Preparation of *m*- and *p*-Substituted Benzalacetones, 2-Phenylcyclopropyl Methyl Ketones and Benzylacetones

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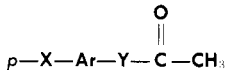
Thirty-seven ketones of the type *m*- or



were prepared; 13 of Y = —CH=CH— (I), 11 of Y = cyclo-C_3H_4 (II), and 13 of Y = —CH_2—CH_2— (III); of new compounds, four of I, 10 of II, and four of III are reported. Since the trans-configuration of ketones I and II was required, procedural modifications of published methods were developed or reaction parameters were varied to affect products in the desired manner. Substituents X include —NO_2, —CN, —Cl, CH_3O—, —CH_3, $(CH_3)_2N$—, and —NH_2. The infrared and ultraviolet spectra are reported.

To investigate the spectral properties of *m*- and *p*-substituted benzalacetones (I), 2-phenylcyclopropyl methyl ketones (II), and benzylacetones (III), a number of compounds were prepared. A search of the literature revealed that, although several ketones I and III are known, only one of ketone II had been reported (*33*) and no recent spectral data had been reported for any.

In the course of extending the synthetic utility of several published methods, it was found that procedural modifications were often necessary to effect good yields. Furthermore, in several instances, the product obtained differed in configuration from that previously reported or was dependent on reaction conditions. Since ketones I and II needed to be prepared in the trans-configuration for valid comparison, efforts were directed toward determining reaction parameters which would produce the desired results. The present communication describes the synthesis and ultraviolet and infrared spectra of 37 compounds, 18 of which had not been previously reported.

EXPERIMENTAL

Melting points were determined on a Thomas Hoover Uni-melt apparatus and were corrected. Elemental analyses were determined by Galbraith Laboratories, Inc., Knoxville, Tenn. Purity of liquid samples was checked on an Aerograph Hy-Fi Model 600C instrument with an SE-30 column. Infrared spectra were obtained using a Perkin-Elmer Model 521 or 527 spectrophotometer, utilizing KBr pellets for solids and NaCl plates with liquid samples. A Varian T-60 or HA-100 spectrometer was used for the nmr spectra with deuterated chloroform–1% TMS as a solvent. Ultraviolet spectra were determined on a Perkin-Elmer Model 202 spectrophotometer in 95% EtOH. Starting materials were obtained commercially except in the cases *m*-cyanobenzylbromide (*23*), *m*-cyanobenzaldehyde (*11*, *39*) and *m*-dimethylaminobenzaldehyde (*8*).

***m*- and *p*-Substituted *trans*-Benzalacetones (I).** The substituted benzalacetones were prepared according to published methods or modifications of published methods. The general procedures and reagents, with any variations, are shown in Table I.

***m*- and *p*-Substituted *trans*-2-Phenylcyclopropyl Methyl Ketones (II).** *Method A.* By use of the method of Corey and Chaykovsky (*10*) and the appropriately prepared *m*- and *m*- or *p*-substituted *trans*-benzalacetone, the ketones were prepared on a 0.06–0.10 mole scale and purified by vacuum distillation.

It was necessary to prepare the nitro isomers by separate procedures as follows:

Method B. A sample of diazoacetyl-2-(*p*-nitrophenyl)cyclopropane was prepared (*26*) starting with commercially available *trans*-2-phenylcyclopropane carboxylic acid. The diazo ketone was dissolved in practical grade dioxane and the solution was in turn treated with 47% hydriodic acid (*44*). Replacement of the chloroform with dioxane improved the yield and purity of product which was recrystallized from hot 95% ethanol.

Method C. From *m*-nitrostyrene, *trans*-2-(*m*-nitrophenyl)cyclopropane carboxylic acid was prepared (*41*) and then converted to the corresponding diazo ketone. Recrystallization from benzene–petroleum ether (30–60° C) gave a solid mp 80–81.5°. Using the same procedure as described for the para isomer, the diazo ketone was converted to the methyl ketone. Several attempts were made to isolate the ketone directly but were not successful. The ketone was therefore recovered as a 2,4-dinitrophenylhydrazone and the yield computed based on this derivative.

