Then 4.2 g. (37 mmoles) of boron trifluoride etherate in 25 ml. of ether was added over a period of one hour. The yield, based on V.P.C. analysis for residual 1-octene, was 94%.

Hydroboration in Tetrahydrofuran with Potassium Borohydride–Lithium Chloride–Boron Trifluoride.—In the reaction flask were placed 1.48 g. (27.5 mmoles) of pulverized potassium borohydride, 1.17 g. (27.5 mmoles) of pulverized lithium chloride (dried at 120° under vacuum) and 52 cc. of tetrahydrofuran. The heterogeneous mixture was stirred for 3 hours at room temperature. (In other experiments analysis of the solution for soluble borohydride indicated conversions of 80 to 90% under these conditions.) To the flask were now added the 100 mmoles of 1-octene and 20 mmoles of cyclohexane. Through the dropping funnel was added 36.6 mmoles of boron trifluoride etherate in 25 cc. of tetrahydrofuran over a period of one hour. After a second hour at room temperature, V.P.C. analysis for 1-octene indicated the yield to be 83%.

Hydroboration in Tetrahydrofuran with Sodium Hydride–Boron Trifluoride.—The sodium hydride oil suspension analyzed for 47% sodium hydride by hydrolysis and measurement of the hydrogen produced.

Sodium hydride, 8.5 g. of the oil suspension (47% analysis, 165 mmoles), was weighed in the reaction flask under 27 cc. of tetrahydrofuran. To the flask was added 11.2 g. (100 mmoles) of 1-octene and 1.68 g. (20 mmoles) of cyclohexane with 50 ml. additional of tetrahydrofuran. Through the dropping funnel was added 18.8 cc. (146 mmoles) of boron trifluoride etherate over a period of 1 hour. There was an obvious exothermic reaction and the solid suspension changed in amount and in color (from dark gray to a very light gray.) After one hour, V.P.C. examination showed 99% of the 1-octene had reacted.

Hydroboration Experiments with Amine-boranes.—In the usual reaction flask was placed 80 ml. of dry benzene, 11.2 g. (100 mmoles) of 1-octene and 37 mmoles of the amine-borane (pyridine-borane or trimethylamine-borane). Experiments were carried out both with and without the addition of 37 mmoles of boron trifluoride etherate. The temperature was maintained at 75°. Samples were removed and analyzed by V.P.C. From the decrease in the peak-height the amount of 1-octene reacted was determined. (No internal standard was used, so the analyses are probably not more reliable than ±5%.) At the end of the reaction, the mixture was hydrolyzed by adding 20 ml. of 6 *N* hydrochloric acid. The hydrogen evolved corresponded to the V.P.C. analyses within the indicated precision.

We attempted to run similar experiments in diglyme as solvent. However, our V.P.C. analyses were erratic. We believe that the difficulty is due to reaction of the olefin with the amine-borane on the hot-stage of the instrument, before the diglyme is vaporized.

Acknowledgments.—We are indebted to the Office of Ordnance Research, to the Ethyl Corporation and to Metal Hydrides, Inc., for the financial assistance which made this study possible. We wish to acknowledge also the assistance of the Ansul Chemical Co. in making available supplies of diglyme and triglyme.

[CONTRIBUTION FROM AVERY LABORATORY, UNIVERSITY OF NEBRASKA]

Ethylenimine Ketones. XV. Absorption Spectra and Stereostructure

BY NORMAN H. CROMWELL, RONALD E. BAMBURY AND JULES L. ADELFANG

RECEIVED JANUARY 20, 1960

A detailed examination of spectroscopic data previously gathered as well as of several new measurements of the infrared and ultraviolet absorption spectra of various arylaroylethylenimines, aroylethylenimines and some related α-aminoketones has led to the following new conclusions: (1) In the solid ground state aroylethylenimines and *cis*-arylaroylethylenimines have a non-conjugated *gauche* conformation, (2) in CCl_4 solutions these ethylenimine ketones exist as mixtures of non-conjugated *gauche* and conjugated *cisoid* rotational isomers, (3) *trans*-arylaroylethylenimines have a conjugated *cisoid* conformation in the ground state in the solid form and in solution, (4) α-aminoketones show conformational isomerism in CCl_4 solution which is similar to that which has been demonstrated for α-halogenated ketones and (5) the ethylenimine ring transmits an electrical effect of a β-phenyl group to the α-carbonyl group in the excited state of the *trans*-arylaroylethylenimines as measured by shifts in ultraviolet absorption spectra, but *p*-substituted groups in the β-phenyl group do not extend the conjugation. Sterically dependent polarity factors responsible for the conformational isomerism shown by these diverse compounds, and the transmission of electrical effects by the ethylenimine ring are discussed.

