

dibromonortricyclene (22.0 min, 17%); *exo,syn*-5,7-dibromonorborene-2 (28.5 min, 10%).¹³ The products were identified by comparison of their glpc retention times with those of authentic samples obtained by the addition of bromine to norbornadiene in carbon tetrachloride and in methanol.¹⁴ The composition of the product mixture in the latter solvent was identical with that reported above.

Reaction of Cyclooctadiene-1,5 with Methanolic Copper(II) Bromide.—A solution of 15.0 g (0.067 mol) of copper(II) bromide in 75 ml of methanol was added dropwise at room temperature to a stirred solution of 11.0 g (0.102 mol) of cyclooctadiene-1,5 in 30 ml of methanol over a period of 30 min. A white precipitate appeared after a few minutes. The complex was separated by filtration and was washed with methanol and pentane. The complex was dried over calcium chloride in a cyclooctadiene atmosphere to give 13.3 g (80.5%) of bis[cyclooctadiene-copper(I) bromide].

Anal. Calcd for $(C_8H_{12}CuBr)_2$: C, 38.18; H, 4.81; Br, 32.76. Found: C, 38.26; H, 5.14; Br, 33.70.

The complex is identical in structure with that of the corresponding copper(I) chloride complex.¹⁵

The reaction filtrate was poured into 200 ml of water and extracted with *n*-pentane (three 150-ml portions). The pentane extracts were combined and dried over magnesium sulfate; the solvent was removed on a rotary evaporator to give 6.7 g of colorless oil. Analysis by glpc (1 m \times 0.25 in. 5% polypropylene glycol, 150°, 110-ml/min helium flow) showed in addition to some unreacted cyclooctadiene the following mixture: 5-bromo-6-methoxycyclooctene (2.2 min, 4.6%); 5,6-dibromocyclooctene (4.4 min, 55.8%); two unidentified compounds at 7.6 min (7.2%) and 9.2 min (32.4%). A 5-g sample of the product was chromatographed over 75 g of acid-washed alumina. Elution with pentane provided a sample of 5,6-dibromocyclooctene of 95% purity (glpc).

Anal. Calcd for $C_8H_{12}Br_2$: C, 35.85; H, 4.51; Br, 59.64. Found: C, 35.87; H, 4.48; Br, 59.54.

The nmr spectrum ($CDCl_3$) had the following pattern: δ 5.68 (m, 2, =CH), 4.67 (m, 2, BrCH), 1.83–3.00 (m, 8, CH_2). Hydrogenation of the olefinic dibromide over 10% palladium on charcoal in ethanol consumed 3 mol of hydrogen/mol of dibromide and yielded cyclooctane; this result indicated that no trans-annular addition reactions had occurred.

Continued elution of the column with 10% ether-pentane permitted the recovery of the two compounds of long retention time. The nmr spectrum ($CDCl_3$) indicated a mixture of polybrominated cyclooctanes; these materials were not characterized further. The addition of bromine to cyclooctadiene in methanol produced a product mixture similar to that previously described; the composition was 9.8% bromo ether, 31.4% dibromocyclooctene, and 59% polybrominated material.

Reaction of Cyclohexene with Methanolic Copper(II) Bromide.—A solution of 8.2 g (0.1 mol) of cyclohexene and 23.0 g (0.1 mol) of copper(II) bromide was stirred at room temperature for 1 hr. The copper(I) bromide (12.9 g, 90%) was separated by filtration, and the filtrate was poured into 100–150 ml of water. The product was extracted with pentane (three 100-ml portions), and the combined pentane extracts were washed with water and dried over magnesium sulfate. The solvent was removed on a rotary evaporator to give 10.2 g of product. Glpc analysis (2 m \times 0.25 in. 20% diethylene glycol succinate, 125°, 200-ml/min helium flow) showed the product to be a mixture of *trans*-1-bromo-2-methoxycyclohexane (4.5 min, 25%) and *trans*-1,2-dibromocyclohexane (9.0 min, 75%). Samples of the individual compounds (>95% pure by glpc) were obtained by preparative glpc (12 ft \times 3/8 in. 20% FFAP¹⁶ column, 175°, 120-ml/min helium flow). The *trans*-dibromide was identical with an authentic sample. The bromomethoxycyclohexane (n_D^{20} 1.4874; lit. n_D^{20} 1.4884¹⁶), had the following nmr pattern: δ 2.74–4.50 (m, 2, CHO, CHBr), 3.33 (s, 3, CH_3O), 0.75–2.50 (m, 8, CH_2).

