triene conjugation in linolenate as shown by the long induction period in the rise of the 2700 band (Fig. 3) and the much more rapid increase of the oxygen compounds sensitive to alkali (Figs. 1, 2 and 9). From this it may be concluded that there is little evidence in these data that a 9,16-dihydroperoxide is formed in more than traces from linolenate. That monohydroperoxides are the chief primary oxidation products of the linolenate and arachidonate is indicated by the fact that the maximum chromophore intensity is at 2350 Å.

These speculations at first seem to contradict earlier findings that peroxides were not responsible for the absorption band near 2300 Å.[5] It should be pointed out that extinction at this wave length is proportional to peroxide content only in the early stages of oxidation or when the oxidizing conditions are not conducive to peroxide destruction. Destruction of the peroxides leads to compounds which still absorb strongly at 2300 Å. These observations do not refute the contention that the conjugation observed in oxidized fats is formed through the conjugated hydroperoxide.

After this paper went to press the authors read a contribution by Sune Bergström in which similar results were reported.[12]

Summary

1. The rates of development of the various chromophores appearing during the oxidation of ethyl linolate, ethyl linolenate and methyl arachidonate have been followed and related to the oxygen absorbed.

2. At 37° oxidation of linolenate, and possibly arachidonate, is accompanied by the formation of chromophores which exhibit fine structure in the spectra of their alcoholic and alkaline solutions. This was not observed with ethyl linolate.

3. The rate of formation of chromophores absorbing at 2325 Å. in oxidizing linolate and the rate of oxygen uptake agrees with the postulated formation of a conjugated monohydroperoxide as suggested by Bolland and Koch.

4. The development of color or of ultraviolet chromophores cannot be taken as a measure of oxygen uptake (degree of oxidation) unless the composition of the fatty acid mixture is known.

(12) Bergström, Arkiv för Kemi, Mineralogi och Geologi, 21A, No. 14 (1945).

Absorption Spectra. III. Cyclic β-Diketones

BY ELKAN R. BLOUT, VIRGINIA W. EAGER AND DOROTHY C. SILVERMAN

Continuing our studies on the relationship between structure and absorption spectra of molecules,[1] we have investigated the spectra of several simple β-diketones and the effect of bromine substitution upon the fundamental diketonic spectrum. Although previous investigators[2,3] have mentioned the influence of bromine atoms adjacent to carbonyl groups upon absorption, no extensive study of this phenomenon has been reported.

The acidic nature of cyclic β-diketones is ascribable to the fact that upon enolization of one of the hydrogen atoms between the carbonyl groups a grouping is formed which has all the properties of, and is vinylogous with, a carboxylic acid. This acidic form (Ib) of a typical cyclic β-diketone, 5,5-dimethylcyclohexanedione-1,3, is one of the possible formulas (I) which may be written for such a compound.

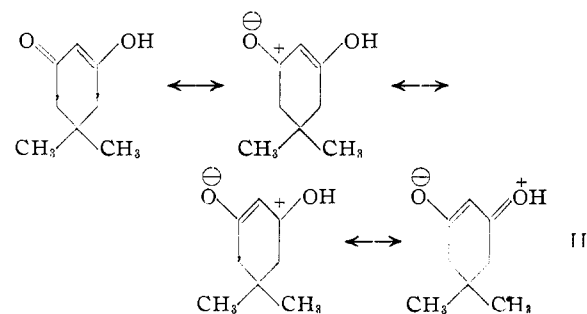The present work shows that form Ib, with contributions of forms such as those shown in II

and their dissociated or ionic forms, III
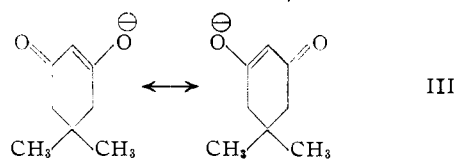
are responsible for many of the light absorptive properties associated with such compounds.

In contrast to isolated carbonyl groups which absorb only very weakly in the ultraviolet (log ϵ 1 → 2, λ max. 270–300 mμ), β-diketones are characterized by intense absorption.[2,4,5] The

(1) Blout and Gofstein, THIS JOURNAL, 67, 13 (1945); Blout and Eager, ibid., 67, 1315 (1945).

(2) Graham and Macbeth, J. Chem. Soc., 121, 2601 (1922).

