6.08 (cyclohexa-2,4-dien-1-one), 9.05 μ (chroman ether); nmr (CCl_4) 1.07 (s, *t*-butyl), 1.29 (s, two equivalent *t*-butyl groups), 1.43 (s, *t*-butyl), 1.25, 1.29 [each of these peaks represents one-half of a doublet arising from the splitting of a methyl group by the adjacent methine proton; the other half of each doublet is under the envelope of the 1.29 signal as determined by the J values of 0.10 and 0.14 (see below)], 2.70 (q, J = 0.13, methine H α to aromatic ring), 4.75 (q, J = 0.10, methine H α to ethereal oxygen), 6.14 (d, J = 0.04 vinylic H), 6.91, 7.03, 7.21 ppm (d for each J = 0.04 one of these doublets represents the other vinylic proton; the other doublets represent the two interacting aromatic protons); mol wt (osmometric), calcd 465, found 504.

Anal. Calcd for $C_{32}H_{48}O_2$: C, 82.70; H, 10.41. Found: C, 82.61; H, 10.51.

Reduction of 3,5,6′,8′-Tetra-*t*-butyl-3′,4′-dihydro-3′,4′-dimethylbenzopyran-2′-spirocyclohexa-3,5-dien-2-one.—A *n*-hexane solution of 50 mg (1.08×10^{-4} mol) of **8** was heated at reflux with excess zinc and glacial acetic acid until the initial yellow color had disappeared. Work-up followed by recrystallization from ethanol (absolute) gave 10 mg (20%) of colorless needles of **6**, 1,2-dimethyl-1,2-bis(3,5-di-*t*-butyl-2-hydroxyphenyl)ethane: mp 185–187°; uv max (cyclohexane) 277 mμ (log ϵ 3.88), 282 (3.88); ir (KBr pellet) 2.77 (hindered O—H), 3.35 (C—H), 6.25 μ (aromatic C=C).

Anal. Calcd. for $C_{32}H_{50}O_2$: C, 82.35; H, 10.80. Found: C, 82.25; H, 10.65.

A 7-mg sample of **6** was oxidized with excess alkaline potassium ferricyanide to yield 4 mg of **8** as evidenced by melting point and uv and ir spectra.

Registry No.—**6**, 17954-01-7; **7**, 17954-02-8; **8**, 17953-99-0; **9**, 17954-00-6; **12**, 17949-23-4.

An Anomalous Hunsdiecker Reaction. The Reaction of the Silver Salts of 1-Hydroxycyclopentyl- and 1-Hydroxycyclohexylacetic Acids

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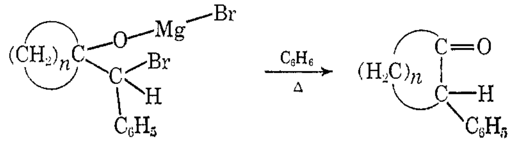
Received July 18, 1968

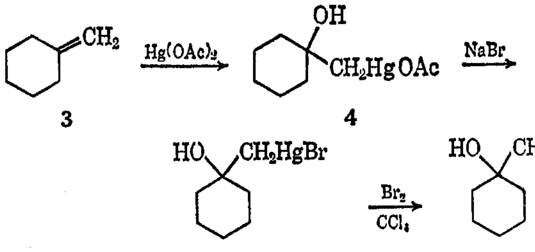
In connection with our studies on ring expansion through the decomposition of the magnesium salts of halohydrins,[1,2] represented by eq 1, a simple method for the preparation of halohydrins became imperative.



1 **2** (1)

n = 4,5,6,7

Besides the action of halogen acids on the epoxide or the action of hypobromous acid on the appropriate olefins,[3,4] the oxymercuration of an olefin in aqueous acetone followed by its conversion into the halohydrin has also been developed[3] (eq 2).



(2)