Anal. Calcd for $C_6H_{10}BrO$: C, 43.54; H, 6.78; Br, 41.39. Found: C, 43.95; H, 7.00; Br, 41.16.

Registry No.—5,6-Dibromocyclooctene, 24165-06-8.

(13) The isomeric nortricyclene derivatives were not resolved under these glpc conditions. The reported toxicity of these materials discouraged a detailed analysis of the reaction products.

(14) S. Winstein and M. Shatavsky, *Chem. Ind. (London)*, 56 (1956).

(15) Varian Aerograph, Walnut Creek, Calif.

(16) S. Winstein and R. B. Henderson, *J. Amer. Chem. Soc.*, **65**, 2196 (1943).

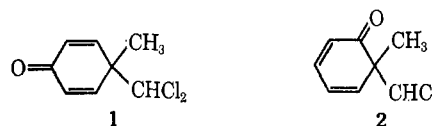
Some Transformations of 1-Methyl-1-dichloromethylcyclohexane Derivatives

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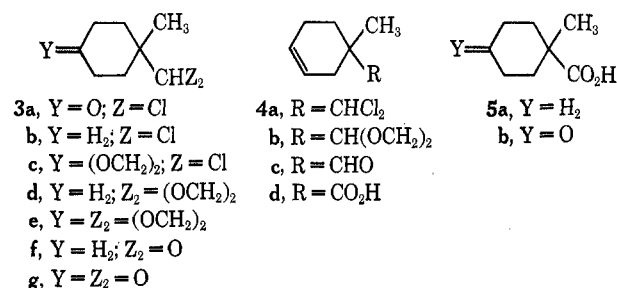
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Recent studies on the chemistry of cyclohexadienones **1** and **2** yielded interesting tangential data which are presented herewith.



4-Dichloromethyl-4-methylcyclohexanone (**3a**), the product of hydrogenation of **1**, was converted to the dichloride **3b** by Wolff-Kishner reduction of its semicarbazone, to the olefin **4a** by a Bamford-Stevens reduction of its tosylhydrazone, and to the ketal **3c** by treatment with ethylene glycol and acid. Exposure of each of the products to sodium ethylene glycolate in ethylene glycol led to the ethylene acetals **3d**, **4b**, and **3e**, respectively, whose acid hydrolyses gave aldehydes **3f**,³ **4c**,⁴ and **3g**, respectively. Oxidation of these aldehydes yielded acids **5a**,³ **4d**,⁵ and **5b**,⁶ respectively.



The acetylation, a consequence of two consecutive chloride displacements or chlorocarbene formation, alcohol addition, and subsequent chloride displacement, represents a crucial step of an unusual method of construction of quaternary carboxyl functions. While the mechanism of the acetylation was not determined, the first step, proton abstraction, of one of the alternate paths, the carbene route, was shown to be operative. Under the reaction conditions the dichloride **3b** underwent deuterium exchange, whereas its acetal **3b** did not.

As a follow-up of a study of hydrogenation of dienone **2**,² hydride reductions of **2** and its hydro derivatives were undertaken. The formation of a single alcohol (**6**) on reduction of the dienone with sodium borohydride in ethanol has been reported already.² Hydrogenation

(1) E. Wenkert, F. Haviv, and A. Zeitlin, *J. Amer. Chem. Soc.*, **91**, 2299 (1969).

(2) E. Wenkert, P. Bakuzis, R. J. Baumgarten, D. Doddrell, P. W. Jeffs, C. L. Leicht, R. A. Mueller, and A. Yoshikoshi, *ibid.*, **92**, 1617 (1970).

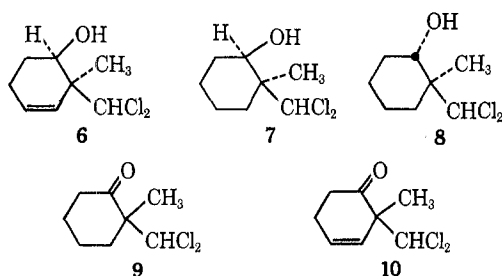
(3) W. Parker and R. A. Raphael, *J. Chem. Soc.*, 1723 (1955).

(4) H. Pines, R. J. Pavlik, and V. N. Ipatieff, *J. Amer. Chem. Soc.*, **73**, 5738 (1951).