Table I. Required Reagents in Preparation of Substituted Benzalacetones

Method	Ref	Aldehyde, moles	NaOH, ml of 10%	Acetone, ml (moles)	H_2O, ml	EtOH, ml
A	(*14*)	2.00	50	400 (5.5)	...	...
B	(*20*)	0.16	100	130 (1.8)	870	...
C[a]	(*32*)	0.13	0.12	60 (0.8)	60	...
D	(*35*)	0.42	(0.06)[b]	165 (2.2)	196	122
E[c]	(*6*)	0.46	12.5	150 (2.0)	40	...
F	(*25*)	0.14	(0.015)[b]	240 (3.3)	460	300
G	(*36*)	0.20	100[a]	148 (2.0)	100	...
H[e]	...	0.10	15[d]	35 (0.5)	15	21

[a] Required a fourfold increase in base with stirring overnight to obtain the *m*-CN isomer. [b] Moles of solid NaOH. [c] The aldol was dehydrated with an ethanol–hydrochloric acid mixture (see Method C). [d] NaOH, 0.5%, in ml. [e] Stirred for 18 hr at 25° C.

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Table II. Physical Properties of X—Ar—Y—CO—CH_3

Substituent	Y = —CH=CH— Method[a]	Yield, %	Bp, °C/mm or mp, °C	Ref	Y = cyclo-C_3H_4 Method	Yield, %	Bp, °C/mm or mp, °C	Ref	Y = —CH_2—CH_2— Method	Yield, %	Bp, °C/mm or mp, °C	Ref
p-NO_2	I-C	69	106–107	(*32*)	II-B	66	98–99[b]		III-A	34	38–39	(*29*)
m-NO_2	I-C	66	93–94	(*43*)	II-C	68	...[c]		III-A	72	43–44	(*4*)
p-CN	I-C	38	105–106[b]		...	...	...		III-A	37	51–52[b]	
m-CN	I-C	34	81–82[b]		...	...	...		III-A	42	109/0.22[b]	
m-Cl	I-B	76	30–31	(*20*)	II-A	36	75/0.2[b]		III-A	44	82/0.50	(*4*)
p-Cl	I-F	44	58–59	(*25*)	II-A	49	94/0.16[e]		III-A	44	73/0.17	(*4*)
m-CH_3O	I-B	78	103/0.03	(*3*)	II-A	41	90/0.16[b]		III-B	87	82/0.15	(*38*)
H	I-A	50	40–41	(*14*)	II-A	57	58/0.2	(*12*)	...	...	...[d]	
p-CH_3	I-A	25	33–34	(*17*)	II-A	54	66/0.07[b]		III-B	89	59/0.15	(*40*)
m-$(CH_3)_2N$	I-H	54	50–51[b]		II-A	39	96/0.01[e]		III-B	72	90/0.01[b]	
p-CH_3O	...	...	...[a]		II-A	53	98/0.3[b]		III-B	60	72/0.02	(*31*)
p-NH_2	I-G	25	97–98	(*13*)	...	...	...		III-B	...	...[f]	(*28*)
p-$(CH_3)_2N$	I-D	83	133–134	(*35*)	II-A	38	47–48[b]		III-B	77	47–48	(*27*)

[a] Refers to method listed in Table I. [b] Elemental analyses (C, H, N, or Cl) in agreement with theoretical values have been obtained (Galbraith Laboratories, Inc., Knoxville, Tenn.) and submitted for review. [c] 2,4-Dinitrophenylhydrazone, mp 167–168°. [d] Commercial source. [e] 2,4-Dinitrophenylhydrazone. [f] 2,4-Dinitrophenylhydrazone.

m- and p-Substituted Benzylacetones (III). *Method A.* The syntheses were repeated as set forth by Boatman *et al.* (*4*), using the appropriately substituted benzyl chloride or bromide. Though the authors (*4*) were unable to isolate the *p*-nitro isomer, this ketone may be obtained if the black residue from the reaction mixture is first washed with water to remove K_2CO_3 and then distilled under reduced pressure.

Method B. The hydrogenation was carried out in a 500-ml pressure bottle on a Parr shaker apparatus at 2.5–3.0 atm of hydrogen. The substituted benzalacetone (0.05–0.10 mole) to be reduced was taken up in 95% ethanol (100–150 ml) to which was added 10% Pd/C (0.05–0.10 gram) as a catalyst. After the correct amount of hydrogen had been taken up, the solution was filtered, the ethanol removed, and the residue vacuum-distilled.

