the lower yields may also reflect the increased difficulty in isolating products from emulsions, or in part of the oxygen being present as oxidized emulsifier. The molecular weights of these polyperoxides from emulsion oxidations are comparable to bulk oxidation products.

The comparison of yield of tetralin hydroperoxide in emulsion and in bulk oxidation (initiated by azobisisobutyronitrile) indicates that the yield drops off with conversion faster in emulsion. Hyde and Verdin[7] observed the same phenomenon with methyl oleate. The hydroperoxide yields in the emulsion oxidation of tetramethylethylene and cyclopentene are nearly identical with those observed in the bulk.[23,24] In the case of tetramethylethylene, the analysis for acetone is complicated by the high solubility of acetone in the aqueous phase. While the conversion of cumene to cumene hydroperoxide is reportedly favorable in thermally initiated basic emulsions,[37] our radiation result gave a very low hydroperoxide yield.

Registry No.—Cobalt-60, 10198-40-0; α-methylstyrene, 98-83-9; cyclohexene, 110-83-8; cyclopentene, 142-29-0; tetramethylethylene, 563-79-1; tetralin, 119-64-2; butadiene, 106-99-0; cumene, 98-82-8; styrene, 100-42-5.

[37] G. P. Armstrong, R. H. Hall, and D. C. Quin, *J. Chem. Soc.*, 666 (1950).

The Chemistry of Carbanions. XX. A Comparison of α-Chloro Enolate Anions and α-Diazo Ketones[1a]

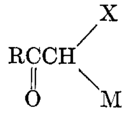
Herbert O. House,*[1b] William F. Fischer, Jr.,[1c] Martin Gall,[1d] Thomas E. McLaughlin, and Norton P. Peet

Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

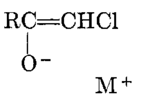
Received March 18, 1971

The α-chloro ketones, 2-chlorocyclohexanone (**5**), chloromethyl cyclohexyl ketone (**7**), and phenacyl chloride (**13**), have been converted to the corresponding enol acetates and trimethylsilyl enol ethers. These enol derivatives have served as precursors for the corresponding lithium α-chloro enolates **6**, **8**, and **16** which are stable intermediates. Even the addition of copper(I) compounds or the formation of α-mercuri derivatives of these enolates does not promote their decomposition to α-ketocarbenes. In contrast, the α-diazo derivatives **17** and **21** of acetophenone and methyl cyclohexyl ketone are readily decomposed by added copper(I) derivatives. The soluble complex, $(n\text{-Bu}_2S)_2CuI$, is an especially convenient catalyst for the decomposition of these α-diazo ketones, compound **21** being rapidly decomposed in solution at 5–10°. With small amounts of this catalyst and excess olefin the norcarane derivative **22** was the major product. With an equimolar amount of this catalyst, the keto sulfide **26** (believed to arise from a sulfur ylide intermediate) became the major monomeric product.

To pursue further the idea[2] that the copper-catalyzed reactions of α-diazo carbonyl compounds may involve copper(I) derivatives such as structure **1a** which possess a good leaving group ($N^+{\equiv}N$) at the α position, we have investigated the behavior of certain metal derivatives of α-chloro enolate ions (**2**). We wished to learn whether certain of these materials (*e.g.*, **1b** or **2**) would show either behavior similar to the copper (I)–diazo ketone reagent or the behavior expected of an α-keto carbene **3**. The metal enolates of α-halo esters and α-halo ketones have served as intermediates in a number of synthetically useful reactions such as the Darzens glycidic ester condensation and related reactions,[3,4] the formation of cyclopropane derivatives by Michael additions involving α-chloro enolates,[5] and the reaction of α-bromo enolates with trialkylboranes.[6] In all of these cases, it is probable that the metal α-halo enolates (*e.g.*, **2**) and not the α-keto carbenes **3**, which might be formed from the enolates, are the actual reactants. Further evidence in support of the view that α-halo enolate anions (*e.g.*, **2**) are not rapidly converted to α-keto carbenes **3** has been obtained by the formation and subsequent acylation of several α-halo enolates to form α-halo enol esters[7-9] such as **4**. In the present study we have generated several metal α-chloro enolate anions **2** from either enol acetate[10] or trimethylsilyl enol ether[11,12] precursors.

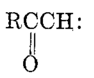


1a, X = $\overset{+}{N}{\equiv}N$, M = Cu
b, X = Cl



$RC(O^-){=}CHCl\ \ M^+$

2



$RC(=O)CH\colon$

3

Preparation of Lithium α-Chloro Enolates.—The most successful of previous preparations[7-9] of α-chloroenol esters have involved acylation of the inter-

---

[1] (a) This research has been supported by Research Grant No. AFOSR-68-1518, from the Directorate of Chemical Sciences, Air Force Office of Scientific Research, and by Public Health Service Grant No. 1-RO1-CA10933 from the National Cancer Institute. (b) Department of Chemistry, Georgia Institute of Technology, Atlanta, Ga. (c) National Institutes of Health Predoctoral Fellow, 1966–1969. (d) National Institutes of Health Predoctoral Fellow, 1968–1970.

[2] (a) H. O. House and C. J. Blankley, *J. Org. Chem.*, **33**, 47, 53 (1968), and references cited therein; (b) W. R. Moser, *J. Amer. Chem. Soc.*, **91**, 1135, 1141 (1969), and references cited therein: (c) V. Dave and E. W. Warnhoff, *Org. React.*, **18**, 217 (1970).

[3] M. S. Newman and B. J. Magerlein, *ibid.*, **5**, 413 (1949).

[4] M. Ballester, *Chem. Rev.*, **55**, 283 (1955).

[5] L. L. McCoy, *J. Org. Chem.*, **25**, 2078 (1960); **29**, 240 (1964); *J. Amer. Chem. Soc.*, **84**, 2246 (1962).

[6] H. C. Brown, M. M. Rogić, M. W. Rathke, and G. W. Kabalka, *ibid.*, **90**, 818, 1911 (1968); **91**, 2150 (1969), and subsequent publications.

[7] R. E. Lyle and R. A. Covey, *ibid.*, **75**, 4973 (1953).

[8] K. G. Rutherford and C. L. Stevens, *ibid.*, **77**, 3278 (1955).

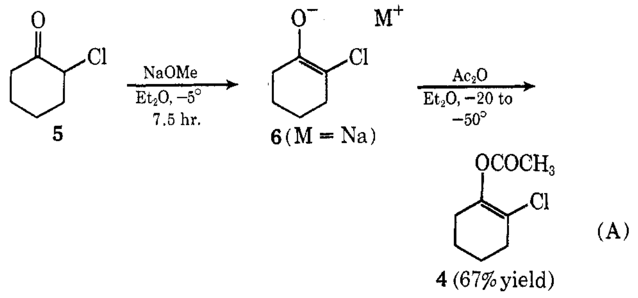
[9] (a) D. J. Cooper and L. N. Owen, *J. Chem. Soc. C*, 533 (1966): (b) L. N. Owen and R. Sridhar, *ibid.*, 564 (1970).

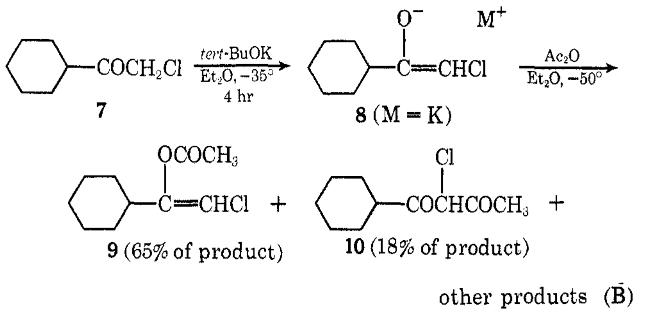
[10] (a) H. O. House and B. M. Trost, *J. Org. Chem.*, **30**, 2502 (1965); (b) H. O. House, *Rec. Chem. Progr.*, **28**, 99 (1967).

[11] G. Stork and P. F. Hudrlik, *J. Amer. Chem. Soc.*, **90**, 4462, 4464 (1968).

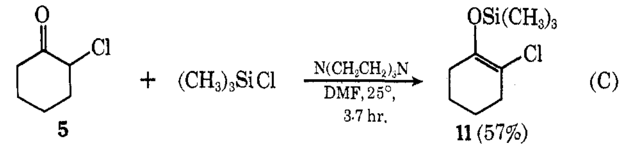
[12] H. O. House, L. J. Czuba, M. Gall, and H. D. Olmstead, *J. Org. Chem.*, **34**, 2324 (1969).