Another sequence for the preparation of halohydrins of the type depicted in **6** appeared to be the Hunsdiecker reaction on the corresponding β-hydroxy acids, as the latter are readily available from the Reformatsky reaction on the appropriate ketone followed by hydrolysis. Studies on the Hunsdiecker reaction with 1-hydroxycyclohexyl- and 1-hydroxycyclopentylacetic acids, however, provided anomalous results, and therefrom mechanistic implications. The dried, powdered silver salt of 1-hydroxycyclohexylacetic acid was added to an equivalent amount of bromine in carbon tetrachloride at 60–65°. The neutral fraction was reduced with lithium aluminum hydride and afforded a bromine-free low-boiling material. This was found to be a mixture of 2-heptanol (90%) and 1-methylcyclohexanol (10%) by vpc analysis. No cyclohexylcarbinol, cyclohexanol or cycloheptanol were detected. The infrared and nuclear magnetic resonance spectra were identical with those of authentic 2-heptanol. The 3,5-dinitrobenzoate was found to be identical with the benzoate of authentic 2-heptanol (mixture melting point and melting point). Similarly the silver salt of 1-hydroxycyclopentylacetic acid gave a neutral fraction which after reduction yielded a bromine-free low-boiling compound which was identical with 2-hexanol from infrared and nuclear magnetic resonance spectra and vpc analysis. Comparison of the 3,5-dinitrobenzoates revealed no depression in melting points between the isolated product and the authentic sample. No 1-methylcyclopentanol, cyclopentanol, cyclohexanol, or cyclopentylcarbinol were detected. Bromohydrin **6** was found experimentally not to be a precursor of the products isolated.

The Hunsdiecker reactions of 1-hydroxycyclopentyl- and 1-hydroxycyclohexylacetic acids are different from those of the unsubstituted acids,[5] the latter reacting normally. The ring opening which takes place may be rationalized as in Scheme I. The primary free radical **10** undergoes preferentially a cleavage reaction to form **11** rather than its collapse to halohydrin **6**. The absence of any compound corresponding to cycloheptanone may be rationalized by the reluctance of an alkyl group to migrate to a free-radical center.[6] In the free-radical rearrangement of **15** to **16**, Berson[7] analogously postulated a ring opening followed by closure (eq 3).

A case more comparable with that reported herein was noted by Kharasch[8] in the free-radical decomposition of *t*-butyl alcohol to acetone which proceeds through a β-hydroxyalkyl radical, **17** (eq 4).

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[1] A. J. Sisti, *J. Org. Chem.*, **33**, 453 (1968).

[2] A. J. Sisti, *Tetrahedron Lett.*, No. 52, 5327 (1967).

[3] A. J. Sisti, *J. Org. Chem.*, **33**, 3953 (1968).

[4] J. Traynham and O. Pascual, *Tetrahedron*, **7**, 165 (1959).

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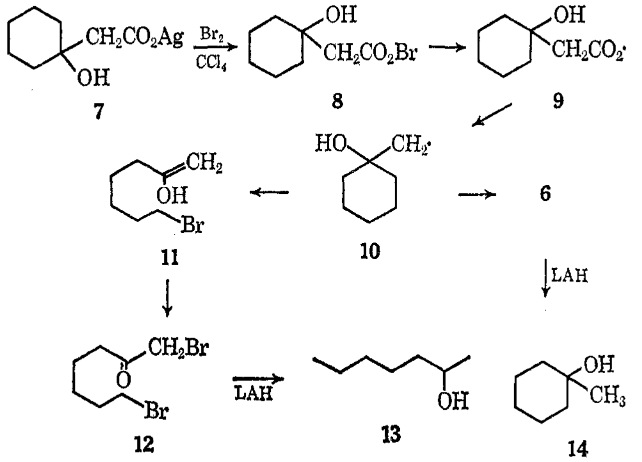
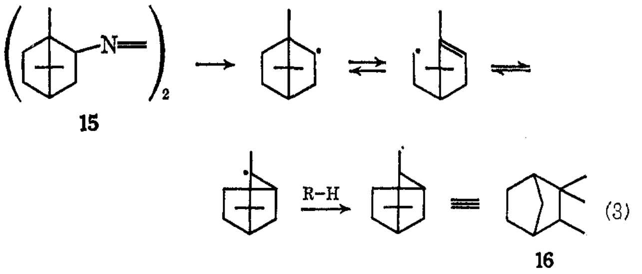
[6] C. Walling in "Molecular Rearrangements," P. DeMayo, Ed., Interscience Publishers, New York, N. Y., 1963, p 407.

[7] J. A. Berson, C. J. Olsen, and J. S. Walia, *J. Amer. Chem. Soc.*, **82**, 5000 (1960).

