Table I

Alkylation of Phenylacetonitrile with Alkyl Halides and 50% Aqueous Sodium Hydroxide in Dimethyl Sulfoxide

$$\underset{\text{I}}{C_6H_5CH_2CN} \xrightarrow[\text{(NaOH)}]{+RX} \underset{\text{II}}{C_6H_5CHRCN} \xrightarrow[\text{(NaOH)}]{+RX} \underset{\text{III}}{C_6H_5CR_2CN}$$

Alkyl halide RX	RX, mol equiv	NaOH, mol equiv	Reaction temp, °C	Yield, %[a] Unalkylated I	Monoalkylated II	Dialkylated III
CH_3Cl	Excess	4.0	45	0	0	93
CH_3Br	1.5	5.0	30	0	79	8
n-C_3H_7Br	1.5	5.0	30	0	75	13
n-C_4H_9Cl	1.0	4.0	26	5	62	8
$C_6H_5CH_2Cl$	3.0	4.0	52	0	0	96[b]

[a] Unless otherwise indicated, all yields were determined by quantitative glpc of the benzene extracts. [b] Product isolated.

promises to be of particular utility whenever the preparation of α-substituted phenylacetonitriles is desired.

Experimental Section

All reagents were the commercially available products (technical grade), used without purification. A typical alkylation reaction is described in the following example.

α,α-Dimethylphenylacetonitrile.—A 500-ml four-necked flask having a gas inlet tube fused to the bottom and equipped with a mechanical stirrer, reflux condenser, two 250-ml dropping funnels (the second one mounted on a side-area adaptor), and a thermowell was charged with 100 ml of dimethyl sulfoxide and methyl chloride was introduced for 15 min. While passage of methyl chloride was continued, to the stirred solution of the gas was added simultaneously 32 g of 50% aqueous sodium hydroxide and 11.7 g of phenylacetonitrile. The reactants were added at such a rate that the temperature of the exothermic reaction was kept between 45 and 50°. After the exothermic reaction had subsided, stirring and introduction of methyl chloride were continued for an additional 60 min. Upon completion of this period, the contents of the reaction flask were diluted with 250 ml of water and the aqueous mixture was extracted with two 100-ml portions of benzene and one 100-ml portion of ether. The combined organic extracts were washed with saturated sodium bicarbonate solution, followed by saturated sodium chloride solution. After drying over anhydrous sodium sulfate, the solvents were evaporated, leaving 14.0 g (93% of theory) of a yellowish oil. Analyses by glpc coupled with a mass spectrograph and by nmr proved this product to be α,α-dimethylphenylacetonitrile.

Registry No.—I, 140-29-4; dimethyl sulfoxide, 67-68-5.

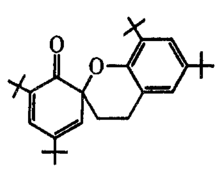
The Dimerization of 2,4-Di-*t*-butyl-6-ethenyl-Quinone Methide. A Possible Diels–Alder Mechanism

Clinton D. Cook[1] and Leroy C. Butler[2]

Department of Chemistry, University of Vermont, Burlington, Vermont

Received June 11, 1968

Work by Waters[3] has shown that lead dioxide oxidation of 2,4-di-*t*-butyl-6-methylphenol (**1**) leads to the ketochroman dimer 2. In connection with our interest in the synthesis of stable relatively simple *o*-quinone methides we have investigated the lead dioxide and alkaline potassium ferricyanide oxidation of the closely related phenol 2,4-di-*t*-butyl-6-ethylphenol (**3**). Our choice of this phenol was dictated by the results in two areas of investigation. First, lead dioxide or alkaline potassium ferricyanide oxidation of the 2,6-di-butyl-4-alkyl-substituted phenolic system has shown that the 4-methyl compound leads to 1,2-bis(3,5-di-*t*-butyl-4-hydroxyphenyl)ethane and its oxidation product, 3,5,-3′,5′-tetra-*t*-butylstilbene-4,4′-quinone,[4] whereas the 4-ethyl compound[5] (or more highly substituted analogs) leads to the stable *p*-quinone methide. Second, several reactions have been reported where an *o*-quinone methide was the expected product but where dimeric or more complex compounds were the only isolated products.[6] In each case the intermediate *o*-quinone methide would possess an unsubstituted methylene group. Therefore, it appeared reasonable that further substitution of the methyl group of **1** might lead to the stable *o*-quinone methide **7**.



