[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

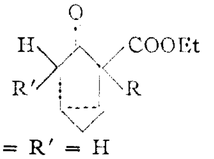
The Infrared Absorption Spectra of Cyclic β-Ketoesters

BY NELSON J. LEONARD, HERBERT S. GUTOWSKY, WILLIAM J. MIDDLETON AND ELIZABETH M. PETERSEN

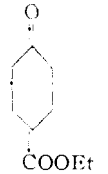
RECEIVED FEBRUARY 29, 1952

The infrared absorption spectra of a number of closely related cyclic β-ketoesters have been observed. In the case of those compounds related to cyclohexanone-2-carboxylic ester in which enolization can occur absorption bands have been found at 1656-1660 cm.$^{-1}$ and 1618-1624 cm.$^{-1}$ in addition to the absorption attributable to the ester carbonyl (1734-1745 cm.$^{-1}$) and the ketone carbonyl (1717-1720 cm.$^{-1}$). The additional bands are considered to be due, respectively, to carbonyl and to carbon-carbon unsaturation in the conjugated chelate enolic form. Analogous but weaker bands were found for compounds similarly related to cyclopentanone-2-carboxylic ester, indicating a lower degree of enolization for the five-membered ring analogs. Also, some of the ester and keto C=O vibrational frequencies differ for correspondingly substituted cyclopentanone and cyclohexanone homologs. The influence of ring strain on bond hybridization provides a basis to account for the differences.

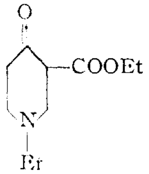
Although there has been some examination of the infrared absorption spectra of acyclic β-ketoesters[1] no detailed characterization of the cyclic β-ketoesters has been reported. The infrared spectra of such compounds are of interest particularly in relation to the influence of ring size and substituents upon the degrees of enolization and chelation, and also upon the keto and ester C=O vibrational frequencies. The infrared absorption bands we have observed in the 6 and 3μ regions for variously substituted β-ketoesters related to cyclohexanone (II through IX)[2] and cyclopentanone (IIa, IVa, VIa, VIIIa)[2] are listed in Table I along with the bond-stretching[3] frequency assignments.



II, R = R' = H
III, R = R' = H; CH_3 at C_5
IV, R = H; R' = COOEt
V, R = H; R' – CH_2COOEt
VI, R = H; R' = CH_2CH_2COOEt
VII, R = CH_2COOEt; R' = H
VIII, R = CH_2CH_2COOEt; R' = H
IX, R = R' = CH_2CH_2COOEt
IIa, IVa, VIa, VIIIa—corresponding compounds in the cyclopentanone series.



I

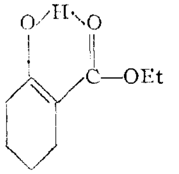


X

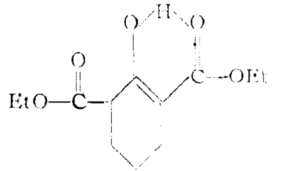
Cyclohexanones.—The non-enolizable β-ketoesters of cyclohexanone have two absorption bands in the 6μ (double bond) region while the enolizable derivatives have usually four, and sometimes apparently three. These absorption bands lie in the ranges 1734-1741 cm.$^{-1}$, 1717-1720 cm.$^{-1}$, 1653-1660 cm.$^{-1}$ and 1615-1624 cm.$^{-1}$.