(3) Woodward, THIS JOURNAL, 63, 1123 (1941).
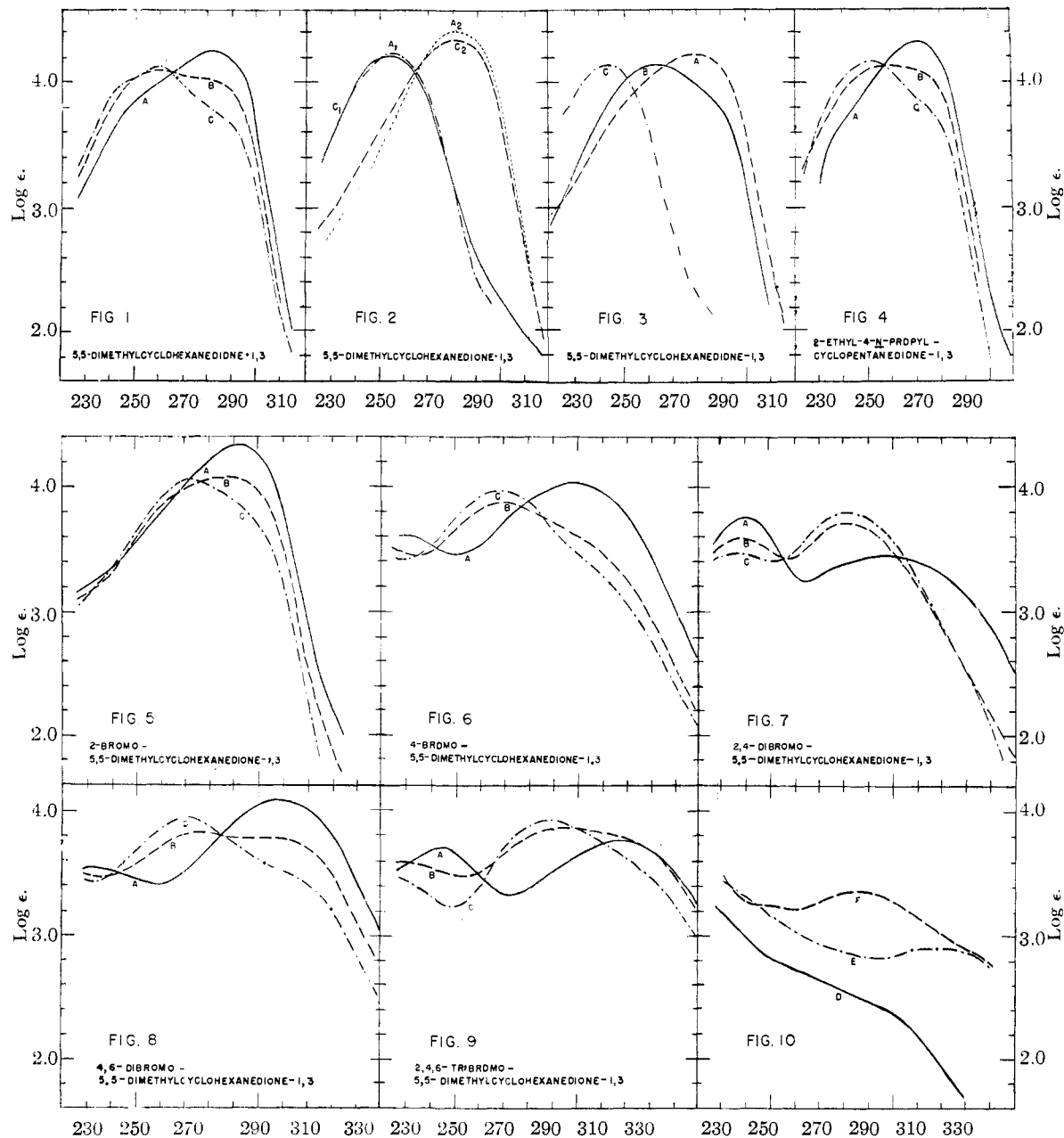
(4) Grossmann, Z. physik. Chem., 109, 305 (1924).

(5) Woodward and Blout, THIS JOURNAL, 65, 562 (1943).

spectrum of 5,5-dimethylcyclohexanedione-1,3 has been reported to have an absorption maximum at 258 mμ[5] and at 282 mμ[2] by different investigators. In the course of our work we noted that the absorption peak of some of the bromine substituted compounds varied with the concentration of the

solution being measured. These anomalies observed with the substitution products led us to undertake a complete investigation of the spectrum of the parent diketone.

