Experimental[33]

Materials.—Isopropenyl acetate and stabilized vinyl acetate from the Matheson Co. were used without further purification. Eastman practical grade vinyl propionate and vinyl butyrate were redistilled prior to use, b.p. 93 and 114°, respectively. Vinyl pivalate was prepared according to the method described by Adelman,[34] b.p. 103.5° uncor. (lit.[34] b.p. 110-112°). Because of the boiling point difference, the structure was confirmed with an n.m.r. spectrum which shows a singlet at τ 8.76 (area 9.4) and an ABC pattern similar to that of vinyl acetate with two groups of peaks centered at τ 2.75 and 5.32, respectively (total area 3.0). For comparison, the singlet methyl peak of vinyl acetate is at τ 7.92 and the singlet butyl group of ethyl pivalate is at τ 8.94.

The solvent used in the kinetic study was prepared as a 1:1 (w./w.) solution of water, and dioxane which had been freshly distilled from sodium. The aqueous solution had n^{26} 1.3805 and $\rho^{20.5}$ 1.022 ± 0.002. Hydrogen chloride was introduced as a dry gas until the normality of acid was *ca.* 0.1.

Kinetic Procedure.—Approximately 0.15 g. of vinyl ester together with a small crystal of *p-t*-butylcatechol[35] were dissolved in 100 ml. of the acidic aqueous dioxane and the solution was sealed in 3-ml. ampoules. After a given period of time in the kinetic bath, each ampoule was quenched, and two 1-ml. aliquots (in excess water) were titrated independently to a phenolphthalein end point with a standardized solution of sodium methoxide in methanol. An infinity titer was obtained after 10 half-lives. Table V contains data from a typical kinetic run.

TABLE V

ACID HYDROLYSIS OF VINYL PROPIONATE[a]

Elapsed time, min.	0.1315 *N* base, ml.[b]	−Ln [ester]
0	1.015	2.60
10	1.083	2.73
20	1.160	2.90
30	1.222	3.06
40	1.270	3.20
50	1.314	3.36
60	1.352	3.51
70	1.380	3.64
	1.579	. . .

[a] At 65.00 ± 0.05° in 50 wt. % aqueous dioxane containing 0.1334 *N* HCl. [b] Each value is the average of two titrations.

Rate constants were determined by the method of least squares[36] and, except for runs pertaining to vinyl pivalate, have a least-squares error less than 0.6% for any individual run. The average deviation among several repeated runs was $\leq 2\%$ with the exception of vinyl butyrate at 55° (±3% deviation) and vinyl pivalate at 75° (±4.5% deviation).

Singular difficulty was encountered with the determination of the vinyl pivalate rate constants. The solubility of the compound in the solvent system was sufficiently low that the solution had to be saturated at a temperature slightly above room temperature. During the initial 10–20% reaction period the titrations would often be erratic apparently associated with the presence of very finely divided droplets of unreacted vinyl pivalate in the cooled ampoules. For reasons as yet unknown, end-point determinations toward the end of the run also became erratic. Because of the apparent curvature in the activation plot, maximum estimates for ΔH^* and ΔS^* were obtained from data at 65 and 75°. Similar difficulties have been reported for the determination of the activation parameters for the acid-catalyzed hydrolysis of ethyl pivalate.[10]

Hydrolysis of Isopropenyl Acetate in a Deuterated Medium.—A solution of 50 vol. % dioxane in deuterium oxide, which contained a trace of hydroquinone and sufficient concentrated hydrochloric acid to make an over-all 0.104 *N* hydrogen ion concentration, was saturated with isopropenyl acetate at room temperature, heated for 1 hr. at 55°, cooled, and diluted with 15 ml. of cold saturated sodium chloride solution. The unreacted starting material was quickly extracted with carbon tetrachloride, washed several times with more salt solution, and dried over magnesium sulfate. A n.m.r. spectrum indicated no deuterium incorporation into the isopropenyl group under conditions which had produced 23% over-all hydrolysis of the starting compound.

That rapid exchange had not taken place during the work-up procedure was ascertained by observing the appearance of the vinyl protons (by n.m.r.) during the course of the hydrolysis. The relative area of the vinyl to acetyl protons in the isopropenyl acetate showed no discernible change during 1 or 2 hr. at 55°.

Acknowledgment.—The author wishes to thank the University of Kansas for the award of an Elizabeth M. Watkins Faculty Fellowship during the summer of 1964. He is also indebted to Professor Richard Schowen for helpful discussions during the course of this work.