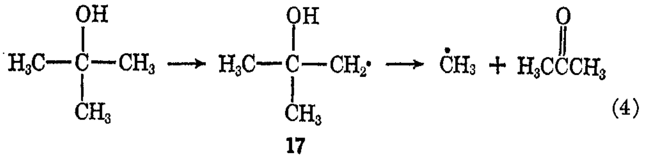
SCHEME I





15

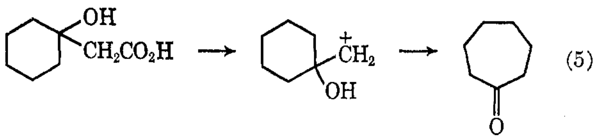
16



$$H_3C-\underset{CH_3}{\overset{OH}{C}}-CH_3 \longrightarrow H_3C-\underset{CH_3}{\overset{OH}{C}}-CH_2\cdot \longrightarrow \dot{C}H_3 + H_3C\overset{O}{\overset{\|}{C}}CH_3 \qquad (4)$$

17

The free-radical nature of the Hunsdiecker reaction is well established[9] although ionic pathways have also been postulated.[10] The formation of mainly open-chain products described herein *via* ring cleavage strongly points to the presence of free radicals. It has been shown[11] that a carbonium ion generated from 1-hydroxycyclohexylacetic acid by electrolysis affords cycloheptanone in 45–53% yield (eq 5). The Hunsdiecker reaction with other β-hydroxy acids is presently under investigation.



Experimental Section[12]

1-Hydroxycyclohexylacetic acid, mp 64–66° (lit.[13] mp 62–64°), was quantitatively converted into the silver salt in the usual manner.[14] To a stirred solution of 8 g (0.05 mol) of bromine in carbon tetrachloride (50 ml) at 60–65° was added 14 g (0.052 mol) of the dried powdered silver salt in portions. Carbon dioxide evolution occurred during the 10-min addition period. The mixture was then refluxed for 30 min, cooled, and filtered. The carbon tetrachloride solution, after dilution with ether, was washed with a sodium bicarbonate solution to remove a considerable amount of the reformed starting acid, 5.8 g (0.037 mol). The carbon tetrachloride was dried (magnesium sulfate) and the solvent removed under vacuum. A yellow liquid residue remained (5 g) which showed infrared absorptions at ν_{CCl_4} 1780, 1740 and 1700 cm^{-1}.

To a stirred refluxing suspension of lithium aluminum hydride (2 g) in dry ether (40 ml) a solution of the crude bromo ketone (5.0 g) in ether (40 ml) was added dropwise. The mixture was stirred and refluxed for 15 hr. It was then cooled and decomposed with saturated sodium sulfate solution. The ether layer was separated and the remaining solid was washed with ether. The combined ether extracts were dried over magnesium sulfate and the solvent removed. The residue upon distillation afforded a fraction of bp 73–75° (20 mm). There was isolated 0.5 g (0.0043 mol) (30% of the recovered acid was taken into account). Vpc analysis on a 4-ft TCEP column and a 4-ft Carbowax column at 100° (40 psi) revealed it to be a mixture of 2-heptanol (90%) and 1-methylcyclohexanol (10%). The infrared and nmr spectra were identical with those of authentic 2-heptanol. The 3,5-dinitrobenzoate was also found to be identical with that of authentic 2-heptanol (melting point and mixture melting point).

The silver salt of 1-hydroxycyclopentylacetic acid[13] under similar conditions (Hunsdiecker followed by lithium aluminum hydride reduction) afforded a liquid, bp 135–136° (15%). This was found to be exclusively 2-hexanol from the infrared and nmr spectra as well as vpc analysis. Comparison of the 3,5-dinitrobenzoates also confirmed the structural assignment.

Registry No.—1-Hydroxycyclopentylacetic acid (Ag salt), 18500-78-2; 7, 18500-79-3.

Acknowledgment.—We are grateful to Mr. T. Kolesar for taking the nmr spectra.

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[12] All melting points and boiling points are uncorrected. Infrared spectra were determined with a Perkin-Elmer Spectrocord infrared spectrophotometer. Nmr spectra were determined with a Varian A-60 instrument.

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N-Alkylanilinomethylenemalononitriles. A Convenient Synthesis through a Variation and Extension of the Meerwein Amide Acetal Reaction

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Amide acetals are readily prepared by reaction of tertiary amides with triethyloxonium tetrafluoroborate,[1] followed by addition of base and alcohol.[2] Meerwein and coworkers[2] have demonstrated the great synthetic utility of amide acetals. One example is the reaction of N,N-dialkylamide acetals with malononitrile to form N,N-dialkylaminomethylenemalononitriles.[2] Desirous of an easy route to N,N-disubstituted aminomethylenemalononitriles, we have explored a variation of this synthetic route and have extended this reaction to a convenient synthesis of N-alkylanilinomethylenemalononitriles.

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[1] Triethyloxonium tetrafluoroborate is quite easily prepared from boron trifluoride etherate and epichlorohydrin: H. Meerwein, *Org. Syn.*, **46**, 113 (1966).

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