Figure 1 shows the absorption spectra of 5,5-dimethylcyclohexanedione-1,3 in absolute ethanol

FIG I — 5,5-DIMETHYLCYCLOHEXANEDIONE-1,3

FIG. 2 — 5,5-DIMETHYLCYCLOHEXANEDIONE-1,3

FIG. 3 — 5,5-DIMETHYLCYCLOHEXANEDIONE-1,3

FIG. 4 — 2-ETHYL-4-N-PROPYL-CYCLOPENTANEDIONE-1,3

FIG. 5 — 2-BROMO-5,5-DIMETHYLCYCLOHEXANEDIONE-1,3

FIG. 6 — 4-BROMO-5,5-DIMETHYLCYCLOHEXANEDIONE-1,3

FIG. 7 — 2,4-DIBROMO-5,5-DIMETHYLCYCLOHEXANEDIONE-1,3

FIG. 8 — 4,6-DIBROMO-5,5-DIMETHYLCYCLOHEXANEDIONE-1,3

FIG. 9 — 2,4,6-TRIBROMO-5,5-DIMETHYLCYCLOHEXANEDIONE-1,3

FIG. 10

Figs. 1, 4, 5, 6, 7, 8, 9.—Ethanol solutions—concentrations: A = 5 × 10⁻⁵ M; B = 10 × 10⁻⁵ M; C = 20 × 10⁻⁵ M.

Fig. 2.—Ethanol solutions—concentrations: A_1 = 5 × 10⁻⁵ M HCl; C_1 = 20 × 10⁻⁵ M HCl; A_2 = 5 × 10⁻⁵ M NaOH; C_2 = 20 × 10⁻⁵ M NaOH.

Fig. 3.—Concentrations: A = 5 × 10⁻⁵ M in water; B = 10 × 10⁻⁵ M in water; C = 5, and 10 and 20 × 10⁻⁵ M in ether.

Fig. 10.—Ethanol solutions—concentrations: 50 × 10⁻⁵ M; D = 2,2-dibromo-5,5-dimethylcyclohexanedione-1,3; E = 2,2,4,6-tetrabromo-5,5-dimethylcyclohexanedione-1,3 measured 15 minutes after solution; F = 2,2,4,6-tetrabromo-5,5-dimethylcyclohexanedione-1,3 measured 60 minutes after solution.

TABLE I

Compound	Figure	Solvent	20 × 10⁻⁴ M λ max. in mμ	Log ε	10 × 10⁻⁴ M λ max. in mμ	Log ε	5 × 10⁻⁴ M λ max. in mμ	Log ε
5,5-Dimethylcyclohexanedione-1,3	1	Abs. ethanol	258	4.10	260	4.10	282	4.25
	2	Acidic abs. ethanol	255	4.22			255	4.23
	2	Basic abs. ethanol	282	4.42			283	4.43
	3	Water	262	4.13			279	4.22
	3	Ether	243	4.14	245	4.13	245	4.14
Cyclohexanedione-1,3		Ethanol	255ᵃ	4.20			280ᵃ	4.30
2-Ethyl-4-n-propylcyclo- pentanedione-1,3	4	Abs. ethanol	252	4.16	258	4.13	272	4.32
Acetylacetone		Abs. ethanol	273ᵇ	3.90	273	3.91	273	3.90
		Aqueous alkali	289.8ᶜ	4.38				
Benzoylacetoneᵈ		Ethanol			310.5	4.14		
		Basic ethanol			325	4.23		
		Piperidine	333.5ᵉ	4.15				

ᵃ Data from Bastron, Davis and Butz (ref. 7). Most concentrated solution, 1.58 × 10⁻⁴ M; most dilute solution, 1.58 × 10⁻⁵ M. ᵇ Grossman (ref. 4) reports 272.5 mμ and log ε 4.02. ᶜ Data from Grossman, (ref. 4). Concentration not stated. ᵈ Data from Morton, Hassan and Calloway (ref. 13). ᵉ Concentration 1 × 10⁻³ M.

solution in three different concentrations.[6] It is apparent there is a large shift in the position of the absorption peak, from 258 to 282 mμ, as the solution is diluted. In a recent paper[7] a similar shift in the absorption spectrum of cyclohexanedione-1,3 is described, and the conjecture is raised whether this behavior may be attributed to a larger amount of the dienolic form (corresponding to Ic) in the more dilute solution. It is quite certain that the foregoing explanation is incorrect since the per cent. enol in tautomeric systems is dependent on the nature of the solvent[8] and not on the molality of the solution. The *dissociation* of weak acids, however, is dependent upon concentration and the observed shift in the absorption of cyclic β-diketones upon dilution may be attributed to increasing ionization.[9] Confirmation of this hypothesis is found in the spectra of 5,5-dimethylcyclohexanedione-1,3 in acidic and basic solutions (Fig. 2). When one equivalent of hydrochloric acid is included in either the most dilute solution (5 × 10⁻⁵ M) or the most concentrated solution (20 × 10⁻⁵ M) the ionization of the cyclic β-diketone is completely repressed and the absorption spectrum (Fig. 2a and b) closely approximates that of the concentrated solution of the non-acidified β-diketone (Fig. 1c). On the