---

[33] All n.m.r. spectra were obtained on a Varian A-60 n.m.r. spectrometer. Unless otherwise specified, chemical shift values are reported in units of τ (internal tetramethylsilane standard).

[34] R. L. Adelman, *J. Org. Chem.*, **14**, 1057 (1949).

[35] Vinyl acetate was used only with the commercial stabilizer present.

[36] L. P. Hammett, "Introduction to the Study of Physical Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1952, p. 410.

The Direction of Enolization of Benzoylacetones[1]

JAMES U. LOWE, JR., AND LLOYD N. FERGUSON

Department of Chemistry, Howard University, Washington, D. C.

Received April 12, 1965

The enolic character and direction of enolization of some substituted benzoylacetones have been studied by infrared, ultraviolet, and n.m.r. spectroscopy. The spectra are interpreted to show that the benzoylacetones are over 90% enolic in a nonpolar solvent and are enolized toward the phenyl group, and some contain a few per cent of a nonchelated enol, thought to be the *trans* isomer **3**.

The keto–enol equilibrium of 1,3 diketones has been the object of many studies, probably because the system provides an interesting case for the application of the prevailing concepts of organic chemistry.[2] Not only is the position of equilibrium of general interest, but also the direction of enolization. Thus, for a 1,3 diketone of the type Ar—CO—CH_2—CO—CH_3, where Ar represents an aryl group, it is desirable to know the population of the enols in the equilibrium mixture A. It is a reasonable assumption that the amount of enol present involving the CH_3 group, Ar—CO—CH_2—C(OH)=CH_2, is insignificant.[2] This is evident from the n.m.r. spectra of the benzoylacetones **6–10**. For almost all diketones studied,[3] even including those of α-keto esters,[4] the per cent and direction of enolization

---

[1] Taken in part from the Ph.D. Dissertation of J. U. Lowe, June 1963.

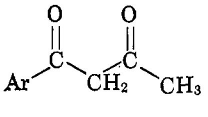
[2] L. N. Ferguson, "Modern Structural Theory of Organic Chemistry," Prentice-Hall, Inc., Englewood Cliffs, N. J., 1963, Chapter 4.

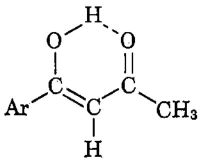
[3] R. P. Barnes, *et al.*, *J. Am. Chem. Soc.*, **69**, 3132 (1947), and earlier papers; R. D. Campbell and H. M. Gilow, *ibid.*, **82**, 2389 (1960); P. B. Russell, *Chem. Ind.* (London), 326 (1956).

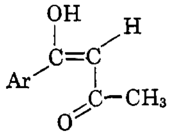
[4] A. M. Stock, N. E. Donahue, and E. D. Amstutz, *J. Org. Chem.*, **23**, 1840 (1958).

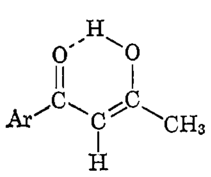
can be explained in terms of the relative amount of resonance stabilization associated with a cinnamoyl system, $\mathrm{Ar{-}C{=}C{-}C{=}O}$. Owing to this resonance and the chelate bond, it was expected that enol **2** should be the major constituent in mixture A. In order to test this notion, a study was made on several substituted benzoylacetones and related intermediates.

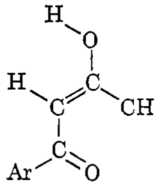
MIXTURE A


1


2


3

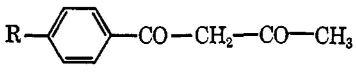

4


5

Results and Discussion

The combined spectral properties of the benzoylacetones included in this study indicate that the compounds are (i) over 90% enolic in a nonpolar solvent, (ii) are enolized toward the phenyl group, and (iii) contain a small per cent of a nonchelated enol. In mixture A, enol **2** is the major constituent. The diketone **1** is not detectable in benzoylacetones **9** and **10** but is present up to 5% in **6–8**. *trans*-Enol **3** is estimated to be present at the 2% level. These deductions are based on the following observations.

(1) The essential n.m.r. data for the benzoylacetones **6–10** are summarized in Table I. All of the


6, R = H **9**, R = Br
7, R = CH$_3$ **10**, R = NO$_2$
8, R = CH$_3$O

benzoylacetones exhibit a broad enolic proton peak[5]: compounds **9** and **10** are 100% enolic, and compounds **6–8** contain *ca.* 5% diketone. The keto methylenic peak of compound **8** falls beneath the strong CH$_3$O peak and therefore is not observed.

