underwent decomposition upon standing in solution. The stability of the compound was also found to be strongly influenced by small variations in the composition of the gc column.

Reaction of Quinone Methide 6 with Di-*t*-butyl Peroxide and Triphenylphosphine.—Triphenylphosphine (13.64 g, 52.0 mmoles) and di-*t*-butyl peroxide (3.80 g, 26.0 mmoles) were added to a freshly prepared solution of quinone methide **6** (13.0 mmoles, generated by dehydrochlorination of 3.31 g of purified 2,6-di-*t*-butyl-4-chloromethylphenol with triethylamine[1]) in chlorobenzene (160 ml), and the mixture was refluxed with stirring under nitrogen for 24 hr. Solvent and other volatile constituents were then removed by evaporation *in vacuo*, and the residue was boiled with 200 ml of *n*-hexane. After cooling to room temperature, the mixture was filtered, and the recovered solid was washed several times with fresh *n*-hexane before drying. This solid (11.29 g) melted at 148–155° and was shown by infrared and nmr analysis to consist almost entirely of triphenylphosphine oxide. The filtrate and washings were combined, concentrated, and subjected to a rough analysis by programmed temperature gc (column B) without using pure reference compounds for calibration. This analysis showed the presence of phenol **3** (13% yield based on **6**), quinone methide **10** (10% yield based on **6**), triphenylphosphine oxide (82% total yield based on the starting phosphine, including material recovered by filtration), and triphenylphosphine (20% recovery). The remainder of the chromatogram consisted primarily of peaks whose long retention times suggested that they were due to compounds formed by dimerization of the starting quinone methide.

Preparation of Quinone Methide 10.—A rapidly stirred solution of phenol **3** (0.69 g, 2.5 mmoles) in benzene (25 ml) was freed of oxygen by bubbling with nitrogen for several minutes. A similarly degassed solution of potassium ferricyanide (4.0 g, 12 mmoles) and potassium hydroxide (2.0 g) in water (50 ml) was then added, and the mixture was stirred vigorously under nitrogen for 1.7 hr. The amber-colored benzene layer was separated, washed with water until a neutral aqueous phase was obtained, dried over Drierite, and evaporated to give 0.59 g of viscous, yellow oil that could not be induced to crystallize, but which was shown by gc analysis (column B) to consist primarily of a single species (85 area %). This species was identified as quinone methide **10** by a variety of spectroscopic measurements. The nmr spectrum ($CDCl_3$) of the crude mixture exhibited weak peaks of equal intensity at τ 3.82 (singlet, olefinic proton of side chain), 3.38 (doublet, $J \sim 2.5$ cps, ring proton *cis* to olefinic proton of side chain), and 2.57 (doublet, $J \sim 2.5$ cps, ring proton *trans* to olefinic proton of side chain), as well as three strong singlets in the *t*-butyl region at τ 8.76, 8.77, and 8.79. Olefinic proton assignments are based on comparisons with the spectra of several similar compounds that are currently under study in these laboratories. Accurate integration of the strong *t*-butyl peaks was not possible because of interference by a number of other small peaks; however, the intensities of the strong peaks were qualitatively in accord with the theoretical values. A purified sample of **10**, trapped after elution from the gas chromatograph, showed no infrared absorption (CS_2) for hydroxyl, but did exhibit a broad, strong band at 1625 cm^{-1} (exact position probably slightly in error owing to solvent interference), as well as a sharp band of medium intensity at 1705 cm^{-1}. The mass spectrum displayed a sizable parent peak at m/e 274.

