acid or acetic anhydride and sulfuric acid, is not affected by refluxing with alcoholic hydrochloric acid, and has an analysis which best fits a dihydroxycholestene. This compound has not been further characterized.
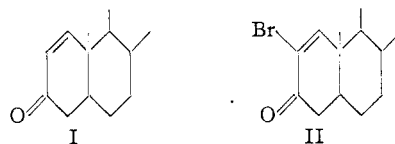

The Effect of Bromine Substitution upon the Ultraviolet Absorption Spectra of α,β-Unsaturated Ketones

BY A. L. NUSSBAUM,[1a] O. MANCERA,[1a] RALPH DANIELS,[1b] G. ROSENKRANZ[1c] AND CARL DJERASSI[1c]

A study of the ultraviolet absorption spectra of a series of aliphatic α-bromo-α,β-unsaturated ketones has demonstrated that α-bromine substitution results in a bathochromic shift of approximately 23 mμ, thus providing additional evidence for the structure of a number of brominated steroid ketones. The presence of a phenyl group in conjugation with either the carbonyl group or the double bond reduces the bathochromic shift due to a bromine atom to 8-14 mμ.

Notably through the work of Woodward[2] and of Gillam[3] it has been possible to correlate with a fair degree of accuracy, ultraviolet absorption spectra with the constitution of α,β-unsaturated ketones. Their measurements and literature analyses, indicating a bathochromic shift of *ca.* 10 mμ for each alkyl substituent and one of 5 mμ for an exocyclic double bond, have proved very valuable in structure assignments of natural products including those of the steroids.

At that time, the tentative suggestion was made[2] that a bromine substituent had almost the same effect as an alkyl group in shifting the maximum. Fieser and Fieser,[4] proceeding on this assumption in correlating ultraviolet absorption with structure in the field of α,β-unsaturated ketosteroids, have been led to question the correctness of structures assigned to the Δ¹-2-bromo-3-ketosteroids (II),[5,6] since they exhibit maxima around 255 mμ as compared to 230 mμ for the unsubstituted Δ¹-3-ketosteroid (I). In our opinion, the structure of the bromo ketones II appeared to be conclusively established by their mode of synthesis (dehydrobromination of a *gem*-2,2-dibromo-3-ketone or bromination of a Δ¹-3-ketone[6c]) and by their reactions, notably the reduction (by zinc in ethanol) to the Δ¹-3-ketone I. On the basis of these observations the bathochromic effect of a bromine substituent upon the spectrum should be close to 25 mμ[7] rather than 10 mμ as believed earlier.[4] This in turn has made untenable the structure assignments[8] of a series of bromination products of Δ⁴-3-ketosteroids and has sub-

sequently led to a revision[9] of their constitution.

From a consideration of the manner in which light in the near ultraviolet region is presumed to be absorbed by α,β-unsaturated ketones to produce activated forms such as —C̈—C=C—O⁻ and a comparison of the electronic environment of a bromine atom *vs.* an alkyl group, it would not be expected *a priori* that they would have the same quantitative effect in shifting the maxima. Bromine might be expected to have an effect intermediate between an alkyl and an alkoxyl or hydroxyl group and in that connection it is pertinent to mention that recent work has indicated a bathochromic shift of 35 mμ for an α-hydroxyl group[10] and one of nearly 50 mμ for a β-hydroxyl substituent.[11] The primary evidence for the assumption by Fieser and Fieser[4] of an equal effect for alkyl and bromine rests on data for three compounds, the structures of which are almost certainly incorrect.[9,12] In or-

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(2) R. B. Woodward, THIS JOURNAL, **63**, 1123 (1941); **64**, 76 (1942).

(3) L. K. Evans and A. E. Gillam, *J. Chem. Soc.*, 815 (1941); A. E. Gillam and T. F. West, *ibid.*, 486 (1942).

(4) L. F. Fieser and M. Fieser, "Natural Products Related to Phenanthrene," Reinhold Publ. Corp., New York, N. Y., 1949, pp. 196-197.

(5) (a) H. H. Inhoffen and G. Zuehlsdorff, *Ber.*, **76**, 233 (1943); (b) B. Ellis and V. Petrow, *J. Chem. Soc.*, 2194 (1939).