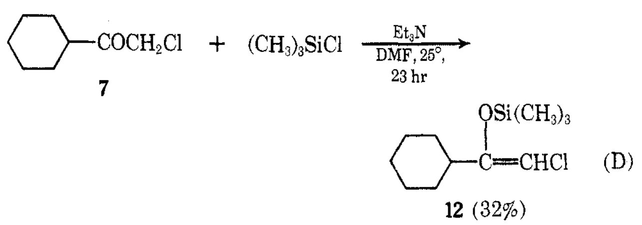
mediate α-chloro enolates formed by reaction of the chloro ketone with a suspension of sodium methoxide in ether at −20 to −50°.[8,9a] This procedure takes advantage of the fact that in unsymmetrical ketones such as **5** or **7** the C–H bond adjacent to both the carbonyl group and the chlorine atom is significantly more acidic (about 2 pK_a units)[13] than C–H bonds adjacent only to a carbonyl group. Although we have successfully adapted this procedure to the formation of the α-chloroenol acetates **4** and **9** (eq A and B),

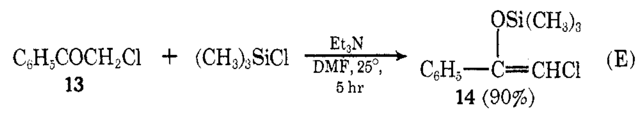




a far more useful synthetic procedure involves the formation of the corresponding trimethylsilyl enol ethers. The procedures, illustrated in eq C, D, and E,

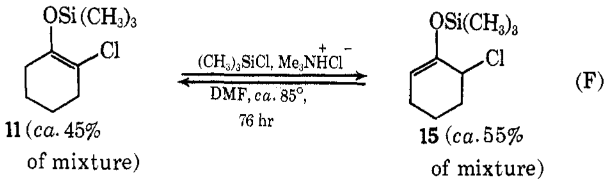






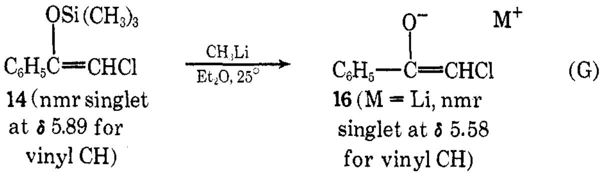
$$C_6H_5COCH_2Cl + (CH_3)_3SiCl \xrightarrow[\text{DMF, 25°, 5 hr}]{Et_3N} C_6H_5\overset{OSi(CH_3)_3}{\overset{|}{C}}{=}CHCl \quad \text{(E)}$$

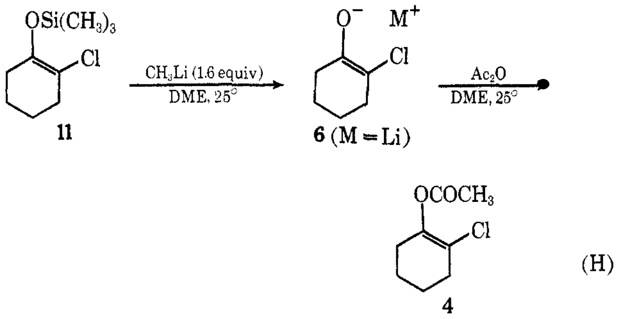
are based on a previously described method[12] and probably also owe their success to the relatively high acidity of the C–H bond adjacent to both the chlorine atom and the carbonyl group. It seems likely that the enol ethers **11** and **12** are formed in kinetically controlled processes since subjection of the enol ether **11** to conditions (eq F) known[12] to equilibrate silyl enol ethers



produced a second substance believed to be the enol ether **15**.

With samples of the enol derivatives **4**, **9**, **11**, **12**, and **14** available, we prepared the corresponding lithium α-chloroenolates **6**, **8**, and **16** and studied their thermal stabilities. As indicated in eq H–K, the

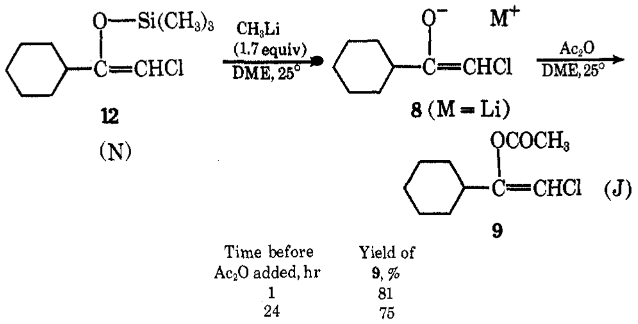




Time before Ac₂O added, hr	Yield of **4**, %
1	90
24	87

$$\mathbf{4} \xrightarrow[\text{DME, 25°}]{\substack{CH_3Li\\(3.1\ \text{equiv})}} \mathbf{6}\ (M = Li) + (CH_3)_3CO^-Li^+ \xrightarrow[\text{DME, 25°}]{(CH_3)_3SiCl} \mathbf{11} \quad \text{(I)}$$

Time before $(CH_3)_3SiCl$ added, hr	Yield of **11**, %
1	83
24	88



Time before Ac₂O added, hr	Yield of **9**, %
1	81
24	75

$$\mathbf{9} \xrightarrow[\text{DME, 25°}]{\substack{CH_3Li\\(3.4\ \text{equiv})}} \mathbf{8}(M = Li) + (CH_3)_3CO^-Li^+ \xrightarrow[\text{DME, 25°}]{(CH_3)_3SiCl} \mathbf{12} \quad \text{(K)}$$

Time before $(CH_3)_3SiCl$ added, hr	Yield of **11**, %
1.0	92
8.0	82

lithium enolates **6** and **8** are very stable and could be recovered as appropriate derivatives in high yield after 24 hr. As a result of these observations it is

---

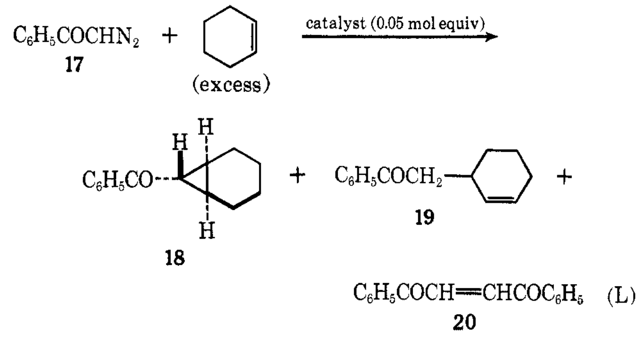
[13] (a) R. G. Pearson and R. L. Dillon, *J. Amer. Chem. Soc.*, **75**, 2439 (1953). (b) R. P. Bell, G. R. Hillier, J. W. Mansfield, and D. G. Street, *J. Chem. Soc. B*, 827 (1967). (c) In a chloro ketone analogous to **7**, the base-catalyzed exchange

$$RCOCH_2Cl + MeOD \overset{NaOMe}{\rightleftharpoons} RCOCHDCl + MeOH$$

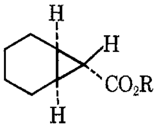
is faster than other possible reactions which may occur: H. O. House and F. A. Richey, Jr., *J. Org. Chem.*, **32**, 2151 (1967).

clear that the lithium α-chloroenolates (**2**, M = Li) do not undergo a ready thermal elimination of lithium chloride to form α-keto carbenes **3**.

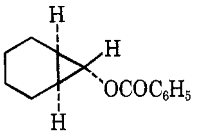
Comparison of α-Diazo Ketones and α-Chloro Enolates.—Before examining the effect of added copper(I) salts on the stability of the α-chloro enolates **2**, we examined the copper-catalyzed decomposition of the related diazo ketones **17** and **21**. The results obtained with the diazo ketone **17** and various copper compounds are summarized in eq L. The stereochemistry of the cyclopropyl ketone **18** was established by a Baeyer-Villiger oxidation and subsequent hydrolysis to form the known acid **24a**.



Catalyst	Reaction time, min	Temp, °C	Product yields, %		
			18	19	20
(MeO)$_3$PCuI (homogeneous)	60	25	11–27	1–3	1–3
(PhO)$_3$PCuI (homogeneous)	90	25	31–33	3–7	5–7
(Bu$_2$S)$_2$CuI (homogeneous)	60	25	37–40	2–3	4–5
C$_6$F$_5$Cu (homogeneous)	10–15	25	24–32	3–5	3–4
CuI (heterogeneous)	15–20	80	55–57	4	7–8
CuO (heterogeneous)	20–25	80	51–53	3–4	5–7



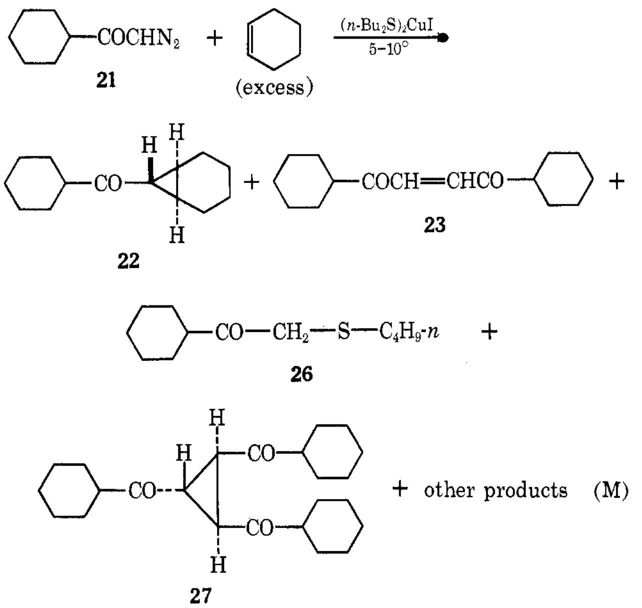
24a, R = H
b, R = C_6H_5
c, R = C_2H_5



25

These results agree with earlier observations, made with α-diazo esters,[2] that reactions involving a catalyst which is initially in solution proceed readily at room temperature. Whether the actual catalyst remains in solution at 25° is less clear, since all of these reaction mixtures became very dark in color as soon as decomposition of the diazo ketone began. Of interest was the fact that the yield of the cyclopropyl ketone **18**, the usual synthetic objective in these decompositions, was consistently higher when one of the insoluble catalysts was employed. The same observation was made in our earlier study of diazo ester reactions.[2a]

The results obtained on decomposition of the diazo ketone **21** in cyclohexene with (n-BuS)$_2$CuI as a catalyst are summarized in eq M. With small amounts (1–5 mol %) of this soluble catalyst the major volatile products were the norcarane **22** and the enedione **23**; although it is likely that a small amount of the triketone **27** was also formed in these reactions, we were not able to obtain quantitative data because the triketone **27** was not eluted from the glpc columns used for analysis. As might be expected, the proportion of norcarane **22** to dimer **23** was increased when dilute solutions of the diazo ketone were employed. A similar concentration effect may be responsible for the improved yields of norcarane **18** obtained when the diazo **17** was decomposed with heterogeneous catalysts. The stereochemistry of the predominant norcarane isomer is believed to be that indicated in structure **22** by analogy with the stereochemistry of the benzoyl analog **18**.



