THE METHYLATION OF THE RESORCINOLATE DIANION

II. PER-METHYLATED RESORCINOL: 2,2,4,6,6-PENTAMETHYLCYCLOHEX-4-EN-1,3-DIONE

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Dedicated to Professor R. B. Sandin on the Occasion of his Sixty-Eighth Birthday

ABSTRACT

Structural evidence for the enedione products, 2,2,4,6,6-pentamethylcyclohex-4-en-1,3-dione and 2,2,6,6-tetramethylcyclohex-4-en-1,3-dione, which are the principal products from the methyl iodide alkylation of the dilithium resorcinol salt in nonpolar aprotic or very polar hydroxylic solvents, is presented. The diimide and lithium aluminium hydride reduction products are presented and, together with the decarboxylated hydrolysis product, 2,4,6-trimethylcyclohex-2-en-5-one, constitute proof of the structure of the 2,2,4,6,6-pentamethylcyclohex-4-en-1,3-dione. Some of the synthesis potential of resorcinolate alkylations is indicated.

INTRODUCTION

Earlier studies in this laboratory on the nuclear alkylation of phenoxides, and, in particular, those studies on 2,6-disubstituted phenoxides, led to the study of the alkylation of polyhydroxylic benzenes under basic conditions. Curtin *et al.* (1) first observed that the sealed-tube methylation of lithium 2,6-dimethylphenoxide with methyl iodide leads to the formation of 2,6-dimethylanisole and a carbonyl-containing species to which was assigned structure I. Some of the many factors which influence the relative amounts of carbon and oxygen alkylation have been discussed by Curtin *et al.* (1), Curtin and Fraser (2), Curtin and Dybvig (3), Kornblum and Lurie (4), Kornblum and Seltzer (5), Kornblum *et al.* (6), Kornblum *et al.* (7), and Barner and Schmid (8). A brief review of the alkylation of analogous systems (e.g. enolates, oxime salts, and thiophenolates) is given in the recent paper by Curtin and Dybvig (3).

By analogy to the phenoxide methylations, the various alkylated *m*-dimethoxybenzenes and, possibly, the dienone analogues II and III would be among the expected neutral products from the methylation of the dilithium salt of resorcinol. It is conceivable that even the higher methylation products IV and V might be formed. It is the last of these, the 2,2,4,6,6-pentamethylcyclohex-4-en-1,3-dione (V), with which this paper deals.

The only previous report of the synthesis of V is the questionable work of Kurzweil in 1903 (9). The 5-methyl substituted compound, however, was reported by Herzig and Wenzel in 1906 (10) as a minor product from the methyl iodide methylation of orcinol (5-methylresorcinol). Herzig and Zeisel (11) have reported that the methylation of phloroglucinol gives 2,2,4,4,6,6-hexamethylcyclohexan-1,3,5-trione (VI), a structure which has recently been confirmed by the independent synthesis of Erickson and Kitchens (12).

This paper deals with the synthesis and structure of 2,2,4,6,6-pentamethylcyclohex-4-en-1,3-dione, VI, and some of its properties and reactions.

RESULTS AND DISCUSSION

Methyl iodide methylations of resorcinol in the presence of excess base in solvents of intermediate polarity (e.g. methanol, ethanol, and tetrahydrofuran) give, among the

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neutral products, a small carbonyl-containing fraction and all seven of the possible 1,3-dimethoxybenzenes—methylation meta to the oxygens was never observed in the products. By use of the less polar solvent mixture of 16% tetrahydrofuran in toluene, it was possible to raise the yield of the carbonyl compounds to about 70%, based upon starting resorcinol, or to about 93–98% of the neutral fraction.