The infrared spectra of these compounds in carbon tetrachloride also confirm the predominance of enol **2** in mixture A. All of the benzoylacetones have a broad, weak band in the 2500–2700-cm.$^{-1}$ region for the chelated hydroxy group,[6] $\mathrm{C{=}O\cdots\cdots H{-}O}$, and a strong band in the 1595–1608-cm.$^{-1}$ region for the chelated carbonyl group. There is no benzoyl band in the 1670–1689-cm.$^{-1}$ region of these spectra. For comparison, the infrared spectra of the α,α-dimethylbenzoylacetones **19** and **20** and of the crotonophenones **16–18** exhibit ν_{CO} bands in the 1687–1689- and 1673–1678-cm.$^{-1}$ regions, respectively, which are characteristic of the Ar—CO and Ar—CO—C═C groups, but are absent in the spectra of the benzoylacetones. Thus, the infrared spectra confirm the completely enolic character of compounds **9** and **10** but do not reveal the presence of the 5% of diketone in compounds **6–8**.

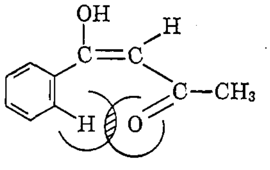
TABLE I

N.M.R. SPECTRAL DATA FOR SOME BENZOYLACETONES[a]

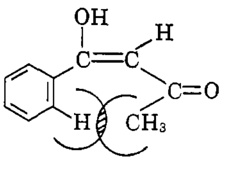
	C.p.s.					
Compound	Enol COCH$_3$	Keto COCH$_3$	Keto CH$_2$	Enol =CH	Enol OH	% Enol
6	128	130	235	365	970	94.5[b]
7[c]	123	131	235	363	960	95.7[b]
8	125	130		359	970	94.7[d]
9	127			360	962	100
10[e]	136			374	954	100

[a] Cycles per second for 0.2–0.5 *M* carbon tetrachloride solutions with tetramethylsilane as internal standard. Measurements were made on Varian DP-60 and A-60 spectrometers. [b] From integrated intensities of vinyl and methylene peaks. [c] Data for neat sample. [d] From weights of paper cut-outs of enol COCH$_3$ and keto COCH$_3$ peaks. Similar estimate for compound **7** agrees with integrated intensity value within 1%. [e] Data for saturated carbon tetrachloride solution (~0.4 *M*).

The presence of a very small amount of the nonchelated enol **3** was detected in the infrared spectra of compounds **6–10**. This was shown by the appearance of very weak hydroxy bands in the 3400–3636-cm.$^{-1}$ region of the spectra of **6–10** and a very low-intensity carbonyl band in the 1708–1722-cm.$^{-1}$ region for compounds **6–8**. The relative intensities of the 3400–3636-cm.$^{-1}$ bands are concentration dependent which suggests that the small amount of nonchelated enol present is associated through intermolecular hydrogen bonds. This nonchelated enol is thought to be enol **3** in mixture A. Enol **5** is excluded on the basis of the absence of a benzoyl group band in the 1670–1689-cm.$^{-1}$ region. The frequency of the —COCH$_3$ band in compounds **6–8** shows that the group is not conjugated with the —C═C— bond. This is no surprise in view of steric hindrance to a planar structure. This forces the acetyl group to rotate out of the plane.



or



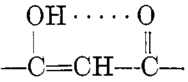
(2) The benzoylacetones **6–10** and the benzalacetones **11–15** all contain a cinnamoyl band in their ultraviolet spectra, which, as to be expected, is absent in the spectra of the crotonophenones **16–18** and the ketonic α,α-dimethylbenzoylacetones **19** and **20**. Thus, $\lambda_{\max}^{n\text{-hexane}}$ values (log ϵ 4–5 in every case) for these chromophoric systems are, for $\mathrm{Ar{-}C{=}C{-}\underset{|}{C}{=}O}$, 281–307; Ar—CO—C═C—, 248–283; Ar—CO—CH$_2$—CO—R, 253; and $\mathrm{Ar{-}\overset{OH\cdots\cdots O}{\overset{|\qquad\quad\|}{C{=}CH{-}C}}{-}}$, >300 m$\mu$. This can be taken as evidence for the direction of enolization of the diketones to be toward the aryl groups to yield **2** or **3** rather than **4** or **5**.