Reaction of Quinone 4 with Di-*t*-butyl Peroxide and Triphenylphosphine.—This reaction was carried out under helium using the apparatus and procedure described for the peroxydienone experiments. After 48 hr at 100 ± 1°, a solution of 0.2203 g (1.00 mmole) of **4**, 0.2924 g (2.00 mmoles) of di-*t*-butyl peroxide, and 1.5738 g (6.00 mmoles) of triphenylphosphine in 25 ml of *n*-heptane gave 0.17 mmole of phenol **12**, 0.47 mmole of triphenylphosphine oxide, 0.70 mmole of unreacted quinone, and 0.17 mmole of isobutene. Product analyses were done by the usual gc methods. The cooled reaction mixture also contained a small amount of brownish solid which was not identified. The low conversion of **4** obtained in this experiment is not surprising in view of the rather slow rate of decomposition of di-*t*-butyl peroxide at 100°.[29]

Acknowledgments.—The authors wish to thank Drs. H. G. Schutze and F. H. Field for their interest and support during the course of this study, and to acknowledge helpful discussions of analytical problems with numerous colleagues in the analytical research section of these laboratories. We are particularly indebted to Mr. H. J. Tarski for his skillful performance of much of the experimental work.

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A New Synthesis of 3-Methylcyclopent-2-en-2-ol-1-one

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The synthesis of 3-methylcyclopent-2-en-2-ol-1-one (I) was accomplished by the hydrolysis and decarboxylation of 5-carbethoxy-5-methylcyclopent-2-en-2-ol-1-one (IV) which was obtained by the nitrosation and hydrolysis of 2-carbethoxy-2-methylcyclopentanone (III). The selenium dioxide oxidation of the ketone III gave the previously unreported ketone, 5-carbethoxy-5-methylcyclopent-2-en-2-ol-1-one (IV), while the DMSO oxidation of 5-bromo-2-carbethoxy-2-methylcyclopentanone (V) gave the unexpected product, 3-bromo-5-carbethoxy-5-methylcyclopent-2-en-2-ol-1-one (VIIa), in good yield.

The potential use of 3-methylcyclopent-2-en-2-ol-1-one (I), cyclotene as a spice, has created a recent interest in new methods for its synthesis. A survey of the literature indicates that I has been obtained by several procedures from divinyl glycol,[1] 2,2-dichloro-5-methylcyclopentan-1-one,[2] 3-methyl-3,5-dicarbethoxy-1,2-cyclopentanedione,[3] and 3-methylcyclopent-2-en-1-one,[4,5] as well as from natural sources.[6] Recently, compound I was reported to be one of the important constituents of coffee aroma[7a] and has been utilized as an intermediate in the synthesis of dihydrojasmone.[7b] Investigations have shown that I[7b,8] rather than Ia[9]

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(1) (a) G. Dupont and E. Urion, *Compt. Rend.*, **197**, 158 (1933); (b) E. Urion, *Ann. Chim.* (Paris), [11] **1**, 5 (1934).

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(3) G. Hesse and K. W. F. Bockmann, *Ann.*, **563**, 37 (1949).

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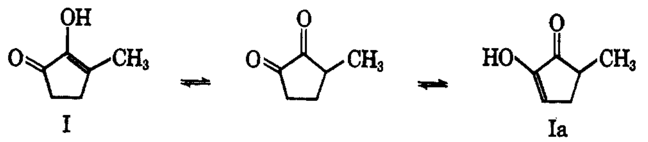
(9) (a) G. Schwarzenbach and C. Wittwer, *Helv. Chim. Acta*, **30** 663 (1947); (b) G. Hesse and K. Breig, *Ann.*, **592**, 120 (1955).

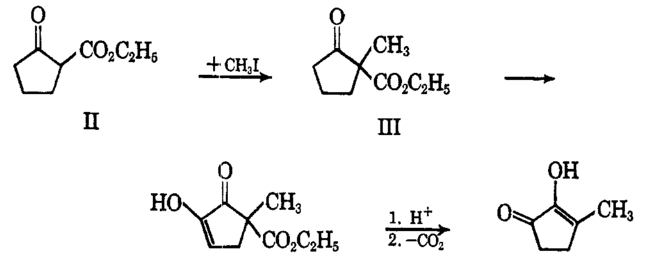


I Ia

represents the correct tautomeric structure of the compound obtained from these syntheses. All the methods cited above for the synthesis of I suffer from low over-all yields and difficulty of obtaining starting materials.

This paper describes our work on the preparation of compound I by the oxidation of 2-carbethoxy-2-methylcyclopentanone (III) as shown in Scheme I.