Ethyl cyclohexanone-4-carboxylate (I)[4] was selected as a model non-enolizable ketoester, and the strong bands in its spectrum at 1736 and 1718 cm.$^{-1}$ suggest that in all of the cyclohexanone derivatives the 1734-1741 cm.$^{-1}$ absorption is that of the ester C=O and the 1717-1720 cm.$^{-1}$, the keto C=O. These assignments follow those for the closely analogous, non-enolizable acyclic β-ketoester, $CH_3COC(CH_3)_2COOEt$, for which the ester C=O band is reported[1] at 1742 cm.$^{-1}$ and the keto C=O at 1718 cm.$^{-1}$. Also, the keto C=O frequency in cyclohexanone has been observed[5] at 1714 cm.$^{-1}$, and in alkyl substituted cyclohexanones[6] at 1695-1720 cm.$^{-1}$. Moreover, the generally accepted non-conjugated ester C=O frequency range is 1725-1755 cm.$^{-1}$,[1,7,8] or more specifically for acetates and propionates, 1735-1740 cm.$^{-1}$ [9] and the reported frequency range for unconjugated keto C=O is 1695-1725 cm.$^{-1}$[1,7,8,10] Conclusive support of the ester and keto C=O assignments in Table I is provided by the increased intensity, in those compounds containing two or more ester C=O groups, of the absorption in the 1734-1741 cm.$^{-1}$ range relative to that at 1717-1720 cm.$^{-1}$

In addition to absorption in the normal ester and keto C=O regions, each of the enolizable β-ketoesters has absorption bands in the 1656-1660 cm.$^{-1}$ and 1615-1624 cm.$^{-1}$ regions. A typical case is ethyl cyclohexanone-2-carboxylate (II) which has somewhat weaker ester and keto C=O bands than the non-enolizable 4-carboxylate (I) and, in addition, a strong broad absorption band at 1656 cm.$^{-1}$ and a sharper one at 1618 cm.$^{-1}$, assigned, respectively, to conjugated chelate C=O and conjugated C=C in the enolic form XI.



XI



XII

---

[1] R. S. Rasmussen and R. R. Brattain, THIS JOURNAL, **71**, 1073 (1949).

[2] (a) H. T. Openshaw and R. Robinson, *J. Chem. Soc.*, 941 (1937); (b) N. N. Chaterjee, B. K. Das and G. N. Barpujari, *J. Indian Chem. Soc.*, **17**, 161 (1940); (c) N. N. Chaterjee and A. Bose, *Science and Culture*, **6**, 724 (1941); (d) R. C. Fuson, W. E. Parham and L. J. Reed, THIS JOURNAL, **68**, 1239 (1946); (e) N. J. Leonard and W. J. Middleton, *ibid.*, in press; (f) W. Dieckmann, *Ann.*, **317**, 27 (1901); (g) M. E. Dobson, J. Ferns and W. H. Perkin, Jr., *J. Chem. Soc.*, **95**, 2015 (1909); (h) H. D. Gardner, W. H. Perkin, Jr., and H. Watson, *ibid.*, **97**, 1756 (1910); (i) M. I. Ushakov, *Zhur. Russ. Fiz. Khim. Obshchestva*, **61**, 795 (1929); (j) A. D. Mitchell and J. F. Thorpe, *J. Chem. Soc.*, **97**, 997 (1910).

[3] G. Herzberg, "Infrared and Raman Spectra of Polyatomic Molecules," D. Van Nostrand Co., Inc., New York, N. Y., 1945, p. 195.

[4] E. Hardegger, Pl. A. Plattner and F. Blank, *Helv. Chim. Acta*, **27**, 793 (1944).

[5] E. J. Hartwell, R. E. Richards and H. W. Thompson, *J. Chem. Soc.*, 1436 (1948).

[6] J. Cabannes, *Compt. rend.*, **225**, 1063 (1947).

[7] R. B. Barnes, R. C. Gore, U. Liddel and V. Z. Williams, "Infrared Spectroscopy," Reinhold Publishing Corp., New York, N. Y., 1944, p. 21.

[8] H. M. Randall, R. G. Fowler, N. Fuson and J. R. Dangl, "Infrared Determination of Organic Structures," D. Van Nostrand Co., Inc., New York, N. Y., 1949, p. 4ff.

[9] H. W. Thompson and P. Torkington, *J. Chem. Soc.*, 640 (1945).

[10] R. S. Rasmussen, D. D. Tunnicliff and R. R. Brattain, THIS JOURNAL, **71**, 1068 (1949).