In a series of papers,[1] beginning in 1951, we have reported on studies of the infrared and ultraviolet absorption spectra of several series of ethylenimine ketones, epoxy ketones and cyclopropyl ketones and discussed the nature of and steric requirements for the electrical interaction of these various three-rings with the carbonyl group. These studies led to the discovery of a practical general method of assigning the geometrical configurations at carbon for the *cis*- and *trans*-arylaroylethylenimines,[1a,c,h] methylaroylethylenimines,[1d] arylacetylethylenimines,[1i] arylaroylethylene oxides[1e] and arylaroylcyclopropanes.[1f,j]

The nature of the electrical interaction between the three-ring and the carbonyl group which results in the latter's increased polarization has been described[1c] as a type of hyperconjugation which results from orbital overlap of the *bent bonds* of the three-rings with the π-orbitals of attached unsaturated groups. The geometrical isomer which shows an inhanced degree of carbonyl associated light absorption in the ultraviolet and/or infrared ranges of the spectrum has been found to possess the *trans* structure.[1]

The steric requirement for maximum three-ring carbonyl hyperconjugation has been assessed[1b,g] to be that *the p-orbitals of attached groups must be free to orient themselves so that their axes approach a parallel relation to the plane of the three-ring and a near symmetrical arrangement with respect to the bent bonds.*

Recently a further consideration of the spectroscopic data which have been gathered to date for these various three-ring carbonyl compounds and

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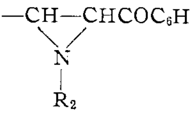
[1] (a) N. H. Cromwell, *et al.*, THIS JOURNAL, **73**, 1044 (1951); (b) N. H. Cromwell and G. V. Hudson, *ibid.*, **75**, 872 (1953); (c) N. H. Cromwell and M. A. Graff, *J. Org. Chem.*, **17**, 414 (1952); (d) N. H. Cromwell and R. J. Mohrbacher, THIS JOURNAL, **75**, 6252 (1953); (e) N. H. Cromwell and R. A. Setterquist, *ibid.*, **76**, 5752 (1954); (f) R. J. Mohrbacher and N. H. Cromwell, *ibid.*, **79**, 401 (1957); (g) R. D. Campbell and N. H. Cromwell, *ibid.*, **79**, 3456 (1957); (h) N. H. Cromwell and G. D. Mercer, *ibid.*, **79**, 3815 (1957); (i) N. H. Cromwell and R. P. Cahoy, *ibid.*, **80**, 5524 (1958); (j) N. H. Cromwell, R. E. Bambury and R. P. Barkley, *ibid.*, **81**, 4294 (1959).

TABLE I

SUMMARY OF SPECTRAL DATA FOR



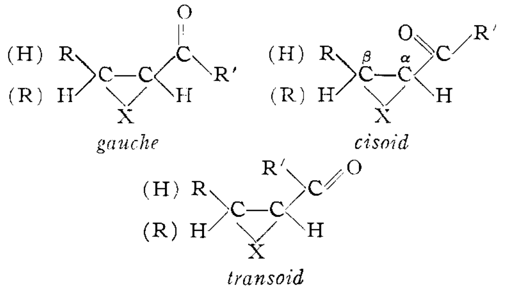
$R_1\text{—}CH\text{—}CHCOC_6H_5$ ($N\text{—}R_2$ bridging the two CH)