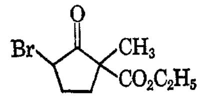
SCHEME I



II III IV I

The methylation of α-carbethoxycyclopentanone (III) in alcoholic solution has been reported[10] to give the C-methylated compound III, in high yield. Since compounds II and III have been shown[11] to undergo ring fission in basic alcohol solution, the previously reported procedure was improved upon (84%) by treating II with methyl iodide using tetrahydrofuran as the solvent and sodium hydride as the base.

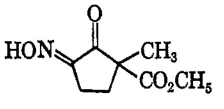
We have examined the following oxidations of III which are of potential importance for the synthesis of I: (1) selenium dioxide oxidation, (2) dimethyl sulfoxide (DMSO) oxidation of 5-bromo-2-carbethoxy-2-methylcyclopentanone (V), and (3) α oximination of III and subsequent hydrolysis.



V

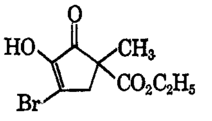
When III was heated under reflux in aqueous dioxane solution, with excess selenium dioxide, for 20 hr, IV was obtained in 44% yield. Compound IV could be readily converted into I (51%) on treatment with 10 *N* sulfuric acid. The structures of I and IV were assigned on the basis of their nuclear magnetic (nmr), infrared, and ultraviolet spectra. The infrared spectra showed hydroxy absorption and gave hydrogen bond information. The ultraviolet spectra may be compared with the data of enolized α-diketone[12] and suggest that I and IV possess enolizable structures. The nmr spectra gave identical informations and moreover suggested that I and IV were enolized in *ca.* 100% (see the Experimental Section).

On the other hand, compound I was also obtained by treatment of III with *n*-butyl nitrite in the presence of dry hydrogen chloride followed by acidic hydrolysis. In this case, neither an expected intermediate IV nor VI could be isolated.

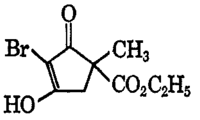


VI

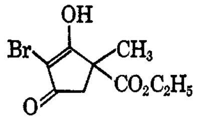
Whereas extensive work on oxidation of α-halo ketones with DMSO to α-diketones has been conducted, little is known of similar oxidations of α-halocycloalkanones.[13] We have found out an anomalous behavior of DMSO toward some α-halocycloalkanones. The oxidation of V, prepared by bromination of III, with DMSO provided, in addition to a very small amount of IV, 70% of white crystals, mp 101.0–101.5°, which contained a bromine atom. Analytical data agreed with the formula $C_9H_{11}O_4Br$, which is in accord with the structure VIIa, VIIb, or VIIc. The infrared spectrum showed a hydroxy absorption in addition to two carbonyl bands and gave a hydrogen bond information. These data can not eliminate from consideration structures such as VIIb or VIIc. The ultraviolet spectrum [λ_{max}^{EtOH} 269 mμ (ε 15,850)] was in substantial agreement with that described above for IV. Finally, a nmr spectrum was obtained which was in accord with the structure VIIa (see the Experimental Section). Conclusive proof for structure VIIa was obtained by synthesis. An authentic sample VIIa readily obtained by bromination of IV was in complete agreement with that obtained by the oxidation. Thus, we conclude that the enolizable α-diketone structure VIIa must be assigned to the DMSO oxidation product from α-bromo ketone V.



VIIa

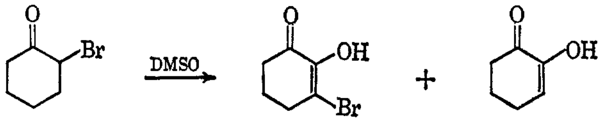


VIIb



VIIc

Attempts to eliminate hydrogen bromide[14] in the oxidation were unsuccessful. For the purpose of exploring the application of anomalous oxidation to general α-halocycloalkanones, the DMSO oxidation of α-bromocyclohexanone (VIII) was furthermore examined.