Reactant concn, M		Product yields, %		
21	(n-Bu$_2$S)$_2$CuI	22	23	26
0.36[a]	0.0088	33	32	
0.065	0.0012	56	11	
0.34[a]	0.34	13	5	22

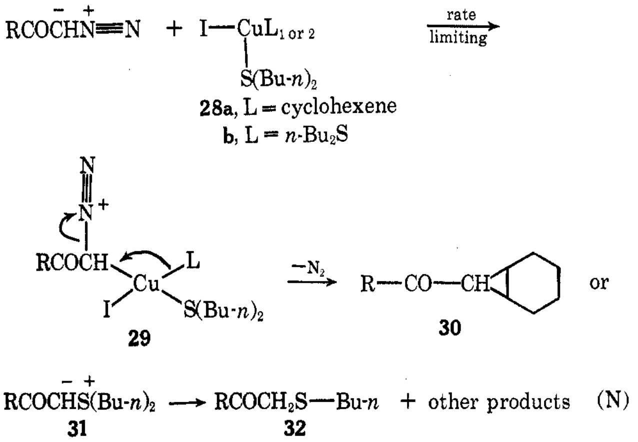
[a] The solvent contained 10% (by volume) of 1,2-dimethoxyethane.

When a full equivalent of the catalyst (n-Bu$_2$S)$_2$-CuI was used to decompose a solution of the diazo ketone **21** in cyclohexene (see eq M), the major volatile product became the keto sulfide **26** and the yields of **22** and **23** were lowered. From a preparative reaction in cyclohexane solution with 100 mol % of the soluble copper complex, the major products isolated by column chromatography were the keto sulfide **26** and the triketone **27** along with a tetramer (see Experimental Section). The structures of these products were confirmed by their physical and spectral properties, particularly the nmr spectra of the materials in which the hydrogen atoms near the carbonyl function were shifted by added europium(III) tri(dipivalolylmethide).[14] The decomposition of the diazo ketone **21** in the presence of (n-Bu$_2$S)$_2$CuI occurred relatively rapidly in the temperature range 5–10°. In this temperature range the reaction mixture remained homogeneous even when 100 mol % of the copper complex was present. Consequently, we were able to follow the course of this reaction by observing the nmr spectrum of a pentane solution containing equimolar amounts of the diazo ketone and (n-Bu$_2$S)CuI. *From these observations we can conclude unambiguously that no appreciable concentration of a diazo ketone–copper(I)*

---

[14] J. K. M. Sanders and D. H. Williams, *J. Amer. Chem. Soc.*, **93**, 641 (1971), and references cited therein.

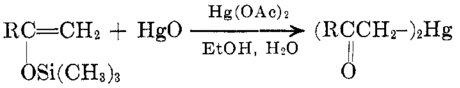
complex such as **1a** *accumulates in the reaction solution as the decomposition proceeds.* From these various observations we believe that the copper(I)-catalyzed diazo ketone reactions are best interpreted as shown in eq N. When low concentrations of a copper(I) complex such as **28** are present, we would expect an



appreciable amount of the complex to be present in solution as a structure such as **28a** with one (or two) olefin molecules as donor ligands. At higher catalyst concentrations, more of the complex should be present as **28b** with two (or three) thioether molecules as donor ligands. Following a rate-limiting coordination of the copper(I) complex **28** with diazo ketone, the resulting diazonium salt **29** undergoes rapid loss of nitrogen and transfer of a donor ligand L from copper to carbon to form either a norcarane **30** or a sulfur ylide **31**.[15,16] Although a sulfur ylide **31** appears to be the most likely precursor of the keto sulfide **32** (by proton transfer and elimination of 1-butene), our data do not allow us to decide whether the known[17] copper-catalyzed decomposition of a sulfur ylide **31** is an important route to the dimeric (*e.g.*, **20** and **23**) and trimeric (*e.g.*, **27**) products. However, it is clear (eq L) that at least dimeric products may arise by reaction paths which do not involve sulfur ylide intermediates.

With this information as a background we then examined the behavior of solutions containing equimolar amounts of $(n\text{-Bu}_2\text{S})_2\text{CuI}$ and each of the lithium α-chloro enolates **8** and **16**. In ether solution at −16°, the nmr spectrum of the lithium enolate **16** was essentially unchanged by the addition of an equimolar amount of the copper(I) complex.[18] When this solution was refluxed for 6 hr and then hydrolyzed, the predominant volatile product was the α-chloro ketone **13**; no 1,2-dibenzoylethylene (**20**) was detected in the reaction product. Solutions of the lithium enolate **8** and either 5 or 100 mol % of $(n\text{-Bu}_2\text{S})_2\text{CuI}$ were allowed to decompose in the same mixture of cyclohexene and 1,2-dimethoxyethane used in studies with the diazo ketone **21**. Although these solutions clearly underwent reaction, as indicated by the separation of a black solid (presumably metallic copper), the only volatile product formed in appreciable amount (72–100% yield) was the chloro ketone **7**. None of the products **22**, **23**, or **26** was detected, indicating that the α-chloro enolate **8** does not react with copper(I) complexes in the same manner (see structure **29**) as α-diazo ketones. These results suggest that the chloro enolates **2** do not form covalent compounds (*e.g.*, **1b**) with the added copper(I) complex. We suggest that the decomposition reaction observed is an electron transfer from the enolate to the copper(I) species to produce metallic copper and a radical of the type $\text{RCO}\dot{\text{C}}\text{HCl}$, which abstracts hydrogen from the solvent to form the observed chloro ketone product **7**. The same type of reaction is apparently involved in the subsequently described thermal decomposition of the α-chloro-α-mercuric ketone **35**.

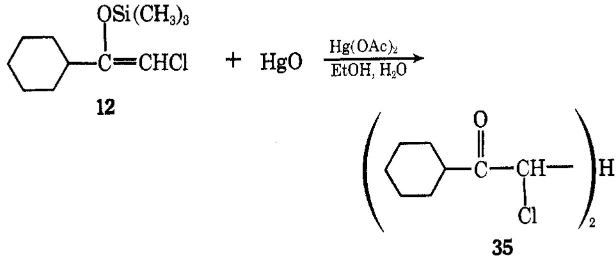
In an effort to produce a substance that has a metal bound to the α carbon of an α-chloro ketone, we examined the reaction of the silyl enol ethers **12** and **14** with HgO. In other studies[19] we have found that use of this reaction with nonhalogenated silyl enol ethers (*e.g.*, **33**) yields the corresponding α-mercuric ketones **34** with nmr absorption, which clearly establishes the



$$\underset{\text{OSi(CH}_3)_3}{\text{RC}}{=}\text{CH}_2 + \text{HgO} \xrightarrow[\text{EtOH, H}_2\text{O}]{\text{Hg(OAc)}_2} (\text{R}\underset{\text{O}}{\overset{\|}{\text{C}}}\text{CH}_2\text{–})_2\text{Hg}$$

33 **34**

presence of C–Hg bond. Application of this reaction to the chlorinated silyl enol ethers **12** and **14** produced high-melting, insoluble materials which were very difficult to purify and characterize. We succeeded in obtaining a sample of one product which had a composition and infrared absorption consistent with structure **35**. However, the insolubility of this product prevented us from obtaining satisfactory nmr data to establish the presence of a C–Hg bond from the magnitude of the coupling constant, $J_{\text{H}-^{199}\text{Hg}}$.



When the product **35** was decomposed at 230°, the chloro ketone **7** was found to distil from the decomposed material. A suspension of **35** in refluxing cyclohexene appeared to undergo no change and after hydrolysis with aqueous acid the chloro ketone **7** was recovered but no norcarane **22** was detected. Although the α-mercuric dichloro ester **36** has been found to decompose slowly (forming products apparently derived from $\text{Cl}\ddot{\text{C}}\text{CO}_2\text{CH}_3$) in refluxing chlorobenzene (132°),[20] our finding that the related mono-

---

[15] For other examples of sulfur ylide formation, see (a) W. Ando, K. Nakayama, K. Ichibori, and T. Migita, *ibid.*, **91**, 5164 (1969); (b) W. Ando, T. Yagihara, S. Tozune, S. Nakaido, and T. Migita, *Tetrahedron Lett.*, 1979 (1969); (c) F. Dost and J. Gosselck, *ibid.*, 5091 (1970); (d) F. Serratosa and J. Quintana, *ibid.*, 2245 (1967).

[16] For examples where donor ligands appear to have been transferred from copper(I) to the α carbon of an α-diazo ketone, see ref 15c and (a) T. Saegusa, Y. Ito, S. Kobayashi, K. Hirota, and T. Shimizu, *J. Org. Chem.*, **33**, 544 (1968); (b) T. Sato and S. Watanabe, *Chem. Commun.*, 515 (1969).

[17] B. M. Trost, *J. Amer. Chem. Soc.*, **89**, 138 (1967).

[18] We have noted previously that the addition of soluble copper(I) compounds seems to have no effect on the rate at which lithium enolates undergo Michael reactions or reaction with alkyl halides: H. O. House and W. F. Fischer, Jr., *J. Org. Chem.*, **34**, 3615 (1969).

[19] H. O. House, M. Gall, H. D. Olmstead, and N. Peet, unpublished work.

[20] (a) D. Seyferth, D. C. Mueller, and R. L. Lambert, Jr., *J. Amer. Chem. Soc.*, **91**, 1562 (1969); (b) D. Seyferth, *Proc. Robert A. Welch Found. Conf. Organometallic Compd.*, 89 (1965).

chloro derivative **35** is stable is in agreement with the general experience that the ease of thermal decomposition of chloroalkyl mercurials lies in the order $RHgCCl_3 > RHgCCl_2R > RHgCClR_2$.[20b]

$C_6H_5HgCCl_2CO_2CH_3$
36

Experimental Section[21]

Starting Material and Reagents.—Commercial samples of 2-chlorocyclohexanone, ω-chloroacetophenone, and halide-free ethereal solutions of methyllithium were employed. The methyllithium solutions were standardized by the titration procedure of Watson and Eastham.[22] Diazomethane was prepared from bis(*N*-methyl-*N*-nitroso)terephthalamide.[23] 1,2-Dimethoxyethane was distilled from $LiAlH_4$ immediately before use. Freshly distilled samples of commercial trimethylsilyl chloride were treated with small amounts of Et_3N and then filtered under anhydrous conditions (to separate any $Et_3NH^+Cl^-$ present) before being used in reactions with solutions of lithium enolates.

