ArCH$_2$CHP), 2.2–2.6 (m, 6, 3 CH$_2$Pr), 1.2–1.7 (m with intense s at 1.34 ppm, 30, 3 CH$_2$CH$_2$CH$_3$ and 2 *t*-Bu), and 0.91 ppm (highly distorted t, 9, $J \cong 6$ Hz, 3 CH$_2$CH$_3$).

Reaction of Phosphonium Chloride (3) with *n*-Butyllithium.—*n*-Butyllithium solution (15.20% in hexane, 1.24 ml, 2.00 mmol) was added to a mixture of **3** (0.914 g, 2.00 mmol) and dry benzene (20 ml) that had previously been degassed by the freeze–thaw method and blanketed with nitrogen. After 2.0 hr of stirring at room temperature, the mixture was stirred for 1.0 hr under vigorous reflux, cooled (all operations described thus far were performed under nitrogen), saturated with anhydrous HCl, and filtered with suction. The precipitate (an infusible, hygroscopic white powder: presumably LiCl) was washed with several small portions of benzene, and the combined filtrate and washings were evaporated under vacuum. Nmr analysis showed that bisphenol **9** (yield, 55–65%) and phosphonium chloride **3** (recovery, 30–40%) were major constituents of the semisolid residue (0.95 g). These identifications were confirmed by peak enhancements produced by the addition of authentic specimens, and the presence of **9** was also indicated by vpc and mass spectral analysis.

***trans*-3,5-Di-*t*-butyl-4-stilbenol (8) from 4-Benzylmethylene-2,6-di-*t*-butyl-2,5-cyclohexadien-1-one (20).**—A solution of quinone methide **20** (0.31 g, 1.0 mmol) in dry benzene (5 ml) was degassed by bubbling with nitrogen. Tri-*n*-butylphosphine (0.20 g, 1.0 mmol) was then added with stirring, and the solution was allowed to stand at room temperature for 3.3 hr. Evaporation under vaccum left an oily residue that solidified when scratched. Drying of the solid on a porous plate gave snow-white microcrystals, mp 89.5–90°, which were shown to be essentially pure **8** by a mixture melting point determination and nmr analysis.

A solution of quinone methide **20** (0.073 *M*) and tri-*n*-butylphosphine (0.160 *M*) in C$_6$D$_6$ was examined by nmr 2–3 min after preparation. The spectrum showed that **20** had undergone quantitative conversion to **8** during the brief reaction period.

Registry No.—Tributylphosphine, 998-40-3; **2,** 2607-52-5; **3,** 24164-84-9; **4,** 24164-85-0; **8,** 21449-69-4; **13,** 24164-86-1; **16,** 24164-87-2; **19a,** 24164-88-3; **19b,** 24164-89-4.

Acknowledgment.—The authors are indebted to Mr. H. J. Tarski for invaluable technical assistance, to Dr. H. G. Schutze for encouragement and support, and to numerous colleagues in the Analytical Division of this laboratory for help with analytical problems.

Diels–Alder Adducts of Acetoxy-1,3-dienes and *p*-Benzoquinone

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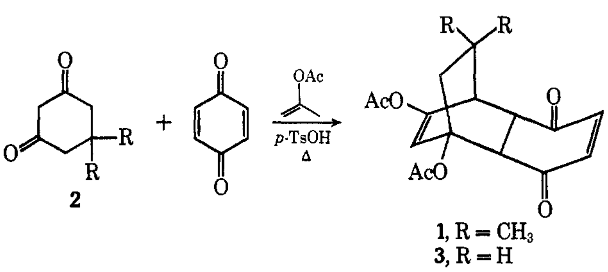
Received September 26, 1969

Cyclic acetoxy-1,3-dienes, generated *in situ* from 1,3-cyclohexanediones or isophorone, undergo Diels–Alder reaction with *p*-benzoquinone to afford 5,8-ethano-4a,5,8,8a-tetrahydro-1,4-naphthoquinone derivatives. The hydrolysis, aromatization, and Grob fragmentation of these derivatives are discussed.