VIII IX X

When VIII was heated in DMSO at 100° for a 0.5 hr, the bromo compound IX was obtained (34%), accompanied by α-diketone X in a very small amount. On the other hand, IX was also obtained in 72% yield

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[10] (a) L. Bouveault, *Bull. Soc. Chim. France,* [3] **21,** 1020 (1899); (b) A. Haller and R. Cornubert, *ibid.,* [4] **39,** 1626 (1926); (c) M. E. Dobson, J. Ferns, and W. H. Perkin, Jr., *J. Chem. Soc.,* 2010 (1909); (d) M. Rysselberghe, *Bull. Soc. Chim. Belgrade,* **35,** 311 (1926); (e) I. N. Nazarov, *et al., Izv. Akad. Nauk SSSR, Otd. Khim. Nauk,* 889 (1953); (f) L. H. Klemm and H. Ziffer, *J. Org. Chem.,* **20,** 182 (1955); (g) R. Mayer, *Angew. Chem.,* **68,** 169 (1956).

[11] (a) R. I. Reed and M. B. Thornley, *J. Chem. Soc.,* 2148 (1954); (b) L. Nicole and L. Berlingnet, *Can. J. Chem.,* **40,** 353 (1962); (c) K. Sisido, *et al., J. Org. Chem.,* **29,** 2781 (1964).

[12] For example, T. A. Geissman, *J. Am. Chem. Soc.,* **75,** 4008 (1953).

[13] (a) R. N. Facona, A. T. Rowland, and H. R. Nace, *J. Org. Chem.,* **29,** 3495 (1964); (b) H. R. Nace and R. N. Facona, *ibid.,* **29,** 3498 (1964).

[14] Hydrogen bromide–DMSO is known to be a halogenating agent.

by bromination of cyclohex-2-en-2-ol-1-one (IX) which was prepared on treatment of cyclohexanone with selenium dioxide.

We are now investigating the scope of this oxidative reaction and the details of its unusual mechanism.

Experimental Section[15]

Materials.—2-Carbethoxycyclopentanone (II) was prepared from ethyl adipate by the procedure of Pinkney.[16] 5-Bromo-2-carbethoxy-2-methylcyclopentanone (V) was obtained by bromination of 2-carbethoxy-2-methylcyclopentanone (III).[17] 2-Bromocyclohexanone (VIII) was prepared by the method of Belcher and co-workers.[18] Cyclohex-2-en-2-ol-1-one (X) was obtained by oxidation of cyclohexanone with selenium dioxide.[19] *n*-Butyl nitrite was prepared by the procedure of Noyes.[20]

2-Carbethoxy-2-methylcyclopentanone (III).—To a stirred mixture of 500 ml of tetrahydrofuran and 33.8 g of sodium hydride (0.7 mole as a 50% suspension in oil), 100.0 g (0.640 mole) of 2-carbethoxycyclopentanone (II) and 109.1 g (0.773 mole) of methyl iodide were added at 0°. After stirring for 2 hr at 0° and an additional 2 hr at room temperature, 200 ml of water was added to the resulting mixture, from which tetrahydrofuran was removed. The organic layer was separated, the water layer was extracted with ether, and the extract was combined with the organic layer. After drying and removal of the ether, distillation of slightly yellow residual oil (95 g) gave 91.4 g (84%) of III, bp 62–65° (2 mm).

Anal. Calcd for $C_9H_{14}O_3$: C, 63.51; H, 8.29. Found: C, 63.27; H, 8.14.

Oxidation of III with Selenium Dioxide.—To a solvent of dioxane (300 ml) and water (150 ml) was added 10.2 g (0.060 mole) of III and 13.3 g (0.120 mole) of selenium dioxide. After stirring and refluxing for 20 hr, the deposited selenium was filtered off, the solvent was removed at reduced pressure, and the residue was extracted with ether. After drying, the ether was evaporated and the resulting oil was distilled to yield 5.2 g of crude product, bp 70–100° (1 mm). Redistillation gave 4.8 g (44%) of 5-carbethoxy-5-methylcyclopent-2-en-2-ol-1-one (IV): bp 97–99° (1 mm); $n^{20}{}_D$ 1.4909; $d^{20}{}_{20}$ 1.0264; λ_{max}^{EtOH} 258 mμ (ε 13,020); ν_{max}^{film} 3249 (OH), 1730 (ester C=O), 1702 (C=O), and 1654 cm^{-1} (C=C); and nmr peaks at *ca.* τ 8.81 (t), 8.65 (s), 7.36 (m), 5.89 (q), 3.43 (t), and 2.85 (s).