(5) T. Inukai and M. Kasai, *J. Org. Chem.*, **30**, 3567 (1965), and references cited therein.

(6) M. Rubin and H. Wishinsky, *J. Amer. Chem. Soc.*, **68**, 338 (1946).

of the alcohol afforded a saturated carbinol (7) which proved to be the major of two epimeric products of lithium aluminum hydride reduction of the saturated ketone 9. The stereochemistry of these alcohols, 7 and 8 (and, hence, of 6 also), was assigned as pictorialized on the basis of their ease of elution on column chromatography and the nature of the proton magnetic resonance (pmr) signal of their hydroxymethine functions. On the assumption of the prevalence of cyclohexane chair and equatorial dichloromethyl conformations in deuteriochloroform solutions of the alcohols, the axial hydroxyl group of 7 would be expected to make this cyclohexanol elute more rapidly than its epimer 8 and display a smaller half band width of its hydroxymethine multiplet than 8. These expectations were in conformity with observation, the spectra revealing half-band widths of *ca.* 7 and 15 cps and hydroxy singlets for alcohols 7 and 8, respectively.



Comparison of the pmr spectra of deuteriochloroform and deuteriopyridine solutions of cyclohexanols 7 and 8 was expected to yield data of value for stereochemical diagnosis.⁷ The axial hydroxyl group of 7 is close to the equatorial dichloromethyl group but distant from the methyl substituent, in consonance with a $\Delta\delta$ value (*i.e.*, $\delta_{\text{CDCl}_3} - \delta_{\text{C}_6\text{D}_6\text{N}}$ in ppm) of -0.49 for the dichloromethyl moiety and merely -0.01 for the methyl unit, whereas the equatorial hydroxyl group of 8 is proximate to both vicinal substituents, in agreement with -0.53 and -0.12 values, respectively. Since, however, the polar dichloromethyl group itself introduces a solvent shift, $\Delta\delta = -0.37$ for the chlorohydrocarbon 3b, and since solvent shifts of neighboring substituents probably are not additive, doubt is cast upon the significance of the aforementioned values (Table I).

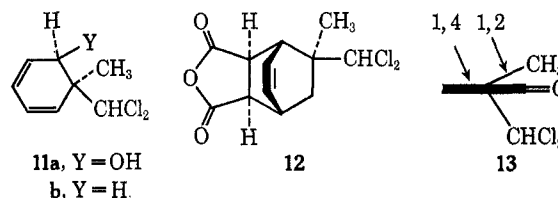
TABLE I

Compd	Group	AROMATIC SOLVENT SHIFTS		
		CDCl ₃	C ₆ D ₆ N	C ₆ D ₆
7	Me	1.10	1.11	0.94
	CHCl ₂	6.01	6.50	6.00
8	Me	1.12	1.24	0.90
	CHCl ₂	6.03	6.56	5.96
3b	Me	1.11	1.06	0.96
	CHCl ₂	5.63	6.00	5.24

The striking difference of the effect of benzene ($\Delta\delta = 0.39$) on the dichloromethine chemical shift of compound 3b from the effect of pyridine ($\Delta\delta = -0.37$) points to dissimilar solute-solvent interactions of the two aromatic solvents. It probably reflects a difference

of orientation of the plane of the aromatic ring to the dipole axis of 3b in the complex responsible for the solvent-induced shifts. Both solvents would be expected to be proximate to the positive end of the dipole. While, however, the benzene plane should be as nearly perpendicular to the dipole axis as possible, thus placing the hydrogen of the dichloromethyl group into the shielding zone of the aromatic ring,⁸ the pyridine plane may lie on the dipole axis and have its nitrogen oriented toward the acidic dichloromethyl hydrogen, thus placing the latter in the deshielding zone of the aromatic nucleus. The minimal effect of benzene on the dichloromethyl groups of compounds 7 and 8, $\Delta\delta = 0.01$ and 0.07 , respectively, contrasted to that of substance 3b, may be due to alcohol-benzene hydrogen-bond complexes being present in lieu of or in addition to the dipole complexes.