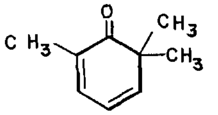
Comparison of the infrared, nuclear magnetic resonance, and ultraviolet spectra of the carbonyl fraction to those of 2,6,6-trimethylcyclohexa-2,4-dienone (I) suggested a similar structure. Thus, the carbonyl fraction collected on the vapor phase chromatograph had carbonyl bands in the infrared at 1 717 and 1 676 cm^{-1} and a geminal dimethyl doublet at 1 382 and 1 362 cm^{-1} compared to those at 1 720 and 1 680 cm^{-1} and at 1 385 and 1 363 cm^{-1} for the Diels–Alder dimer of I (14). In its nuclear magnetic resonance spectrum, the carbonyl fraction had signals at 8.74 and a narrow doublet at 8.16 τ compared to those at 8.80 and 8.13 τ in I. Even the coupling constant giving rise to the doublet was about 1.45 c.p.s. for both species. The ultraviolet absorbance maxima at 231 mμ ($\epsilon = 8\,450$) and at 305 mμ ($\epsilon \simeq 57$) suggest that the fraction contains both a conjugated and non-conjugated carbonyl. This conclusion is confirmed by the infrared carbonyl absorption frequencies quoted above.

A molecular weight and elemental analysis determination gave the molecular formula $C_{11}H_{16.5}O_{2.05}$ for one carbonyl fraction. The nuclear magnetic resonance spectrum of this particular fraction showed the aforementioned signals at 8.74 τ (area = 12.97, a singlet), at 8.16 τ (area = 3.05, a doublet, $J \simeq 1.5$ c.p.s.), and at 3.47 τ (area = 1.00, a quartet, $J \simeq 1.5$ c.p.s.) and two pairs of doublets at 3.98 and 3.21 τ (area 0.09, $J \simeq 10.5$ c.p.s.). The relative intensities of the olefinic quartet and pair of doublets varied from reaction to reaction, so that they must be caused by two separate components. Indeed, the spectrum of the carbonyl fraction collected on the vapor phase chromatograph from the methylation of mesorcinol (dihydroxymesitylene) was completely free of the olefinic doublets. It showed only the signals at 3.47, 8.16, and 8.74 τ (relative areas, 1:3:12) and analyzed for $C_{11}H_{16}O_2$.

Nuclear magnetic resonance spin-decoupling studies confirmed that the pairs of olefinic doublets were coupled to each other and that the olefinic quartet at 3.47 τ and the doublet at 8.16 τ were spin coupled. Upon expansion, the 8.74 τ signal was found to be a narrow jagged doublet with separation of about 0.8 c.p.s. The signal was unaffected by temperature variations between −35° and 65°.

From the spectral evidence discussed above, it was concluded that the carbonyl-containing fraction from the methylation of resorcinolate dianion must be a mixture of IV and V. The percentage of IV present varied from 8 to 30%, with the higher end of the range occurring in the reactions with lower conversions of resorcinol to the enediones, as would be expected from the data presented in Part I of this series (13).

While attempts to make the usual derivatives of the double bond or carbonyls in V were unsuccessful, additional evidence for the structure of the enedione (V) is found in some of its reactions. By using pure V derived from the methylation of mesorcinol under conditions identical with those used in the methylation of resorcinol, a diimide reduction of the carbon–carbon double bond was performed by the procedure of van Tamelen *et al.* (15). The reduced material, 2,2,4,4,6-pentamethylcyclohexan-1,3-dione, VII, showed carbonyl absorption frequency shifts from 1 727 and 1 683 cm^{-1} to 1 695 and 1 724 cm^{-1} and disappearance of the 900 cm^{-1} vinyl proton bending frequency. In its nuclear magnetic resonance spectrum, VII showed a pair of overlapping multiplets ($J = 6.5$ c.p.s.) centered at 7.28 and 7.49 τ of total area one, a narrow doublet ($J = 1.5$ c.p.s.) at 8.15 τ



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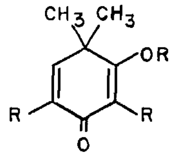

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R' = H or CH_3

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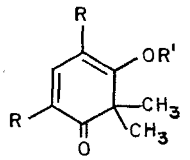

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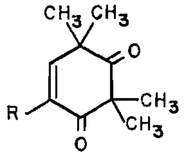
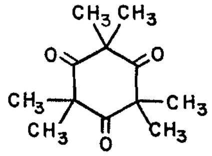


IV R = H
V R = CH_3



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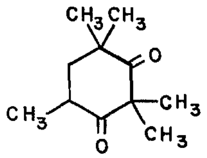