The position of $\lambda_{\max}$ of the benzoylacetones cannot be attributed to a bathochromic effect of the —OH

---

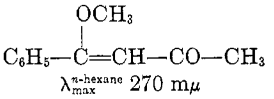
[5] J. L. Burdett and M. T. Rogers, *J. Am. Chem. Soc.*, **86**, 2105 (1964); J. K. O'Loane, C. M. Combs, and R. L. Griffith, *J. Org. Chem.* **29**, 1730 (1964).

[6] S. Bratoy, D. Hâdzi, and G. Rossmy, *Trans. Faraday Soc.*, **52**, 464 (1956).

on the Ar—CO—C=C system because it has been observed that the auxochromic effect of the OH and OCH_3 groups on the CO—C=C—R (R = alkyl) system does not shift λ_{max} beyond the 300-mμ region.[7] Thus, all reported values of λ_{max} for enols and their methyl ethers of the type R—CO—CH=C(OH)—R and R—CO—CH=C(OCH_3)—R are below 300 mμ. This is true even for the methyl ethers of the two enols of benzoylacetone.[8] On the other hand, the  $\overset{OH\cdots\cdots O}{Ar—\overset{|}{C}=CH—\overset{\|}{C}—}$ chromophore, when steric requirements do not prevent coplanarity of the aromatic and chelated enol rings, has λ_{max} >300 mμ.[9] Therefore, the λ_{max} values reported in this work for the benzoylacetones, all larger than 300 mμ, provide evidence for the direction of enolization of the diketones, *i.e.*, enol **2** or **3** in mixture A. The shift of λ_{max} with a change of solvent is in the direction expected for a transition in which absorption produces a more polar excited state.

$C_6H_5—CH=CH—CO—CH_3$

$\lambda_{max}^{n\text{-hexane}}$ 281 mμ

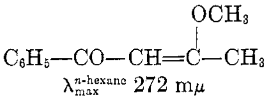


$C_6H_5—\overset{OCH_3}{\overset{|}{C}}=CH—CO—CH_3$

$\lambda_{max}^{n\text{-hexane}}$ 270 mμ

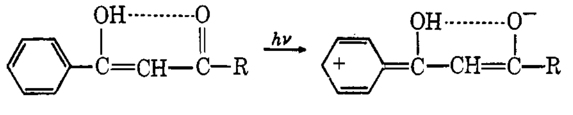
$C_6H_5—CO—CH=CH—CH_3$

$\lambda_{max}^{n\text{-hexane}}$ 248 mμ



$C_6H_5—CO—CH=\overset{OCH_3}{\overset{|}{C}}—CH_3$

$\lambda_{max}^{n\text{-hexane}}$ 272 mμ



Bromine titrations[10] for enol content were run in carbon tetrachloride in order to compare the results with the spectroscopic data. The titration results were far from quantitative. This situation has been reported previously for other ketones.[11]

Experimental

Preparation of Compounds.—Compounds **6**, **11**, and **13** were commercial samples purified by recrystallization. The remainder of the compounds were prepared by methods cited in the literature. The benzoylacetones were purified by formation of their copper chelates and regeneration with sulfuric acid. The copper chelates had infrared absorption bands in the 1550–1640-cm.$^{-1}$ *and* 1520–1540-cm.$^{-1}$ regions which is characteristic of a 1,3 diketone unsubstituted at the methylenic group.[12]

In all cases, solutions were allowed to equilibrate at least 24 hr. in the dark before spectra were measured.

Infrared Absorption Measurements.—The majority of the infrared spectra were measured using a Perkin-Elmer Model 21 double-beam recording spectrophotometer with sodium chloride optics. The control settings were maintained constant: resolution, 927; response, 1; gain, 5; speed, 6; and suppression, 3. Concentrations were in the range 30–40 mg./ml. of spectroanalyzed carbon tetrachloride. Matched 0.2-mm. cells were used in standard double-beam operation. The benzoylacetones were also examined in the 3700–3400- and 2700–2500-cm.$^{-1}$ regions as Nujol mulls and in carbon tetrachloride solutions (concn., 20 mg./ml.) in 14.4-mm. matched cells on a Beckman IR-8 double-beam grating spectrophotometer. The copper chelates of the benzoylacetones were recorded as Nujol mulls on the Beckman IR-8 spectrophotometer.