Cpd.[a]	R_1	R_2	Config.	Solv.[b]	λ, mμ	ε × 10^{-3}	$\gamma_{C=O}$/% abs
1	H	C_6H_{11}		h.c.	243	11.9	1695/90; 1673/85
				m	247	13.4	
2	C_6H_5	C_6H_{11}	*trans*	m	253	14.6	1675/89
			cis	m	247	12.0	1695/83; 1670/45
3	C_6H_5	$C_6H_5CH_2$	*trans*	m	251	14.4	1673/89
			cis	m	248	12.8	1695/87; 1675/80
4	*p*-$CH_3C_6H_4$	$C_6H_5CH_2$	*cis*	m	248	13.1	1694/70; 1677/30
5	*o*-$NO_2C_6H_4$	C_6H_{11}	*trans*	e	254	21.5	1675/64
			cis	e	254	17.9	1687/70
6	*p*-$NO_2C_6H_4$	C_6H_{11}	*trans*	e	257	18.6	1668/S
					277	16.3	
			cis	e	251	16.7	1694/S
					281	12.1	
7	*p*-$NO_2C_6H_4$	H	*trans*	e	255	20.5	1675/85
					279	19.4	
8	*m*-$NO_2C_6H_4$	$C_6H_5CH_2$	*cis*	m	253	19.8	1692/82; 1677/52
9	*p*-$CH_3OC_6H_4$	C_6H_{11}	*trans*	m	231	15.6	1673/76
					249	14.6	
					(280)	6.5	
			cis	m	231	16.5	1695/75; 1673/33
					(246)	12.5	
					(276)	4.4	

[a] For compound preparation, see for, 1, ref. 1a; 2, ref. 1a; 3, ref. 1a; 4, N. H. Cromwell, THIS JOURNAL, **69**, 258 (1947); 5, ref. 1h; 6, P. L. Southwick and R. J. Shozda, *ibid.*, **82**, 2888 (1960); 7, N. H. Cromwell and G. D. Mercer, *ibid.*, **79**, 3819 (1957); 8, same as for 4; 9, this paper. [b] Solvents for ultraviolet determinations: h.c., 2,2,4-trimethylpentane; m, methanol; e, 95% ethanol.

several new measurements reported here for the first time has led to more detailed conclusions concerning, (1) the nature of the three-ring carbonyl electrical interaction, (2) the abilities of three rings to transmit electrical effects between contiguous unsaturated groups, (3) the occurrence of conformational isomerism with some of these compounds.[2] The ethylenimine ketones are discussed in this connection in the present paper.

Discussion of the Infrared Absorption Spectra.—The earlier studies[1a,c,d] employing Nujol mulls showed only a single carbonyl band between 1675–1685 cm.$^{-1}$ for the aroylethylenimines and the *cis*-aryl (or methyl) aroylethylenimines. This is now[2] interpreted as meaning that in the solid, ground state these molecules are in the more stable *gauche* conformation in which there is little or no orbital overlap of the carbonyl π-bonds with the three-ring bent-bond orbitals (for, RCH_2CH_2-COAr, $\gamma_{C=O}$, 1680–1685 cm.$^{-1}$ in Nujol, see ref. 1d and Table III).



rotational conformations for cis and trans configurations

Solution infrared spectra for these same compounds (see ref. 1d and Table I) usually show two carbonyl bands, one between 1685–1695 cm.$^{-1}$ and a weaker one between 1660–1677 cm.$^{-1}$. This indicates that two molecular species are present in solution.[1d] The stronger, higher frequency band is now assigned to the more prevalent and stable *gauche* form and the weaker, lower frequency band to the less stable and less prevelant conjugated *cisoid* conformer. Models clearly indicate the improbability of the very sterically crowded *transoid* arrangement for the *cis*-aryl (and methyl) aroylethylenimines.

Variation in the nature of the β- R group (H, aryl, methyl) has no effect on the ground state polarity of the carbonyl group in conjugated *cisoid* conformations of the ethylenimine ketones. Even for α,β-unsaturated ketones ($\overset{\beta}{C}{=}\overset{\alpha}{C}\text{—CO—}\underset{}{\overset{\alpha'}{C}}{=}\overset{\beta'}{C}$) conjugation beyond the first unsaturated groups (α,β and α',β') is without effect on the ground state polarity of the carbonyl group.[3] The increased non-bonded interactions in the *cis*-aryl (or methyl) aroylethylenimines (as contrasted with the aroylethylenimines) accounts for the observed decrease in the relative intensities of the bands associated with the *cisoid* conformations of the former compounds (*i.e.*, see Table I, for cpd. 1, a_2/a_1 = 0.944; for cpd. 2, *cis*, a_2/a_1 = 0.536).

