a steam-bath for an additional 30 minutes, cooled, and filtered to give 1.38 g. (77%) of 1-phenyl-3-(4′-biphenylyl)-pyrazoline. Recrystallizations from chloroform–ethanol mixture, and benzene and petroleum ether gave chartreuse colored clusters, m.p. 203–205°.

Anal. Calcd. for $C_{21}H_{18}N_2$: C, 84.53; H, 6.08; N, 9.39. Found (M): C, 84.58; H, 6.03; N, 9.57.

This compound gave a strong Knorr[12] test for pyrazolines. The Raiford test[12] was doubtful; on exposure of 1-phenyl-3-(4′-biphenylyl)-pyrazoline to bromine vapor the sample turned black in color. Solutions of this pyrazoline fluoresced vividly upon exposure to ultraviolet light.

(v) A sample of β-ethoxy-4-phenylpropiophenone was de-ethoxylated by the action of phosphorus pentoxide in toluene to give a small yield of 4-phenylacrylophenone (II).

Phenyldiazomethane.—Benzalhydrazine (b.p. 99° (1.7 mm.), 102° (2 mm.)) was prepared in 76% yield according to the procedure of Lock and Stach.[36] In a dry, smooth-glass, bicarbonate-washed erlenmeyer flask was placed 5 g. of anhydrous magnesium sulfate, 14.8 g. (0.064 mole) of silver oxide, 200 ml. of absolute ether and 7.4 g. (0.062 mole) of benzalhydrazine. The flask was stoppered with a new rubber stopper, fitted with a thermometer, and shaken mechanically at 25–30° for 40 minutes. The stopper was occasionally removed to relieve internal pressure. The silver and magnesium sulfate were removed from the deep red solution by filtration and aliquot portions were analyzed by benzoic acid assay. Yields ranged from 58–65% of theory. In one experiment petroleum ether was employed as the solvent (60% yield).

Initial attempts to prepare phenyldiazomethane by alkaline decomposition of 1-benzyl-1-nitroso-3-nitroguanidine, following the method of McKay[37a] (reported yield 75%), gave yields of 10–20%. Recently McKay[37b] has confirmed the low yields reported here.

Reaction of 4-Phenylacrylophenone with Phenyldiazomethane.—A petroleum ether solution of phenyldiazomethane (containing *ca.* 0.12 mole) was added to a well-stirred solution of 2 g. (0.01 mole) of 4-phenylacrylophenone in 50 ml. of dry toluene over a period of 75 minutes at −15 to −5°. A white granular solid separated during the addition. The mixture was stirred for 20 minutes while the temperature was allowed to rise to 0°. After overnight storage in the ice-box, acetic acid in benzene was carefully added until the red color of the mixture changed to yellow. The solution was evaporated to a volume of 20 ml. and petroleum ether was added. From the precipitated material a trace of 1-(4′-phenylbenzoyl)-2-phenylcyclopropane (Ia), m.p. 128–130°, identified by a mixed m.p. experiment, was isolated by a chromatographic separation on alumina.

2-Phenylcyclopropanecarbonitrile (IV).—A 63.1-g. (1.18 moles) sample of freshly distilled acrylonitrile was added to a solution of *ca.* 0.16 mole of phenyldiazomethane in 785 ml. of absolute ether over a period of 35 minutes at 5°. After standing overnight the ether and excess acrylonitrile were boiled off on a steam-bath. The resulting oil was heated for 3 hours at 100–120° *in vacuo* (water jet) until gas evolution became negligible. The tan oil was then distilled rapidly at 114° (3.2 mm.) to give 22.7 g. (65% of theory based on benzalhydrazine) of yellow oil. A sample of this oil was fractionated; a slightly yellow fraction of 2-phenylcyclopropanecarbonitrile (b.p. 102° (1.4 mm.), m.p. 27–30°, $n^{30}D$ 1.5441) was analyzed.

Anal. Calcd. for $C_{10}H_9N$: C, 83.88; H, 6.34; N, 9.78. Found (M): C, 83.99; H, 6.57; N, 9.90.

A sample of 2-phenylcyclopropanecarbonitrile was hydrolyzed in ethanolic sodium hydroxide to give an 89% yield of the low melting isomer of 2-phenylcyclopropanecarboxylic acid.[17]

Reaction of 2-Phenylcyclopropanecarbonitrile with 4-Biphenylylmetallic Compounds.—A solution of 2 g. (0.014 mole) of 2-phenylcyclopropanecarbonitrile in 10 ml. of absolute ether was added to the stirred, refluxing ether mixture of 4-biphenylyllithium, prepared from 6.9 g. (0.03 mole) of 4-bromobiphenyl,[7b] over a period of 12 minutes. The mixture was stirred under reflux for 30 minutes and poured onto crushed ice and aqueous ammonium chloride solution. The decomposition mixture was heated on the steam-bath for one hour to remove the ether, and to ensure complete hydrolysis of the intermediate ketimine. The mixture was cooled and the aqueous phase decanted from a red oil. The oil was dissolved in absolute ethanol. Charcoal treatment and cooling yielded 1.4 g. of yellow solid, m.p. 71–103°. After two recrystallizations, once from isopropyl ether and once from 95% ethanol, the solid melted at 128–130°. A mixed m.p. experiment with 1-(4′-phenylbenzoyl)-2-phenylcyclopropane (Ia) showed no depression.