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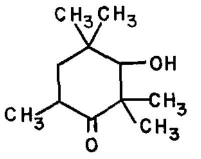

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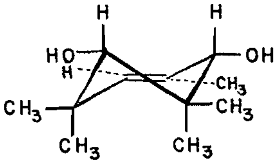

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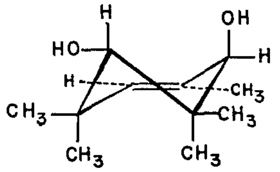
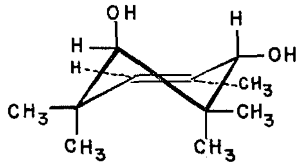


X



XI

of area one, a doublet (J = 6.5 c.p.s.) at 8.30 τ of area one, and an unsymmetrical quartet at 8.84 τ of area 15. Spin-decoupling studies confirmed that the downfield multiplets were coupled both to the protons at 8.15 and 8.30 τ and to the methyl protons at 8.84 τ. The protons at 8.15 τ were also coupled with the methyl protons. Further confirmation of the structure of VII was found in its ultraviolet spectrum, which showed absorption maxima at 290 mμ ($\epsilon = 47$) and at 214 mμ ($\epsilon = 725$).

Lithium aluminium hydride reduction of V gave three fractions upon vapor phase chromatographic separation. The minor constituent (11% of the product) showed infrared absorptions attributed to hydroxyl and to carbonyl (1 709 cm^{-1}). No olefinic proton signal appeared on the nuclear magnetic resonance spectrum and, in the ultraviolet, maxima appeared at 280 mμ ($\epsilon = 44$) and at 235 mμ ($\epsilon = 143$) as a shoulder on end absorption. This spectral evidence is consistent with structure VIII, arising from V by the 1,4- or Michael addition of the hydride to the conjugated carbonyl (16) and simple reduction of the other carbonyl.

The infrared spectra of the two remaining fractions, IX and (X + XI), showed no carbonyl absorption but did show very weak carbon–carbon double bond absorption at about 1 650 cm^{-1} and very strong broad hydroxyl absorption. The ultraviolet spectra showed only weak absorptions at about 230 mμ with $\epsilon \simeq 53$ and 38, respectively, for the major (52% yield) and final (37% yield) fractions. Nuclear magnetic resonance and spin-decoupling results are summarized in Table I.

TABLE I

The products of LiAlH$_4$ reduction of the enedione V: n.m.r. and spin-decoupling studies

Compound	Signal	Chemical shift (τ)	Relative area	Multiplicity	J (c.p.s.)	Double resonance
VII	A	6.85	1.2	Multiplet	—	—
	B	7.41	1.8	Multiplet	—	—
	C	8.35	2.0	Multiplet	—	—
	D	9.0	15.0	Multiplet	—	—
IX	A	4.87	0.9	Quartet	1.0	At F gave a singlet
	B	5.54	1.8	Doublet	7.0	" E " " "
	C	5.72		Doublet	7.0	" D " " "
	D	6.56	2.1	Doublet	7.0	" C " " "
	E	6.72		Doublet	7.0	" B " " "
	F	8.30	2.7	Doublet	1.0	" A " " "
	G	9.1	12.0	Unsym. triplet		Unaffected
X + XI	A	4.87	0.6	Multiplet	—	At E gave a narrow doublet
	B	5.51	1.4	Overlapping	7.5	Indeterminable
	C	5.55		doublets	6.0	At D gave a singlet
	D	6.92	0.8	Doublet	6.0	" C " " "
	E	8.37	2.0	Multiplet	—	" A " " narrow doublet
	F	9.1	12.0	Unsym. quintet		Unaffected

After IX had stood in d_6-dimethylsulfoxide for several weeks, or after a small amount of water had been added and the mixture had stood for a few minutes, the nuclear magnetic resonance spectrum of IX was simplified. The pair of doublets at 5.54 and 5.72 τ became a broad singlet, while the doublets at 6.56 and 6.72 τ became two singlets. The rest of the spectrum was unchanged. The low-field doublets then are caused by the hydroxylic protons, and their spin coupling to the protons on the hydroxylic carbon is confirmed.