(6) (a) A. L. Wilds and C. Djerassi, THIS JOURNAL, **68**, 2125 (1946); (b) C. Djerassi and C. R. Scholz, *ibid.*, **69**, 2404 (1947); (c) **70**, 1911 (1948); (d) *J. Org. Chem.*, **13**, 697 (1948); (e) C. Djerassi and G. Rosenkranz, *Experientia*, **7**, 93 (1951).

(7) R. Adams and W. Herz, THIS JOURNAL, **71**, 2546 (1949), recorded a shift of 25 mμ in the conversion of helenalin to bromohelenalin in excellent agreement with the values observed in the steroid series (refs. 5 and 6).

(8) A. Butenandt, G. Schramm and H. Kudszus, *Ann.*, **531**, 176 (1937); H. H. Inhoffen, *Angew. Chem.*, **53**, 473 (1940).

(9) C. Djerassi, G. Rosenkranz, J. Romo, St. Kaufmann and J. Pataki, THIS JOURNAL, **72**, 4534 (1950). It was also pointed out in this paper that a bromine atom in the γ-position has a variable influence depending upon the configuration. In the steroid series, a 6α-substituent showed a very slight bathochromic shift, while the 6β-isomer exhibited a bathochromic shift of nearly 8 mμ. This has since been confirmed by D. H. R. Barton, University of London (private communication).

(10) L. F. Fieser, M. Fieser and S. Rajagopalan, *J. Org. Chem.*, **13**, 800 (1948).

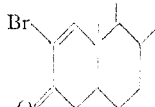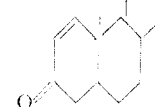(11) C. H. Shunk and A. L. Wilds, THIS JOURNAL, **71**, 3947 (1949), footnote 8.

(12) Of the three compounds (Nos. 43-45 in ref. 4), Δ⁴-4-bromocholesten-3-one (No. 43) is the most important one and the fallacy in its structure assignment is herewith illustrated. The Fiesers (ref. 4) obtained the spectrum from Dannenberg's monograph, who in turn quotes Barkow, Dissertation, Danzig, 1938 (publ. 1940). An inspection of this thesis (a copy was obtained from the Library of the University, Basle) yields the following information: Δ⁴-cholesten-3-one was tetra- or hexabrominated for 24 hours, the resulting solution was refluxed to complete spontaneous loss of hydrogen bromide and the polyunsaturated dibromo derivative refluxed in amyl alcohol in an atmosphere of hydrogen with palladium–barium sulfate catalyst for eight hours. The product, isolated in poor yield, was characterized by a bromine analysis (2.4% *too high*) and an ultraviolet maximum at 250 mμ, and *on the basis of the latter* was assigned the Δ⁴-4-bromocholesten-3-one structure. According to our present results (*cf.* ref. 9, footnote 16) such a substance should exhibit a maximum at *ca.* 265 mμ.

der to clarify this situation, it appeared desirable to examine the influence of bromine substitution on the ultraviolet absorption spectra of a series of *simple*, α,β-unsaturated ketones. The present contribution, dealing with such a systematic study, clearly proves that our earlier structure assignments[6,9] in the steroid series are correct, and that bromine substitution results in a large bathochromic shift of *ca.* 23 mμ.

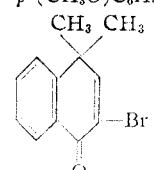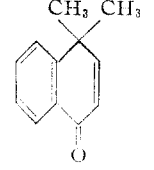The results are summarized in two tables. With one exception, Table I contains aliphatic α,β-unsat-

urated carbonyl derivatives and their α-bromo substituted analogs. The results are in excellent agreement with those observed in the steroid series[5,6] and indicate a bathochromic shift of 21–25 mμ for α-bromine substitution with a somewhat variable effect on the extinction coefficient. A single illustration (Nos. 9 and 10) indicates that the same order of magnitude can be expected with α,β-unsaturated acids. As can be judged from an example taken from the literature (Nos. 12 and 13), bromine substitution on the β-carbon atom pro-