Reaction of cyclohexanecarboxylic acid with excess $SOCl_2$ in CH_2Cl_2 yielded the acid chloride, bp 44–45° (5 mm) [lit.[24] bp 184–188° (755 mm)], which was converted to the chloro ketone **7** by reaction with cold (0°), ethereal diazomethane as previously described.[25] The chloro ketone **7** was collected in 74% yield as a colorless liquid, bp 75–85° (3.1 mm), $n^{25}D$ 1.4762–1.4775 [lit. mp 1–2.5°,[15] bp 114–115° (20 mm),[26] $n^{25}D$ 1.4773[26]], which contained [glpc analysis, 1,2,3-tris-(β-cyanoethoxy)propane on Chromosorb P] the chloro ketone **7** accompanied by small amounts of low-boiling impurities. A pure sample of the chloro ketone **7** was collected (glpc): ir (CCl_4) 1740 and 1712 cm^{-1} (C=O); nmr (CCl_4) δ 4.03 (2 H, s, $COCH_2Cl$) and 1.0–2.9 (11 H, m, aliphatic CH); mass spectrum *m/e* (rel intensity), 162, 160 (2, M^+), 111 (25), 83 (100), 55 (44), and 41 (20).

Preparation of the Trimethylsilyl Enol Ethers. A. From ω-Chloroacetophenone (13).—A solution of 21.6 g (140 mmol) of ω-chloroacetophenone in 20 ml of Me_2NCHO was treated with a solution of 23.9 g (220 mmol) of Me_3SiCl and 38.4 g (380 mmol) of Et_3N in 80 ml of Me_2NCHO. After the initial exothermic reaction subsided, the mixture was stirred at 25° for 5 hr and then partitioned between pentane and saturated, aqueous $NaHCO_3$. The organic extract was dried, concentrated, and distilled to separate 28.6 g (90%) of the silyl enol ether **14**: bp 75–75.5° (1 mm); $n^{25}D$ 1.5214; ir (CCl_4) 1620 (shoulder) and 1615 cm^{-1} (enol C=C); nmr (CCl_4) δ 7.1–7.6 (5 H, m, aryl CH), 5.89 (1 H, s, vinyl CH),[27] and 0.20 [9 H, $(CH_3)_3Si$]; mass spectrum *m/e* (rel intensity), 228 (13) and 226 (33, M^+), 190 (24), 183 (22), 177 (22), 157 (22), 155 (58), 95 (37), 93 (100), 73 (97), and 45 (36).

Anal. Calcd for $C_{11}H_{15}ClOSi$: C, 58.23; H, 6.65. Found: C, 58.16; H, 6.65.

B. From Chloromethyl Cyclohexyl Ketone (7).—A solution of 32.6 g (300 mmol) of Me_3SiCl, 20.2 g (200 mmol) of Et_3N, and 9.5 g (59 mmol) of the chloro ketone **7** in 100 ml of Me_2NCHO was stirred for 4 hr and subjected to the previously described isolation procedure. Fractional distillation afforded early fractions, bp 80–81° (3.5 mm), containing the chloro ketone **7** and 4.40 g (32%) of the silyl ether **12**: bp 85–86° (3.5 mm); $n^{25}D$ 1.4692–1.4699; ir (CCl_4) 1637 cm^{-1} (enol C=C); nmr (CCl_4) δ 5.25 (1 H, s, vinyl CH),[27] 0.8–2.1 (11 H, m, aliphatic CH), and 0.27 [9 H, s, $(CH_3)_3Si$]; mass spectrum *m/e* (rel intensity), 234 (12) and 232 (33, M^+), 183 (24), 177 (53), 149 (26), 147 (37), 93 (39), 83 (33), 79 (28), 73 (100), 55 (25), and 41 (20).

Anal. Calcd for $C_{11}H_{21}ClOSi$: C, 56.74; H, 9.09; Cl, 15.23. Found: C, 56.70; H, 8.90; Cl, 15.39.

C. From 2-Chlorocyclohexanone (5).—The same procedure was followed with a solution of 25.2 g (250 mmol) of 1,4-diazabicyclo[2.2.2]octane, 19.98 g (184 mmol) of Me_3SiCl, and 15.37 g (116 mmol) of the chloro ketone **5** in 50 ml of Me_2NCHO. The silyl enol ether **11** was collected as 13.5 g (57%) of colorless liquid, bp 82° (4 mm), $n^{25}D$ 1.4638. A sample for analysis was collected from a glpc column (Carbowax, 20M, on Chromosorb P): ir (CCl_4) 1675 cm^{-1} (enol C=C); nmr (CCl_4) δ 1.3–2.6 (8 H, m, aliphatic CH) and 0.20 [9 H, s, $(CH_3)_3Si$]; mass spectrum *m/e* (rel intensity) 206 (16) and 204 (40, M^+), 191 (23), 189 (65), 95 (35), 93 (100), 75 (28), 73 (92), and 45 (37).

Anal. Calcd for $C_9H_{17}ClOSi$: C, 52.79; H, 8.37. Found: C, 52.81; H, 8.31.

In experiments where triethylamine rather than 1,4-diazabicyclo[2.2.2]octane was used, the conversion of the chloro ketone **5** to the silyl enol ether **11** was slower. Heating the reaction mixture resulted in the appearance of a new glpc peak (Carbowax 20M on Chromosorb P) believed to be the enol ether **15** (retention time 21.0 min) as well as peaks corresponding to the enol ether **11** (17.4 min) and the chloro ketone **5** (35.6 min). A suspension of 153 mg (1.6 mmol) of Me_3NHCl (freshly sublimed), 25.7 g (236 mmol) of Me_3SiCl, and 6.12 g (29.9 mmol) of the enol ether **11** in 60 ml of Me_2NHCO was heated to *ca.* 85° with stirring and aliquots of the reaction mixture were removed periodically and subjected to the usual isolation procedure followed by glpc analysis. After 76 hr, when equilibration appeared to be complete, the low-boiling components were distilled from the mixture and the residue was partitioned between pentane and aqueous $NaHCO_3$. The pentane solution was washed successively with aqueous $NaHCO_3$ and aqueous NaCl and then dried over $CaSO_4$, decolorized with charcoal, and concentrated. The residual pale yellow liquid (4.88 g) exhibited glpc peaks corresponding to the enol ethers **11** (*ca.* 34%) and **15** (*ca.* 44%) and to the chloro ketone **5** (*ca.* 22%). Collected samples of **11** and **5** were identified with authentic samples by comparison of ir spectra and glpc retention times. A collected sample of the silyl enol ether **15** was obtained as a colorless liquid: ir (CCl_4) 1660 cm^{-1} (enol C=C); nmr (CCl_4) δ 4.8–5.0 (1 H, m, vinyl CH), 4.2–4.4 (1 H, m, COCHCl), 1.4–2.5 (6 H, m, aliphatic CH), and 0.20 [9, H, s, $(CH_3)_3Si$]; mass spectrum *m/e* (rel intensity) 206 (11) and 204 (29, M^+), 191 (27), 189 (76), 169 (36), 95 (28), 93 (67), 79 (26), 75 (58), 73 (100), 68 (35), 55 (37), and 45 (26). Attempts to store or work with this material were complicated by its rapid conversion or mixtures containing the isomer **11** and the ketone **5**.

Anal. Calcd for $C_9H_{17}ClOSi$: C, 52.79; H, 8.37. Found: C, 53.11; H, 8.28.

Preparation of the Enol Acetates. A. From 2-Chlorocyclohexanone (5).—To a cold (−7°) suspension of 17.05 g (315 mmol) of NaOMe in 300 ml of Et_2O was added 9.33 g (70.3 mmol) of the chloro ketone **5**. After the resulting mixture had been stirred at −5° for 7.5 hr, it was cooled to −50° and 92.4 g (904 mmol) of Ac_2O was added. The reaction mixture, which initially warmed to −20°, was stirred at *ca.* −50° for 20 min and then allowed to warm to room temperature over 60 min. The resulting suspension was poured into a mixture of 200 ml of pentane and 150 ml of saturated, aqueous $NaHCO_3$, and additional solid $NaHCO_3$ was added until all the HOAc was neutralized. The organic phase was separated, washed successively with aqueous $NaHCO_3$ and H_2O, dried, and concentrated. An 8.52-g portion of the residual orange liquid (10.02 g) was distilled through a 40-cm spinning-band column to separate 5.69 g (67%) of the enol acetate **4** as a colorless liquid, bp 107–108° (24 mm), $n^{28}D$ 1.4740, which contained (glpc, Carbowax 20M on Chromosorb P) the enol acetate **4** (retention time 40.1 min) accompanied by small amounts (3–5%) of the chloro ketone **5** (33.1 min). A collected (glpc) sample of the enol acetate **4** was characterized: ir (CCl_4) 1765 (enol ester C=O) and 1685 cm^{-1} (enol C=C); nmr ($CDCl_3$) δ 1.5–2.7 (multiplet, aliphatic CH); mass spectrum *m/e* (rel intensity) 176 (3) and 174 (9, M^+), 134 (27), 132 (100), 104 (26), 97 (58), and 43 (82).

Anal. Calcd for $C_8H_{11}ClO_2$: C, 55.02; H, 6.35; Cl, 20.30. Found: C, 55.14; H, 6.53; Cl, 20.15.