Lithium aluminum hydride reduction of 2 in ether solution at Dry Ice-acetone bath temperature produced ketone 10 and dienol 11a, while similar reduction at salt-ice bath temperature led to these products in minor amounts in accompaniment with the diene 11b in major quantity. Reduction at room temperature in tetrahydrofuran solution gave some diene 11b and alcohol 6, but mostly ketone 10. Reduction of 10 with lithium aluminum hydride afforded alcohol 6 exclusively. Oxidation of the dienol 11a with manganese dioxide reverted it to the dienone 2, and hydrogenation transformed it into the saturated alcohol 7 and some ketone 9. The liquid diene 11b was characterized as its maleic anhydride adduct 12 whose stereochemistry was determined by analysis of its pmr spectrum and that of its dihydro derivative.



The diverse results of the reduction of 2 by lithium aluminum hydride can be explained on the basis of the initial reaction occurring at the site of the carbonyl group and the primary reduction intermediate either surviving, undergoing carbon-oxygen bond scission,⁹ or suffering double-bond isomerization and even experiencing further reduction, the last two procedures conceivably taking place during aqueous work-up.¹⁰ The most interesting features of the chemical reductions were the preponderant formation of axial alcohols in the reactions of ketones 2, 9, and 10, and the high stereoselectivity of especially the first and third processes. These observations can be interpreted most readily in terms of the reactant-like transition-state model of Felkin for ketone addition reactions.¹¹ The following can be offered as rationale for the transformation of ketone 2 into a single cyclohexadienol (11a) and for the contrasting liberation of a *ca.* 3:2 mixture of stereo-

(8) T. Ledaal, *ibid.*, 1683 (1968).(9) Cf. M. P. Cava and K. Narasimhan, *J. Org. Chem.*, **34**, 3641 (1969).(7) (a) A. C. Huitric, J. B. Carr, and W. F. Trager, *J. Pharm. Sci.*, **55**, 211 (1966); (b) P. V. Demarco, E. Farkas, D. Doddrell, B. L. Mylari, and E. Wenkert, *J. Amer. Chem. Soc.*, **90**, 5480 (1968), and references therein; (c) C. R. Narayanan, N. R. Bhadane, and M. R. Sarma, *Tetrahedron Lett.*, 1561 (1968).(10) D. I. Schuster, J. M. Palmer, and S. C. Dickerman, *ibid.*, **31**, 4281 (1966); J. A. Marshall, N. H. Anderson, and A. R. Hochstetler, *ibid.*, **32**, 113 (1967).(11) M. Chérest, H. Felkin, and N. Prudent, *Tetrahedron Lett.*, 2199 (1968); M. Chérest and H. Felkin, *ibid.*, 2205 (1968).

isomeric cyclohexadienols in the hydride reduction of 6-methyl-6-allyl-2,4-cyclohexadienone.¹² The bulky, polar dichloromethyl group of **2** would be expected to assume a quasiaxial stance in order to minimize non-bonded interactions with its neighbors and dipole-dipole repulsions. Hence both steric and electronic factors invite hydride attack on **2** from the methyl side of the nuclear plane (*cf.* **13**). The lack of significant steric or electronic dissimilarity of methyl and allyl groups leads to lowered directional discrimination in the hydride reduction of the cyclohexadienone containing these α -alkyl substituents. The powerful polar effect of the dichloromethyl group is illustrated strikingly in the 1,4 addition reactions of **2** with Grignard reagents. Despite the absence of steric factors, the nucleophile shows preference for the methyl side of the nearly planar substance (*cf.* **13**).^{2,13}

Experimental Section

Melting points were determined on a Reichert micro hot stage and are uncorrected. Infrared spectra were obtained on Perkin-Elmer Model 137 and 137B spectrophotometers. Proton magnetic resonance spectra of deuteriochloroform solutions (unless otherwise noted) containing tetramethylsilane (δ 0 ppm) as internal standard were taken on Varian Associates Model A-60 and HA-100 spectrometers. Solvent-shift studies were carried out on 3% solutions.

4-Dichloromethyl-4-methylcyclohexanone (3a).—A mixture of 1.91 g of ketone **1** and 200 mg of 10% palladium-charcoal in 15 ml of ethyl acetate was hydrogenated at atmospheric pressure and room temperature. Upon cessation of hydrogen uptake the catalyst was filtered and the filtrate evaporated. Crystallization of the residual oil from hexane gave 1.90 g of ketone **3a**: mp 44–46°; infrared (Nujol) C=O 5.85 (s) μ ; pmr δ 1.40 (s, 3, Me), 5.83 (s, 1, CHCl₂).