The first paper[2] in this series described the *in situ* generation of acetoxy-1,3-dienes by the reaction of isopropenyl acetate with a variety of cyclic enones and diones, and their reaction with maleic anhydride. We now report the reaction of these acetoxy-1,3-dienes with *p*-benzoquinone and describe the hydrolysis products obtained from the resulting adducts.

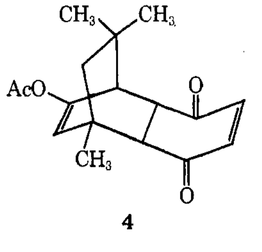
When dimedone (**2**, R = CH$_3$) or 1,3-cyclohexanedione is heated with an equivalent amount of *p*-benzoquinone in isopropenyl acetate containing a catalytic amount of *p*-toluenesulfonic acid, crystalline adducts **1** and **3** are obtained in about 55% yield.



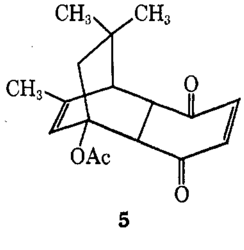
2

1, R = CH$_3$
3, R = H

Isophorone, which gives two different enol acetates, similarly afforded a mixture of adducts **4** and **5** in a 42:58 ratio.

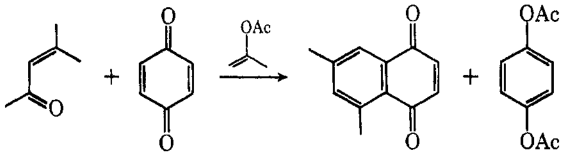


4



5

Attempts to condense *p*-benzoquinone with other conjugated carbonyl compounds such as crotonaldehyde, tiglaldehyde, and 2-cyclopentylidene-cyclopentanone[3] gave tars and no recognizable products other than hydroquinone diacetate. Mesityl oxide also gave a complicated mixture from which 4,7-dimethyl-1,4-naphthoquinone (14%) and hydroquinone diacetate (43%) were isolated. The naphthoquinone probably arises by elimination of acetic acid and dehydrogenation of the 1:1 adduct produced from 4-acetoxy-2-methyl-1,3-pentadiene.



The isolation of adducts **1**, **3**, **4**, and **5** is surprising in view of the powerful enol acetylating conditions employed in this Diels–Alder condensation. The failure to induce aromatization may in part be attributed to the inherent strain of the bicyclo[2.2.2]octadiene system which would be produced since treatment of **1** and **3** with aqueous acid resulted in hydrolysis of both acetate groups and aromatization to give ketoquinols **6a**

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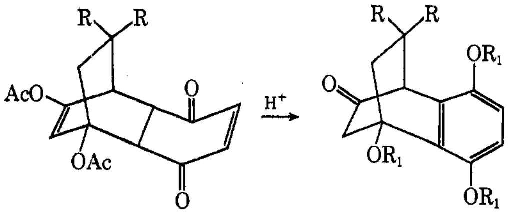
[1] David Ross Fellow, 1968–1969.

[2] C. M. Cimarusti and J. Wolinsky, *J. Amer. Chem. Soc.*, **90**, 113 (1968).

[3] This conjugated ketone reacts readily with maleic anhydride under the conditions of this Diels–Alder reaction to give a 1:2 adduct, which will be described in a forthcoming publication.

and **6b**, which are readily characterized as triacetate derivatives **7a** and **7b**. Adduct **4** behaves in a similar fashion.



1 or **3**

6a, R = CH_3; R_1 = CH_3
b, R = R_1 = H
7a, R = CH_3; R_1 = Ac
b, R = H; R_1 = Ac