---

[21] All melting points are corrected and all boiling points are uncorrected. Unless otherwise stated magnesium sulfate was employed as a drying agent. The infrared spectra were determined with a Perkin-Elmer Model 237 infrared recording spectrophotometer fitted with a grating. The ultraviolet spectra were determined with a Cary recording spectrophotometer, Model 14. The nmr spectra were determined at 60 Mc with a Varian Model A-60 or Model T-60 nmr spectrometer. The chemical shift values are expressed in δ values (ppm) relative to a tetramethylsilane internal standard. The mass spectra were obtained with an Hitachi (Perkin-Elmer) mass spectrometer. All reactions involving strong bases or organometallic intermediates were performed under a nitrogen atmosphere.

[22] S. C. Watson and J. F. Eastham, *J. Organometal. Chem.*, **9**, 165 (1967).

[23] J. A. Moore and D. E. Reed, *Org. Syn.*, **41**, 16 (1961).

[24] R. E. Lutz and J. W. Wilson, *J. Org. Chem.*, **12**, 767 (1947).

[25] R. B. Loftfield and L. Schaad, *J. Amer. Chem. Soc.*, **76**, 35 (1954).

[26] M. Mousseron, R. Jaquier, and A. Fontaine, *Bull. Soc. Chim. Fr.*, 767 (1952).

[27] Although the narrow line widths observed for the nmr peaks would suggest that this product is a single stereoisomer, we have no compelling evidence on this point.

B. From Chloromethyl Cyclohexyl Ketone (7).—A mixture of 3.90 g (35.1 mmol) of *tert*-BuOK, 1.98 g (12.3 mmol) of the chloro ketone **7**, and 60 ml of Et$_2$O was stirred at −35° for 4 hr and then cooled to −50° and mixed with 21.7 g (212 mmol) of Ac$_2$O. After the resulting solution had been stirred at −50° for 10 min it was allowed to warm to 25° over a 60-min period and then subjected to the previously described isolation procedure. The crude liquid product contained (glpc analysis, silicone gum, SE-30, on Chromosorb P) four volatile components: the chloro ketone **7**, *ca.* 11%, retention time 16.5 min; the enol acetate **9**, *ca.* 65%, 37.5 min; a product thought to be the diketone **10**, *ca.* 18%, 44.8 min;[28] and an unidentified component, *ca.* 6%, 102.6 min. Samples of each of the major components **7**, **9**, and **10** were collected (glpc) and the starting ketone was identified by comparison of glpc retention times and ir spectra. The enol acetate **9** was obtained as a colorless liquid: ir (CCl$_4$) 1775 (enol ester C=O) and 1650 cm^{-1} (C=C); nmr (CCl$_4$) δ 5.7 (1 H, partially resolved doublet, vinyl CH), 2.16 (3 H, s, CH$_3$CO), and 0.9–2.3 (11 H, m, aliphatic CH); mass spectrum *m/e* (rel intensity) 204 (1) and 202 (3, M$^+$), 162 (17), 160 (51), 111 (38), 83 (36), and 43 (100).

Anal. Calcd for $C_{10}H_{15}ClO_2$: C, 59.26; H, 7.41. Found: C, 59.60; H, 7.43.

The material thought to be diketone **10** has ir absorption at 1715 and 1610 (broad) cm^{-1} (enolic β diketone); mass spectrum *m/e* (rel intensity), 204 (9) and 202 (26, M$^+$), 121 (19), and 119 (52, $O^+{\equiv}CCHClCOCH_3$), 111 (32), 83 (100), 55 (65), 43 (48), and 41 (33).

Preparation of the Lithium Chloro Enolate 6. A. From the Silyl Ether 11.—A solution of 8.25 mmol of MeLi and several milligrams of 2,2-bipyridyl (as an indicator) in 8.0 ml of 1,2-dimethoxyethane was treated with 1.076 g (5.25 mmol) of the silyl enol ether **11** and the resulting solution was stirred at 25°. Periodically, 1-ml aliquots were removed, quenched in 2.0 ml of Ac$_2$O, stirred for 10 min, and then partitioned between pentane and aqueous NaHCO$_3$. The organic phase was mixed with an internal standard (tetralin) and analyzed to give the results summarized in eq H. On the glpc column (Carbowax 20M on Chromosorb P) used for analysis the retention times were: silyl ether **11**, 17.4 min; tetralin, 23.8 min; chloro ketone **5**, 34.6 min; enol acetate **4**, 42.0 min. The gas chromatography equipment was calibrated with known mixtures of authentic samples and collected (glpc) samples of each of the peaks were identified with authentic samples by comparison of glpc retention times and ir spectra.

B. From the Enol Acetate 4.—A solution prepared from 6.6 mmol of MeLi and 370 mg (2.12 mmol) of the enol acetate **4** in 6.0 ml of 1,2-dimethoxyethane was stirred at 25° and 1.0-ml aliquots were removed periodically and quenched in 2.0 ml of Me$_3$SiCl. The resulting mixtures were stirred for 10 min and then subjected to the previously described isolation and analysis procedures to give the results summarized in eq I.

Preparation of the Lithium Chloro Enolate 8. A. From the Silyl Ether 12.—The enolate solution, prepared from 8.25 mmol of MeLi and 1.122 g (4.83 mmol) of the silyl enol ether **12** in 6.0 ml of 1,2-dimethoxyethane, was stirred at 25° and aliquots were removed, quenched in Ac$_2$O, and then subjected to the previously described isolation procedure. An internal standard (pentamethylbenzene) was added to each crude product and it was analyzed to give the results indicated in eq J. On the glpc column used (silicone gum, SE-30, on Chromosorb P), the retention times were: chloro ketone **7**, 14.6 min; pentamethylbenzene, 20.7 min; enol acetate **9**, 31.6 min; silyl enol ether **12**, 34.3 min. The gas chromatography equipment was calibrated with known mixtures of authentic samples, and collected (glpc) samples of the reaction products were identified with authentic samples by comparison of glpc retention times and ir spectra.

B. From the Enol Acetate 9.—The enolate solution, prepared from 6.6 mmol of MeLi and 387 mg (1.9 mmol) of the enol acetate **9** in 4.0 ml of 1,2-dimethoxyethane, was stirred at 25° and aliquots were removed periodically and quenched in Me$_3$SiCl. The mixtures were subject to the previously described isolation and analytical procedures to give the results indicated in eq K.

Copper-Catalyzed Decomposition of Diazo Ketones. A. Materials.—Reaction of benzoyl chloride with excess ethereal CH$_2$N$_2$ in the presence of Et$_3$N[29] afforded α-diazoacetophenone (**17**) as yellow needles from hexane: mp 47.4–48.6° (lit.[29] mp 47.8–48.4°); ir (CCl$_4$) 2110 and 1635 cm^{-1} (α-diazo ketone); uv (95% EtOH) 252 mμ (ϵ 11,500) and 297 (12,000); nmr (CCl$_4$) δ 7.2–8.0 (5 H, m, aryl CH) and 6.15 (1 H, s, COCHN$_2$). A similar reaction of 8.704 g (59.3 mmol) of cyclohexanecarboxylic acid chloride with excess ethereal CH$_2$N$_2$ yielded 6.59 g (73%) of the diazo ketone **21** as yellow needles from pentane (at −20°): mp 14.5–16° (lit.[30] 11–13°); ir (CCl$_4$) 2130 and 1655 cm^{-1} (α-diazo ketone); nmr (CDCl$_3$) δ 5.31 (1 H, s, COCHN$_2$) and 0.8–2.5 (11 H, m, aliphatic CH).

Commercial samples of CuI and CuO were employed. The bis(di-*n*-butyl sulfide) complex of CuI was described previously,[31] pentafluorophenylcopper was obtained from Dr. W. A. Shepard,[32] and the triphenyl phosphite complex of CuI was obtained from Dr. J. San Filippo.[33] A mixture of 1.24 g (10 mmol) of (MeO)$_3$P, 1.90 g (10 mmol) of CuI, and 20 ml of benzene was refluxed for 8 hr and then filtered while hot and concentrated. The residual solid (2.63 g, mp 175–185°) was recrystallized from an Et$_2$O–CHCl$_3$ mixture to separate the trimethyl phosphite complex of CuI as white needles, mp 192–193° (lit.[34] 175–177°).

Anal. Calcd for $C_3H_9CuIO_3P$: C, 11.46; H, 2.88; Cu, 20.20; I, 40.35. Found: C, 11.54; H, 2.82; Cu, 20.12; I, 40.05.

A solution of the lithium enolate of acetophenone, prepared in the usual way from 37.2 mmol of MeLi, 7.15 g (37.2 mmol) of α-trimethylsiloxystyrene, and 38 ml of 1,2-dimethoxyethane, was treated with 6.62 g (37.2 mmol) of 3-bromocyclohexene. After the mixture had been stirred at 25° for 5 hr, it was partitioned between pentane and aqueous NH$_4$Cl. The organic layer was washed with H$_2$O, dried, concentrated, and distilled to separate 2.02 g (27%) of the **ketone 19** as a colorless liquid: bp 95–95.6° (0.1 mm); n^{25}D 1.5508; ir (CCl$_4$) 1690 cm^{-1} (conjugated C=O); uv max (95% EtOH) 243 mμ (ϵ 11,300) and 280 (994); nmr (CCl$_4$) δ 7.2–8.2 (5 H, m, aryl CH), 5.74 (2 H, broad, vinyl CH), 2.6–3.1 (3 H, m, CH$_2$CO and allylic CH), and 1.1–2.3 (6 H, m, aliphatic CH); mass spectrum *m/e* (rel intensity) 200 (14, M$^+$), 105 (100), 77 (40), and 43 (34).

Anal. Calcd for $C_{14}H_{16}O$: C, 83.96; H, 8.05. Found: C, 84.19; H, 8.20.