On the basis of this evidence, the major fraction was assigned structure IX. Because of the marked similarity of the spectra of the major and final fractions, it was concluded that they were isomeric. That the third fraction was about an equal-part mixture of the two possible isomers of IX was inferred from the nuclear magnetic resonance spectrum and especially from the fact that, in the spin-decoupling studies, a narrow "doublet" was obtained from several signals, while the corresponding signals in IX decoupled to a sharp singlet. Structures X and XI were assigned to the components of this mixture.

Aqueous base cleavage of V did not give reverse aldol cleavage at the double bond but did give a quantitative yield of a sharp-melting solid with the molecular formula $C_{11}H_{18}O_3$, corresponding to the addition of the elements of water to the enedione. The infrared spectrum contained the characteristic very broad carboxylic acid hydroxyl absorption between 3 600 and 2 400 cm^{-1}. The ultraviolet spectrum showed only a strong maximum at 233 mμ ($\epsilon = 2.7 \times 10^3$).

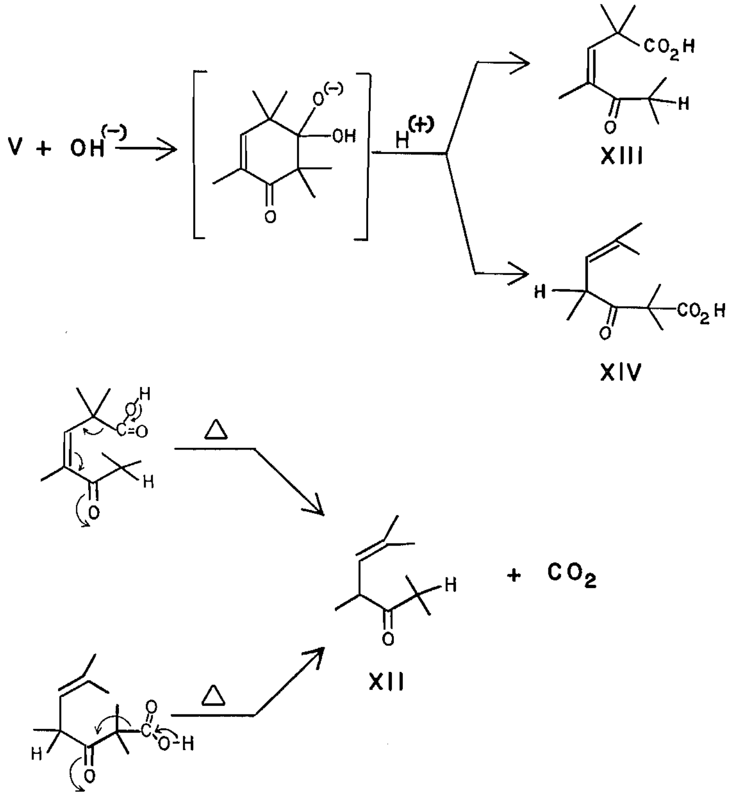
Heating the acid above 150° resulted in decarboxylation to give $C_{10}H_{18}O$. The decarboxylated material showed a single sharp carbonyl absorption at 1 720 cm^{-1}, which is in the region of non-conjugated carbonyl groups. At 845 cm^{-1}, a band characteristic of C—H bending in trisubstituted ethylenes was present. In the ultraviolet region absorption maxima were present at 293 mμ (ϵ = 220) and at 212 mμ (ϵ = 3.2×10^3). The nuclear magnetic resonance signals and the results of spin decoupling for the decarboxylated compound are summarized in Table II.

TABLE II

Nuclear magnetic resonance and double resonance studies on 2,4,6-trimethylhept-2-en-5-one (XII)

Signal	τ value	Area ratio	Multiplicity	J (c.p.s.)	Double resonance
A	5.02	1	Pair of heptets	10.0 and 1.3	At B gave a single heptet (J = 1.3) " D " " " doublet (J = 10.0)
B	6.53	1	Pair of overlapping quartets	10.0 and 7.0	" A " " " quartet (J = 7.0) " E–F " " " doublet (J = 10.0)
C	7.34	1	Heptet	7.0	" E–F " " singlet
D	8.28	6	Narrow doublet	1.3	" A " " "
E	8.98	6	Pair of overlapping doublets	7.0	" B " an unsymmetrical triplet
F	9.02	3		6.9	" C " " " "

From this spectral evidence, the decarboxylated material was assigned structure XII. This 2,4,6-trimethylcyclohex-2-en-5-one can arise by decarboxylation of either or both of the acids derived from attack of the hydroxide ion at the 1-carbonyl in V, that is, from either XIII or XIV.