Ultraviolet Absorption Measurements.—Stock solutions for each compound were prepared by dissolving an accurately weighed amount of the sample in 100 ml. of Fisher spectroanalyzed grade isopropyl alcohol or *n*-hexane. Solutions with concentrations of 1×10^{-3} to 1×10^{-5} *M* were prepared by dilution of the stock solutions using certified National Bureau of Standards 2-, 3-, and 5-ml. pipets and volumetric flasks.

The survey runs were carried out either on a Beckman DK-2 recording spectrophotometer or a Bausch and Lomb 505 grating spectrophotometer. The spectra of these compounds were then determined with a Beckman DU battery-powered spectrophotometer with the same pair of matched 1-cm. silica cells. The spectrum of each compound was measured at least twice.

Nuclear Magnetic Resonance Measurements.—The H^1 spectra were measured by N. Judge King of Howard University on a Varian A-60 spectrometer and by R. Barefoot of the U. S. Naval Propellant Plant on a Varian DP-60 spectrometer operated at 60 Mc.p.s. All measurements were made in carbon tetrachloride at concentrations of 0.2 to 0.5 *M* with tetramethylsilane as internal standard. The solutions were degassed and vacuum sealed in 5-mm.-o.d. glass tubes.

Bromine Titrations.[10]—Aliquots (50-ml.) of 2×10^{-3} *M* carbon tetrachloride solutions of the diketonic substances were brominated with 25 ml. of 1.87×10^{-2} *M* ethanolic bromine. After the excess bromine was destroyed with diisobutylene, 15 ml. of 20% aqueous sodium iodide was added. The solution was equilibrated at 35° and the endpoint was determined with 0.1046 *N* sodium thiosulfate.

Physical Constants.—**Benzoylacetone** (**6**) had m.p. 57°, (lit.[13] m.p. 57–58°); copper chelate m.p. 193–196° (lit.[14] m.p. 195–196°); % enol[10] 101 ± 0.8; ν 3574 w, 3461 (assoc. OH), 2520–2460 w (intramolecular OH····O=C), 1714 w (CH_3—C=O), and 1610–1598 cm.$^{-1}$ s (C=O·····H—O); λ^{I}_{max}[15] 307 mμ (ε 15,800), λ^{H}_{max}[15] 307 mμ (ε 38,000); n.m.r. τ 7.87 (enol —CH_3), 7.84 (keto —CH_3), 6.09 (CH_2), 3.92 (vinyl), multiplet with center at 2.34 (aromatic), and −6.02 (OH).

p-**Methylbenzoylacetone** (**7**) had b.p. 96–98° (4 mm.), n^{25}D 1.5907 [lit.[16] b.p. 126–132° (6 mm.)]; copper chelate m.p. 228–229° (lit.[17] m.p. 229°); % enol[10] 96 ± 7; ν 3610 (free OH), 3497 w (assoc. OH), 2700–2500 w (intramolecular OH····O=C), 1722 w (CH_3C=O), and 1606–1596 cm.$^{-1}$ s (C=O····H—O); λ^{I}_{max} 312 mμ (ε 35,600); λ^{H}_{max} 306 mμ (ε 44,600); n.m.r. τ 7.95 (enol —CH_3), 7.82 (keto —CH_3), 7.64 (Ar—CH_3), 3.95 (vinyl), 2.38 (aromatic quartet, *J* = 8 c.p.s.), and −6.02 (OH).

p-**Methoxybenzoylacetone** (**8**) had m.p. 54.5° (lit.[14] m.p. 54.5°); copper chelate m.p. 229° (lit.[18] 210–211.5°); % enol[10] 89 ± 6; ν 3636 w (free OH), 3484 w (assoc. OH), 2793–2591 w (intramolecular OH····O=C), 1712 w (CH_3—C=O), and 1635–1577 cm.$^{-1}$ s (broad, C=O····H—O + C=C); λ^{I}_{max} 320 mμ (ε 56,300); λ^{H}_{max} 309 mμ (ε 49,000); n.m.r. τ 7.92 (enol —CH_3), 7.84 (keto —CH_3), 6.23 (CH_3O), 4.03 (vinyl), 2.71 aromatic quartet (*J* = 9 c.p.s.), and −6.16 (OH).

p-**Bromobenzoylacetone** (**9**) had m.p. 92–93° (lit.[16] m.p. 92.5°); copper chelate m.p. 288–290°; % enol[10] 94 ± 0.5; ν 3450 w, 3360 w (assoc. OH), 2725–2590 w (intramolecular OH·····O=C), 1615–1585 s (broad, C=O····H—O + C=C); λ^{I}_{max} 314 mμ (ε 18,200), λ^{H}_{max} 309 mμ (ε 18,700); n.m.r. τ 7.84 (keto —CH_3), 4.00 (vinyl), 2.38 aromatic multiplet (*J* = 10 c.p.s.), and −6.03 (OH).