The *p*-amino isomer was prepared by the reduction of the corresponding *p*-nitrobenzalacetone ketal which was synthesized by reaction of the ketone with ethylene glycol (*34*). The *p*-nitro ketal was a light yellow solid with a melting point of 116–117° C. Following reduction, the amino ketal was hydrolyzed in 25% HCl to obtain the ketone. The physical data for the compounds prepared are shown in Table II, and spectral data are contained in Table III. Table IV lists the elemental analysis for previously unreported ketones.

Table III. Spectral Data for X—Ar—Y—CO—CH_3 Compounds

X Substituent	Y = —CH=CH— λ^a_{max}	$\epsilon \times 10^{-4}$	C=O, cm^{-1}	Y = cyclo-C_3H_4 λ^a_{max}	$\epsilon \times 10^{-4}$	C=O cm^{-1}	Y = —CH_2—CH_2— λ^a_{max}	$\epsilon \times 10^{-1}$	C=O cm^{-1}
p-NO_2	216	1.25	1665[b,c]	216	1.05	1687[b]	276	0.98	1705[b]
	306	2.13	1688[d]	290	1.13				
m-NO_2	268	2.52	1678[b]	(264)[e]	(0.65)	1699[f]	265	0.72	1709[b]
			1692						
p-CN	219	1.31	1665[b]	...	...	...	233	1.72	1703[b]
	287	2.72	...						
m-CN	228	2.22	1671[b]	...	...	...	228	1.03	1715[f]
	276	1.95	1708						
m-Cl	224	1.45	1668[f]	220	1.07	1698[f]	213	0.94	1695[f]
	282	1.88	1691						
p-Cl	223	1.14	1657[b]	230	1.44	1700[f]	221	1.10	1710[f]
	290	2.29	1683						
m-CH_3O	239	0.95	1660[f]	...	...	1697[f]	217	0.71	1705[f]
	287	1.54	1685	281	0.25	...	...	...	...
H	221	1.21	1678[f]	226	0.97	1694[f]	...	...	1720[f]
	289	2.14	1694						
m-CH_3	225	1.12	1670[f]	229	0.91	1690[f]	208	0.90	1715[f]
	291	1.80	1692						
p-CH_3	226	1.08	1663[f]	230	1.00	1693[f]	212	0.91	1715[f]
	298	2.24	1688						
m-$(CH_3)_2N$	272	2.46	1667[b]	253	1.24	1694[f]	255	1.14	1716[f]
	384	0.22	1688	302	0.24		301	0.22	...
p-CH_3O	233	1.04	1630[b]	237	1.06	1695[f]	225	0.90	1710[f]
	320	2.35	1655						
p-NH_2	244	0.79	1627[b]	...	...	...	245	1.03	1690[b]
	367	2.40	1658						
p-$(CH_3)_2N$	252	1.00	1647[b]	265	1.20	1693[e]	255	1.33	1700[b]
	389	2.88	1665	393	0.10	...	304	0.19	...

[a] Spectra obtained in 95% ethanol. [b] KBr pellet. [c] Band due to *s*-trans conformer. [d] Band due to *s*-cis conformer. [e] Oxime derivative. [f] Thin film.

Table IV. Analysis of New Ketones

No.	X	Formula	No.	X	Formula
	m- and *p*-Substituted Benzalacetones			2-(*m*- and *p*-Substituted Phenyl)-cyclopropyl Methyl Ketones	
1	*p*-CN	$C_{11}H_9NO$	10	*m*-CH_3	$C_{12}H_{14}O$
2	*m*-CN	$C_{11}H_9NO$	11	*p*-CH_3	$C_{12}H_{14}O$
3	*m*-CH_3	$C_{11}H_{12}O_2$	12	*m*-$(CH_3)_2N$[b]	$C_{13}H_{17}NO$
4	*m*-$(CH_3)_2N$	$C_{12}H_{15}NO$	13	*p*-CH_3O	$C_{12}H_{14}O_2$
	2-(*m*- and *p*-Substituted Phenyl)-cyclopropyl Methyl Ketones		14	*p*-$(CH_3)_2N$	$C_{13}H_{17}NO$
				m- and *p*-Substituted Benzylacetones	
5	*p*-NO_2	$C_{11}H_{11}NO_3$			
6	*m*-NO_2[a]	$C_{11}H_{11}NO_3$	15	*p*-CN	$C_{11}H_{11}NO$
7	*m*-Cl	$C_{11}H_{11}ClO$	16	*m*-CN	$C_{11}H_{11}NO$
8	*p*-Cl	$C_{11}H_{11}ClO$	17	*m*-CH_3	$C_{11}H_{14}O$
9	*m*-CH_3O	$C_{12}H_{14}O_2$	18	*m*-$(CH_3)_2N$	$C_{12}H_{17}NO$

[a] 2,4-Dinitrophenylhydrazone, mp 167–168° C. [b] 2,4-Dinitrophenylhydrazone, mp 149–150° C.