Both Nujol mull and solution infrared spectra (see ref. 1a,c,d, and Table I) show only a single

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(2) Some of these conclusions, based only on older data, were included in N. H. Cromwell, *Rec. Chem. Progress*, **19**, 215 (1958).

(3) N. H. Cromwell, *et al.*, THIS JOURNAL, **71**, 3337 (1949).

strong symmetrical carbonyl band for the *trans*-aryl (and methyl) aroylethylenimines. The carbon tetrachloride solution values all fall between 1667–1677 cm.$^{-1}$ and thus the *trans*-aryl (and methyl) aroylethylenimines seem to have a conjugated *cisoid* conformation under these conditions. Both the *cis* and *trans* forms of 2-(*o* nitrophenyl)- and 2-(*p*-nitrophenyl)-1-cyclohexyl-3-benzoylethylenimine show single symmetrical carbonyl bands in solution (see Table I), with the *trans* forms showing frequencies at 1675 and 1668 cm.$^{-1}$ and the *cis* isomers at 1687 and 1694 cm.$^{-1}$, implying *cisoid* conjugated arrangements for the *trans* isomers and non-conjugated gauche conformations for the *cis* forms. The *cis* configuration of 1-benzyl-2-(*m*-nitrophenyl) - 3 - benzoylethylenimine, however, shows a strong band at 1692 cm.$^{-1}$ for a *gauche* conformation and a weaker one at 1677 cm.$^{-1}$ for the *cisoid* rotational isomer. The effect of solvent variation on rotational isomerism for various carbonyl compounds is to be reported in a later paper.[4]

It seems quite unlikely that any combination of inductive and coulombic field effects of the imine nitrogen in these ethylenimine ketones can wholly account for the locations of the two carbonyl stretching frequencies observed for the aroylethylenimines and *cis*-aryl (and methyl) aroylethylenimines. An inductive (-I) effect of the imine nitrogen as well as its coulombic field effect would be expected to increase the carbonyl stretching frequency. The fact that all of the *trans* forms and most of the *cis* isomers of the ethylenimine ketones show at least one carbonyl stretching frequency which is considerably lower than that of the parent saturated ketone, the propiophenone (see Tables II and III) clearly indicates that the three-ring is able to polarize the carbonyl group (increase its single bond character) in the ground state. This seems best accounted for by the hyperconjugation mode suggested previously.[1a–c]

TABLE II

SUMMARY OF SPECTRAL DATA FOR $C_6H_5COCH_2Y$

Y	Solv.[a]	λ, mμ	ε × 10^{-3}	$\gamma_{C=O}$/% abs.
H	m	242	11.8	1692[c]
		280	2.0	
NC_5H_{10}	m	242	10.7	1701/70; 1685/80
		280	1.0	
NC_4H_8O	m	242	12.0	1704/75; 1688/80
		280	1.0	
CH_3	e	242[b]	13.5	1694
$C_6H_5CH_2$	m	243	13.3	1694
		280	0.1	
p-$NO_2C_6H_4CH_2$[d]	e	246	12.3	1686
		274	10.7	
o-$NO_2C_6H_4CH_2$[e]	e	244	15.8	1690

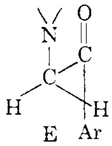
[a] Solvents for ultraviolet determinations: e, ethanol; m, methanol. [b] E. A. Braude and F. Sondheimer, *J. Chem. Soc.*, 3764 (1955). [c] L. J. Bellamy and R. L. Williams, *ibid.*, 4294 (1957). [d] N. H. Cromwell and G. D. Mercer, THIS JOURNAL, **79**, 3819 (1957). [e] *Ibid.*, **79**, 3815 (1957).