(6) Our choice of concentrations (5 × 10⁻⁵, 10 × 10⁻⁵, and 20 × 10⁻⁵ M) was made with two criteria in mind. First, to use solutions having as wide a range of concentrations as possible which would show the highly intense absorption maxima of *all* the cyclic β-diketones and secondly, to remain within the limits of the optimum extinction coefficients for the Beckman spectrophotometer used in these determinations. Vandenbelt, Forsyth and Garrett, *Ind. Eng. Chem. Anal. Ed.*, 17, 235 (1945), have shown that optimum extinction coefficients were obtained with instrument densities of 0.5 to 1.9. All our measurements were made in this range, although in some cases it was necessary to vary the length of the cell containing the solution.

(7) Bastron, Davis and Butz, *J. Org. Chem.*, 8, 515 (1943).

(8) Baker, "Tautomerism," D. Van Nostrand Co., New York, N. Y., 1934, pp. 57–58, 113–114.

(9) 5,5-Dimethylcyclohexanedione-1,3 is a fairly weak acid. Schilling and Vorlander, *Ann.*, 308, 193 (1899), report $K_{25}° = 0.71 × 10⁻⁵$. Scharzenbach and Lutz, *Helv. Chim. Acta*, 23, 1147, 1162 (1940). give pK at 25° = 5.253.

other hand, if one or more equivalents of sodium hydroxide are dissolved in the dilute and concentrated solutions, the ionization of the β-diketone is complete and the spectra are identical with that of the dilute neutral solution of the β-diketone (*cf.* Fig. 2a₂ and 2c₂ with Fig. 1a). Thus it is evident that the spectrum observed in concentrated solution (20 × 10⁻⁴ M or greater) is that of the un-ionized molecule (II); while the spectrum obtained in dilute solution (5 × 10⁻⁵ M or less) is essentially due to ionic forms (III) of the compound.

Upon investigation of the spectrum of 5,5-dimethylcyclohexanedione-1,3 in aqueous solution we noted that the compound absorbs at approximately the same wave lengths as in alcoholic solution (Table I, Fig. 3). This means in effect that the compound is dissociated to approximately the same degree in both of these hydroxylic solvents. Unfortunately, its solubility in a hydrocarbon solvent such as hexane is so low[10] that measurement of the spectrum in the desired concentrations is impossible. However, it is sufficiently soluble in diethyl ether to allow spectral determinations (Fig. 3). The maximum at 243 mμ is probably indicative of transitions to higher energy levels which involve absorption at correspondingly shorter wave lengths. The greater energy necessary to effect the transition is in turn due to the environment; that is, the lower dielectric constant of ether as compared with water or alcohol. The fact that there is no shift in absorption upon dilution indicates that dissociation is repressed more in ethereal solution than in hydroxylic solvents.

By analogy it is reasonable to assume that 1,3-cyclopentanediones will show similar effects. A member of this class of compounds, 2-ethyl-4-n-propylcyclopentanedione-1,3, does indeed show the typical shift in absorption spectrum upon

(10) The solubility of 5,5-dimethylcyclohexanedione-1,3 in hexane is less than 1 × 10⁻⁵ M.

dilution (Fig. 4). We assume that this phenomenon of increasing dissociation upon dilution and the related shift in absorption is typical of all cyclic β-diketones having at least one enolizable hydrogen on the carbon between the carbonyl groups.

On the other hand, the spectra of non-cyclic β-diketones do not show this same effect, which is consistent with the fact that these compounds are considerably weaker acids.[11] For example, we have reëxamined the spectrum of acetylacetone at three different concentrations and found in each case that the curves were identical, all having maxima at 273 mμ (Table I). This is theoretically explicable upon consideration of the intramolecular hydrogen bonding that exists in open-chain β-diketones,[12] but which cannot exist in cyclic β-diketones due to the fixed spatial arrangement of the carbon–carbon bonds. Because of this hydrogen bonding, increasing ionization of acetylacetone does not occur upon dilution and, hence, there is no change in the spectrum. Strong alkali, however, will ionize even a hydrogen-bonded β-diketone, and the ionic forms show the typical shift in absorption observed with the cyclic compounds (Table I). Further support for this argument may be adduced from the work of Morton[13] upon benzoylacetone where completely analogous effects were noted. It should be emphasized that our results show that the shift in absorption is due to ionization of the compound and not to chelation as postulated by Morton, et al.

Several bromo derivatives of 5,5-dimethyl-cyclohexanedione-1,3 have been described[14] and the spectra of the 2-bromo and the 2,2-dibromo compounds have been measured.[2] During the present investigation the bromo derivatives noted in Table II were prepared and their absorption spectra determined.