p-**Nitrobenzoylacetone** (**10**) had m.p. 113° (lit.[17] m.p. 112.5–113°); copper chelate m.p. >355° (lit.[19] >320°); % enol[10] 85 ±

---

(7) *Cf.* G. S. Hammond, W. G. Bordium, and G. A. Guter, *J. Am. Chem. Soc.*, **81**, 4682 (1959); R. D. Campbell and H. M. Gilow, *ibid.*, **82**, 2389 (1960); S. T. Yoffe, E. M. Popov, K. V. Vatsuro, E. K. Tulikova, and M. I. Kabachnik, *Tetrahedron*, **18**, 923 (1962).

(8) B. Eistert and E. Merkel, *Ber.*, **86**, 904 (1953).

(9) L. N. Ferguson and R. P. Barnes, *J. Am. Chem. Soc.*, **70**, 3907 (1948); G. S. Hammond, W. G. Bordium, and G. A. Guter, *ibid.*, **81**, 4682 (1959).

(10) S. R. Cooper and R. P. Barnes, *Ind. Eng. Chem., Anal. Ed.*, **10**, 379 (1938); A. Gero, *J. Org. Chem.*, **19**, 1960 (1954).

(11) In some cases values up to 202% enol have been reported: *cf.* J. D. Park, H. A. Brown, and J. R. Lacher, *J. Am. Chem. Soc.*, **75**, 4753 (1953); K. Meyer, *Ber.*, **45**, 2843, 2848, 2858 (1912); J. C. Reid and M. Calvin, *J. Am. Chem. Soc.*, **72**, 2952 (1950); R. Filler and S. M. Naqui, *J. Org. Chem.* **26**, 2571 (1961).

(12) R. P. Dryden and A. Winston, *J. Phys. Chem.* **62**, 635 (1938); R. W. Kuiber, *J. Am. Chem. Soc.*, **82**, 4839 (1960); H. F. Holtzclaw, Jr., and J. P. Collman, *ibid.*, **79**, 3318 (1957).

(13) W. Wislicenus and W. Stoeber, *Ber.*, **35**, 545 (1902).

(14) H. G. Walker, Jr., J. J. Sanderson, and C. R. Hauser, *J. Am. Chem. Soc.*, **75**, 4109 (1953).

(15) Ultraviolet spectral solvents: I, isopropyl alcohol; H, *n*-hexane.

(16) K. v. Auwers and P. Heinke, *Ann.*, **458**, 219 (1927).

(17) U. Basu, *J. Indian Chem. Soc.*, **8**, 119 (1931); *Chem. Abstr.*, **25**, 4881 (1931).

(18) E. Besthorn and G. Jaegle, *Ber.*, **27**, 910 (1894); E. Chapman, A. G. Perkin, and R. Robinson, *J. Chem. Soc.*, 3033 (1927).

(19) H. G. Walker and C. R. Hauser, *J. Am. Chem. Soc.*, **68**, 2742 (1946).

0.8; ν 3610 w (free OH), 3472 w (assoc. OH), 2732–2704 w (intramolecular OH····O=C), 1602 s (broad chelated C=O····H—O), 1527 s (asym. NO_2), and 1342 cm.$^{-1}$ s (sym. NO_2); $\lambda^{I}_{\max}$ 327 mμ (ϵ 50,200); n.m.r. τ 7.73 (keto —CH_3), 3.77 (vinyl), 3.5 aromatic quartet (J = 10 c.p.s.), and −5.9 (OH).

Benzalacetone (11) had m.p. 42° (lit.[20] m.p. 42°); dibromide m.p. 124–125° (lit.[21] m.p. 124°); ν 1683 s (conj. C=O), and 1254 cm.$^{-1}$ vs (*trans* C=C); $\lambda^{I}_{\max}$ 285 mμ (ϵ 21,500); $\lambda^{H}_{\max}$ 281 mμ (ϵ 24,100); n.m.r. τ 7.77 (CH_3) and 3.77 (vinyl).

p-**Methylbenzalacetone** (12) had b.p. 97–98 (7 mm.) [lit.[22] b.p. 142–145 (15 mm.)]; ν 1685 s (conj. C=O) and 1252 cm.$^{-1}$ vs (*trans* C=C); $\lambda^{I}_{\max}$ 296 mμ (ϵ 21,500); $\lambda^{H}_{\max}$ 285 mμ (ϵ 31,800).