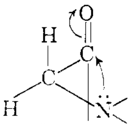
TABLE III

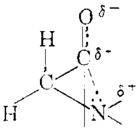
SUMMARY OF SPECTRAL DATA FOR *p*-$C_6H_5C_6H_4COCH_2Y$

Y	H	NC_5H_{10}	NC_4H_8O
I.r. $\gamma_{1C=O}$	1690	1695(s)/70	1700/62
$\gamma_{2C=O}$		1682/85	1684/70
I.r. $\gamma_{C=O}$ Nujol mull	1682	1684	1690
U.v. λ/ε × 10^{-4} 95% ethanol	. .	287/2.26	284/2.15
U.v. λ/ε × 10^{-4} methanol	283/2.4	286/2.36	285/2.36
U.v. λ/ε × 10^{-4} isoöctane	275/2.5	280/2.32	280/2.28

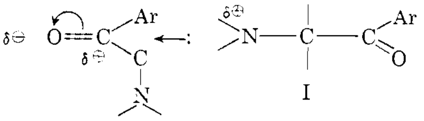
A study, reported here for the first time, of the infrared spectra of some α-aminoketones has also revealed conformational isomerism for such substances, similar to that which has been extensively investigated for α-halogenated ketones.[5] Thus α-piperidino-and α-morpholino acetophenone (see Table II) show split carbonyl bands in CCl_4 solution at $\gamma_{1C=O}$, 1701–1704 cm.$^{-1}$ and $\gamma_{2C=O}$, 1685–1688 cm.$^{-1}$, with an intensity ratio of a_2/a_1 = 1.14–1.06. Since acetophenone[5c] shows a single symmetrical carbonyl frequency at $\gamma_{C=O}$, 1692 cm.$^{-1}$ in CCl_4 solution it is suggested that the bands with the elevated frequencies (1701–1704 cm.$^{-1}$) should be assigned to conformations of the α-aminoacetophenones with the C=O and C—N bonds in an eclipsed *cis* arrangement (E). The lower frequency bands (1685–1688 cm.$^{-1}$) are assigned to a *gauche* conformation P in which a small polarization of the carbonyl group might be expected from the resonance implied by $P_1 \leftrightarrow P_2$ resulting from an intramolecular three-ring interaction of the amino nitrogen with the carbonyl carbon. This intramolecular interaction for α-aminoketones is related to transannular interactions.[6] For steric reasons a similar interaction of the imino nitrogen is not expected to be significant with the ethylenimine ketones. Table III reports similar split carbonyl bands for the α-amino-*p*-phenylacetophenones which also indicates that these ketones exist as conformational isomers in CCl_4 solution.


E


P_1


P_2

A study of the effect of dilution on the infrared carbonyl band intensity ratio, a_2/a_1, for α-morpholino-*p*-phenylacetophenone clearly indicated that the polarization responsible for the lowered frequency, $\gamma_{2C=O}$, 1682–1684 cm.$^{-1}$ (*p*-$C_6H_5C_6H_4COCH_3$, $\gamma_{C=O}$, 1690 cm.$^{-1}$), cannot be due to intermolecular polarization effects (I). The band intensity ratio, a_2/a_1, was essentially unchanged


I

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[4] In this study, N. H. Cromwell and S. F. D. Orr, unpublished, it was found that in more polar solvents the lower frequency band was reduced in intensity. This seems to be the usual situation for rotational isomers according to L. J. Bellamy, "The Infrared Spectra of Complex Molecules," Methuen and Co., London, 2nd Ed., 1958, pp. 139, 140 and 401.

(5) For example see, (a) Ref. 4; (b) L. J. Bellamy, L. C. Thomas and R. L. Williams, *J. Chem. Soc.*, 3704 (1956); (c) L. J. Bellamy and R. L. Williams, *ibid.*, 4294 (1957).

(6) For a good discussion of transannular interactions and infrared spectra studies see the ref. given in footnote 4, pp. 149 and 403.

upon a twelve-fold dilution of the CCl_4 solution.

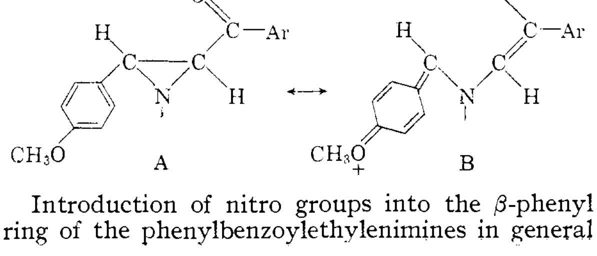
In the solid form the α-amino-*p*-phenylacetophenones show only single symmetrical carbonyl bands indicating that in this state they exist as single conformations as would be expected.