TABLE I

INFRARED ABSORPTION BANDS IN THE 6 AND 3μ REGIONS[a]

No.	Six-membered ring compounds	Ester C=O	Ketone C=O	Chelated conjugated C=O	Conjugated C=C	C=O overtone or combination
I	Ethyl cyclohexanone-4-carboxylate[4]	1736 vs	1718 vs			3440 w
II	Ethyl cyclohexanone-2-carboxylate[2f]	1744 s–m	1718 s–m	1656 s,br	1618 s	
III	Ethyl 5-methylcyclohexanone-2-carboxylate[2h]	1745 s–m	1718 s–m	1656 s,br	1618 s	
IV	Diethyl cyclohexanone-2,6-dicarboxylate[2i]	1738 vs,br		1660 s,br	1621 s	3450 w
V	Diethyl cyclohexanone-6-acetate-2-carboxylate[2e]	1736 vs,br	1718 vw(?)	1653 w	1615 w	3445 vw
VI	Diethyl cyclohexanone-2-carboxylate-6-β-propionate[2k]	1734 vs,br		1656 vw	1624 w	3445 m–w
VII	Diethyl cyclohexanone-2-acetate-2-carboxylate[2c]	1736 vs	1718 s			3445 m–w
VIII	Diethyl cyclohexanone-2-carboxylate-2-β-propionate[2a]	1736 vs	1717 s			3440 m–w
IX	Triethyl cyclohexanone-2-carboxylate-2,6-di-β-propionate[2l]	1735 vs	1718 m			3445 vw
X	Ethyl 1-ethyl-4-piperidone-3-carboxylate[2d]	1741 s–m	1720 s–m	1660 s,br	1624 s	

No.	Five-membered ring compounds	EtOOC- C=O	Ketone and $EtOOC(CH_2)_2$- C=O	Chelated conjugated C=O	Conjugated C=C	C=O overtone or combination
IIa	Ethyl cyclopentanone-2-carboxylate[2f,g]	1756 vs	1725 vs	1660 w	1618 w	3440 w
IVa	Diethyl cyclopentanone-2,5-dicarboxylate[2j]	1763 s	1736 vs,br	1671 m	1625 w	3440 w
VIa	Diethyl cyclopentanone-2-carboxylate-5-β-propionate[2b]	1751 m	1733 vs,vbr	1666 w	1624 vw	3445 m–w
VIIIa	Diethyl cyclopentanone-2-carboxylate-2-β-propionate[2b]	1755 w(?)	1736 vs,vbr			3445 w

vs, very strong; s, strong; s–m, strong to medium; m, medium; m–w, medium to weak; w, weak; vw, very weak; br, broad. [a] Tabulated frequencies are in cm.$^{-1}$.

The assignment of the absorption in the 1656–1660 cm.$^{-1}$ region to conjugated chelate C=O follows Rasmussen and Brattain[1] who found the ester C=O frequency in salicylic esters and enolized β-ketoesters displaced to near 1667 cm.$^{-1}$. They also found their β-ketoesters to have ester C=O vibrational frequencies corresponding to the non-enolized as well as the chelate form. Thus, in ethyl acetoacetate and ethyl methylacetoacetate absorption maxima were found at 1730 cm.$^{-1}$, a normal ester C=O, and at 1650 cm.$^{-1}$, the conjugate chelate C=O. Conjugation alone displaces the ester C=O to about 1720 cm.$^{-1}$ [1] and the keto C=O to about 1667–1695 cm.$^{-1}$.[10] Specifically, the keto C=O frequency is displaced by conjugation to 1686 cm.$^{-1}$ in 1-acetyl-2-methyl-Δ^1-cyclohexene[11] and to 1666–1670 cm.$^{-1}$ in steroids of the type Δ^{16}-one-20.[12] Chelation alone has been found[13] to decrease the ester C=O frequencies by 45–75 cm.$^{-1}$ in several aromatic systems. Accordingly, for the cyclic β-ketoesters a combination of conjugation and chelation appears to be the most reasonable interpretation of the large displacements to 1656–1660 cm.$^{-1}$ of what otherwise would be a normal ester C=O absorption band.