The cis isomer of 1,2-dibenzoylethylene (**20**), obtained by photoisomerization[35] of the commercially available trans isomer, crystallized as white needles: mp 132–133° (lit.[35] mp 134°); ir (CHCl$_3$) 1670 (conjugated C=O) and 1610 cm^{-1} (conjugated C=C); uv max (95% EtOH), 262 mμ (ϵ 17,100); nmr (CDCl$_3$) δ 7.3–8.2 (10 H, m, aryl CH) and 7.21 (2 H, s, vinyl CH); mass spectrum *m/e* (rel intensity), 236 (5, M$^+$), 105 (29), 78 (100), 77 (31), 52 (20), 51 (22), and 50 (16).

B. Reaction of the Diazo Ketone with Cyclohexene.—A mixture of 6.5 g (45 mmol) of the diazo ketone **17**, 1.00 g (5.3 mmol) of CuI, and 250 ml of cyclohexene was heated under reflux. After 40 min a vigorous exothermic reaction occurred which consumed all the diazo ketone within 10 min. During this time, the color of the reaction mixture became very dark. The reaction mixture was filtered and the filtrate was concentrated and distilled to separate 2.46 g (28%) of the crude cyclopropyl ketone **18** as a pale yellow liquid, bp 96.5–99° (0.1 mm), n^{25}D 1.5602 [lit.[36] bp 145° (1 mm)], which contained (glpc, Versamid 900 on Chromosorb P) *ca.* 10% of lower boiling impurities. A pure sample of the ketone **18** was collected (glpc) as a colorless liquid: n^{25}D 1.5629; ir (CCl$_4$) 1670 cm^{-1} (conjugated C=O); uv max (95% EtOH) 245 mμ (ϵ 17,100); nmr (CCl$_4$) δ 7.2–8.2 (5 H, m, aryl CH), 2.2–2.5 (1 H, m, COCH), and 1.1–2.2 (10 H, m, aliphatic CH); mass spectrum *m/e* (rel intensity) 200 (53, M$^+$), 157 (81), 105 (100), 77 (82), 51 (29), 44 (75), 43 (84), and 39 (27).

The stereochemistry assigned to the cyclopropyl ketone **18** was based upon its preparation[37] from derivatives of the known

---

[28] In an experiment where a solution of the enolate **8** was added slowly to excess Ac$_2$O, none of the C-acylated product **10** was detected. This suggests that diketone **10** is formed by reaction of the enolate **8** with the initially formed enol acetate **9**.

[29] M. S. Newman and P. Beal, *J. Amer. Chem. Soc.*, **71**, 1506 (1949).

[30] R. B. Wagner and J. A. Moore, *ibid.*, **72**, 2884 (1950).

[31] H. O. House and W. F. Fischer, Jr., *J. Org. Chem.*, **33**, 949 (1968).

[32] A. Cairncross and W. A. Shepard, *J. Amer. Chem. Soc.*, **90**, 2186 (1968).

[33] G. M. Whitesides and J. San Filippo, unpublished work.

[34] A. E. Arbusoff, *Ber.*, **38**, 1171 (1905).

[35] L. Horner and E. Lingnau, *Justus Liebigs Ann. Chem.*, **591**, 21 (1955).

[36] D. O. Cowan, M. M. Couch, K. R. Kopecky, and G. S. Hammond, *J. Org. Chem.*, **29**, 1922 (1964).

[37] M. Mousseron, R. Jacquier, and R. Fraisse, *C. R. Acad. Sci.*, **243**, 1880 (1956).

acid **24a**. To verify this assignment, the ketone **18** (704 mg or 3.5 mmol) was oxidized with peroxytrifluoroacetic acid [from 12 mmol of $(CF_3CO)_2O$ and 10 mmol of H_2O_2] in 7.5 ml of CH_2Cl_2 containing 3.55 g (25 mmol) of suspended Na_2HPO_4. After the mixture had been refluxed for 12 hr, it was filtered and the filtrate was washed with aqueous Na_2CO_3 and then concentrated. The residual pale yellow liquid (501 mg) contained (glpc, Versamide 900 on Chromosorb P) a component believed to be the ester **25** [*ca.* 50%, retention time 14.6 min, ir (CCl_4) 1730 cm^{-1} (conjugated ester)], the ester **24b** [*ca.* 25%, 17.6 min, ir (CCl_4) 1750 cm^{-1} (ester C=O)], and the starting ketone **18** (*ca.* 25%, 20.2 min, identified by ir and glpc retention time). The phenyl ester **24b** was selectively saponified by stirring a solution containing the crude esters **24b** and **25** and 2.0 ml of aqueous 0.5 *M* KOH in 10 ml of EtOH at 25° for 2 hr. The crude acidic product was separated by appropriate extractions and recrystallized from hexane to separate 25 mg (5.1% based on the starting ketone **18**) of the acid **24a** as white needles, mp 94.8–96° (lit.[38] 96.5°), identified with an authentic sample by a mixture melting point and comparison of ir spectra. To obtain an authentic sample of this acid **24a** for comparison, ethyl diazoacetate was decomposed in boiling cyclohexene in the presence of suspended copper powder. The crude ethyl ester **24c** [bp 111–115° (18 mm), $n^{25}D$ 1.4631–1.4642] was saponified (KOH in EtOH–H_2O) and the acid was recrystallized from hexane: mp 95–96.2°; ir (CCl_4) 1695 cm^{-1} (carboxyl C=O); nmr (CCl_4) δ 1.0–2.2 (multiplet, aliphatic CH); mass spectrum *m/e* (rel intensity) 140 (43, M^+), 105 (31), 97 (49), 95 (42), 86 (49), 81 (37), 80 (100), 79 (31), 68 (33), 67 (45), 55 (46), 41 (51), and 39 (46).

The quantitative experiments summarized in eq L were performed by adding 0.034 mmol of the indicated catalyst to solutions of 100 mg (0.69 mmol) of the diazo ketone **17** in 5.0 ml of cyclohexene. The progress of the reactions was monitored by use of the ir absorption at 2110 cm^{-1} characteristic of the starting diazo ketone. When the diazo ketone was consumed, the mixtures were partitioned between PhH and aqueous NH_4Cl containing NH_3. The organic extracts were mixed with known amounts of an internal standard (2-phenylnaphthalene) and analyzed (glpc, silicone gum, SE-52, on Chromosorb P). The retention times were: ketone **19**, 10.2 min; ketone **18**, 12.7 min; 2-phenylnaphthalene, 17.1 min; and the *cis*- and *trans*-1,2-dibenzoylethylenes **20** (not resolved), 27.0 min. Collected samples of each component were identified with authentic samples by comparison of glpc retention times and ir spectra.

C. Reaction of the Diazo Ketone 21 with Cyclohexene.—A solution of 2.73 g (17.9 mmol) of the diazo ketone **21** in 30 ml of cyclohexene at 23° was treated with 87 mg (0.18 mmol) of $(n\text{-}Bu_2S)_2CuI$. An immediate exothermic reaction occurred and the color of the solution changed from pale yellow to dark brown. After 10 min the reaction had subsided and all the diazo ketone **21** had been consumed (ir analysis). The reaction solution was concentrated and a solution of the residue (2.88 g) in petroleum ether (bp 30–60°) was cooled to separate 272 mg (6%) of the enedione **23**, mp 87–88.5°. After this material had been washed with aqueous NH_4Cl and NH_3, recrystallization afforded the pure **enedione 23** as pale yellow needles: mp 88–89.5°; ir (CCl_4) 1685 (conjugated C=O) and 990 cm^{-1} (trans CH=CH); uv max (95% EtOH) 234 mμ (ϵ 12,500) and 349 (96); nmr ($CDCl_3$) δ 7.03 (2 H, s, vinyl CH), 2.3–3.0 (2 H, m, CHCO), and 0.9–2.3 (20 H, m, aliphatic CH_2); mass spectrum *m/e* (rel intensity), 248 (1, M^+), 137 (20), 83 (54), 55 (99), 43 (26), 41 (100), and 39 (30).

Anal. Calcd for $C_{16}H_{24}O_2$: C, 77.37; H, 9.74. Found: C, 77.10; H, 9.82.

The mother liquors remaining after crystallization of the enedione **23** contained (glpc analysis, silicone fluid, no. 710, on Chromosorb P) the norcarane **22** (retention time, 10.4 min), the enedione **23** (retention time, 42.4 min), and two minor unidentified components (retention times, 9.2 min and 21.5 min). A sample of the norcarane **22** was collected (glpc) as a colorless liquid, which crystallized on cooling. Recrystallization from pentane gave the pure **norcarane 22** as colorless needles: mp 36–37.5°; ir (CCl_4) 3030 (cyclopropyl CH) and 1690 cm^{-1} (C=O); nmr ($CDCl_3$) δ 0.9–2.6 (multiplet); mass spectrum *m/e* (rel intensity), 206 (22, M^+), 123 (100), 95 (39), 83 (23), 81 (23), 67 (22), 55 (63), and 41 (43).

Anal. Calcd for $C_{14}H_{22}O$: C, 81.50; H, 10.75. Found: C, 81.23; H, 10.68.

A portion of material from the mother liquors was also subjected to a short-path distillation to separate the bulk of the norcarane **22**. The residue (1.64 g) from the distillation was chromatographed on 100 g of alumina (activity grade III) with mixtures of hexane and Et_2O as the eluent. From ir and nmr analysis of the various fractions we conclude that the major component in the mixture is the enedione **23**. The latter fractions from the chromatograph contained small amounts of material with ir and nmr spectra corresponding to the triketone **27** and the subsequently described tetramer.