2

Oxidation by **3** lead dioxide or alkaline potassium ferricyanide did not result in the isolation of the *o*-quinone methide **7** but instead produced three new compounds—ketochroman dimers, **8** and **9**, and an unidentified compound, a trimer based on the starting phenol **3** (see Experimental Section). The structures of **8** and **9** were established by chemical means, molecular weights, and ultraviolet, infrared, and nmr spectroscopy.

Oxidation of **3** produces phenoxy radical **5** as evidenced by the immediate appearance of a deep green color with an absorption maximum at 580 mμ.[7] The possible fates of this radical are represented in Chart I. Most probably phenoxy radical **5** disproportionates[8] to phenol **3** and *o*-quinone methide **7**, which subsequently reacts with itself *via* a Diels–Alder mech-

---

[1] Support of the Petroleum Research Foundation under Grant 1156-A4 is gratefully acknowledged.

[2] To whom inquiries should be sent: Department of Chemistry, Windham College, Putney, Vt. 05346.

[3] W. Waters, *J. Chem. Soc.*, 243 (1954).

[4] C. D. Cook, *J. Org. Chem.*, **18**, 261 (1953).

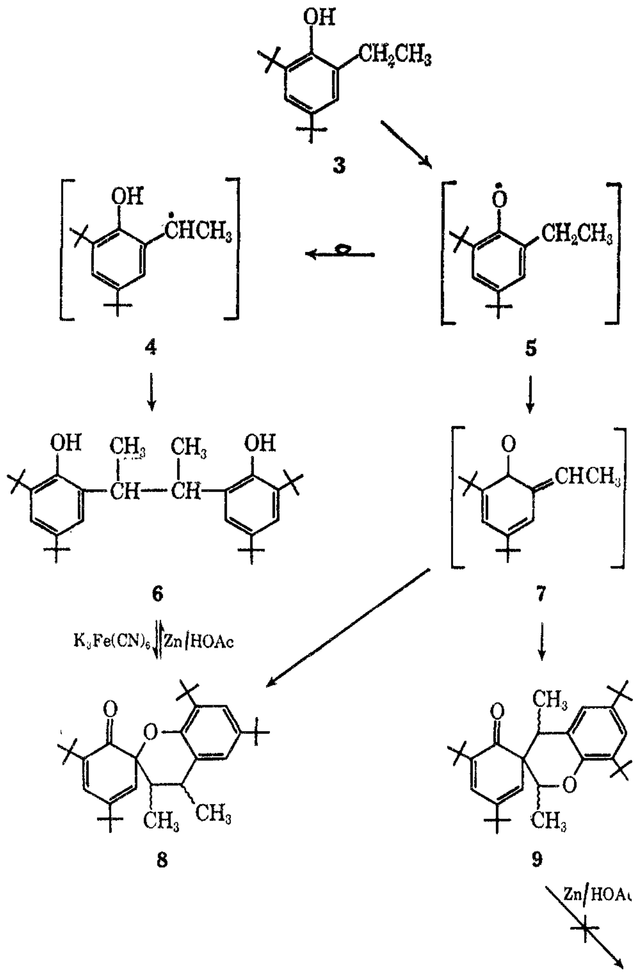
[5] C. D. Cook and B. E. Norcross, *J. Amer. Chem. Soc.*, **78**, 3797 (1956).

[6] (a) L. Smith and J. Horner, Jr., *ibid.*, **60**, 670 (1938); (b) P. Gardner and H. Sarrafizadeh R., *J. Org. Chem.*, **25**, 641 (1960); (c) S. Cavitt, H. Sarrafizadeh R., and P. Gardner, *ibid.*, **27**, 1211 (1962); (d) A. B. Turner, *Quart. Rev.* (London), **18**, 347 (1964).

[7] For λ_{max} of other phenoxy radicals, see C. D. Cook, D. A. Kuhn, and P. Fianu, *J. Amer. Chem. Soc.*, **78**, 2002 (1956).