TABLE II

Cyclohexane-dione-1,3 derivative[a]	Fig-ure	$20 \times 10^{-5} M$		$10 \times 10^{-5} M$		$5 \times 10^{-5} M$	
		λmax	Log ε	λmax	Log ε	λmax	Log ε
2-Bromo-5,5-dimethyl-	5	273	4.06	287	4.08	293	4.34
4-Bromo-5,5-dimethyl-	6	268	3.96	270	3.88	300	4.03
2,4-Dibromo-5,5-dimethyl-	7	282	3.87	282	3.72	297	3.45
						240	3.77
4,6-Dibromo-5,5-dimethyl-	8	270	3.95	278	3.82	308	4.09
2,4,6-Tribromo-5,5-dimethyl-	9	290	3.93	295	3.87	320	3.77

[a] All compounds measured in absolute ethanol.

It should be noted that all the derivatives which are not dibrominated in the 2-position, i. e., those capable of forming systems vinylogous

(11) Scharzenbach and Lutz (ref. 9) report for acetylacetone pK = 8.94 which is, of course, equivalent to stating that it is more than 1000 times a weaker acid than 5,5-dimethylcyclohexanedione-1,3.

(12) Pauling, "The Nature of the Chemical Bond," 2nd ed., Cornell University Press, Ithaca, N. Y., 1942, p. 318.

(13) Morton, Hassan and Calloway, J. Chem. Soc., 883 (1934).

(14) Voitila, Ann. Acad. Sci. Fennicae, A49, 7 (1938).

with carboxylic acids (vide supra), show the same type of shift in absorption maximum upon dilution as that of parent β-diketone. In all cases the shift due to increasing dissociation is toward longer wave lengths. It is also apparent that the spectral shift upon bromination cannot be correlated at this time with the position of the substituent; for example, the spectrum of the 2-bromo compound shifts more in concentrated and less in dilute solution than does its non-centrally brominated isomer, 4-bromo-5,5-dimethylcyclohexanedione-1,3. In general, increasing the number of bromine atoms in the molecule shifts the maximal absorption toward longer wave lengths.

In a previous paper,[5] attention was called to the facile oxidative decomposition of centrally C-alkylated cyclic β-diketones. This decomposition was postulated as a consequence of the high electron density induced in the unsaturated system by the electron repelling alkyl group. It would therefore be expected that centrally C-halogen substituted cyclic β-diketones would be stable under the same conditions because of the electron-attracting properties of halogen atoms. We have found this to be the case with all of the above-noted derivatives of 5,5-dimethylcyclohexanedione-1,3 having one bromine in the 2-position.

The lack of discrete absorption of centrally disubstituted β-diketones has been described.[2,13] The two centrally dibrominated diketones investigated by us showed similar spectral characteristics (Fig. 10) in that no high intensity bands were observed. In addition, both these compounds are unstable to ultraviolet radiation in alcoholic solution. In fact, unless the spectrum of 2,2,4,6-tetrabromo-5,5-dimethylcyclohexanedione-1,3 was run immediately upon solution, the spectrum obtained was similar to that of the symmetrical tribromo compound (cf. Fig. 9 and 10). After this observation was made, a solution of the tetrabromo compound in a Vycor tube was found to give 2,4,6-tribromo-5,5-dimethylcyclohexanedione-1,3 in 65% yield upon irradiation with a high intensity ultraviolet source for five minutes. Further irradiation yielded only uncrystallizable oils. Similarly, an alcoholic solution of the 2,2-dibromo compound upon irradiation for one hour gave a good yield of 2-bromo-5,5-dimethylcyclohexanedione-1,3. Evidently this reaction represents photochemical reduction of the labile 2,2-dibromo compounds with the ethanol serving as a source of hydrogen.

Experimental[15]

5,5-Dimethylcyclohexanedione-1,3.—Commercial grade material (Eastman Kodak Co. dimethyldihydroresorcinol)

(15) All melting points are corrected. Elementary analyses by Dr. Carl Tiedcke.

was used as starting material for the bromination reactions. The spectral sample was recrystallized twice from 20% ethanol and melted at 148.5–149°.

2-Ethyl-4-n-propyl-cyclopentanedione-1,3.—This diketone was prepared by the method of Woodward and Blout.[5] The sample used for the spectral determination was recrystallized once from water, once from ethyl acetate–petroleum ether, and had a melting point 120–120.5°.

Acetylacetone.—The material used had a boiling point of 135–135.5° (760 mm.); $n^{22.2}$D 1.44676.