RESULTS AND DISCUSSION

The preparation of substituted benzalacetones (I) proceeded smoothly using the Claisen-Schmidt reaction to condense acetone with the appropriate aldehyde. The most difficult ketone on this series to prepare was the *m*-dimethylamino derivative (Table II). Unlike the conditions used in the synthesis of *p*-dimethylaminobenzalacetone, the meta-isomer required only 0.5% NaOH to catalyze its formation, and though 3-dimethylaminobenzaldehyde is apparently stable to concentrated base (*8*), the condensation with acetone at higher base strengths led to polymeric mixtures.

The nmr spectra of ketones I, II, and III showed an acetyl methyl signal between 7.58 and 7.90 τ as expected for methyl protons deshielded by a carbonyl group. Absorption in the aromatic region was typical for the disubstituted ring and supported the proposed structure, and, for the benzalacetones, the geometry about the carbon-carbon double bond was established as trans- since the olefinic protons exhibited a coupling constant of 16 Hz.

The preparation of the benzylacetones (III) was achieved in a one-step reaction either by hydrogenation of the analogous benzalacetone or by an alkylation-cleavage reaction involving a substituted benzyl halide and acetylacetone in an ethanol–potassium carbonate mixture (*4*).

Though substituted cyclopropyl ketones can be prepared in a number of ways (*9*), the general method developed by Corey and Chaykovsky (*10*) was found to be the most useful. It has been reported that methylene insertion into an α,β-unsaturated ketone using the dimethyloxosulfonium methylide leads to a cyclopropane product composed of cis- and trans- isomers (*1*). This was not observed within the series of *m*- and *p*-substituted cyclopropyl ketones prepared here. Only the trans disubstituted cyclopropane derivative was obtained from the mixture. No cis- isomer could be detected by nmr or vapor phase chromatography (VPC).

It appears from our work that the reaction conditions employed by Agami and Prevost (*2*) led to the thermodynamic product and that the reaction was indeed stereospecific. To support this, a sample of the *trans*-2-phenylcyclopropyl methyl ketone was refluxed in methanol containing a trace of sodium methoxide for several hours. The nmr or the base-treated ketone gave rise to a new peak at 0.27 ppm higher field than that for the *trans*-acetyl-methyl group, suggesting the presence of the cis-isomer.

To prepare the *m*- and *p*-nitro isomers of Series II, it was necessary to turn to other methods of synthesis due to the side reactions that a nitro group undergoes in the presence of a strong nucleophile (*18, 37*). Though Traynelis and McSweeney (*42*) have reported the methylation of various nitro-substituted aromatic compounds with dimethyloxosulfonium methylide, attempts to prepare 2-(*m*-nitrophenyl)cyclopropyl methyl ketone by methylene transfer to the appropriate ethylenic ketone produced only a black viscous tar. On the other hand, nitration of 2-phenylcyclopropyl methyl ketone in the presence of acetic anhydride (*5*) gave a dark yellow oil from which was isolated the *p*-nitro isomer in a 14% yield.

Attention was therefore directed toward a reaction sequence which gave good yields and terminated with the disubstituted cyclopropane in the trans- configuration. An isomeric mixture of *cis*- and *trans*-phenylcyclopropane carboxylic acids can be converted to pure *trans*- through the acid chloride (*7*), and, in the preparation of deoxysugars, a method was reported for the conversion of acid chlorides to the corresponding acetyl group using diazomethane (*44*). The *trans*-2-(*m*- and *p*-nitrophenyl)cyclopropane carboxylic acids were therefore converted to the acid chlorides, reacted with diazomethane, and the resultant diazo ketones treated with hydriodic acid to give the methyl ketones.