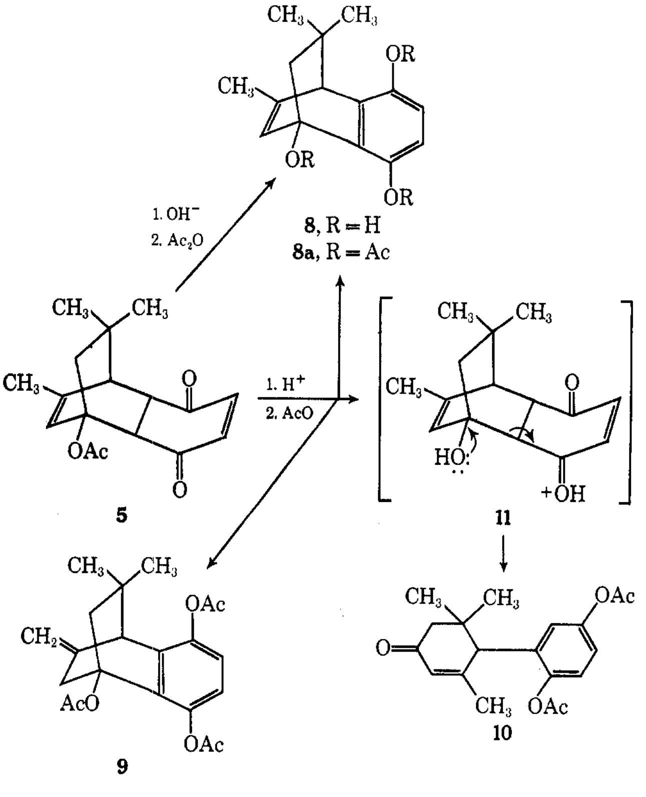
Base-catalyzed aromatization, on the other hand, proceeds rapidly; **1**, **3**, and **5** are transformed into **6a**, **6b**, and **8**, respectively, by brief heating with aqueous sodium bicarbonate solution. Aromatization of **3** with triethylamine in benzene followed by acetylation gave triacetate **7b**.

By contrast, acid hydrolysis of **5** proceeds slowly and after acetylation affords a mixture of **8a**, **9**, and **10**, Scheme I. **8a** and **9** crystallize together from the reaction mixture and analysis of their nmr spectra indicates the presence of 25% **8a**. Column chromatography permits the isolation of **9** (50%) and **10** (25%) in pure form.

Structural assignments for these compounds were based on their spectral properties. Triacetate **9** displayed a molecular ion at m/e 372 and infrared absorption at 11.22 μ characteristic of a terminal methylene group. A broad nmr doublet at 4.82 ppm integrating for two protons confirmed the presence of this group.

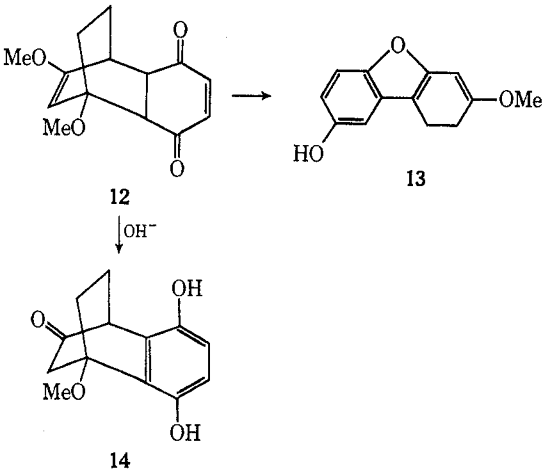
Diacetate **10**, an oil, displayed absorption at 5.68 and 6.0 μ indicative of aromatic acetate and α,β-unsaturated carbonyl groups. The molecular ion at m/e 330 and the nmr spectrum showing three aromatic protons centered at 7.0, a single vinyl hydrogen at 6.1, a singlet benzylic proton at 3.43, two acetate resonances at 2.35 and 2.25, and a vinyl methyl resonance at 1.79 ppm confirm the structural assignment **10**.

SCHEME I



The formation of **10** undoubtedly involves a Grob type of fragmentation[4] of an intermediate hydroxyenedione **11** as pictured in Scheme I.

Birch and coworkers[5] have observed a facile Grob fragmentation of the methoxy derivative **12** on treatment with acid. We have confirmed that **12** is converted into vinyl ether **13** under conditions as mild as heating in aqueous methanol. Compound **12** even undergoes a Grob fragmentation on standing in deuteriochloroform. In basic media Birch[5] found that **12** is converted into ketoquinol **14**, with the hydrolysis of the vinyl ether most likely occurring during the acid workup. The quinols **14**, **8**, **6a**, and **6b** have not been observed to undergo Grob fragmentation in acid media.