2-Bromo-5,5-dimethylcyclohexanedione-1,3.—This compound was prepared by the method of Voitila[13] in 71% yield. A pure sample was observed to melt at 175.0° with no decomposition. The same yield was obtained when the reaction was carried out at room temperature using 2 moles of bromine, 2.2 moles of potassium acetate for 1 mole of 5,5-dimethylcyclohexanedione-1,3.

4-Bromo-5,5-dimethylcyclohexanedione-1,3.—To 3.25 g. (0.01082 mole) of 2,4-dibromo-5,5-dimethylcyclohexanedione-1,3 dissolved in cold 95% alcohol were added 1.80 g. (0.01082 moles) of potassium iodide dissolved in the least amount of cold water and 0.87 cc. (0.01082 moles) of concentrated hydrochloric acid. The solution became colored with iodine and potassium bromide precipitated on addition of the hydrochloric acid. The iodine was taken up by dropwise addition of cold, saturated sodium thiosulfate solution, the potassium bromide was filtered off, and the solvent evaporated at room temperature by a stream of air. The residue was a yellow oil which set to 2.25 g. (91%) of a yellow solid on cooling. After two recrystallizations from 5% ethanol saturated with the compound at 60–70°, long white needles, melting point 149.5–150°, were obtained. In spite of its relatively high melting point, this compound shows a marked tendency to oil out of concentrated solutions when impure. The pure compound gives a reddish-purple color with ferric chloride in water. Calculated for $C_8H_{11}O_2Br$: C, 43.85; H, 5.06. Found: C, 43.67; H, 5.15.

2,2-Dibromo-5,5-dimethylcyclohexanedione-1,3.—This compound was prepared in 50% yield (*cf.* Voitila[13]) by using 4 moles of bromine and 4 moles of potassium acetate for 1 mole of 5,5-dimethylcyclohexanedione-1,3. (When only 2 moles of bromine were used for 2.2 moles of potassium acetate and 1 mole of 5,5-dimethylcyclohexanedione-1,3, the *monobromo* derivative was isolated.) The 2,2-dibromo derivative was formed in 58% yield when 2 moles of bromine, 1.1 moles of potassium acetate, and 1 mole of 5,5-dimethylcyclohexanedione-1,3 were used, and the reaction mixture worked up at once. On recrystallization from 40% ethanol, it gave flat white plates, melting point 150.5–151°. It gave a negative ferric chloride test in water. Calculated for $C_8H_{10}O_2Br_2$: C, 32.24; H, 3.38. Found: C, 32.35; H, 3.56.

2,4-Dibromo-5,5-dimethylcyclohexanedione-1,3.—This derivative was postulated by Voitila as a necessary intermediate in the known rearrangement reactions. Five grams (0.0357 mole) of 5,5-dimethylcyclohexanedione-1,3, 3.85 g. (1.1 × 0.0357 mole) of potassium acetate were dissolved in 345 cc. of cold glacial acetic acid and 442 cc. of 0.322 N bromine–glacial acetic acid (2 × 0.0357 mole, 11.42 g.) were added in fifteen minutes with stirring and cooling. The solution became orange after about one third of the bromine had been added. After standing eighteen hours the potassium bromide was precipitated with ether, and the solvent evaporated at reduced pressure. The residual green oil set on cooling to 1.66 g. (26%) of a light green solid. On recrystallization from 40% ethanol, it oiled and solidified, but after several recrystallizations from 20% alcohol, it gave long white needles, melting point 149–150.5°. An aqueous solution gave a reddish-purple color with ferric chloride solution. A mixed melting point with the 2,2-dibromo derivative (melting point 149–149.5°) melted at 122°. When the reaction mixture was worked up after standing only one hour, 58% yield of the 2,2-dibromo derivative was isolated, showing that the 2,4-dibromo derivative is indeed produced by a rearrangement reaction which requires some time to take place.

The 2,4-dibromo derivative is quite soluble in water and cannot be precipitated from the glacial acetic acid–ether solution by adding a large amount of water. Calculated for $C_8H_{10}O_2Br_2$: C, 32.24; H, 3.38. Found: C, 32.35; H, 3.56.

4,6-Dibromo-5,5-dimethylcyclohexanedione-1,3.—This bromo derivative was prepared in 74% yield by the same method used for the 4-bromo-5,5-dimethylcyclohexanedione-1,3. On recrystallization from 20% ethanol it gave white prisms, melting point 146–146.5°. Mixed melting point with 2,2-dibromo derivative (melting point 150.5–151°) gave 120°+. Mixed melting point with 2,4-dibromo derivative (melting point 149.5–150°) 125°+. In water solution it gives a reddish-purple color with ferric chloride. This compound decomposes unless it is isolated from a cold reaction solution. It shows a tendency to form an oil. Calculated for $C_8H_{10}O_2Br_2$: C, 32.24; H, 3.38. Found: C, 32.41; H, 3.63.