Anal. Calcd for C₈H₁₂OCl₂: C, 49.25; H, 6.20. Found: C, 48.96; H, 5.99.

Its semicarbazone was crystallized from ethanol (mp 191–193°).

Anal. Calcd for C₉H₁₅ON₂Cl₂: C, 42.85; H, 5.95; N, 16.64. Found: C, 42.81; H, 6.17; N, 16.65.

Its *p*-toluenesulfonylhydrazone was crystallized from aqueous ethanol (mp 158–160°).

Anal. Calcd for C₁₅H₂₀O₂N₂SO₂: C, 49.58; H, 5.51. Found: C, 49.54; H, 5.79.

4-Dichloromethyl-4-methylcyclohexanone Ethylene Ketal (3c).—A solution of 970 mg of ketone **3a**, a few crystals of *p*-toluenesulfonic acid, and 340 mg of ethylene glycol in 50 ml of benzene was refluxed for 12 hr, while water was being removed azeotropically. Upon addition of sodium bicarbonate the cooled mixture was extracted with ether. The extract was dried over sodium sulfate and evaporated. Crystallization of the solid residue, 850 mg, from hexane yielded ketal **3c**: mp 99–100°; pmr δ 1.15 (s, 3, Me), 3.96 (s, 4, oxymethylenes), 5.72 (s, 1, CHCl₂).

Anal. Calcd for C₁₀H₁₆O₂Cl₂: C, 50.21; H, 6.69. Found: C, 50.41; H, 6.56.

1-Dichloromethyl-1-methylcyclohexane (3b).—A mixture of 20.5 g of **3a** semicarbazone and 13.0 g of potassium hydroxide in 500 ml of diethylene glycol was refluxed for 4 hr. The cooled mixture was diluted with water and extracted with ether. The extract was dried and evaporated. Filtration of the residual oil through a short alumina column and distillation yielded 11.0 g of liquid **3b**: bp 55° (1.7 Torr); pmr δ 1.11 (s, 3, Me), 5.68 (s, 1, CHCl₂).

Anal. Calcd for C₈H₁₄Cl₂: C, 53.04; H, 7.74. Found: C, 52.88; H, 7.65.

4-Dichloromethyl-4-methylcyclohexene (4a).—A mixture of 640 mg of **3a** *p*-toluenesulfonylhydrazone and sodium ethylene glycolate, from 1.2 g of sodium, in 15 ml of ethylene glycol was

refluxed for 2 hr. The mixture was distilled, taken up in ether, dried, and evaporated. Filtration of the oil through a short alumina column and distillation gave 300 mg of liquid **4a**: bp 45–46° (1.7 Torr); infrared (neat) C=C 6.01 (w) μ ; pmr δ 1.12 (s, 3, Me), 1.6–1.8 (m, 2, methylene), 1.9–2.2 (m, 4, allyl H's), 5.6–5.8 (m, 2, olefinic H's), 5.70 (s, 1, CHCl₂).

Anal. Calcd for C₈H₁₂Cl₂: C, 53.63; H, 6.70. Found: C, 53.93; H, 6.67.

Ethylene Acetals.—A solution of sodium ethylene glycolate, from 1.3 g of sodium, and 540 mg of **3b** in 20 ml of ethylene glycol was refluxed under nitrogen for 20 hr. The cooled mixture was diluted with 200 ml of water and extracted with hexane. The extract was dried, concentrated, filtered through a short alumina column, and evaporated. Purification of the residue by gas chromatography on a Carbowax 20M column gave 320 mg of liquid **3d** [pmr δ 0.90 (s, 3, Me), 1.2–1.7 (m, 10, methylenes), 3.88 (s, 4, oxymethylenes), 4.50 (s, 1, oxymethine)], which was used as such in further experiments.

The same reaction for 48 hr and the same work-up was carried out on 360 mg of **4a**. It produced 150 mg of liquid **4b** [pmr δ 0.92 (s, 3, Me), 1.3–1.7 (m, 2, methylene), 1.7–2.2 (m, 4, allyl H's), 3.89 (s, 4, oxymethylenes), 4.61 (s, 1, oxymethine), 5.6–5.7 (m, 2, olefinic H's)], which was used as such in further experiments.

A similar reaction for 48 hr and a similar work-up was performed on 1.92 g of **3c**. It led to 650 mg of liquid **3e** [pmr δ 0.95 (s, 3, Me), 1.5–1.8 (m, 8, methylenes), 3.89–4.01 (m, 8, oxymethylenes), 4.58 (s, 1, oxymethine)] which was used as such in further experiments.