Discussion of the Ultraviolet Absorption Spectra.—The aroylethylenimines and *cis*-phenyl (and methyl)-aroylethylenimines show nearly identical three-ring aroyl ultraviolet absorption maxima (see ref. 1d and Table I), and three-ring carbonyl hyperconjugation is apparent on comparison with the parent propiophenone derivatives (see Table II and ref. 1d,f). The fact that the *cis*-phenyl(and methyl)-aroylethylenimines show ultraviolet maxima at about the same wave lengths and intensities as the corresponding aroylethylenimines indicates that an electrical effect by these β-substituents is not being transmitted to the carbonyl group *via* the three-ring in these configurations.

A comparison of the aroyl ultraviolet maxima obtained for the *trans*-phenyl(and methyl)-aroylethylenimines with those observed for the *cis* isomers (and the aroylethylenimines) shows a significant increase in wave length and/or intensity (see Table I and ref. 1d). This clearly indicates that an electrical effect by the β-substituent is being transmitted *via* the three-ring to the carbonyl group to inhance its polarization in these cross-conjugated systems of the *trans* configurations.

It was of interest to learn if introduction of groups into the *p*-position of the β-phenyl group in the *trans*-arylaroylethylenimine would have an effect on the polarization of the aroyl group as measured by a shift in the ultraviolet maximum. Admittedly such studies are not necessarily definitive with such complex cross-conjugated systems and a chemical measure of such polarization changes with simpler substances is the subject of a further investigation.

Of special interest for the present ultraviolet absorption spectra studies were the newly synthesized *cis*- and *trans*-1-cyclohexyl-2-(*p*-anisyl)-3-benzoylethylenimines, described in the Experimental section. The *trans* isomer showed a small increase in wave length and intensity (λ 249 mμ, ε 14,600), for what is probably the benzoyl band, over that observed for the same band with the *cis* isomer (λ 246 mμ, ε 12,500). However, there are three bands between 231 and 280 mμ for these compounds and introduction of the *p*-methoxy group on the β-phenyl ring of *trans*-1-cyclohexyl-2-phenyl-3-benzoylethylenimine (λ 253 mμ, ε 14,600) has actually had an opposite effect on the wave length of the benzoyl band to what would be predicted assuming resonance A ↔ B to make a contribution to structure.



Introduction of nitro groups into the β-phenyl ring of the phenylbenzoylethylenimines in general caused increased absorption in the ultraviolet range of the spectrum as might be expected since the nitrophenyl group is itself a strong chromophore.

A comparison of the isoöctane solution ultraviolet maxima for the α-amino-*p*-phenyacetophenones with that of the parent *p*-phenylacetophenone showed an increase in λ of 5–6 mμ which may be taken as further evidence for the three-ring transannular-like interaction polarization for these α-aminoketones discussed in the infrared spectra section of this paper. This effect is less pronounced in methanol or ethanol, being swamped out by the polarizing effect of the solvent.

Acknowledgment.—This work was supported in part by a grant, NSF G-10,034, from the National Science Foundation.

Experimental

***cis*- and *trans*-Cyclohexyl-2-(*p*-anisyl)-3-benzoylethylenimine.**—The procedure used to prepare this isomeric pair of arylaroylethylenimines was the same as has been reported[7] for *trans*-1-cyclohexyl-2-phenyl-3-(*p*-phenylbenzoyl)-ethylenimine. A 94% yield of the mixture of isomers, m.p. 75–100°, was obtained from *p*-methoxychalcone,[8] iodine and cyclohexylamine which showed infrared bands at 1695 and 1675 cm.$^{-1}$. Extraction of the more soluble *trans* isomer from the mixed product was accomplished with petroleum ether (b.p. 60–70°). Recrystallization of the crude separated isomers from methanol produced about two parts of the *trans* isomer, m.p. 93–95°, and one part of the *cis* isomer, m.p. 115–117°. This same approximate isomer ratio was verified by a comparison of the intensity of carbonyl bands in the infrared spectrum of the mixed product, m.p. 75–100°, with those of the pure *cis* and *trans* forms.