TABLE I
ULTRAVIOLET ABSORPTION SPECTRA OF ALIPHATIC α-BROMO-α,β-UNSATURATED CARBONYL COMPOUNDS

No.	Compound	Ultraviolet maximum (mμ) in 95% ethanol	log ϵ	$\Delta\lambda$ (mμ)
1	CH_3CO—CBr=CH_2	240	3.73	21–30
2	CH_3CO—CH=CH_2	210–219[a,b]	3.81	
3	CH_3CO—CBr=$CHCH_3$	244	4.03	20
4	CH_3CO—CH=$CHCH_3$	224[a,b]	3.99	
5	CH_3CO—CBr=CCH_3CH_3	(218), 260	(3.47) 3.73	24
6	CH_3COCH=CCH_3CH_3	236	3.95	
7	CH_3COCBr=CH—CH=$CBrCOCH_3$	319	4.36	21/bromine atom
8	CH_3COCH=CH—CH=$CHCOCH_3$	278	4.54	
9	CH_3CH=CBr—$COOH$	228[c]	3.85	24
10	CH_3CH=CH—$COOH$	204[c]	4.00	
11	$BrCH$=CBr—CO—$CH_2CH_2CH_3$	259[c] (hexane)	3.85	22
12	$BrCH$=CH—CO—$CH_2CH_2CH_3$	237[c] (hexane)	3.70	30 (β-subst.)
13	CH_2=CH—CO—$CH_2CH_2CH_3$	207[c] (hexane)	3.90	
14		254–256 (6 examples)[5,6]		
				25
15		230 (6 examples)[5,6]		

[a] Ref. 3. [b] K. Bowden, I. M. Heilbron, E. R. H. Jones and B. C. L. Weedon, *J. Chem. Soc.*, 42 (1946). [c] Ref. 14.

TABLE II
ULTRAVIOLET ABSORPTION SPECTRA OF AROMATIC α-BROMO-α,β-UNSATURATED KETONES

No.	Compound	Ultraviolet maximum (mμ)	log ϵ	$\Delta\lambda$ (mμ)
16	C_6H_5CO—CBr=CH_2	254	3.92	12
17	C_6H_5CO—CH=CH_2	242[a]	4.32	
18	p-$(CH_3O)C_6H_4CO$—CBr=CH_2	(224) 286	(4.08) 4.23	12
19	p-$(CH_3O)C_6H_4COCH$=CH_2	(218) 274	(4.21) 4.28	
20		256	4.20	
21		242	4.09	14
22	CH_3CO—CBr=CH—C_6H_5	(222) 294	(4.00) 4.38	8
23	CH_3CO—CH=CH—C_6H_5	(220) 286[17]	(4.08) 4.37	
24	CH_3CO—CBr=$CHC_6H_4(OCH_3)$-p	(236) 326	(3.99) 4.45	8
25	CH_3COCH=$CHC_6H_4(OCH_3)$-p	(232) 318[17]	(4.02) 4.39	

[a] Bowden, *et al.* (ref. 13), report a maximum at 247.5 for a specimen prepared by semihydrogenation of phenyl ethynyl ketone (ultraviolet max. 264.5 mμ). It is conceivable that their vinyl ketone was contaminated by the ethynyl derivative.

duces an even larger shift toward the red (30 mμ). The additive effect of two bromine atoms in diacetylbutadiene (Nos. 7 and 8) is noteworthy.

Table II consists of examples in which a benzene ring is situated adjacent to the carbonyl group (Nos. 16–21), whereupon the bathochromic effect of bromine substitution is reduced to 12–14 mμ, or in the β-position (Nos. 22–25), which resulted in a still further reduction to 8 mμ.

It has already been pointed out in the case of amino,[13,14] alkoxy[14] and halogen[14] substituted α,β-unsaturated ketones that in addition to species such as III (e.g., R = Br) associated with simple α,β-unsaturated ketones (III, R = H), ionic forms in which the amino, alkoxy or halogen atom assumes a partial positive charge must be chiefly responsible for the relatively large bathochromic shift observed with these derivatives. Taking the compounds shown in Table I as specific examples, it is somewhat difficult to write formal structures for such species. Bromonium ions of types IV and V appear attractive, but in contrast to the ground state and III (R = Br, H) where all six atoms are coplanar, this would not be the case with IV and V where a distortion of the valence angles and a twisting of the C=C bond by 90°[15] would be involved. Since two essential requirements for resonance are relatively fixed atomic nuclei and, in this case, coplanarity of all bonds, the resonance stabilization in the excited state provided by forms IV and V would be expected to be low. Similarly, species such as VI are probably of minor importance since they represent cross-conjugated systems.