Aldehydes.—Treatment of acetal **3d** with acid and 2,4-dinitrophenylhydrazine yielded an aldehyde derivative. Crystallization from methanol gave **3f** 2,4-dinitrophenylhydrazone, mp 154–155° (lit.³ mp 154–155°).

A solution of 80 mg of acetal **4b** in 3 ml of a 50% aqueous dioxane solution of 10% sulfuric acid was kept at room temperature for 12 hr. Sodium bicarbonate was added, and the mixture extracted with chloroform. The extract was dried and evaporated. The residual oily aldehyde, 50 mg, was converted into a derivative. Crystallization from ethanol gave **4c** semicarbazone, mp 170° (lit.⁴ mp 170–172°).

Acetal **3e**, 100 mg, was hydrolyzed in the same manner as **4b** and the crude ketoaldehyde **3g** [infrared (CCl₄) aldehyde CH 3.70 (w), C=O 5.80 (s) μ] was used immediately for oxidation to an acid (*vide infra*).

Acids.—A mixture of 100 mg of **3d** and 1 ml of Jones reagent in 2 ml of acetone was stirred at room temperature for 30 min. It was extracted with ether; the extract was dried and evaporated. Sublimation of the residual oil, 70 mg, gave 1-methylcyclohexanecarboxylic acid (**5a**), mp 36–38° (lit.³ mp 37–38°).

A mixture of 50 mg of aldehyde **4c**, 100 mg of sodium hydroxide, and 80 mg of silver nitrate in 3 ml of dioxane and 7 ml of water was stirred at 0° for 24 hr. The precipitate was filtered, and the filtrate was acidified and extracted with chloroform. The extract was dried and evaporated. Sublimation of the residual oil, 30 mg, gave 1-methyl-3-cyclohexanecarboxylic acid (**4d**): mp 77–79° (lit.⁵ mp 78–79°), mmp 78°; infrared spectrum identical with that of an authentic sample.

Crude **3g** was treated with 2 ml of Jones reagent at 0° for 5 min. Work-up as above yielded 35 mg of oil whose sublimation led to 4-carboxy-4-methylcyclohexanone (**5b**): mp 79–81° (lit.⁶ mp 78–79°); pmr δ 1.42 (s, 3, Me).

Deuterium Exchange.—The above acetylation of **3b** was carried out in O-deuterated ethylene glycol¹⁴ for 24 hr, and starting material was separated by gas chromatography. Its pmr spectrum revealed all signals characteristic of **3b** except that at 5.68 ppm. A 48-hr "acetalation" of **3d** in O-deuterated ethylene glycol gave **3d** unchanged.

Lithium Aluminum Hydride Reductions.—A mixture of 1.00 g of 2-methyl-2-dichloromethylcyclohexanone (**9**)² and 200 mg of lithium aluminum hydride in 100 ml of ether was stirred at room temperature for 2 hr. Sodium sulfate decahydrate was added and the mixture was shaken thoroughly and filtered. The filtrate was washed with water, dried, and evaporated. Chromatography of the residue on silica gel and elution with benzene yielded 625 mg of an oil whose distillation [bath temperature 80° (0.2 Torr)] and sublimation [45° (0.1 Torr)] gave alcohol **7**: mp 43–44°; infrared (Nujol) OH 2.85 (m) μ ; pmr δ 3.85 (m, 1, oxymethine).

(12) H.-J. Hansen, B. Sutter, and H. Schmid, *Helv. Chim. Acta*, **51**, 828 (1968).

(13) *Cf.* D. M. S. Wheeler and M. M. Wheeler, *J. Org. Chem.*, **27**, 3796 (1962), and references therein.

(14) D. J. Cram and B. Rickborn, *J. Amer. Chem. Soc.*, **83**, 2178 (1961).

Anal. Calcd for $C_8H_{10}OCl_2$: C, 48.75; H, 7.16. Found: C, 48.91; H, 7.22.

Continued elution with benzene led to 159 mg whose distillation [bath temperature 80° (0.2 Torr)] gave alcohol **8**: mp $41-42^\circ$; infrared (Nujol) OH 2.91 (m) μ , fingerprint region vastly different from that of **7**; pmr δ 3.85 (m, 1, oxymethine).