In conclusion it is seen that the hydrolysis of 5,8-ethanotetrahydro-1,4-naphthoquinone derivatives depends upon the nature of the bridgehead substituent and on the use of acidic or basic conditions. Basic conditions rapidly aromatizes these adducts yielding the corresponding quinols.[6] Aromatization is much slower under acidic conditions and appears to be especially slow when a double bond is present in the bicyclic ring system. The presence of a bridgehead methoxy group induces a facile Grob-type fragmentation. This is attributed[5] to the ability of a methoxy group to stabilize the incipient positive charge which develops during the fragmentation reaction. Grob fragmentation does not compete favorably with aromatization when the bridgehead substituent is acetoxy, but may do so when it is hydroxy.

Experimental Section[7]

1,3-Diacetoxy-10,10-dimethyl-1,4,4a,8a-tetrahydro-1,4-ethanonaphthalene-5,8-dione (1).—A solution of 7.0 g of dimedone and

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[4] C. A. Grob and P. W. Schiess, *Angew. Chem., Int. Ed., Engl.*, **6**, 1 (1967).

[5] A. J. Birch, D. N. Butler, and J. B. Siddall, *J. Chem. Soc.*, 2932, 2944 (1964).

[6] The conversion of thebainequinone to the thebainequinol appears to fall in this category; *cf.* K. W. Bentley and J. C. Ball, *J. Org. Chem.*, **23**, 1720 (1958), and references cited therein.

[7] All melting points are uncorrected. Infrared spectra were measured with a Perkin-Elmer Infracord spectrometer. Nmr spectra were determined with a Varian Associates A-60 spectrometer. The mass spectra were measured with a Hitachi RMU-6D mass spectrometer. The microanalyses were performed by Dr. C. S. Yeh and associates.

5.4 g of *p*-benzoquinone in 60 ml of isopropenyl acetate containing 25 mg of *p*-toluenesulfonic acid was refluxed for 40 hr. The volume was reduced to 30 ml under diminished pressure and the resulting solution was cooled to −20°. The solid, 8.13 g, was removed and recrystallized from hexane (Norit) to give pale yellow crystals: mp 121–123°; ir (Nujol) 5.65 (sh), 5.73, and 5.99 μ; nmr δ ($CDCl_3$) 0.98 (s, 3, CH_3), 1.18 (s, 3, CH_3), 1.42 and 2.41 (AB q, 2, *J* = 12.5 Hz, $-CH_2-$), 2.07 (s, 6, -OAc), 2.57 (m, 1), 3.32 (d of d, 1, *J* = 2.5 Hz, *J* = 9 Hz, $C—H_{8a}$), 3.87 (d, 1, *J* = 9 Hz, $C—H_{4a}$), 5.8 (d, 1, *J* = 2.0 Hz, -C=CH), 6.62 ppm (s, 2, CO—CH=CH—CO); mass spectrum (75 eV) *m/e* (relative intensity) 332 (0.15), 290 (17.5), 248 (16), 230 (10), 182 (19), 140 (35), 125 (40), 110 (12), 69 (15), 43 (100).

Anal. Calcd for $C_{18}H_{20}O_6$: C, 65.05; H, 6.07. Found: C, 65.10; H, 6.05.

Hydrolysis of 1.—A mixture of 370 mg of adduct **1** and 30 ml of 0.1 *N* hydrochloric acid was refluxed for 24 hr. The mixture was cooled and extracted with ether. The ether solution was washed with saturated salt solution and dried ($MgSO_4$). The ether was evaporated leaving an oil which was purified by thick layer chromatography using silica gel and ether to give 262 mg (96%) of liquid ketohydroxyquinol **6a**: ir (neat) 3.0 and 5.82 μ; nmr δ (CD_3CN) 0.74 (s, 3, CH_3), 1.1 (s, 3, CH_3), 1.92 (m, 2, $-C^9H_2$), 2.45 (d, 2, C^2H_2), 3.54 (s, 1, C^8H), 6.55 and 6.79 (AB q, 2, Ar—H), 6.1, 7.76, 8.94 ppm (s's, 3, -OH).