[8] C. D. Cook and B. E. Norcross, *ibid.*, **81**, 1176 (1959).

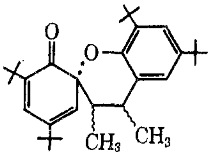
Chart I



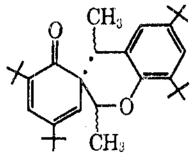
anism to give the observed dimers. It is also possible for the phenoxy radical to rearrange to the corresponding substituted benzyl radical 5 in a manner analogous to that suggested for the 2,6-di-*t*-4-methylphenoxyradical.[9] Benzyl radical 4 could then dimerize to the substituted dihydroxydiphenylethane 6, which upon oxidation would give dimer 8. The latter reaction has been observed by us and constitutes half of the chemical proof of the structure of 8, *i.e.*, 6 is produced upon treating 8 with zinc and acetic acid, thus completing the chemical proof. In contrast, 9 is unreactive toward zinc and acetic acid.

This path does not, however, account for the isomeric ketochroman dimer 9. Therefore, dimerization of the intermediate *o*-quinone methide is most likely operative in the formation of both dimers with the additional possibility that the benzyl radical pathway is accounting for some of 8.[10]

If dimers 8 and 9 are produced *via* the Diels–Alder reaction of one *o*-quinone methide molecule with another, it marks the first instance, to our knowledge, that intermediate *o*-quinone methides react to give more than one of a number of possible arrangements of diene and dienophile in the product, *i.e.*, in all recorded instances only the product analogous to 8 was isolated.[6d] The observed behavior is reasonable, however, if one considers the Diels–Alder mechanism to consist of initial orientation of diene and dienophile with concomitant formation of one bond followed by formation of the other bond at the "diradical" end of the reacting species. This type of mechanism has been suggested recently as a possibility for the Diels–Alder reaction.[11] This view correctly predicts that the product arises from the most stabilized "diradical" orientation. In the case of "diradicals" **10** and **11** there is probably almost equal stabilization of each radical fragment.[12] Consequently, it would not be surprising for **8** and **9** to be formed in comparable amounts.



10



11

Experimental Section

2,4-Di-*t*-butyl-6-ethylphenol was prepared according to the method employed by Stillson.[13]

Oxidation of 2,4-Di-*t*-butyl-6-ethylphenol.—A benzene solution of 10.0 g (0.0052 mol) of **3** was treated with an 8 *M* excess of alkaline potassium ferricyanide according to the general method of Cook and Norcross.[5] The work-up produced 9.60 g of a viscous liquid. After trituration with *n*-hexane and allowing the solution to stand, a crop of yellow crystals was obtained. Close examination revealed crystals of two types: some pale yellow and the others bright yellow. The majority of each shade of crystals were separated with a pair of tweezers. The pale yellow crystals were recrystallized twice from *n*-hexane to give a trimeric compound **12** based on the starting phenol. The total yield of **12** was 1.10 g (11%): mp 181–183°; uv max (cyclohexane) 288 mμ (log ϵ 3.86), 310 (3.93), 375 (sh) (2.71); ir (KBr pellet) 3.40 (C—H), 6.00, 6.08 (cyclohexa-2,4-dien-1-one), 9.25 μ (chroman ether); nmr (CCl_4) 0.75, 0.88, 1.13, 1.25, 1.35, 1.40 (all s) six nonequivalent *t*-butyl groups, 0.62, 1.33 and probably under *t*-butyl group at 1.13 (all s), three nonequivalent methyl groups, 2.40 (m, 2 or 3 H), 5.32, 5.50, 6.38, 6.80, 6.92, 7.21 ppm (all d, J = 0.04 ppm for each, 1 H); mol wt (osmometric) calcd for trimer of *o*-quinone methide 697, found 702.

Anal. Calcd for $(C_{16}H_{24}O)_3$: C, 82.70; H, 10.41. Found: C, 82.91; H, 10.56.