In comparable decompositions of the diazo ketone **21** in cyclohexene, catalyzed by the heterogeneous catalysts CuO or CuI, the major volatile product (glpc) was the norcarane **22**. To obtain the products from reaction of the diazo ketone **21** with $(n\text{-}Bu_2S)CuI$ a cold (5°) solution of 2.158 g (14.2 mmol) of the diazo ketone **21** in 60 ml of cyclohexane was treated with 7.021 g (14.5 mmol) of $(n\text{-}Bu_2S)_2CuI$ and the resulting solution was allowed to warm slowly. Evolution of N_2 began at about 7° and continued for 10 min, during which time the color of the solution changed from pale yellow to brown; ir analysis indicated that the reaction was complete after 30 min. The reaction solution was diluted with pentane, washed with aqueous NH_4Cl and NH_3, dried, and concentrated. The residual liquid (5.87 g) contained (glpc and tlc) $n\text{-}Bu_2S$, the keto thioether **26**, and the cyclopropane **27** as well as a number of minor unidentified components. Chromatography on 102 g of alumina (activity grade III) separated 0.26 g of the crude sulfide **26** and 0.36 g of the crude cyclopropane **27**, mp 80–110°. A collected (glpc, silicone gum, SE-52, on Chromosorb P) sample of the **keto sulfide 26** was obtained as a colorless liquid: $n^{25}D$ 1.4915; ir (CCl_4) 1705 cm^{-1} (C=O); uv max (95% EtOH) 214 mμ (ϵ 720), 245.5 (449), and 305 (285); nmr (CCl_4) δ 3.16 (2 H, s, $COCH_2S$) and 0.8–3.0 (20 H, m, aliphatic CH); nmr [CCl_4 + $Eu(DPM)_3$] δ 8.02 (2 H, s, $COCH_2S$), 6.77 (1 H, m, CHCO), 5.16 (2 H, t, J = 7.0 Hz, CH_2S), 4.6–5.0 (4 H, m, CH_2), 2.1–2.9 (6 H, m, CH_2), 1.1–1.8 (2 H, m, CH_2), and 0.83 (3 H, t, J = 6.5 Hz, CH_3); mass spectrum *m/e* (rel intensity) 214 (2, M^+), 83 (100), 61 (24), 55 (69), 41 (66), and 39 (21).

Anal. Calcd for $C_{12}H_{22}OS$: C, 67.23; H, 10.34. Found: C, 67.50; H, 10.42.

Crystallization of the crude cyclopropane from hexane afforded the pure **triketone 27** as white needles: mp 111–112°; ir (CCl_4) 1715 (shoulder) and 1695 cm^{-1} (C=O); uv max (95% EtOH) 289 mμ (ϵ 177); nmr ($CDCl_3$) δ 2.89 (1 H, t, J = 5.5 Hz, CHCO), 2.50 (2 H, d, J = 5.5 Hz, CHCO), and 0.9–2.6 (33 H, m, aliphatic CH); nmr [CCl_4 + $Eu(DPM)_3$] δ 3.88 (1 H, t, J = 5.5 Hz, trans COCH), 3.48 (2 H, d, J = 5.5 Hz, cis COCH), and 0.8–3.0 (33 H, m, aliphatic CH); mass spectrum *m/e* (rel intensity), 372 (1, M^+), 289 (26), 95 (21), 83 (97), 55 (100), 41 (63), and 39 (19).

Anal. Calcd for $C_{24}H_{36}O_3$: C, 77.37; H, 9.74. Found: C, 77.10; H, 9.62.

The mother liquors remaining after crystallization of the triketone **27** were subjected to a series of fractional crystallizations from hexane to separate 33.4 mg of a **tetramer** as white needles: mp 159–160° (recrystallization raised the melting point to 161–162°); ir (CCl_4) 1762 (strong) and 1710 cm^{-1} (medium); uv max (95% EtOH) 214 mμ (ϵ 25,000) and 289 (110); nmr ($CDCl_3$) δ 7.06 (1 H, s), 4.08 (1 H, m), and 0.6–2.9 (*ca.* 46 H, m); mass spectrum *m/e* (rel intensity) 496 (6, M^+), 413 (10), 312 (15), 249 (12), 248 (10), 247 (30), 111 (23), 83 (100), 55 (66), and 41 (37).

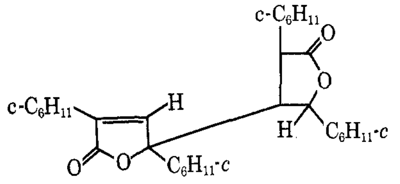
Anal. Calcd for $C_{32}H_{48}O_4$: C, 77.37; H, 9.74. Found: C, 77.56; H, 9.90.

These data and earlier investigations of the products from the thermal or photolytic decomposition of α-diazo ketones[15d,39] suggest that our tetramer may have the structure **37**. Our uv data are consistent with the value [λ_{max} 212 mμ (ϵ 11,300)] reported[39a] for conjugated lactone **38** and our nmr data indicate the presence of one vinyl CH and one >CHO function. Relatively abundant fragments in the mass spectrum at *m/e* 249 and 247 are compatible with the fragmentation of the molecular ion from **37** to form **39** and **40**, and such a fragmentation process is supported by the presence of a metastable ion at *m/e* 125.0 (calcd $249^2/496$ = 125.0). The presence of strong ir absorption

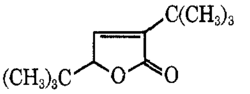
---

[38] H. Musso and U. Biethan, *Chem. Ber.*, **97**, 2282 (1964).

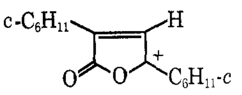
[39] (a) K. B. Wiberg and T. W. Hutton, *J. Amer. Chem. Soc.*, **76**, 5367 (1954); (b) P. Yates and T. J. Clark, *Tetrahedron Lett.*, 435 (1961); (c) R. Huisgen, H. König, G. Binsch, and H. J. Sturm, *Angew. Chem.*, **73**, 368 (1961).



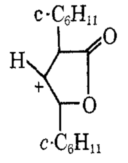
37



38



39 (*m/e* 247)



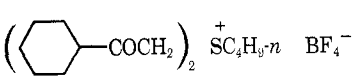
40 (*m/e* 249)

at 1762 cm^{-1} is also consistent with the presence of a γ-lactone and an α,β-unsaturated γ-lactone;[40] it is not clear whether or not the medium-intensity peak at 1710 cm^{-1} in the ir should be attributed to Fermi resonance.[41]

In a similar experiment, a cold ($-15°$) solution of 0.28 mmol of the diazo ketone **21** and 0.34 mmol of $(n\text{-Bu}_2\text{S})_2\text{CuI}$ in a mixture of 0.50 ml of pentane and 0.15 ml of tetramethylsilane was placed in an nmr probe and the temperature of the solution was slowly raised to 0°. Comparable observations were made with separate solutions of the diazo ketone **21** and the $(n\text{-Bu}_2\text{S})_2$-CuI. The nmr singlet at δ 5.39 (at $-15°$) [δ 5.26 at 0°], attributable to the grouping COCHN_2, and the triplet (J = 7 Hz) at δ 2.53, attributable to the CH_2S grouping, were essentially the same in solutions of the separate components and the mixture. The diazo ketone signal at δ 5.26 was observed to diminish slowly and disappear as the solution was allowed to stand at 0°, but no new low-field nmr signal was observed during this period.

To obtain an authentic sample of the keto thioether **26**, a solution of 1.37 g (8.9 mmol) of the crude diazo ketone **21** in 10 ml of n-BuSH was treated dropwise with $\text{BF}_3\text{–OEt}_2$ until gas evolution was no longer observed. The resulting mixture was concentrated and then partitioned between pentane and H_2O. After separation of an insoluble product (143 mg, mp 113–118°), the pentane solution was dried, concentrated, and distilled (0.5 mm and 50–80° bath) to separate 703 mg of liquid which contained (glpc) the keto thioether **26** and a number of other unidentified components. A collected (glpc) sample of the keto sulfide **26** was identified with the previously described sample by comparison of glpc retention times and ir spectra.

The pentane-insoluble product from this reaction was recrystallized from an acetone–pentane mixture to separate a product, believed to be the sulfonium salt **41**, as colorless needles:



$$\left(\text{C}_6\text{H}_{11}\text{–COCH}_2\right)_2\overset{+}{\text{S}}\text{C}_4\text{H}_9\text{-}n\quad\text{BF}_4^-$$

41

mp 123–124°; ir (CHCl_3) 1705 cm^{-1} (C=O); uv max (95% EtOH) 231 mμ (ϵ 349) and 275 (172); nmr (CDCl_3) δ 4.77 (4 H, s, COCH_2S), 3.37 (2 H, t, J = 7 Hz, CH_2S), and 0.8–3.1 (29 H, m, aliphatic CH).

Anal. Calcd for $\text{C}_{20}\text{H}_{35}\text{BF}_4\text{O}_2\text{S}$: C, 56.35; H, 8.27. Found: C, 56.07; H, 8.41.

The quantitative data summarized in eq M were obtained by dissolving the appropriate amounts of the diazo ketone **21**, the catalyst, $(n\text{-Bu}_2\text{S})_2\text{CuI}$, and a weighed amount of n-hexadecane (an internal standard) in either 35.0 ml of cyclohexene or a mixture of 5.0 ml of cyclohexene and 0.50 ml of 1,2-dimethoxyethane. The resulting solutions were warmed until decomposition began (*ca.* 7°) and allowed to stand at this temperature until all the diazo ketone **21** was consumed (ir analysis). The resulting solutions were then diluted with pentane, washed with aqueous NH_4Cl and NH_3, dried, concentrated, and analyzed (glpc, silicone gum, SE-52, on Chromosorb P, programmed temperature rise 5 deg/min from 90 to 230°). On the glpc column employed the retention times were: $n\text{-Bu}_2\text{S}$, 7.2 min; n-hexadecane, 22.9 min; the keto sulfide **26**, 24.9 min; a minor component believed to be the epimer of ketone **22**, 25.8 min; the ketone **22**, 26.8 min; the enedione **23**, 35.7 min. With the glpc equipment used the triketone **27** was not eluted. Collected (glpc) samples of the products **22**, **23**, and **26** were identified with authentic samples by comparison of glpc retention times and ir spectra, and the glpc equipment was calibrated with known mixtures of authentic samples.