Quinol **6a** was dissolved in 1 ml of acetic anhydride and 2 ml of pyridine and kept at ambient temperature for 24 hr. The excess reagents were evaporated under diminished pressure and the resulting oil was dissolved in ether and the solution washed with saturated salt solution and dried ($MgSO_4$). The ether was removed and the resulting solid recrystallized from benzene–pentane to give 200 mg of triacetate **7a**: mp 161–162°; ir (Nujol) 5.66 and 5.75 μ; nmr δ ($CDCl_3$) 0.74 (s, 3, CH_3), 1.19 (s, 3, CH_3), 2.11, 2.26, 2.28 (s's, 9, -OAc), ~2.1 (m, 2, $-CH_2$), 2.91 (d, 2, C^2H_2), 3.38 (s, 1, C^4H), 6.88 and 7.1 ppm (AB q, 2, *J* = 9 Hz, Ar—H).

Anal. Calcd for $C_{20}H_{22}O_7$: C, 64.16; H, 5.92. Found: C, 64.14; H, 5.67.

1,3-Diacetoxy-1,4,4a,8a-tetrahydro-1,4-ethanonaphthalene-5,8-dione (3).—The reaction of 8.8 g of 1,3-cyclohexanedione and 8.5 g of *p*-benzoquinone was carried out as described above and gave 10 g (58%) of adduct **3**. Several recrystallizations from ethyl acetate–hexane gave an analytical sample: mp 114–115.5°; ir (Nujol) 5.7 and 6.0 μ; nmr δ ($CDCl_3$) 2.08 (s, 6, OAc) and 5.79 ppm (d, 1, *J* = 1.8 Hz, -C=CH); mass spectrum (75 eV) *m/e* (relative intensity) 304 (1.5), 262 (55), 220 (72), 192 (25), 162 (22), 154 (57), 112 (88), 82 (28), 43 (100).

Anal. Calcd for $C_{16}H_{16}O_6$: C, 63.15; H, 5.30. Found: C, 62.92; H, 5.38.

Hydrolysis of Adduct 3. A. Acidic Conditions.—A mixture of 1.0 g of **3** and 40 ml of 0.1 *N* hydrochloric acid was refluxed for 100 min, cooled, saturated with salt, and extracted with ether. After drying, the ether was evaporated to give 750 mg of ketohydroxyquinol **6b**: ir 3.06 and 5.82 μ; nmr [$(CD_3)_2SO$] 6.5 and 6.7 ppm (AB q, 2, *J* = 9 Hz, Ar—H).

Hydrolysis of **3** with ethanolic hydrochloric acid gave the same quinol **6b**.

The triacetate **7b** was obtained by treatment with acetic anhydride and pyridine and after recrystallization from benzene–pentane exhibited mp 157–158°.

Anal. Calcd for $C_{18}H_{18}O_7$: C, 62.42; H, 5.24. Found: C, 62.27; H, 5.05.

B. Basic Conditions.—Adduct **3** (1.0 g) was heated with sodium bicarbonate in aqueous methanol for 15 min. Work-up gave a product whose nmr spectrum showed the absence of acetate methyl signals. Acetylation of the crude hydrolysis product afforded 600 mg of a crystalline solid, mp 157–158°, which was identical with the triacetate obtained by acid hydrolysis of **3**.

3-Acetoxy-1,10,10-trimethyl-1,4,4a,8a-tetrahydro-1,4-ethanonaphthalene-5,8-dione (4) and 1-Acetoxy-3,10,10-trimethyl-1,4,4a,8a-tetrahydro-1,4-ethanonaphthalene-5,8-dione (5).—The condensation of 25.6 g of isophorone with 20 g of *p*-benzoquinone gave a first crop of 10 g of adduct **5**. An analytical sample of **5** was obtained by sublimation *in vacuo* and displayed mp 119–121°; ir (Nujol) 5.74 and 6.0 μ; nmr 0.9 and 1.18 (s's, 6, $CH_3—C—CH_3$), 1.7 (d, 3, *J* = 1.5 Hz, $CH_3C=C$), 2.1 (s, 3, OAc), and 6.64 ppm (s, 2, CO—CH=CH—CO); mass spectrum (75 eV) *m/e* (relative intensity) 288 (9), 246 (10), 190 (20), 180 (48), 139 (18), 136 (20), 123 (42), 109 (31), 108 (39), 91 (16), 82 (86), 79 (17), 77 (22), 54 (28), 43 (100).