Nuclear magnetic resonance spectroscopy should readily distinguish between the two acids, XIII and XIV. Unfortunately, even the sharp-melting (88.5–88.8°) analytical sample of the acid gave a spectrum which could be either of, or more likely a mixture of, the two acids. The ultraviolet maximum at 233 mμ ($\epsilon = 2.7 \times 10^3$), corresponding to that at 231 mμ ($\epsilon = 8.5 \times 10^3$) for V, suggests that approximately 30–35% of the "enone" chromophore is present in the acid mixture. This approximately 1:2 composition of XIII and XIV is consistent with the nuclear magnetic resonance spectrum of the acids.

Analogies for the ring cleavage by aqueous base treatment are to be found in a study by Stetter (17) of the formation of δ-ketocarboxylic acids by the treatment of 1,3-cyclohexandiones with aqueous base.

All of the physical data presented for the major product from the methylation of resorcinol in basic nonpolar solution, 2,2,4,6,6-pentamethylcyclohex-4-en-1,3-dione, and some of its reaction products are consistent only with the structure proposed. Potential synthetic uses for the enedione or its analogues produced by substituting other alkyl halides for the methyl iodide at any point along the alkylation sequence, as presented in the previous paper (13), are numerous and varied.

EXPERIMENTAL

Infrared spectra reported were obtained for the most part with a Perkin–Elmer model 21 on 10% solutions in carbon tetrachloride. Nuclear magnetic resonance spectra were obtained with a Varian A-60 on 10–30% solutions in carbon tetrachloride or deuterochloroform, except in those cases (IX, X, and XI) where the sample was not soluble. d_6-Dimethylsulfoxide was then used. Spin-decoupling studies were performed on a Varian HR-60 with side-band double resonance. Ultraviolet spectra were obtained in ethanolic solution on a Bausch and Lomb Spectronic 505 spectrophotometer.

Preparation of 2,2,4,6,6-Pentamethylcyclohex-4-en-1,3-dione (Enedione)

Into a 500-ml Morton (creased) flask continually purged with dry nitrogen, 6.568 g (0.0596 mole) of resorcinol in 25 ml of tetrahydrofuran, which had been freshly distilled from lithium aluminium hydride, was very slowly added to 3.162 g (0.358 mole) of lithium hydride powder while the mixture was gently stirred. In the violent evolution of hydrogen, considerable tetrahydrofuran vapors were entrained. After hydrogen evolution had ceased, 125 ml of toluene, which had been freshly distilled from lithium aluminium hydride, was added, and heating and vigorous high-speed stirring commenced. At gentle reflux, 50 ml (114 g, 0.800 mole) of methyl iodide, which had been freshly distilled from calcium hydride, was dropped in over an 8-h period. The milky-white slurry turns brilliant yellow with the first drops of methyl iodide.

After it was refluxed and stirred for 24–30 h, the solution was allowed to settle and cool before the supernatant liquid was poured off and concentrated on a rotary evaporator. The residue from both the flask and the solvents was taken up in 100 ml each of ether and 1:1 aqueous Claisen's alkali (13). Extraction and re-extraction of each of the ethereal layers until the fresh alkali extracts were colorless, and drying and removal of the ether, gave 6.18 g of neutral fraction. Vapor phase chromatographic analysis on a 16-ft 20% liquid-phase Ucon 50-HB-2000 column at 188° showed the neutral fraction to be 98% enediones and 2% dimethoxymesitylene.

The enedione fraction collected from the vapor phase chromatograph was found to be 93% V and 7% IV. The oil (b.p. 75–82° at 2.3 mm and 62–66° at 0.9 mm) had an average molecular weight of 178.