It was not possible to isolate the *m*-nitro ketone in the pure state by this method due to contamination with the intermediate α-iodo ketone which on heating or standing decomposed to an entractable black residue. As a consequence, the 2,4-dinitrophenylhydrazone or oxime was prepared immediately after work-up of the product. Subsequent acid hydrolysis of the oxime derivative yielded the *m*-nitro isomer as a light yellow liquid. Interestingly, the preparation of the oxime derivative of the *m*-nitro isomer under basic conditions (pH 9–10) led quickly to a mixture of *cis*- and *trans*-methyl oximes as indicated by the nmr spectrum (70% trans–30% cis). The two forms were separated on a silicic acid column eluting with a benzene–ether mixture. Again it was observed in the nmr spectra that the methyl peak in the cis- derivative appeared at a higher field than that of the trans- form.

The ultraviolet spectra of the α,β-unsaturated ketones were generally characterized by two absorption maxima (Table III). Both bands can be assigned to transitions of the substituted benzene ring, the ^1L_a primary band transition occurring at the shorter wavelength and the "enone chromophore" (*21*) band at the longer wavelength. The position of both bands changed as the substituent was varied, and with the exception of the *p*-NO_2 compound, the maxima underwent a bathochromic shift with electron donating substituents.

An exception to the assignment of bands exists for the *m*-NO_2, *p*-NO_2, and *p*-CN compounds. The *m*-NO_2 derivative gave only one maximum, that arising from the ^1L_a transition. The *p*-NO_2 and CN isomers gave two bands, but in these cases the shorter wavelength maximum can be assigned to the ^1B transition and the longer wavelength maximum to the ^1L_a transition (*22*).

In the spectra of the ketones II and III, the most prominent adsorption was the primary band of the substituted phenyl ring. The longer wavelength ^1L_b band was of very weak intensity and in some cases was overlapped by the primary band. The spectra of these two ketone series compare with those of the analogously substituted toluenes (*19*), and carbonyl transitions were masked by the much stronger phenyl ring absorption.

The infrared spectra of the α,β-ethylenic ketones gave rise to two carbonyl stretching bands between 1650 and 1700 cm^{-1}. As noted by Kronenberg and Havinga (*24*), the second weaker carbonyl band occurred at approximately 20–25 cm^{-1} higher in the spectra arising from the presence of the *s*-cis conformer. The carbonyl frequency for the other two ketones (II and III) fell in the region between 1690–1720 cm^{-1} with the benzylacetones generally appearing at the higher frequency. Table III shows that the carbonyl maxima of the cyclopropyl ketones falls into a region

intermediate between the benzal- and benzylacetones in agreement with previous reports (*15, 16, 30*). The ketones containing a nitro substituent on the phenyl ring gave two strong bands in the 1520 and 1345 cm^{-1} regions while those bearing a nitrile group exhibited the characteristic strong absorption band at 2225 cm^{-1}.

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Reaction of Hydroxylamine with Reissert Compounds

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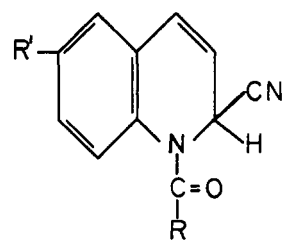
Some new amidoximes have been prepared from Reissert compounds, and the unusual acid-catalyzed hydrolysis of these amidoximes has been studied.

A previous paper (*10*) reported the reaction of 1-benzoyl-1,2-dihydroquinaldonitrile (I, R = C_6H_5; R′ = H) with hydroxylamine to give 1-benzoyl-1,2-dihydroquinaldamidoxime (II, R = C_6H_5; R′ = H). Acid-catalyzed hydrolysis of this product gave an unusual result—benzaldehyde was obtained along with the expected benzoic acid much as benzaldehyde was formed by the acid-catalyzed hydrolysis of Reissert compounds (I, R = C_6H_5; R′ = H and III, R = C_6H_5) (*2, 9*).



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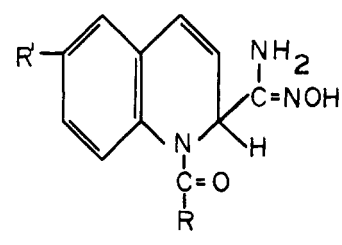

II

Several new amidoximes listed in Table I have been prepared by the reaction of hydroxylamine with the appropriate Reissert compound.

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