p-**Methoxybenzalacetone** (13) had m.p. 74–75° (lit.[20] m.p. 72–74°); oxime m.p. 125° (lit.[23] m.p. 123–124°); ν 1682 s (conj. C=O) and 1247 cm.$^{-1}$ vs (*trans* C=C); $\lambda^{I}_{\max}$ 317 mμ (ϵ 24,000); $\lambda^{H}_{\max}$ 307 mμ (ϵ 44,700).

p-**Bromobenzalacetone** (14) had m.p. 83–84° (lit.[24] m.p. 83–84°); ν 1686 s (conj. C=O) and 1259 cm.$^{-1}$ vs (*trans* C=C); $\lambda^{I}_{\max}$ 289 mμ (ϵ 48,000); $\lambda^{H}_{\max}$ 288 mμ (ϵ 100,500).

p-**Nitrobenzalacetone** (15) had m.p. 107–108° (lit.[24,25] m.p. 110°); ν 1692 m (conj. C=O), 1344 vs (asym. NO_2), and 1247 cm.$^{-1}$ m (sym. NO_2); $\lambda^{I}_{\max}$ 298 mμ (ϵ 15,800); $\lambda^{H}_{\max}$ 295 mμ (ϵ 49,000).

Crotonophenone (16) had b.p. 58° (0.14 mm); n^{25}_{D} 1.5567 [lit.[26] b.p. 98.6–98.9 (3.9–4.0 mm.); n^{25}_{D} 1.5586]; ν 1673 cm.$^{-1}$ vs (arom. C=O); $\lambda^{I}_{\max}$ 254 mμ (ϵ 17,000); $\lambda^{H}_{\max}$ 248 mμ (ϵ 46,900); n.m.r. τ 8.1 and 8.2 (CH_3) and 3.22 and 2.87 (vinyl) (J = 21 c.p.s.).

p-**Methylcrotonophenone** (17) had b.p. 77–78° (0.2 mm); n^{26}_{D} 1.5549; ν 1674 cm.$^{-1}$ vs (arom. C=O); $\lambda^{I}_{\max}$ 255 mμ (ϵ 31,600); $\lambda^{H}_{\max}$ 254 mμ (ϵ 37,200); n.m.r. τ 8.09 (doublet, CH_3), 7.67 (arom. CH_3), and 3.25 (doublet, vinyl).

Anal. Calcd. for $C_{11}H_{12}O$: C, 82.46; H, 7.55. Found: C, 82.27; H, 7.79.

p-**Methoxycrotonophenone** (18) had m.p. 22–23° (lit.[27] m.p. 23°), b.p. 107° (0.2 mm); ν 1670 cm.$^{-1}$ vs (arom. C=O); $\lambda^{I}_{\max}$ 292 mμ (ϵ 18,200); $\lambda^{H}_{\max}$ 283 mμ (ϵ 19,500); n.m.r. τ 8.09 (doublet, CH_3), 6.23 (CH_3O), and 3.85 (doublet, vinyl).

α,α-**Dimethylbenzoylacetone** (19) had b.p. 83–84° (11 mm.); $n^{27.5}_{D}$ 1.5151 [lit.[28] b.p. 84° (2 mm.), 125–128 (14 mm.)]; ν 1748 m, 1718 s (aliphatic C=O), and 1677 cm.$^{-1}$ vs (arom. C=O); $\lambda^{I}_{\max}$ 242 mμ (ϵ 15,500); $\lambda^{H}_{\max}$ 253 mμ (ϵ 19,500).

α,α-**Dimethyl-*p*-methylbenzoylacetone** (20) had b.p. 130° (1 mm.); n^{23}_{D} 1.5228; ν 1735 m, 1705 s (aliphatic C=O), and 1667 cm.$^{-1}$ vs (arom. C=O); $\lambda^{I}_{\max}$ 254.5 mμ (ϵ 13,500); $\lambda^{H}_{\max}$ 253 mμ (ϵ 28,000).

Anal. Calcd. for $C_{13}H_{16}O_2$: C, 76.45; H, 7.90. Found: C, 76.38; H, 8.21.

---

[20] N. L. Drake and P. Allen, Jr., "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1941, p. 77.

[21] N. H. Cromwell and R. Benson, "Organic Syntheses," Coll. Vol. III, John Wiley and Sons, Inc. New York, N. Y., 1955, p. 105.