Anal. Calcd. for $C_{22}H_{25}NO$: C, 78.77; H, 7.51; N, 4.18. Found, for *cis* isomer: C, 78.80; H, 7.72; N, 4.41. For *trans* isomer: C, 78.78; H, 7.51; N, 4.48.

Preparation of α-Aminoketones for Spectral Studies.—These compounds were prepared from two equivalents of the amine (morpholine or piperidine) and one equilvalent of the α-bromoacetophenone or α-bromo-*p*-phenylacetophenone in benzene solution at room temperature. The morpholine and piperidine hydrobromide by-products were removed by filtration and the benzene solutions well washed with water and dried.

α-Piperidinoacetophenone and α-morpholinoacetophenone were isolated and purified as their hydrochloride, m.p. 223°[9a] and 222–223°,[9b] respectively. Weighed samples of the hydrochlorides were dissolved in water and the solutions made basic with potassium carbonate. Extraction of these water solutions with ether, drying and evaporation gave the oily α-piperidino- and α-morpholinoacetophenone samples which were dissolved in the proper solvents for spectral analysis.

α-Piperidino- and α-morpholino-*p*-phenylacetophenones were isolated as the free bases and recrystallized from benzene and petroleum ether mixtures. The piperidine[10] derivative showed a m.p. at 82.5–83.5°, while the morpholine derivative, which has not been previously reported, showed its m.p. at 114.5–115.5°.

Anal. Calcd. for $C_{18}H_{19}NO_2$: C, 76.84; H, 6.81: N, 4.98. Found: C, 77.02; H, 6.80; N, 4.84.

Absorption Spectra Measurements.—All newly determined ultraviolet spectra were done with a Cary recording instrument, model 11 MS, employing methanol solutions of freshly recrystallized materials unless otherwise indicated. The new infrared spectra were measured over the range of 700–4000 cm.$^{-1}$ using a Perkin-Elmer model 21 double-beam

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[7] N. H. Cromwell, R. P. Cahoy, W. E. Franklin and G. D. Mercer, THIS JOURNAL, **79**, 922 (1957).

[8] F. Pond and A. Shoffstall, *ibid.*, **22**, 666 (1900).

[9] (a) P. Rabe and W. Schneider, *Ber.*, **41**, 874 (1908); (b) N. Rubin and A. R. Day, *J. Org. Chem.*, **5**, 54 (1940).

[10] H. King and T. S. Work, *J. Chem. Soc.*, 1307 (1940), report a m.p. 86°, while B. R. Carpenter and E. E. Turner, *J. Chem. Soc.*, 869 (1934), reported the m.p. at 93–94°.

instrument employing sodium chloride optics and CCl_4 solutions of freshly purified materials in matched 1.0-mm. sodium chloride cells unless otherwise indicated.

A study of the effect of dilution on the split carbonyl band in the infrared spectrum of α-morpholino-*p*-phenylacetophenone gave the results: 9.21 mg./ml. CCl_4 in a 1.0-mm. cell, $\gamma_{1C=O}$, 1700/62, $\gamma_{2C=O}$, 1686/70 (a_2/a_1 = 1.13); 3.78 mg./ml. CCl_4 in a 1.0 mm. cell, $\gamma_{1C=O}$ 1702-38, $\gamma_{2C=O}$, 1686/47 (a_2/a_1 = 1.23); 0.75 mg./ml. CCl_4 in a 5.0-mm. cell, $\gamma_{1C=O}$, 1701/46, $\gamma_{2C=O}$, 1684/56 (a_2/a_1 = 1.21).

LINCOLN, NEBR.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CALIFORNIA, BERKELEY]

The Reaction of 1,5-Diketones with Sulfuric Acid

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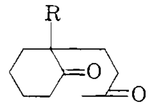
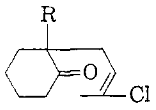
RECEIVED DECEMBER 7, 1959

It has been found that certain 1,5-diketones upon treatment with sulfuric acid give rise to products with bridged bicyclic structures rather than the expected fused ring systems. The strain in certain 3,2,1-bicyclic systems is discussed.