Anal. Calcd. for $C_{11}H_{16}O_2$: C, 73.30; H, 8.95. Calcd. for $C_{10}H_{14}O_2$: C, 71.65; H, 8.44. Found: C, 72.91; H, 8.78.

Attempted Preparation of Derivatives of the Enedione V

2,4-Dinitrophenylhydrazone

The procedure of Shriner *et al.* (18) was followed, but the small amount of solid obtained after it had stood at 3° for 5 days melted over a 50° range, even after six recrystallizations from ethanol.

Semicarbazone

The procedure of Shriner *et al.* (19) was followed, but even after 2 months in the refrigerator no precipitate had formed.

Bromine Addition

Bromine failed to add to the double bond with carbon tetrachloride or acetic acid solutions of bromine or pure bromine. Aqueous bromine solution gave some paste-like material which failed to crystallize in 15 months.

Diimide Reduction of the Enedione

By the procedure of Thiele (20), 20 g (0.172 mole) of azodicarboxamide was hydrolyzed with 50 ml of carbon dioxide free 50% aqueous potassium hydroxide at 0° under a nitrogen blanket in a 1-l beaker. The dipotassium azodicarboxylate was vacuum-filtered in a chilled Büchner funnel, again under a blanket of nitrogen. The salt was promptly dissolved in water (100 ml) at 0° and filtered through a chilled sintered-glass funnel into 400 ml of cold absolute ethanol, where the salt again precipitated as a fine bright yellow powder. The product was recovered from the ethanolic solution by filtration and was thoroughly washed with three 400-ml portions of absolute methanol at 0° and under a nitrogen blanket. The yellow salt was transferred to a vacuum desiccator and dried overnight to yield 27.2 g or 83% of the theoretical amount of dipotassium diazodicarboxylate.

Following the general procedure of van Tamelen *et al.* (15), 3.50 g (0.021 mole) of the enedione was added to 75 ml of methanol containing 10.0 g (0.0515 mole) of dipotassium diazodicarboxylate. With magnetic stirring at 0°, 11 ml (11 g, 0.18 mole) of glacial acetic acid in 30 ml of methanol was very slowly added under a nitrogen atmosphere. After several hours at 0°, the solution was allowed to warm slowly to room temperature, where it was stirred for 6 h.

The methanol was removed on a rotary evaporator and the slurry was taken up in ether and water. The ether layer was washed twice with 50-ml portions of 1:1 aqueous Claisen's alkali to remove the excess acetic acid and then washed with water before being dried by an extraction with saturated aqueous sodium chloride and filtration through a cone of sodium sulfate.

Vapor phase chromatographic analysis showed the enedione to be only 15% reduced, so that the reduction procedure was repeated three additional times to give an overall yield of 3.35 g (90%) of a material which was 3.4% enedione, 3.4% miscellaneous products, and 93.4% 2,2,4,6,6-pentamethylcyclohexan-1,3-dione. Analysis of a fraction of VII collected on the vapor phase chromatograph follows.

Anal. Calcd. for $C_{11}H_{18}O_2$: C, 72.49; H, 9.95. Found: C, 72.33; H, 9.90.

Lithium Aluminium Hydride Reduction of the Enedione

Under an atmosphere of dry nitrogen, 1.00 g (0.006 mole) of the enedione was dissolved in 75 ml of reagent grade ether, and 0.696 g (0.0183 mole) of lithium aluminium hydride was added.

After the solution was refluxed for 20 h with magnetic stirring, 1.5 ml of water was cautiously added to destroy the excess hydride and the solution was stirred overnight, before the precipitated salt was removed by filtration and washed with several portions of ether. The ethereal solution was dried with sodium sulfate and the ether removed to leave 0.95 g of white solid (m.p. 106–122°). The three components which were separated on the vapor phase chromatograph were assigned the structures 2,2,4,4,6-pentamethylcyclohexan-3-ol-1-one, VIII (10.6%), 1,3,3,5,5-pentamethylcyclohex-1-en-4*e*,6*e*-diol, IX (52.0%), and the two stereoisomers with pseudo-axial and equatorial hydroxyl groups, X and XI (37.4%).