III   IV

V   VI
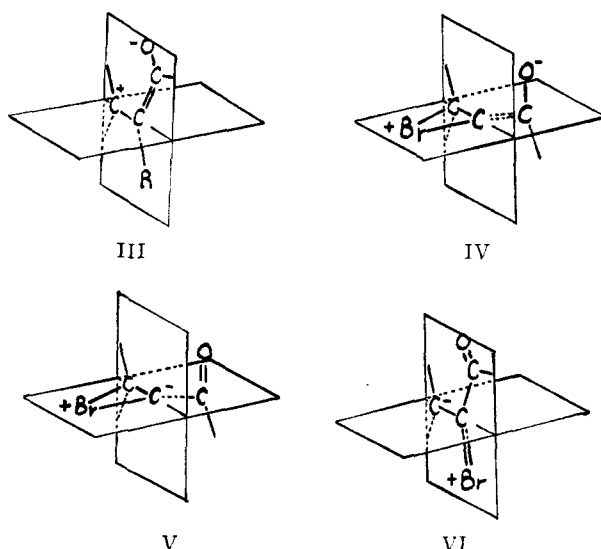
The three carbon atoms and the α-substituent are in the vertical plane in III and VI and in the horizontal plane in IV and V.

The shift in the maximum of the β-bromo ketones (VII) compared with that of the α-isomer may be

(13) K. Bowden, E. A. Braude, E. R. H. Jones and B. C. L. Weedon, J. Chem. Soc., 49 (1946); N. H. Cromwell and W. R. Watson, J. Org. Chem., 14, 411 (1949).

(14) K. Bowden, E. A. Braude and E. R. H. Jones, J. Chem. Soc., 952 (1946).

(15) Such an assumption would be particularly difficult to make in the case of cyclic ketones (I).

rationalized on the basis of a contribution from structure VIII.
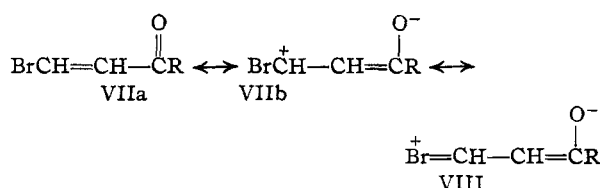
The phenyl substituted derivatives (Table II) can be divided into two classes. With respect to those bearing the phenyl ring on the carbonyl carbon atom (IX), stabilization results mainly from species such as IXa since the acyl phenones absorb at the same wave length as phenyl vinyl ketone.[16] In view of this, forms analogous to III–V in the aliphatic case but not carrying any positive charge in the ring (e.g., IXb) are clearly of minor importance and the contribution of the bromine atom which involves these forms would be expected to be smaller (12–14 mμ) than that in the aliphatic series.

IX   IXa   IXb
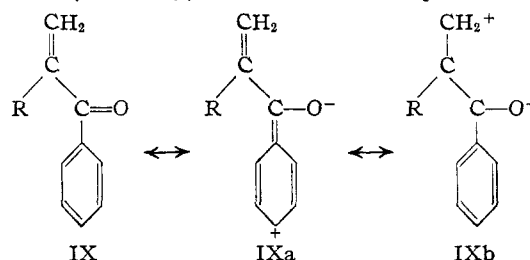
When the phenyl group is substituted in the β-position (X), structures involving the aromatic ring can again be assumed to be of major importance since the effect of a p-methoxyl group is the same here as in case IX (cf. Nos. 16, 17 vs. 18, 19 and 22, 23 vs. 24, 25).[17] As in IX, the aliphatic moiety would contribute little, but now Xb would be more stable[17a] (secondary, benzyl carbonium ion) so that species in which bromine carries a partial positive charge would contribute even less in case X, thus affording an explanation for the smaller bathochromic effect observed in this series.