Several recrystallizations of the bright yellow crystals from *n*-hexane gave 2.1 g (21%) of **8**, 3,5,6′,8′-tetra-tert-butyl-3′,4′-dihydro-3′,4′-dimethylbenzo-pyran-2′-spirocyclohexa-3,5-dien-2-one; mp 179–181°; uv max (cyclohexane) 270 mμ (log ϵ 3.79), 283 (3.81), 306 (3.65), 335 (2.77), 349 (2.84), 361 (2.77), 375 (2.44); ir (KBr pellet) 3.35 (C—H), 5.85, 6.00, 6.05 (cyclohexa-2,4-dien-1-one), 9.28 μ (chroman ether); nmr (CCl_4) 0.86 (d, J = 0.12 ppm, methyl), another methyl group is under the envelope of the *t*-butyl groups, 2.30 (m, J = 0.04 methine H, smaller coupling constants not clearly discernible), 2.79 (m, J = 0.04 methine H), 6.22 (d, J = 0.04 vinylic H), 6.85 (d, J = 0.04 vinylic H), 7.03 (d, J = 0.04 aromatic H), 7.25 ppm (d, J = 0.04, aromatic H); mol wt (osmometric) calcd 465, found 494.

Anal. Calcd for $C_{32}H_{48}O_2$: C, 82.70; H, 10.41. Found: C, 82.73; H, 10.37.

The original mother liquor from which **12** and **8** were obtained afforded another crop of yellow crystals whose intensity was between that of **12** and **8**. Two recrystallizations from petroleum ether (bp 30–60°) produced 1.5 g (15%) of **9**: mp 129–131°; uv max (cyclohexane) 277 mμ (sh) (log ϵ 3.66), 284 (3.76), 308 (3.76), 375 (sh) (2.52); ir (KBr pellet) 3.35 (C—H), 6.00,

---

(9) C. D. Cook, N. G. Nash, and H. R. Flanagan, *J. Amer. Chem Soc.*, **77**, 1783 (1955).

(10) One referee has pointed out that **9** might be formed by the attack of **5** on **7** followed by further oxidation and closure or by the coupling of **4** and **5** followed by corresponding oxidation and closure.

(11) J. D. Roberts and M. C. Caserio, "Basic Principles of Organic Chemistry," W. A. Benjamin, Inc., New York, N. Y., 1964, p 267.

(12) It is realized, however, that **11** is probably somewhat less stable than **10** since a phenoxy radical is expected to be more stable than the corresponding benzyl radical. See A. L. Buchachenko, "Stable Radicals" (translation from the Russian), Consultants Bureau, New York, N. Y., 1965, p 35.

(13) A. Stillson, *J. Amer. Chem. Soc.*, **68**, 722 (1946).

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.

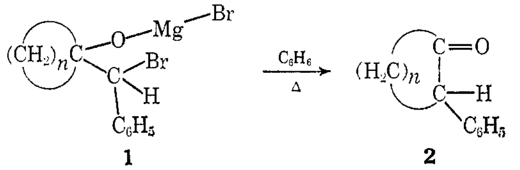
An Anomalous Hunsdiecker Reaction. The Reaction of the Silver Salts of 1-Hydroxycyclopentyl- and 1-Hydroxycyclohexylacetic Acids

NITYA G. KUNDU AND ANTHONY J. SISTI

Department of Chemistry, Adelphi University, Garden City, New York

Received July 18, 1968

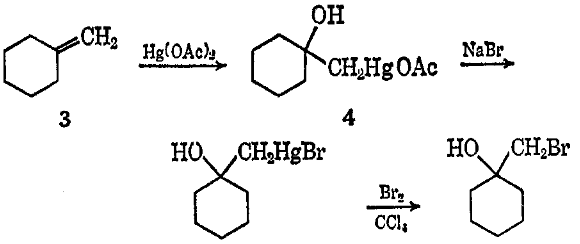
In connection with our studies on ring expansion through the decomposition of the magnesium salts of halohydrins,[1,2] represented by eq 1, a simple method for the preparation of halohydrins became imperative.



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).



3 4 5 6 (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).

---

[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).

[5] C. Hunsdiecker, H. Hunsdiecker, and E. Vogt, German Patent 730,410 (1942); *Chem. Abstr.*, **38**, 374 (1944). W. Parker and R. A. Raphael, *J. Chem. Soc.*, 1723 (1955).

[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).