Anal. Calcd for $C_8H_{10}OCl_2$: C, 48.75; H, 7.16. Found: C, 48.73; H, 7.12.

A mixture of 1.00 g of ketone **10** and 0.38 g of lithium aluminum hydride in 100 ml of ether was stirred at 0° for 1 hr. Work-up as above gave 970 mg of alcohol **6**, mp $61-62^\circ$.

A mixture of 270 mg of alcohol **6** and 50 mg of 10% palladium-charcoal in 5 ml of ethanol was hydrogenated at room temperature and atmospheric pressure. Usual work-up yielded 270 mg of alcohol **7**, mp $43-44^\circ$.

A solution of 5.00 g of ketone **2** in 10 ml of ether was added over a 1.5-hr period to a suspension of 500 mg of lithium aluminum hydride in 50 ml of ether under nitrogen in a Dry Ice-acetone bath. The mixture was stirred for 3 hr, 3 ml of methyl formate added, and the stirring continued for 30 min. After the mixture was warmed to 0° , 1 ml of water and 1 ml of 10% sodium hydroxide solution were added and the mixture was filtered. The filtrate was washed with 5% sodium bicarbonate solution and with water, dried, and evaporated. Crystallization of the residue from 5 ml of 3:1 hexane-benzene yielded 1.74 g of **10**. Chromatography of the mother liquor on Florisil and elution with petroleum ether gave 0.87 g more of **10**. Elution with 3:1 petroleum ether-benzene led to 1.64 g of a solid whose sublimation [45° (0.1 Torr)] yielded dienol **11a**: mp $57-57.5^\circ$; infrared (Nujol) OH 3.01 (s) μ ; pmr δ 1.21 (s, 3, Me), 4.09 (m, 1, oxymethine), 5.95-6.15 (m, 4, olefinic H's), 6.23 (s, 1, $CHCl_2$); pmr (pyridine) δ 1.27 (s, 3, Me), 4.20 (m, 1, oxymethine), 5.85-6.10 (m, 4, olefinic H's), 6.64 (s, 1, $CHCl_2$).

Anal. Calcd for $C_8H_{10}OCl_2$: C, 49.76; H, 5.23. Found: C, 49.64; H, 5.24.

A mixture of 88 mg of **11a** and 600 mg of manganese dioxide in 75 ml of ether was stirred at room temperature for 3 hr and then filtered. Evaporation of the filtrate gave 86 mg of the dienone **2**.

A mixture of 70 mg of **11a** and 10 mg of 10% palladium-charcoal in 5 ml of ethyl acetate was hydrogenated at room temperature and atmospheric pressure. After cessation of hydrogen uptake the mixture was filtered and the filtrate evaporated. A benzene solution of the residue was passed through a column of silica gel and evaporated. Pmr analysis of the residual mixture, 64 mg, showed it to consist of 90% alcohol **7** and 10% ketone **9**.

A solution of 13.6 g of ketone **2** in 40 ml of tetrahydrofuran was added over a 10-min period to a suspension of 1.95 g of lithium aluminum hydride in 140 ml of tetrahydrofuran under nitrogen. The mixture was stirred for 0.5 hr, sodium sulfate decahydrate then added, and the mixture filtered. The filtrate was dried and evaporated and the residue chromatographed on Florisil. Elution with petroleum ether yielded 500 mg of liquid diene **11b**: infrared ($CHCl_3$) $C=C$ 6.01 (s), 6.12 (m) μ ; pmr δ 1.20 (s, 3, Me), 2.38 (q, 2, $J = 18.0, 2.5$ cps, methylene), 5.4-6.0 (m, 4, olefinic H's), 5.66 (s, 1, $CHCl_2$). It was characterized as a maleic anhydride adduct (*vide infra*). Elution with 20:1 petroleum ether-ether gave 7.6 g of ketone **10**, while elution with a 4:1 mixture afforded 1.2 g of alcohol **6**.