X   Xa

Xb
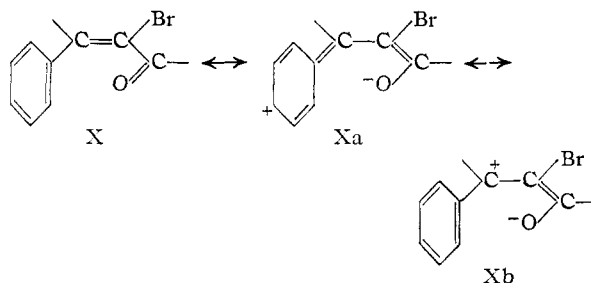
Experimental

Ultraviolet Absorption Measurements.—All of the spectra were measured in a Beckman quartz photoelectric spectro-

(16) For example, acetophenone absorbs at 241 mμ [T. W. Campbell, S. Linden, S. Godshalk and W. G. Young, THIS JOURNAL, 69, 880 (1947)], propiophenone at 244 mμ, butyrophenone at 243 mμ and valerophenone at 241 mμ [D. Biquard, Bull. soc. chim., [5] 8, 55 (1941)].

(17) The effect of a p-methoxyl group (Nos. 16 and 18, 22 and 24) in the bromine substituted substances is of the same magnitude (30–32 mμ) as was reported for the corresponding halogen-free compounds [A. L. Wilds, L. W. Beck, W. J. Close, C. Djerassi, J. A. Johnson, T. L. Johnson and C. H. Shunk, THIS JOURNAL, 69, 1985 (1947)].

(17a) We are indebted to the referee for this suggestion.

photometer (model DU) in the region 216 mμ to 360 mμ; ϵ = $(1/c)$ log I_0/I, where c is the concentration in moles per liter. Since most of the compounds were rather unstable liquids, at least three distillation cuts of similar boiling point and refractive index were used and the triplicate spectral determinations (in 95% ethanol) were carried out immediately after distillation.

Preparation of Compounds.—In spite of the fact that most of the substances are known, their purity was checked by elementary analysis in addition to b.p. and refractive index. Compounds 1, 3, 16 and 22 were prepared according to Nield,[18] No. 5 according to Pauly and Lieck,[19] Nos. 17 and 19 by decomposition of the corresponding Mannich bases,[20] while Nos. 20 and 21 were gifts of Dr. Jay S. Buckley of the University of Minnesota.[21] The synthesis of diacetylbutadiene (No. 8)[22] will be published at a later date.[23] The following compounds are new:

3,6-Dibromo-3,5-octadien-2,7-dione (No. 7).—This compound was obtained in 56% yield from the corresponding dilactone[23] by following the general method described by Nield.[18] Two recrystallizations from 95% ethanol afforded the desired compound in rosettes of yellow needles, m.p. 102-103°.

Anal. Calcd. for $C_{10}H_8O_2Br_2$: C, 32.46; H, 2.72. Found: C, 32.60; H, 2.79.

(18) C. H. Nield, THIS JOURNAL, **67**, 1145 (1945).

(19) H. Pauly and H. Lieck, *Ber.*, **33**, 500 (1900).

(20) K. Mannich and G. Heilner, *ibid.*, **55**, 356 (1922); K. Mannich and D. Lammering, *ibid.*, **55**, 3510 (1922).

(21) R. T. Arnold, J. S. Buckley and J. Richter, THIS JOURNAL, **69**, 2322 (1947).

(22) P. Karrer, C. H. Eugster and S. Perl, *Helv. Chim. Acta*, **32**, 1013, 1934 (1949); F. Sondheimer and B. C. L. Weedon, *Nature*, **165**, 482 (1950).

(23) R. B. Woodward and R. Daniels; *cf.* R. Daniels, Ph.D. Thesis, Harvard University, 1950.

3-Bromo-4-(p-methoxyphenyl)-3-buten-2-one (No. 24).—α-Keto-β-acetyl-γ-(p-methoxyphenyl)-butyrolactone was synthesized in 32% yield by exactly the same procedure employed by Nield[18] for the corresponding γ-phenyl derivative; m.p. 157-158°.