Treatment of the Enedione with Refluxing Aqueous Potassium Hydroxide

Under a slight positive pressure of nitrogen, 1.05 g of V (b.p. 59° at 0.75 mm, m.p. 5–8°) was refluxed for 2 h in 50 ml of 10% aqueous potassium hydroxide made with freshly opened reagent grade potassium hydroxide and degassed distilled demineralized water. Still under nitrogen, the flask was allowed to cool to room temperature. The solution was extracted with two 75-ml portions of ether which were, in turn, washed with water and dried, and the ether removed to give 0.009 g of neutral fraction, all of which was recovered enedione.

The alkaline solution was acidified with hydrochloric acid and the white solid which separated was recovered with two 50-ml ether extractions. The ethereal layers were washed once with 10 ml of water and dried as usual before the ether was removed on a rotary evaporator. From the $C_{11}H_{18}O_3$ formula calculated from the analysis of a recrystallized portion of the white solid, the 1.127 g of acid fraction obtained corresponds to a 97.8% yield.

Recrystallization of 100 mg of the product from 2 ml of hexane gave 75 mg of very fluffy solid carboxylic acid mixture (m.p. 88.5–88.8°).

Anal. Calcd. for $C_{11}H_{18}O_3$: C, 66.63; H, 9.15. Found: C, 66.67; H, 9.09.

Either collection of the material which passes through the v.p.c. or heating the acid or mixture of acids above 150° for several minutes results in decarboxylation to give a colorless liquid, XII.

Anal. Calcd. for $C_{10}H_{18}O$: C, 77.84; H, 11.77. Found: C, 77.54; H, 11.74.

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REFERENCES

1. D. Y. CURTIN, R. J. CRAWFORD, and M. WILHELM. J. Am. Chem. Soc. **80**, 1391 (1958).
2. D. Y. CURTIN and R. FRASER. J. Am. Chem. Soc. **80**, 6016 (1958).
3. D. Y. CURTIN and D. H. DYBVIG. J. Am. Chem. Soc. **84**, 225 (1962).
4. N. KORNBLUM and A. P. LURIE. J. Am. Chem. Soc. **81**, 2705 (1959).
5. N. KORNBLUM and R. SELTZER. J. Am. Chem. Soc. **83**, 3668 (1961).
6. N. KORNBLUM, P. J. BERRIGAN, and W. J. LE NOBLE. J. Am. Chem. Soc. **85**, 1141 (1963).
7. N. KORNBLUM, R. SELTZER, and P. HABERFIELD. J. Am. Chem. Soc. **85**, 1148 (1963).
8. R. BARNER and H. SCHMID. Helv. Chim. Acta, **43**, 1393 (1960).
9. P. KURZWEIL. Monatsh. **24**, 910 (1903).
10. J. HERZIG and F. WENZEL. Monatsh. **27**, 781 (1906).
11. J. HERZIG and S. ZEISEL. Monatsh. **9**, 217, 882 (1882); **11**, 219, 311 (1890).
12. J. L. E. ERICKSON and G. C. KITCHENS. J. Org. Chem. **27**, 460 (1962).
13. A. R. STEIN. Can. J. Chem. This issue.
14. T. L. BROWN, D. Y. CURTIN, and R. FRASER. J. Am. Chem. Soc. **80**, 4339 (1958).
15. E. E. VAN TAMELEN, R. S. DEWEY, and R. J. TIMMONS. J. Am. Chem. Soc. **83**, 3725 (1961).
16. N. G. GAYLORD. Reductions with complex metal hydrides. Interscience Publishers, Inc., New York. 1956. p. 956.
17. H. STETTER. Angew. Chem. **67**, 769 (1955).
18. R. L. SHRINER, R. C. FUSON, and D. Y. CURTIN. Systematic identification of organic compounds. 4th ed. John Wiley and Sons, Inc., New York. 1956. p. 219.
19. R. L. SHRINER, R. C. FUSON, and D. Y. CURTIN. Systematic identification of organic compounds. 4th ed. John Wiley and Sons, Inc., New York. 1956. p. 218.
20. J. THIELE. Ann. **271**, 127 (1892).