A solution of 5.00 g of ketone **2** in 10 ml of ether was added over a 30-min period to a suspension of 500 mg of lithium aluminum hydride in 50 ml of ether at *ca.* -5° . The mixture was stirred for 30 min, 1 ml of 10% sodium hydroxide solution added, and the mixture filtered. The filtrate was washed with sodium bicarbonate solution and with water, dried, and evaporated. Distillation [45° (0.5 Torr)] of the residue yielded 1.86 g of a mixture, shown by gas phase chromatography (SE-30 column) to consist of 90% **11b** and 10% **10**. Chromatography of the distillation residue on silica gel and elution with petroleum ether gave 56 mg of diene **11b**. Elution with 1:1 benzene-petroleum ether led successively to 338 mg of **10** and 1.08 g of a complex alcohol mixture whose distillation [75° (0.4 Torr)] afforded 577 mg of a mixture shown by manganese dioxide oxidation (*vide supra*) to contain *ca.* 40% dienol **11a**.

Anhydride 12.—A solution of 340 mg of diene **11b** and 350 mg of maleic anhydride in 1 ml of benzene was refluxed for 48 hr and then evaporated. Chromatography of the residue on Florisil and elution with 4:1 benzene-petroleum ether gave 215 mg of a mixture of Diels-Alder adducts from which 120 mg of **12**

could be obtained on crystallization from benzene-petroleum ether. Recrystallization from benzene yielded **12**: mp $146-146.5^\circ$; infrared (Nujol) $C=O$ 5.38 (w), 5.46 (w), 5.64 (s) μ ; pmr δ 1.37 (s, 3, Me), 1.4-1.7 (m, 2, methylene), 3.0-3.7 (m, 4, methines), 5.42 (s, 1, $CHCl_2$), 6.2-6.5 (m, 2, olefinic H's).

Anal. Calcd for $C_{12}H_{14}O_3Cl_2$: C, 52.38; H, 4.39. Found: C, 52.53; H, 4.31.

Analysis of the pmr spectrum of the first mother liquor showed it to contain predominantly **12** but also some of its isomer epimeric at the methyl-substituted site: pmr δ 1.18 (s, 3, Me), 5.63 (s, 1, $CHCl_2$).

A mixture of 100 mg of **12** and 10 mg of 10% palladium-charcoal in 5 ml of ethyl acetate was hydrogenated at room temperature and atmospheric pressure. The mixture was filtered and the filtrate evaporated. A benzene solution of the residue, 100 mg, was passed through a Florisil column and evaporated. Sublimation [80° (0.1 Torr)] of the residue yielded dihydro-**12**: mp $161-162^\circ$; infrared (Nujol) $C=O$ 5.37 (m), 5.63 (s) μ ; pmr δ 1.31 (s, 3, Me), 5.82 (s, 1, $CHCl_2$).

Anal. Calcd for $C_{12}H_{14}O_3Cl_2$: C, 52.00; H, 5.09. Found: C, 51.98; H, 5.22.

Registry No.—**3a**, 24463-33-0; semicarbazone of **3a**, 24463-34-1; *p*-toluenesulfonylhydrazone of **3a**, 24463-35-2; **3b**, 24147-13-5; **3c**, 24463-37-4; **3d**, 24463-38-5; **4a**, 24463-39-6; **4b**, 24463-40-9; **5b**, 24463-41-0; **6**, 24463-42-1; **7**, 24463-43-2; **8**, 24463-44-3; **11a**, 24463-45-4; **11b**, 24463-46-5; **12**, 24463-47-6; dihydro-**12**, 24463-48-7.

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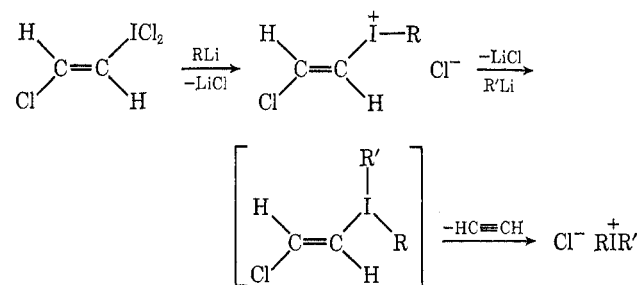
Iodonium Salts from Organolithium Reagents with *trans*-Chlorovinylidioso Dichloride^{1,2}

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The aim of the present work was to adapt a recently reported synthesis of diaryliodonium salts³ to the synthesis of iodonium salts having one or two heterocyclic, alkyl, or bicycloalkyl groups, according to the following scheme.



Di-2-thienyliodonium and phenyl-2-thienyliodonium salts, previously obtained by direct electrophilic substitution of thiophene,⁴ were prepared in 72 and 38%

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(2) Taken from the dissertation of R. A. Nathan submitted in partial fulfillment of the requirements for the Ph.D. degree, 1969.

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