Anal. Calcd for $C_9H_{12}O_4$: C, 58.69; H, 6.57. Found: C, 58.40; H, 6.62.

Acidic Hydrolysis of 5-Carbethoxy-5-methylcyclopent-2-en-2-ol-1-one (IV).—A mixture of 10.0 g (0.054 mole) of IV and 15 ml of 10 *N* sulfuric acid was stirred for 9 hr maintaining bath temperature at 100–105°. The resulting black paste was cooled and extracted with a chloroform. The chloroform was distilled off and crude 3-methylcyclopent-2-en-2-ol-1-one (I) was obtained. Recrystallization from water gave 3.1 g (51%) of pure I: mp 104.8–105.7° [a mixture melting point with an authentic sample from natural sources (mp 106–107°) showed no depression]; λ_{max}^{EtOH} 257 mμ (ε 13,350); ν_{max}^{KBr} 3380 (OH), 1709 (C=O), and 1659 cm^{-1} (C=C); and nmr peaks at *ca.* τ 8.03 (s), 7.63 (s), and 3.67 (s).

Anal. Calcd for $C_6H_5O_2$: C, 64.27; H, 7.19. Found: C, 64.37; H, 7.08.

Reaction of 5-Bromo-2-carbethoxy-2-methylcyclopentanone (V) with DMSO.—A solution of 10.0 g (0.040 mole) of V in 100 ml of DMSO was stirred at 70° for 10 hr. The reaction mixture was cooled and poured into ice water and extracted with ether. After drying, removal of the ether gave 8.1 g of crude VIIa and small quantity of red oil. By filtration and recrystallization from benzene–petroleum ether (bp 30–70°), 7.3 g (70%) of pure VIIa was obtained: mp 101.0–101.5° (no depression at melting point was observed on admixture with the VIIa prepared by the bromination of IV); λ_{max}^{EtOH} 269 mμ (ε 15,850); ν_{max}^{KBr} 3360 (OH), 1747 (ester C=O), 1793 (C=O), and 1655 cm^{-1} (C=C); and nmr peaks at *ca.* τ 8.78 (t), 8.55 (s), 6.96 (q), 5.78 (q), and 2.54 (s).

Anal. Calcd for $C_9H_{11}BrO_4$: C, 41.09; H, 4.21. Found: C, 41.26; H, 4.21.

The filtrate was distilled, bp 80–110° (2 mm), and IV was shown by the gas chromatographic analysis.

3-Bromo-5-carbethoxy-5-methylcyclopent-2-en-2-ol-1-one (VIIa) by Bromination of IV.—To a solution of 2.0 g (0.11 mole) of IV in 20 ml of ether was added 1.8 g (0.11 mole) of bromide at 0–5°. The ether was evaporated and 1.8 g (63%) of VIIa was obtained, mp 99.0–100.5°.

Anal. Calcd for $C_9H_{11}BrO_4$: C, 41.09; H, 4.21. Found: C, 41.05; H, 4.32.

Reaction of 2-Bromocyclohexanone (VIII) with DMSO.—Freshly distilled VIII (10.0 g, 0.056 mole) was dissolved in 50 ml of DMSO and stirred for 30 min at 100°. After cooling, the reaction mixture was poured into 50 ml of ice water and repeatedly extracted with ether. The extract was dried and removal of the ether gave 4.7 g of crystals and 4.5 g of heavy red oil. The crystals were filtered and recrystallization from benzene gave 3.8 g (34%) of 3-bromocyclohex-2-en-2-ol-1-one (IX): mp 103.5–104.0° (a mixture melting point with IX prepared by bromination of X showed no depression); λ_{max}^{EtOH} 273 mμ (ε 9600); ν_{max}^{KBr} 3250 (OH), 1680 (C=O), and 1643 cm^{-1} (C=C).