2,4,6-Tribromo-5,5-dimethylcyclohexanedione-1,3.—By the rearrangement of 2,2-dibromo-5,5-dimethylcyclohexanedione-1,3 in glacial acetic acid–hydrogen bromide, 18% yield of impure 2,4,6-tribromo-5,5-dimethylcyclohexanedione-1,3 was obtained. Direct bromination of 5,5-dimethylcyclohexanedione-1,3 with 6 gram-atoms of bromine gave 55% yield after nine days. Eighty-five per cent. yield was obtained on direct bromination with 9 gram-atoms of bromine after two days by frequently breaking up the slushy clumps of 2,2-dibromo derivative. Recrystallization from 40% ethanol produced either fine white grains or chunky prisms, melting point 172–173° (dec.). The melting point of a well-purified sample may vary from 170–175° depending on the rate of heating. Voitila[13] reports a melting point of 175° (dec.). The pure compound gives a reddish-purple ferric chloride test in aqueous solution.

2,2,4,6-Tetrabromo-5,5-dimethylcyclohexanedione-1,3.—This compound was prepared in 35% yield by the method of Voitila.[13] On fractional precipitation from the reaction mixture by the addition of water the first fraction was almost the entire product. This material had the highest melting point, 109.5–111°, and gave a negative ferric chloride test in cold water or in dilute cold alcohol. This compound readily decomposes to the 2,4,6-tribromo derivative and cannot be purified by recrystallization.

Photochemical Decomposition of 2,2-Dibromo-5,5-dimethylcyclohexanedione-1,3.—A solution of 0.50 g. of 2,2-dibromo-5,5-dimethylcyclohexanedione-1,3 in 20 cc. of absolute ethanol was placed in a stoppered Vycor test tube and irradiated two hours one foot away from a Luxor S mercury arc made by the Hanovia Chemical and Mfg. Co. At the end of this time the solution was faintly yellow. The solvent was evaporated by an air stream, leaving a yellow oil which set to 0.20 g. (55%) of yellow crystals, melting point 138–142°. After two recrystallizations from 40% ethanol, there were formed white plates, melting point 169–170°. A mixed melting point with an authentic sample of 2-bromo-5,5-dimethylcyclohexanedione-1,3 (melting point 175°) melted at 171–172°.

Photochemical Decomposition of 2,2,4,6-Tetrabromo-5,5-dimethylcyclohexanedione-1,3.—A solution of 1.00 g. of 2,2,4,6-tetrabromo-5,5-dimethylcyclohexanedione-1,3 in 25 cc. of absolute ethanol was irradiated five minutes. On evaporation of the solvent, there was formed a yellow oil which set to 0.55 g. (66% yield) of yellow crystals; m. p., 110–120° (dec.). One recrystallization from 40% ethanol gave white grains, melting point 173° (dec.). A mixed melting point with 2,4,6-tribromo-5,5-dimethylcyclohexanedione-1,3 (melting point 173° dec.) melted at 172° (dec.).

All absorption spectra were measured on Beckman quartz spectrophotometer, model DU, with a hydrogen tube as an ultraviolet source, using 1 and 0.5 cm. quartz cells. All measurements were made upon absolute ethanolic solutions unless otherwise noted under the figures.

Summary

The absorption spectra of solutions of non-centrally disubstituted β-diketones have been

shown to be dependent upon enolization and the dissociation of enolic forms. Increasing dissociation occurs upon dilution for cyclic β-diketones, but does not occur for non-cyclic β-diketones. In both cases, however, dissociation does take place upon the addition of alkali and the absorption spectra are shifted toward longer wave lengths.

The spectra of several bromo derivatives of 5,5-dimethylcyclohexanedione-1,3 have been determined. Photochemical reduction of 2,2-dibromo derivatives of 5,5-dimethylcyclohexanedione-1,3 has been shown to occur with the formation of the corresponding 2-monobromo compounds.