By elimination, the absorption observed in the 1615–1624 cm.$^{-1}$ region is assigned to the conjugated C=C in the chelate enol form (XI). No report appears to have been made previously of the C=C stretching frequency to be expected in enolized β-ketoesters, but in α,β-unsaturated ketones an absorption band assigned to the conjugated C=C is found generally in the 1621–1647 cm.$^{-1}$ region[10] and at 1605 cm.$^{-1}$ for 5,5-dimethyl-1,3-cyclohexanedione (enol).[10] A band at about 1616 cm.$^{-1}$ appears in the infrared absorption spectrum of 1-acetyl-2-methyl-Δ^1-cyclohexene, reported by Turner and Voitle,[11] and we suggest it be assigned to the conjugated C=C in the molecule.

The weak absorption bands observed at about 3445 cm.$^{-1}$ for most of the compounds are in the 3μ OH region.[7,8] However, the character and position of these bands, as well as their appearance for all of the non-enolizable compounds, demonstrate they are not due to OH in, say, a non-chelated enol form. Instead the most likely assignment is as an overtone or combination of the ester and/or the keto C=O vibrational frequency. A counterpart to the weak broad absorption reported near 2700 cm.$^{-1}$ in conjugated enolized β-diketones and attributed[10] to the chelated OH vibration was not found in the spectra of the β-ketoesters. It is inferred that the enol present occurs primarily as the chelated form (XI) in which the hydroxyl OH is perturbed beyond recognition.

The data in Table I show that all of the cyclic β-ketoesters with α-hydrogen (II–VI, X) form the chelated enol to a greater or less degree, while those in which the α-hydrogen is replaced by an alkylenecarboxylate residue (VII–IX) do not. The change in structure from ethyl cyclohexanone-4-carboxylate (I) to the isomeric 2-carboxylate (II) not only permits formation of the chelated enol, but also raises the ester C=O frequency in the non-enolic form from 1736 to 1744 cm.$^{-1}$. This agrees with the observation of Grove and Willis[14] that two carboxyl groups will interact and produce small increases in their vibrational frequencies when they are in 1,2-, 1,3- or 1,4-positions. Methyl substitution at C_5 in ethyl cyclohexanone-2-carboxylate (II) to form III leaves the 6μ region unaffected. The substitution of C_2H_5–N for C_3 in II as with ethyl 1-ethyl-4-piperidone-3-carboxylate[2d] (X) also

---

[11] R. B. Turner and D. M. Voitle, *ibid.*, **73**, 1403 (1951).

[12] R. N. Jones, P. Humphries, E. Packard and K. Dobriner, *ibid.*, **72**, 86 (1950).

[13] I. M. Hunsberger, *ibid.*, **72**, 5626 (1950).

[14] J. F. Grove and H. A. Willis, *J. Chem. Soc.*, 877 (1951).

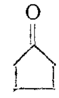
has virtually no effect; the very small shifts observed may be real and if so are attributable to inductive and ring strain differences.[5,14]

The disappearance of the 1718 cm.$^{-1}$ keto C=O absorption band in the diethyl cyclohexanone-2,6-dicarboxylate (IV) suggests that this molecule resides almost exclusively in the chelated forms (XII). This assumption seems reasonable as the intensities of the 6μ absorption bands of the monoester (II) indicate it to be about half-conjugated enol, and in the diester the statistical probability of enolization is twice as great. The presence of alkylenecarboxylate residues at C_6 in II (V, VI) weakened the bands assigned to the chelated forms. This appears to be a variety of steric effect since the ethyl propionate group (V) reduces the extent of chelation more than does the ethylacetate (VI). Presumably inter- as well as intramolecular effects are involved, particularly as the ester C=O absorption regions in V and VI are broadened toward longer wave lengths, with the keto C=O no longer resolvable.