Anal. Calcd. for $C_{13}H_{12}O_5$: C, 62.90; H, 4.88. Found: C, 63.17; H, 5.29.

The bromination and cleavage of the butyrolactone derivative was carried out according to Nield's method[18] at 5° in 85% methanol solution; yield 45%, b.p. 153-155° (0.01 mm.), $n^{19}D$ 1.6579.

Anal. Calcd. for $C_{11}H_{11}O_2Br$: C, 51.79; H, 4.35. Found: C, 51.56; H, 4.62.

α-Bromovinyl-p-methoxyphenyl Ketone (No. 18).—The synthesis of α-keto-β-(p-methoxybenzoyl)-butyrolactone as modeled after that of the corresponding benzoyl derivative[18]; yield 34%, m.p. 153-154°.

Anal. Calcd. for $C_{12}H_{10}O_5$: C, 61.54; H, 4.30. Found: C, 61.66; H, 4.69.

The bromo derivative was prepared from the above lactone in the usual manner[18] in 41% yield, b.p. 130-131° (0.005 mm.), $n^{19}D$ 1.6028.

Anal. Calcd. for $C_{10}H_9O_2Br$: C, 49.82; H, 3.76. Found: C, 49.71; H, 3.99.

Reactions of Nitrous Acid. I. Ammonium Nitrite Decomposition[1]

BY JOSEPH H. DUSENBURY AND RICHARD E. POWELL

The rate law for the reaction of nitrous acid with ammonia is $d(N_2)/dt = k_r (NH_4^+)(HNO_2)$, where $k_r = (kT/h)$ exp $(-7.75/R)$ exp$(-20,000/RT)$ sec.$^{-1}$ mole^{-1} liter. The rate-determining step of the reaction is proposed to be reaction of nitrosyl ion with molecular ammonia.

The kinetics of the reaction between ammonium ion and nitrite ion

$$NH_4^+ + NO_2^- = N_2 + 2H_2O$$
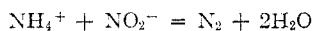
was studied by Abel and co-workers in 1931.[2] They reported the reaction to be kinetically third order: first order with respect to ammonium ion, to nitrite ion and to molecular nitrous acid. Reaction mechanisms involving such an extra molecule of nitrous acid have seemed to us implausible, so we have reinvestigated the kinetics.

Experimental

The reaction vessel was a three-necked flask equipped with a gas-tight motor stirrer,[3] a pressure-equalizing funnel for adding the sodium nitrite solution to the other reactants, and a gas buret in which the evolved nitrogen was measured. The reactor was immersed in an oil thermostat whose temperature was controlled to ±0.05°. The apparatus was swept with nitrogen before each run. At the completion of each run the evolved gas was shaken with permanganate solution to determine the nitric oxide liberated by the in-

(1) Presented at the 115th National Meeting of the American Chemical Society, San Francisco, California.

(2) E. Abel, H. Schmid and J. Schafranik, *Z. physik. Chem.*, Bodenstein Festband, 510 (1931).

(3) W. G. Dauben, J. C. Reid and P. E. Yankwich, *Anal. Chem.*, **19**, 828 (1947).

cidental decomposition of nitrous acid. Under our experimental conditions the amount of such decomposition was negligible.

Reaction mixtures were made up from stock solutions of sodium nitrite and ammonium perchlorate, whose concentrations were checked by analysis. The acidity of the reaction mixtures was controlled by phosphate buffers made with phosphoric acid and NaH_2PO_4, and was measured before and after each run with a glass-electrode pH meter. The ionic strength was brought to the desired value with sodium perchlorate.

Individual measurements of initial rates were reproducible within about 2%.

Results and Discussion

In one series of rate measurements, only the initial concentration of ammonium ion was varied (Table I, Fig. 1). In another series, only the initial concentration of total nitrous acid was varied (Table II, Fig. 2). These data demonstrate that the reaction is first order with respect to (stoichiometric) ammonia and first order with respect to (stoichiometric) nitrous acid. We find no evidence of the second-order dependence on stoichiometric nitrous acid which Abel, *et al.*, reported. The probable explanation of the discrepancy is that we buffered our reaction mixtures, whereas they omitted doing so.