[22] V. Hanzlik and A. Bianchi, *Ber.*, **32**, 2282 (1899).

[23] R. E. Corbett and C. L. Davey, *J. Chem. Soc.*, 296 (1955).

[24] R. E. Lutz, T. A. Martin, J. F. Codington, T. M. Amacker, R. K. Allison, N. H. Leake, R. J. Rowlett, Jr., J. D. Smith, and J. W. Wilson, III, *J. Org. Chem.*, **14**, 994 (1949).

[25] A. Baeyer and P. Becker, *Ber.*, **16**, 1969 (1882).

[26] R. P. Mariella and R. R. Rause, *J. Am. Chem. Soc.*, **74**, 521 (1952).

[27] K. v. Auwers, *Ann.*, **439**, 150 (1924).

[28] R. A. Morton, A. Hassan, and T. C. Galloway, *J. Chem. Soc.*, 891 (1934); A. R. Pinder and R. Robinson, *ibid.*, 3341 (1955).

Reactivities of Bicycloalkenes toward Free-Radical Addition of Thiols[1]

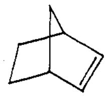
EARL S. HUYSER AND RICHARD M. KELLOGG[2]

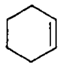
Department of Chemistry, University of Kansas, Lawrence, Kansas

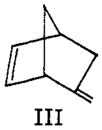
Received May 4, 1965

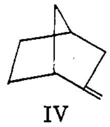
The reactivity ratio of norbornene with respect to methylenenorbornane toward free-radical addition of ethanethiol was shown to vary with both the ethanethiol concentration and temperature. At 40°, norbornene is 2.1 times more reactive than methylenenorbornane when the mole fraction of ethanethiol is 0.87, and 6.7 times more reactive when the mole fraction of ethanethiol is 0.24. At 0°, the relative reactivity ratio was considerably lower and varied between 1.13 and 1.55 as the mole fraction of ethanethiol was decreased from 0.85 to 0.55. These concentration and temperature effects are explained in terms of reversibility of the ethanethiyl radical addition to alkenes, a factor more important with methylenenorbornane than with norbornene.

The relative reactivities of alkenes have been demonstrated to be quite similar toward addition by thiyl radicals[3] and trichloromethyl radicals.[4] One notable exception is the considerably higher reactivity of endocyclic double bonds of bicycloalkenes toward addition by thiyl radicals compared with addition by trichloromethyl radicals. Norbornene (I) was shown to be 45 times more reactive than cyclohexene (II) toward addition of *p*-toluenethiol[5] but only five times more reactive than cyclohexene toward addition by trichloromethyl radicals.[4a] A more striking anomaly was recently pointed out by Cristol and co-workers who found the products formed in the addition of benzenethiol to 5-methylenenorbornene (III) resulted from addition of benzenethiyl radicals only to the endocyclic double bond with complete exclusion of any addition to the exocyclic double bond.[6] A comparison of the reactivity of I with methylenenorbornane (IV) toward addition of the trichloromethyl radical showed that IV, an alkene with an exocyclic double bond, was at least four times more reactive at 78° than I, an alkene with an endocyclic double bond.[7] Cristol and co-workers suggested that the rate of addition to an endocyclic double bond in such a system would be expected to be greater than to an exocyclic double bond


I


II


III


IV

---

[1] This work was supported in part by a grant (GP-739) from The National Science Foundation.

[2] National Science Foundation Cooperative Fellow, 1963–1965. The work described was taken from the thesis submitted by R. M. K. in partial fulfillment of the requirements for the Ph.D. degree from the University of Kansas, 1965.

[3] C. Walling and W. Helmreich, *J. Am. Chem. Soc.*, **81**, 1144 (1959).

[4] (a) M. S. Kharasch and H. N. Friedlander, *J. Org. Chem.*, **14**, 239 (1949); (b) M. S. Kharasch and M. Sage, *ibid.*, **14**, 537 (1949); (c) M. S. Kharasch, E. Simon, and W. Nudenberg, *ibid.*, **18**, 328 (1953).

[5] S. J. Cristol and G. D. Brindell, *J. Am. Chem. Soc.*, **76**, 5699 (1954).

[6] S. J. Cristol, T. W. Russell, and D. I. Davies, *J. Org. Chem.*, **30**, 207 (1965).

[7] E. S. Huyser and G. Echegaray, *ibid.*, **27**, 429 (1962).