Anal. Calcd for $C_6H_7BrO_2$: C, 37.72; H, 3.69. Found: C, 37.72; H, 3.92.

Ethereal solution of the filtrate was stirred with 10% potassium hydroxide solution. The ether layer was separated, washed with water, dried, and concentrated yielding 1.2 g of yellow oil. This oil was distilled and analyzed by vapor phase chromatography. By comparing the retention time of peaks with that of authentic samples, it was found that this product consisted of 2-cyclohexenone, cyclohexanone, and starting material VIII. The water layer was acidified with hydrogen chloride and extracted with ether. Removal of the ether gave 2.7 g of red oil. Distillation of this oil gave small quantity of cyclohex-2-en-2-ol-1-one (X), bp 68–70° (13 mm); the rest polymerized in a Claisen flask.

3-Bromocyclohex-2-en-2-ol-1-one (IX) by Bromination of Cyclohex-2-en-2-ol-1-one (X).—To a solution of 5.0 g (0.045 mole) of X in 45 ml of ether, 7.2 g (0.045 mole) of bromine was added at 0°, dropwise and with stirring. White crystals were obtained by removal of the ether from the reaction mixture. Recrystallization gave 6.5 g (72%) of IX, mp 103.5–104.0°.

Anal. Calcd for $C_6H_7BrO_2$: C, 37.72; H, 3.69. Found: C, 37.98; H, 3.71.

Reaction of 2-Carbethoxy-2-methylcyclopentanone (III) with *n*-Butyl Nitrite.—To a solution containing 10.0 g (0.058 mole) of III in 40 ml of absolute ether, dry hydrogen chloride was passed through for 15 min below 5°, and 10.0 g (0.097 mole) of *n*-butyl nitrite was added dropwise with bubbling hydrogen chloride flow for 20 min below 10°. After stirring for 1 hr, hydrogen chloride flow was stopped and the reaction mixture was stirred for additional 30 min. Throughout the reaction, temperature was kept at 5–10°. The ether was evaporated under reduced pressure below 5° and 60 ml of 2 *N* hydrogen chloride was added to the residue, which was stirred for 1 hr at 60–70°. The reaction mixture was chilled, extracted with ether, and concentrated to yield 8 g of dark red oil. Attempts to isolate IV or VI from this oil by simple distillation were unsuccessful. Then mixture of 10 g this oil and 15 ml of 10 *N* sulfuric acid was stirred in the same way with the acidic hydrolysis of IV and was extracted with chloroform. Removal of the chloroform and recrystallization gave 2.3 g of I, mp 106.5–107.0°. No depression at melting point was observed on admixture with an authentic specimen (mp 106–107°) which was prepared from natural sources.

Acknowledgment.—The authors wish to express their gratitude to Mr. M. Funaki and T. Hirai in our laboratory for their help in carrying out the study presented in this paper and to the Asahi Glass Co. and Seimi Chemical Co. for generous gifts of literature and materials. The authors are also indebted to professor S. Abe for his kind advice.

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[15] Melting points and boiling points are uncorrected. Infrared spectra were recorded on Hitachi Model EPI-S2 spectrophotometer and nmr spectra were measured with a Varian A-60 instrument, using tetramethylsilane as an internal standard. Vapor phase chromatographic analyses were carried out on Shimazu Model GC-IC. The column employed was 3.75 m and Reoplex 400 on Chromosorb P.

[16] P. S. Pinkney, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N.Y., 1943, p 116.

[17] P. C. Dutta, *J. Indian Chem. Soc.*, **26**, 106 (1949).

[18] R. Belcher, W. Hoyle, and T. S. West, *J. Chem. Soc.*, 2743 (1958).

[19] L. W. Butz, B. L. Davis, and A. M. Gaddis, *J. Org. Chem.*, **12**, 122 (1947).

[20] W. A. Noyes, ref 16, page 108.