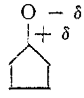
Cyclopentanones.—The major features of the spectra of the five-membered ring β-ketoesters are analogous to those of the corresponding six-membered ring compounds (Table I). However, some informative differences exist.

The ethyl carboxylate C=O vibrational frequencies are about 15 cm.$^{-1}$ higher in the cyclopentanones (IIa, IVa, VIa, VIIIa) than in the corresponding cyclohexanones (II, IV, VI, VIII); also, the keto C=O vibrational frequencies are about 10 cm.$^{-1}$ higher in the cyclopentanones, although still 10–20 cm.$^{-1}$ lower than the 1744 cm.$^{-1}$ band in cyclopentanone itself.[5] On the other hand, the 1717–1720 cm.$^{-1}$ keto C=O absorption bands in the substituted cyclohexanones (I–X) are essentially undisplaced from the 1714 cm.$^{-1}$ band in cyclohexanone itself.[5] To consider a particular case, we infer that for ethyl cyclopentanone-2-carboxylate (IIa) the 19 cm.$^{-1}$ decrease in the keto C=O frequency, compared to cyclopentanone, is associated with the 12 cm.$^{-1}$ increase in the ester C=O frequency, compared to the cyclohexanone homolog (II).

An explanation of these displacements can be based on electronic effects associated with ring strain in the cyclopentanones. It has been pointed out[15] that differences in the C=O vibrational frequency are related to the polarity of the C=O bond and the corresponding differing amounts of double-bond and ionic character, structures XIII and XIV. Greater polarity or ionic character (XIV) reduces the C=O vibrational frequency.[15] In unstrained ketones the C=O bond is, to a given degree, a π-bond formed by p^2 hybridization. The R_1-C-R_2 angle in $R_1R_2C=O$ is determined by sp-hybridization and is near 120°; however, in the cyclopentanone this angle is constrained to a considerably smaller value. Pure p-bonds are at angles of 90°, so that the ring strain increases the p-character of the C–R bonds, and at the same time transfers some s-character to the C=O bond. The electron density at the carbon end of the C=O bond is increased by the s-character, and thereby the bond polarity decreased and the vibrational frequency increased. When the ethyl carboxylate is substituted in the cyclopentanone, a similar interaction can be invoked to raise the ester C=O vibrational frequency and reduce the ring strain. However, the effect is attenuated by the carbon atom between the oxygen and the ring. The relief of the ring strain by the ester C=O of course partially reduces the original effect of the strain on the keto C=O.



XIII



XIV

The 6μ absorption of the diesters is complicated somewhat by the second ester C=O. In VIa and VIIIa, the ethyl β-propionate is removed sufficiently from the ring for the ester C=O vibrational frequency to be near the normal 1735 cm.$^{-1}$. It combines apparently with the ring keto C=O near 1725 cm.$^{-1}$ to give the observed strong unresolved absorption. Something similar occurs in the case of diethyl cyclopentanone-2,5-dicarboxylate (IVa); however, the effects of the two ethyl carboxylate groups appear to be antagonistic, with the result that only one is displaced to higher frequencies.

The absorption maxima of the conjugated chelate form of ethyl cyclopentanone-2-carboxylate (IIa) at 1656 and 1618 cm.$^{-1}$ are weak, whereas the corresponding bands for the hexanone homolog (II) are strong. This indication that there is less enolization in the five-membered ring is a substantiation of earlier chemical[16] and physical data[17] supporting the same conclusion. It is fortified further by the observation that the other enolizable cyclopentanones (IVa, VIa) have consistently weaker absorption bands in the conjugated chelate region than the corresponding cyclohexanones (IV, VI). One reason the degree of enolization is less in the five- than in the six-membered ring β-ketoesters may be seen by reference to structure XIV. This structure and a similar one for the cyclohexanone are likely intermediates to enolization. Thus, the smaller polarity of the cyclopentanone structure decreases the enolization. Probably a more important factor is that introduction of the C=C bond in the cyclopentane ring requires more bond angle distortion than in cyclohexane, so that enolization is energetically less favored in the cyclopentanones.[11,18]