# Aromatic Cyclodehydrogenation. III. Experiments with 2-Ethylbiphenyl[1]

BY MILTON ORCHIN[2]

Previous communications[3] have dealt with the cyclodehydrogenation of 2-methylbiphenyl and 2,2'-dimethylbiphenyl and their conversion to the fluorene nucleus by vapor-phase treatment with a palladium catalyst. It was of interest to determine the fate of 2-ethylbiphenyl (I) under the same conditions. If cyclodehydrogenation proceeded without the loss of a carbon atom, either 9-methylfluorene (II) or phenanthrene (III) or both could be formed.

$$ H_2 + \quad II \quad \longleftarrow \quad I \quad \longrightarrow \quad III \quad + 2H_2 $$
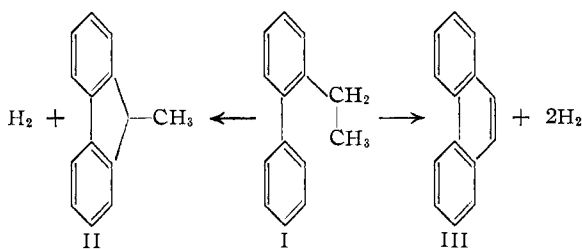
2-Ethylbiphenyl was synthesized by the reaction of ethylmagnesium bromide with 2-phenyl-cyclohexanone. The gas evolved in this reaction corresponded to about 10% enolization which is considerably less than the 50% reported[4] for this ketone in the Reformatsky reaction. The crude carbinol isolated from the Grignard reaction was dehydrated to 2-ethyltetrahydrobiphenyl (IV), and IV dehydrogenated to I by treatment with sulfur.

Treatment of ethylbiphenyl at about 480° with palladium-charcoal gave both 9-methylfluorene and phenanthrene, but the major product was fluorene (V). Similar treatment of the tetrahydro derivative, IV, likewise gave all three conversion products. Since both phenanthrene, III, and fluorene, V, were isolated after similar cyclodehydrogenation of 9-methylfluorene, there is a possibility that the latter may be an intermediate in the formation of III and V. Graebe[5] achieved

the thermal conversion of 9-methylfluorene to phenanthrene by passing the former through a glowing tube but made no mention of the loss of a methyl group. The survival of 9-methylfluorene under the conditions of the present experiments and its presence in the conversion products from ethylbiphenyl and the ethyl-tetrahydrobiphenyl is probably a function of the contact time with the catalyst, a factor which is difficult to control with small quantities and the type of catalyst used in these experiments.

Experimental[6]

2-Ethyl-tetrahydrobiphenyl, IV.—To the Grignard solution prepared from 78 g. of ethyl bromide, 18 g. of magnesium and 440 cc. of dry ether, there was added dropwise with stirring, a solution of 118 g. of 2-phenyl-cyclohexanone[4] in 200 cc. of benzene and 50 cc. of ether. During the addition about 1.3 liters (N. T. P.) of gas was liberated. The mixture was refluxed eighteen hours. About 200 cc. of ether was then distilled from the mixture, whereupon it was decomposed with ammonium chloride solution. The organic fraction, on distillation through a Widmer column, gave 117.4 g. (85%) 1-ethyl-2-phenylcyclohexanol, b. p. 120-121° (5-6 mm.). The carbinol (101 g.) was refluxed with 350 cc. of 90% formic acid for three and one-half hours. The top layer was separated and combined with a benzene extract of the acid bottom layer. The benzene solution was washed, dried and evaporated and the residue distilled. There was obtained 65.6 g, (71%) ethyl-tetrahydrobiphenyl, colorless liquid, b. p. 103-105° (5-6 mm.). Analysis indicated the presence of a small quantity of an oxygenated compound. A second treatment with formic acid did not remove the oxygen. An ethanol solution of the material was then treated with semicarbazide hydrochloride and sodium acetate. The material recovered after this treatment had b. p. 93-93.5° (3-4 mm.), $n^{20}D$ 1.5417, d^{20}_4 0.961. Anal. Calcd. for $C_{14}H_{18}$: C, 90.26; H, 9.74. Found: C, 90.1; H, 9.8. No attempt was made to prove the location of the double bond.

2-Ethylbiphenyl, I.—A mixture of 14.7 g. of IV and 5.05 g. of sulfur was heated at 210-240° for one and one-half hours and distilled in vacuo. The crude distillate (8.1 g.) was dissolved in petroleum ether and chromatographed on alumina. The first portion to come through was rejected. The balance of the hydrocarbon was recovered from the petroleum ether by distillation whereupon there was obtained 6.1 g. (42%) 2-ethylbiphenyl, b. p. 93-94° (2-3 mm.), $n^{20}D$ 1.5808. Anal. Calcd. for $C_{14}H_{14}$: C, 92.26; H, 7.74. Found[7]: C, 92.0; H, 8.0.

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(3) (a) Orchin and Woolfolk, THIS JOURNAL, 67, 122 (1945); (b) Orchin, ibid., 67, 499 (1945).

(4) Newman and Farbman, ibid., 66, 1550 (1944).

(5) Graebe, Ber., 37, 4146 (1904).

(6) All melting points corrected. Analyses by Dr. T. S. Ma, University of Chicago, unless otherwise noted.

(7) Bureau of Mines, Coal Analysis Section.