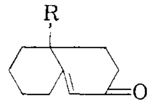
There are two general synthetic routes which have been employed to fuse an additional carbocyclic ring to a cyclic ketone. The first procedure, that of Robinson,[2] is the cyclization of a 1,5-diketone, such as Ia, with dilute acid or base. The second procedure, discovered by Wichterle[3] and widely employed by Prelog,[4,5] is the cyclization of a 2-(3′-chlorocrotyl)-cyclonone, such as IIa, with concentrated sulfuric acid. Although the reaction conditions of these two processes are very different, in both reactions the octalone IIIa is obtained in good yield. It has been proposed that the vinyl chloro group acts as a disguised ketone and upon treatment with strong acid gives rise to the same 1,5-diketone employed in the Robinson reaction.



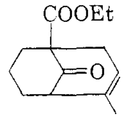
Ia, R = H
b, R = COOEt



IIa, R = H
b, R = COOEt



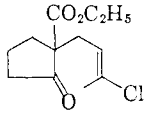
IIIa, R = H
b, R = COOEt



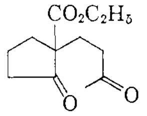
IV

One particular facet of these reactions which is of special interest arises when the potential angular grouping is carbethoxy. In this case, Ib under Robinson conditions[2] yields the expected octalone IIIb, while IIb under Wichterle conditions[4] gives rise to the bicyclic ketone IV. If the vinyl chloro group is acting as a disguised carbonyl group, then the strongly acidic conditions used in the Wichterle reaction must be a controlling factor directing ring closure to a bicyclic system. Such now has been found to be the case since Ib upon reaction with concentrated sulfuric acid yields bicyclic ketone IV in good yield.

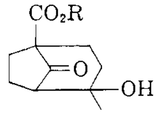
In contrast to the excellent reaction of IIb with sulfuric acid, Prelog and Zimmermann[5] found that ethyl 2-(3′-chlorocrotyl)-cyclopentanone-2-carboxylate (V) yielded only an intractable mixture of materials. In this reaction, the presumed intermediate would be ethyl 2-(3′-oxobutyl)-cyclopentanone-2-carboxylate (VI) whose reaction has now been studied. When the diketone VI was allowed to react with 95% sulfuric acid, a solid isomeric product ($C_{12}H_{18}O_4$) was obtained in good yield. The material could be hydrolyzed in either dilute acid or base to a carboxylic acid which, in turn, upon treatment with diazoethane was reconverted to the original ester. The infrared spectrum of the ester in carbon tetrachloride showed a single strong band at 1740 cm.$^{-1}$ and in chloroform showed two bands at 1732 and 1720 cm.$^{-1}$. The spectrum of the acid in chloroform possessed bands at 1750 and 1719 cm.$^{-1}$. These data indicate the presence of a cyclopentanone and a carboxyl function. No direct chemical evidence for the carbonyl group could be obtained since the product would not react with 2,4-dinitrophenylhydrazine, semicarbazide or thiosemicarbazide, even under forcing conditions. The fourth and remaining oxygen function was shown to be a hydroxy group by the presence of a weak but definite band at 3450 cm.$^{-1}$ in the infrared spectrum, and by the presence of one active hydrogen as determined by the Zerewitinoff reaction.



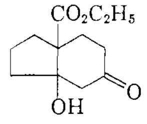
V



VI



VII, R = C_2H_5
VIII, R = H



IX

Based upon these data and assuming no deep seated rearrangement, there are two possible formulations for the reaction product, VII and IX.

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[1] United States Rubber Co. Fellow in Chemistry, 1955-1956; Dow Chemical Co. Fellow in Chemistry, 1956-1957.

[2] E. C. DuFeu, F. J. McQuillin and R. Robinson, *J. Chem. Soc.*, 53 (1937).

[3] O. Wichterle, J. Prochazka and J. Hofman, *Coll. Czech. Chem. Comm.*, **13**, 300 (1948).

[4] V. Prelog, P. Barman and M. Zimmermann, *Helv. Chim. Acta*, **32**, 1284 (1949).

[5] V. Prelog and M. Zimmermann, *ibid.*, **32**, 2360 (1949).