Experimental

The infrared spectra were obtained with a Perkin–Elmer Model 12B automatic recording infrared spectrometer equipped with rock salt optics. An internal calibration was provided in each spectrum by the 3 and 6 μ atmospheric water vapor absorption. The sharpness of the bands was the main factor limiting accuracy. The estimated error of the data in Table I for the 6 μ region is ±3 cm.$^{-1}$ except for the broader or weaker bands where it is ±5 cm.$^{-1}$; and in the 3 μ region it is ±10 cm.$^{-1}$.

---

(15) A. D. Walsh, *Trans. Faraday Soc.*, **43**, 158 (1947).

(16) (a) V. Grignard and H. Blanchon, *Bull. soc. chim.*, [4] **49**, 23 (1931); (b) C. Mannich and V. H. Hâncu, *Ber.*, **41**, 564 (1908); (c) W. Dieckmann, *ibid.*, **55**, 2470 (1922).

(17) Buu-Hoï and P. Cagniant, *Bull. soc. chim.*, **10**, 251 (1943).

(18) E. A. Braude and W. F. Forbes, *J. Chem. Soc.*, 1755 (1951).

The samples[2] were redistilled prior to being observed as the pure liquids at room temperature. The reported relative intensities are based on the apparent per cent. transmission at a constant sample thickness of 0.025 mm. Thinner samples were used occasionally to resolve the keto and ester C=O absorption bands.

URBANA, ILLINOIS

[CONTRIBUTION FROM THE BAKER LABORATORY OF CHEMISTRY AT CORNELL UNIVERSITY]

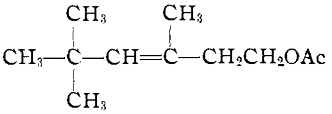
2-Neopentyl-1,3-butadiene. Preparation and Proof of Structure[1]

BY A. T. BLOMQUIST AND JEROME C. WESTFAHL[2]

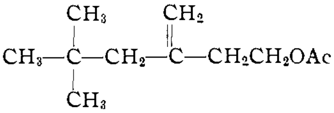
RECEIVED MARCH 7, 1952

The isomeric nonenyl acetates obtained by the condensation of diisobutylene, paraformaldehyde and glacial acetic acid when pyrolyzed yield 2-neopentyl-1,3-butadiene, diisobutylene, acetic acid and formaldehyde. The structure of 2-neopentyl-1,3-butadiene was established. Its formation of an adduct with maleic anhydride, which on aromatization and degradation gave trimellitic acid, demonstrated the presence of one alkyl group in the 2-position of the 1,3-butadiene chain. Oxidation of the diene to *t*-butylacetic acid showed that the alkyl group is a neopentyl group.

Recent studies in this Laboratory of the condensation of olefins with paraformaldehyde and glacial acetic acid had shown that the principal products are acetates of unsaturated alcohols having one more carbon atom than the original olefins and having the same degree of unsaturation. The structure of individual isomers in the mixture of acetates obtained from commercial diisobutylene (80% 2,4,4-trimethyl-1-pentene and 20% 2,4,4-trimethyl-2-pentene) has been studied by means of ozonolysis and the isomeric acetates I and II are believed to be present.[3]

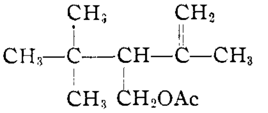

$CH_3-\overset{CH_3}{\underset{CH_3}{C}}-CH=\overset{CH_3}{C}-CH_2CH_2OAc$

I


$CH_3-\overset{CH_3}{\underset{CH_3}{C}}-CH_2-\overset{CH_2}{\overset{\|}{C}}-CH_2CH_2OAc$