Anal. Calcd for $C_{17}H_{20}O_4$: C, 70.81; H, 6.99. Found: C, 70.88; H, 6.90.

The mother liquor obtained from the crystallization of **5** was saturated with pentane and cooled to −20° overnight to give 17.5 g of solid. Concentration and cooling gave a second crop of 6.5 g. Nmr analysis of these solids indicated the presence of adduct **4** contaminated by *ca.* 17% of **5**. A sublimed sample of **4** showed mp 68–72°; ir 5.7 and 6.0 μ; nmr ($CDCl_3$) 0.98 and 1.12 (s's, 6, $CH_3—C—CH_3$), 1.19 (s, 3, CH_3), 2.06 (s, 3, OAc), 2.68 (m, 2, $-CH_2-$), 3.35 (d of d, *J* = 9 Hz, *J* = 3 Hz, CH), 5.5 (d, 1, *J* = 2 Hz, H—C=C), and 6.61 ppm (s, 2, CO—CH=CH—CO); mass spectrum (75 eV) *m/e* (relative intensity) 288 (14), 273 (11), 246 (24), 231 (32), 228 (25) 213 (7), 190 (11), 180 (19), 138 (58), 137 (15), 124 (13) 123 (100), 91 (10), 82 (32), 43 (25).

Hydrolysis of 4.—A solution of 3.71 g of **4** in 40 ml of 50% aqueous methanol containing a few milliliters of concentrated hydrochloric acid was refluxed for 24 hr. Work-up gave an oil whose nmr spectrum showed the absence of acetate methyl signals. Treatment with acetic anhydride–pyridine yielded 1 g of a ketoquinol diacetate derivative which was recrystallized from benzene–hexane and exhibited mp 141–142°.

Anal. Calcd for $C_{19}H_{22}O_5$: C, 69.07; H, 6.77. Found: C, 69.07; H, 6.71.

Hydrolysis of 5. A. Acidic Conditions.—A solution of 2.50 g of **5** in 50 ml of ethanol containing 0.5 ml concentrated hydrochloric acid was refluxed for 72 hr. The solution was concentrated to a volume of 30 ml, and 200 ml of ice water was added. The mixture was extracted with ether and the ether solution was washed with dilute sodium bicarbonate solution and saturated brine solution. The ether solution was dried and evaporated leaving an oil which was taken up in 20 ml of acetic anhydride and 10 ml of pyridine. The solution was kept at ambient temperature for 30 hr. The usual work-up gave 1.75 g of white solid and 1.13 g of oil. Nmr analysis of the solid indicated it was comprised of 40% **8a** and 60% **9**. The oil showed two components on tlc (silica gel). Chromatography of the oil on silica gel and elution with hexane–ether gave **10**, while elution with hexane–ethyl acetate gave **9**.

A sample of **9** was recrystallized from benzene and showed mp 116–117°; ir ($CHCl_3$) 5.67 and 11.22 μ; nmr ($CDCl_3$) 0.68 and 1.13 (s's, 6, $CH_3—C—CH_3$), 2.11, 2.22, and 2.29 (s's, 9, -OAc), 4.82 (broad d, 2, $C=CH_2$), 6.8 and 7.01 ppm (AB q, 2, Ar—H); mass spectrum *m/e* (relative intensity) 372 (38), 368 (8.2), 330 (18), 316 (17), 274 (13), 232 (42), 190 (30), 43 (100).

Quinol diacetate **10** showed ir ($CHCl_3$) 5.68 and 6.0 μ; nmr ($CDCl_3$) 0.78 and 1.15 (s's, 6, $CH_3—C—CH_3$), 1.79 (d, 3, *J* = 1 Hz, $CH_3C=C$), 2.12 (s, 2, $-CH_2-$), 2.25 and 2.35 (s's, 6, -OAc), 3.43 (s, 1, Ar—CH-), 6.1 (s, 1, C=CH), 7.0 ppm (ABC m, 3, Ar—H); mass spectrum (75 eV) *m/e* (relative intensity) 330 (15), 288 (37), 272 (15), 246 (58), 232 (10), 231 (52), 190 (25), 161 (14), 147 (12), 83 (44), 43 (100).