In another experiment 4-biphenylylmagnesium bromide was prepared following Gilman's[38] procedure except that the ether mixture of magnesium (0.8 g., 0.033 mole) and 4-bromobiphenyl (6.9 g., 0.03 mole) was refluxed for 13 hours (nitrogen atmosphere). This was treated with 2-phenylcyclopropanecarbonitrile (2.0 g., 0.014 mole) in a manner similar to that described above for 4-biphenylyllithium. A 33% yield of crude 1-(4′-phenylbenzoyl)-2-phenylcyclopropane (Ia) was obtained.

Reaction of 2-Phenylcyclopropanecarbonitrile with Phenylmagnesium Bromide.—A solution containing *ca.* 0.046 mole of phenylmagnesium bromide was treated with an ethereal solution of 6 g. (0.042 mole) of 2-phenylcyclopropanecarbonitrile in a manner similar to that described above to give an 85% yield of crude 1-benzoyl-2-phenylcyclopropane (V) as a yellow oil. The oil was fractionated twice. A slightly yellow fraction (b.p. 114° (0.001 mm.), $n^{25}D$ 1.6022) was analyzed. This material slowly crystallized on standing in the ice-box, m.p. 32–34°.

Anal. Calcd. for $C_{16}H_{12}O$: C, 86.45; H, 6.35. Found (M): C, 86.07; H, 6.60.

A 2,4-dinitrophenylhydrazone derivative of 1-benzoyl-2-phenylcyclopropane was prepared, m.p. 215–217°.

Anal. Calcd. for $C_{22}H_{18}N_4O_4$: C, 65.66; H, 4.51; N, 13.92. Found (M): C, 65.78; H, 4.72; N, 13.95.

4-Phenylbenzoylcyclopropane (VI).—A solution of 4-biphenylyllithium[7b] was prepared from 2.75 g. (0.40 gram atom) of lithium and 46.2 g. (0.20 mole) of dry 4-bromobiphenyl in 410 ml. of absolute ether with vigorous stirring. After 15 minutes spontaneous reflux and 5 minutes reflux with external heating almost all of the lithium metal was consumed. A 5.0-g. (0.079 mole) sample of cyclopropyl cyanide[39] in 25 ml. of absolute ether was added and the reaction was carried out as described above to give a 51% yield of crude solid, m.p. 102–106°. Recrystallizations from aqueous ethanol, and benzene and petroleum ether mixtures gave white plates of 4-phenylbenzoylcyclopropane (VI), m.p. 114–115°.

Anal. Calcd. for $C_{16}H_{14}O$: C, 86.44; H, 6.36. Found (M): C, 86.41; H, 6.44.

A 2,4-dinitrophenylhydrazone derivative of 4-phenylbenzoylcyclopropane was prepared, m.p. 227–228°.

Anal. Calcd. for $C_{22}H_{18}N_4O_4$: C, 65.66; H, 4.51; N, 13.93. Found (M): C, 65.48; H, 4.52; N, 14.02.

***cis*- and *trans*-*p*-Nitrobenzyl 2-Phenylcyclopropanecarboxylate.**—The procedure followed was essentially that of Vogel.[40] A sample of *trans*-2-phenylcyclopropanecarboxylic acid[17] was converted to the silver salt in 80% yield. The silver salt was treated with a benzene solution of *p*-nitrobenzyl bromide and stirred under reflux for 36 hours. An 89% yield of ester, m.p. 60–64°, was obtained. Recrystallizations from benzene and petroleum ether and then 95% ethanol gave white needles of *trans*-*p*-nitrobenzyl 2-phenylcyclopropanecarboxylate, m.p. 65–66°.

Anal. Calcd. for $C_{17}H_{15}NO_4$: C, 68.67; H, 5.08. Found (C): C, 68.87; H, 4.56.

A sample of *cis*-2-phenylcyclopropanecarboxylic acid[17] was changed into the silver salt in 57% yield, and the salt was converted to the ester in 70% yield. Recrystallizations from benzene and petroleum ether then aqueous ethanol gave white needles of *cis*-*p*-nitrobenzyl 2-phenylcyclopropanecarboxylate, m.p. 74–75°.

Anal. Calcd. for $C_{17}H_{15}NO_4$: C, 68.67; H, 5.08. Found (M): C, 68.74; H, 5.11.

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(36) G. Lock and K. Stach, *Ber.*, **76**, 1252 (1943).

(37) (a) A. F. McKay, W. L. Ott, G. W. Taylor, M. N. Buchanan and J. F. Crooker, *Can. J. Res.*, **28B**, 683 (1950); (b) private communication, A. F. McKay to R. J. Mohrbacher, May 9, 1956.

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