II

The structures of I and II indicate that they are both formed from the major isomer of diisobutylene. Since the condensation of pure 2,4,4-trimethyl-2-pentene with paraformaldehyde and glacial acetic acid has been shown to produce a nonenyl acetate,[4] an isomer such as III may be assumed to be present in the mixture of isomeric acetates prepared from diisobutylene. The compounds I, II and III each contain the $-CH=\underset{|}{C}-\underset{|}{CH}-CH_2OAc$ group


$CH_3-\overset{CH_3}{\underset{CH_3}{C}}-\underset{CH_2OAc}{CH}-\overset{CH_2}{\overset{\|}{C}}-CH_3$

III

and, accordingly, pyrolysis of the mixture of nonenyl acetates should yield a mixture of alkyl substituted 1,3-butadienes.

Pyrolysis at 475° of the nonenyl acetate fraction of b.p. 78–85.5° (10 mm.) and n^{20}D 1.442–1.444 gave a mixture of 2-neopentyl-1,3-butadiene (IV), diisobutylene, acetic acid, paraformaldehyde and unpyrolyzed nonenyl acetate. Repyrolysis of the recovered nonenyl acetate under the same conditions produced IV and acetic acid with only traces of diisobutylene and paraformaldehyde. This indicated that the more thermolabile nonenyl acetates responsible for the production of diisobutylene and formaldehyde were almost completely decomposed in the first pyrolysis.

The structure of IV was established by the series of reactions shown in the chart. Reaction of the diene (IV) with maleic anhydride in benzene solution gave 4-neopentyl-4-cyclohexene-1,2-dicarboxylic anhydride (V). Aromatization of V, carried out with a 30% palladium-on-norit catalyst[5] by the method of Fieser[6] or by heating with sulfur at 200–250°, produced VI. Oxidation of the sodium salt of VII, obtained from VI, by refluxing with an excess of aqueous potassium permanganate failed to give trimellitic acid (XII) but produced instead the stable intermediate oxidation product pivalophenone-3,4-dicarboxylic acid (VIII).

The possibility of establishing the position and structure of the acyl group in VIII by means of a Beckmann rearrangement of the oxime of VIII was investigated. The keto acid (VIII) was converted to the N-phenyl imide (IX) by a modification of the method of Tingle and Cram[7] in order to simplify the preparation of an oxime. The oxime X was prepared by a standard method.[8] In studying the Beckmann rearrangement of pivalophenone ketoxime Schroeter[9] observed that treatment with phosphorus pentachloride gave benzonitrile. However, treatment of the oxime with anhydrous hydrogen chloride in acetic acid effected rearrangement to trimethylacetanilide. When Schroeter's anhy-

---

[1] The work reported here was done as part of a research project at the Baker Laboratory of Chemistry, Cornell University, sponsored by the B. F. Goodrich Company.

[2] Abstracted from the dissertation submitted by Jerome C. Westfahl in September, 1950, to the Graduate Faculty of Cornell University in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

[3] A. T. Blomquist, L. I. Diuguid, M. Passer and C. S. Schollenberger, unpublished; M. Passer, Thesis, Cornell University, 1948; C. S. Schollenberger, Thesis, Cornell University, 1947.

[4] Private communication from Dr. Fred T. Fiedorek, Research Center, The B. F. Goodrich Co., Brecksville, Ohio.

[5] R. P. Linstead and S. L. C. Thomas, *J. Chem. Soc.*, 1127 (1940).

[6] L. F. Fieser, "Experiments in Organic Chemistry," 2nd Ed., D. C. Heath and Co., Boston, Mass., 1941, pp. 461–462.

[7] J. B. Tingle and M. P. Cram, *Am. Chem. J.*, **37**, 596 (1907).

[8] S. M. McElvain, "The Characterization of Organic Compounds," The Macmillan Co., New York, N. Y., 1945, p. 198.

[9] G. Schroeter, *Ber.*, **44**, 1201 (1911).