B. Basic Conditions.—A solution of 1.0 g of **5** in 15 ml of methanol and 15 ml of saturated sodium bicarbonate solution was refluxed for 15 min, cooled, and added to 100 ml of saturated salt solution. Extraction with ether, followed by washing the ether solution with 10% hydrochloric acid, and then evaporation of the ether gave an oil which showed no carbonyl absorption in the ir. The oil was dissolved in 15 ml of acetic anhydride and 7 ml of pyridine. The resulting solution was kept at ambient temperature for 17 hr and after removing the volatile reagents *in vacuo* and crystallization from benzene–hexane there was obtained 800 mg of a white solid, **8a**: mp 166.5–167.5°; nmr ($CDCl_3$) 0.61 and 1.05 (s's $CH_3—C—CH_3$), 1.87 (d, 3, *J* = 1.1 Hz, $CH_3C=C$), 2.15, 2.21, and 2.28 (s's, 9 OAc), 6.1 (broad s, 1, C=CH), 6.66 and 6.88 ppm (AB q, 2, *J* = 9 Hz, Ar—H); mass spectrum (75 eV) *m/e* (relative intensity) 372 (<1), 316 (14), 274 (18), 232 (22), 190 (29), 111 (61), 97 (85) 95 (72), 71 (82), 55 (100), 43 (100).

Reaction of Mesityl Oxide and *p*-Benzoquinone.—The reaction of 3.0 g of mesityl oxide and 3.3 g of *p*-benzoquinone was conducted in the usual manner and afforded 6.0 g of solid which showed several components on tlc. Chromatography of 1.0 g of this solid on silica gel gave 140 mg of 5,7-dimethyl-1,4-naphthoquinone, mp 124–126° (lit.[8] mp 128–129°), 426 mg of 1,4-diacetoxybenzene, and 434 mg of unidentified tars.

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(8) H. V. Euler and H. Hasselquist, *Ark. Kemi*, **2**, 367 (1950).

Registry No.—*p*-Benzoquinone, 106-51-4; **1**, 24097-79-8; **3**, 24097-80-1; **4**, 24097-81-2; ketoquinol diacetate derivative of **4**, 24097-82-3; **5**, 24097-83-4; **6a**, 24215-68-7; **6b**, 24097-84-5; **7a**, 24097-85-6; **7b**, 24097-86-7; **8a**, 24097-87-8; **9**, 24097-88-9; **10**, 24097-89-0.

Halomethyl Metal Compounds. XXXII. Insertion of Phenyl(bromodichloromethyl)mercury-Derived Dichlorocarbene into Carbon–Hydrogen Bonds. Alkanes and Alkylbenzenes[1]

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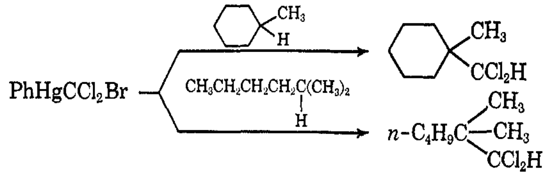
Received October 17, 1969

Phenyl(bromodichloromethyl)mercury has been found to insert CCl_2 into aliphatic C–H bonds. Most reactive in this reaction are tertiary C–H bonds; secondary C–H bonds are less reactive and no such insertion into methyl group C–H bonds was observed. The cases of 3-methylcyclohexene and *trans*-$Me_3SiCH{=}CHCHMe_2$ showed that a tertiary C–H bond can even compete for CCl_2 in some measure with a C=C bond. In the case of alkylbenzenes such as ethylbenzene and cumene, CCl_2 insertion occurred exclusively in the benzylic position. These reactions are of preparative utility. A mechanism involving a transition state (III) in which the carbon atom at which the C–H insertion is occurring bears a partial positive charge is suggested. The first case of an insertion of CBr_2 into a C–H bond (of ethylbenzene) is described.

The insertion of singlet state CH_2 into C–H bonds of of alkanes (→ C–CH_3 groups) is a well-known reaction,[6] but in 1962 an analogous insertion of a dihalocarbene into any kind of a C–H bond had not yet been encountered. During our early work on the CX_2 transfer reactions of phenyl(trihalomethyl)mercury compounds,[7] we sought to study the thermolysis of $PhHgCCl_2Br$ and $PhHgCCl_3$ in an inert medium. In view of the apparent lack of reactivity of CCl_2 derived from other sources toward C–H linkages, *n*-heptane was chosen as the "inert" medium. When phenyl(trichloromethyl)mercury was heated at reflux in *n*-heptane solution under nitrogen, phenylmercuric chloride precipitated (*ca.* 80% yield), and one of the volatile products obtained in very low yield upon work-up of the filtrate (glpc) was found by combustion analysis to have the empirical formula $C_8H_{16}Cl_2$, *i.e.*, (C_7H_{16} + CCl_2), an insertion product of CCl_2 into heptane. Because several isomeric (dichloromethyl)heptanes were possible, it was decided to study this novel reaction with a simpler substrate, cyclohexane. The decomposition of phenyl(bromodichloromethyl)mercury in refluxing cyclohexane during 3 hr gave phenylmercuric bromide (77%), tetrachloroethylene[8] (26%), cyclohexyl bromide (22%, based on available bromine), and a new compound identified by analysis and its nmr and ir spectra as (dichloromethyl)cyclohexane (32%). Dichlorocarbene insertion into a completely unactivated C–H bond in a preparatively useful yield was unprecedented and most surprising. Clearly, further studies were called for.

The unactivated secondary C–H bond is very low on the scale of reactivity toward CCl_2. Under the usual conditions which serve in the high yield dichlorocyclopropanation of olefins (3 mol of substrate to 1 mol of $PhHgCCl_2Br$ in benzene solution at 80°), the reaction of phenyl(bromodichloromethyl)mercury with cyclohexane proceeded very poorly, (dichloromethyl)-cyclohexane being obtained in only trace yield. However, tertiary aliphatic C–H bonds were found to be more reactive. Thus, under these standard reaction conditions $PhHgCCl_2Br$ served to convert methylcyclohexane to 1-methyl-1-(dichloromethyl)cyclohexane in 15% yield and 2-methylhexane to 1,1-dichloro-2,2-dimethylhexane in 20% yield (eq 1). In neither case was any insertion into CH_2 or CH_3 groups observed; insertion into the methine C–H appeared to be the exclusive process. These limited data suggest a reactivity sequence for aliphatic C–H bonds in the order tertiary C–H > secondary C–H > primary C–H. Indirect confirmation for this was provided in experiments with cyclohexene and 3-methylcyclohexene. In the case of the former, reaction with $PhHgCCl_2Br$ at 80° gave 7,7-dichloronorcarane as the sole product (eq 2),[9] but with 3-methylcyclohexene, where a tertiary C–H bond is available to compete with the C=C bond for CCl_2, both C=C addition and C–H insertion were



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[6] (a) W. Kirmse, "Carbene Chemistry," Academic Press, New York, N. Y., 1964, Chapter 2; (b) J. Hine, "Divalent Carbon," Ronald Press Co., New York, N. Y., 1964, Chapter 2; (c) D. F. Ring and B. S. Rabinovitch, *Can. J. Chem.*, **46**, 2435 (1968), and earlier references cited therein.

[7] First report: D. Seyferth, J. M. Burlitch, and J. K. Heeren, *J. Org. Chem.*, **27**, 1491 (1962).

[8] Tetrachloroethylene is the product of decomposition of $PhHgCCl_2X$ (X = Cl or Br) in the absence of substrate capable of trapping dichlorocarbene and usually is found in low to moderate yield in reactions where the substrate is only poorly reactive toward CCl_2.[9]

[9] D. Seyferth, J. M. Burlitch, R. J. Minasz, J. Y.-P. Mui, H. D. Simmons, Jr., A. J.-H. Treiber, and S. R. Dowd, *J. Amer. Chem. Soc.*, **87**, 4259 (1965).