Treatment of the Lithium α-Chloroenolates with a Copper(I) Complex. A. The Chloroenolate 16.—A solution of the lithium enolate **16** was prepared by adding a solution of 4.7 mmol of MeLi in 3.0 ml of Et_2O to 1.06 g (4.7 mmol) of the silyl enol ether **14**. After the ethereal solution had been stirred at 25° for 1 hr, it exhibited nmr absorption at δ 7.0–8.0 (5 H, m, aryl CH) and 5.58 (1 H, s, vinyl CH). For comparison, a solution containing 20 mmol of the lithium enolate of acetophenone (from α-trimethylsiloxystyrene) in 22 ml of Et_2O exhibited nmr peaks at δ 7.0–8.0 (5 H, m, aryl CH), 4.42 (1 H, s, vinyl CH), and 4.16 (1 H, s, vinyl CH). In a similar experiment, a cold ($-16°$), ethereal solution containing 4.7 mmol of the lithium chloroenolate was treated with 2.24 g (4.7 mmol) of $(n\text{-Bu}_2\text{S})_2\text{CuI}$ and then centrifuged to remove a small amount of yellow precipitate (presumably MeCu). The nmr spectrum of the supernatant liquid was essentially identical with the previously described lithium chloroenolate spectrum except for the presence of additional multiplets at δ 2.5–2.8 and 1.3–1.9 attributable to the protons of Bu_2S. A similar solution was refluxed for 6 hr, allowed to stand at 25° for 12 hr, and then partitioned between benzene and an aqueous solution of NH_4Cl and NH_3. Analysis (glpc, silicone gum, SE-52, on Chromosorb P) of the benzene solution indicated the presence of $n\text{-Bu}_2\text{S}$ (retention time 3.2 min), the chloro ketone **13** (7.2 min), and a small amount of the silyl enol ether **14** (10.4 min); no peak was observed corresponding to 1,2-dibenzoylethylene **20** (28.4 min). A collected sample of the chloro ketone **13** was identified with an authentic sample by comparison of ir spectra and glpc retention times.

B. The Chloroenolate 8.—A solution of the lithium enolate **8**, prepared from 2.0 mmol of MeLi and 451 mg (1.94 mmol) of the silyl enol ether **12** in 0.5 ml of 1,2-dimethoxyethane, was cooled to $-55°$ and then treated successively with 5.0 ml (48 mmol) of cyclohexene, 196 mg of n-hexadecane (an internal standard), and 762 mg (1.58 mmol) of $(n\text{-Bu}_2\text{S}_2\text{CuI}$. The resulting solution was warmed to 22° and stirred for 20 min, during which time the reaction solution darkened and a black solid separated. The reaction mixture was partitioned between pentane and an aqueous solution of NH_4Cl and NH_3. After the pentane extract had been dried and concentrated, analysis (glpc, silicone gum, SE-52, on Chromosorb P) indicated the presence of $n\text{-Bu}_2\text{S}$ (retention time 7.2 min), the chloro ketone **7** (100% yield, 11.4 min), n-hexadecane (22.1 min), and a very small unidentified peak (16.2 min); no peaks were observed corresponding to the cyclopropyl ketone **22** (25.8 min) or the enedione **23** (37.1 min). A collected (glpc) sample of the chloro ketone product **7** was identified with an authentic sample by comparison of ir spectra and glpc retention times.

A comparable experiment was performed with the lithium enolate **8** [from 2.0 mmol of MeLi and 436 mg (1.88 mmol) of the silyl enol ether **12**], 0.5 ml of 1,2-dimethoxyethane, 5.0 ml (48 mmol) of cyclohexene, and 44 mg (0.09 mmol) of $(n\text{-Bu}_2\text{S})\text{CuI}$. The resulting solution was warmed to 25° and stirred; aliquots were removed periodically and subjected to the previously described isolation and analysis procedures. After 20 min, the yield of chloro ketone **7** was quantitative; after 140 min the yield of chloro ketone **7** was 72% and a minor unidentified component was detected (retention time 18.8 min), but no peaks were present corresponding to the cyclopropyl ketone **22** or the enedione **23**. A number of similar experiments with various copper(I) salts and various reaction and isolation conditions give comparable results.

Preparation of the α-Chloro-α-mercuri Ketone 35.—A mixture of 2.7 g (12.5 mmol) of HgO, 0.1 g (0.3 mmol) of Hg(OAc)_2, 5.8 g (25 mmol) of the silyl enol ether **12**, 1 ml of H_2O, and 5 ml of EtOH was warmed on a steam bath with mixing for 30 min. After the resulting white solid had been dissolved in 700 ml of boiling tetrahydrofuran and filtered, the filtrate was allowed to

---

[40] R. N. Jones, C. L. Angell, T. Ito, and R. J. D. Smith, *Can. J. Chem.*, **37**, 2007 (1959).

[41] C. L. Angell, P. J. Krueger, R. Lauzon, L. C. Leitch, K. Noack, R. J. D. Smith, and R. N. Jones, *Spectrochim. Acta*, **15**, 926 (1959).

stand in the cold. The bisketo mercurial **35** separated as 1.8 g (28%) of white solid, mp 230–232° dec, ir (Nujol) 1665 cm^{-1} (C=O). We were unsuccessful in obtaining other spectra for this substance because of its insolubility.

Anal. Calcd for $C_{16}H_{24}Cl_2HgO_2$: C, 36.96; H, 4.56; Cl, 13.64; Hg, 38.59. Found: C, 37.21; H, 4.67; Cl, 13.66; Hg, 38.85.

When a sample of the mercurial **35** was thermally decomposed in a sealed melting point tube, the volatile liquid which distilled from the decomposing sample was collected and identified with an authentic sample of the chloro ketone **7** by comparison of ir spectra. No evidence of decomposition was observed when a slurry of the mercurial **35** in cyclohexene was refluxed for 6 hr. After the reaction mixture had been partitioned between pentane and an aqueous solution of NH_4Cl, KI, and HCl, the calculated yield (glpc analysis) of the chloro ketone **7** was quantitative. The reaction of this bisketo mercurial **35** with excess AcCl yielded a mixture of products containing (glpc, Apiezon L on Chromosorb P) primarily the enol acetate **9** accompanied by lesser amounts of the chloro ketone **7** and several unidentified components. A collected (glpc) sample of this product **9** was identified with an authentic sample by comparison of ir spectra and glpc retention times.

Registry No.—**4**, 31151-32-3; **7**, 1892-09-7; **9**, 311180-45-7; **10**, 31151-34-5; **11**, 31180-46-8; **12**, 31151-35-6; **14**, 31151-36-7; **15**, 31151-37-8; **17**, 3282-32-4; **18**, 31152-14-4; **19**, 31151-39-0; **20**, 959-27-3; **21**, 31151-40-3; **22**, 31152-16-6; **23**, 31152-17-7; **24c** acid, 21448-77-1; **26**, 31151-41-4; **27**, 31152-19-9; **35**, 31151-42-5; **37**, 31151-43-6; **41**, 31152-20-2.

Conformational Analysis. LXXVI. The Perhydrodurenes[1-3]

NORMAN L. ALLINGER*[4] AND NICHOLAS A. PAMPHILIS

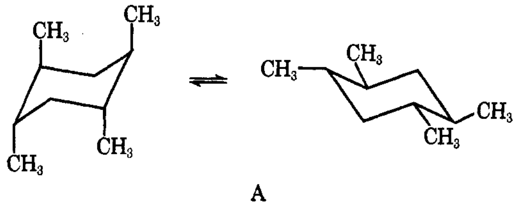
Departments of Chemistry, Wayne State University, Detroit, Michigan 48202, and
University of Georgia, Athens, Georgia 30601

Received December 11, 1970

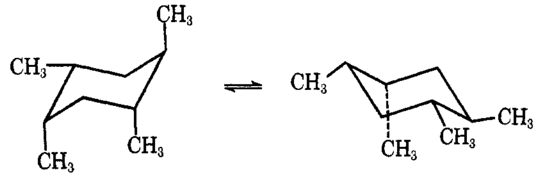
The five stereoisomeric perhydrodurenes (1,2,4,5-tetramethylcyclohexanes) have been prepared and equilibrated over palladium at elevated temperatures, and the thermodynamic quantities for the equilibria have been established. Nmr spectra of the compounds have been recorded, and structures have been assigned for each isomer.

While mono- and disubstituted cyclohexane rings have been extensively studied from the conformational point of view,[5] more highly substituted rings have been rarely examined.[6] It is known that with simple molecules conformational energies in general tend to be additive quantities; so with certain exceptions it is possible to determine *a priori* the relative energies of substituted cyclohexane systems. The present paper is concerned with extending this study experimentally to more complicated systems, specifically to the 1,2,4,5-tetramethylcyclohexane system. This particular ring system was chosen because it is reasonably typical of a polymethylated cyclohexane, there are five stereoisomers which can be individually examined, and each of them has a different energy. Thus it should be possible to assign unambiguously the structures of the isomers by studying the equilibrium between them. Finally, none of the energies is so high that it should not be possible to isolate all of the isomers from equilibrations at elevated temperatures.

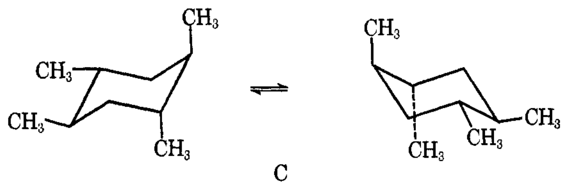
The five isomers can be given the letters A–E for convenience of discussion. Each of these isomers is in principle an equilibrium mixture of two chair conformations, together with what is assumed to be a minor amount of boat forms. Thus, for isomer A, all of the methyl groups are equatorial, or they are all axial. For isomer B, one methyl is axial and the rest equatorial, or vice versa. Isomer C has two methyls equatorial and two axial, and the two conformations are superimposable mirror images. For isomer D, again two methyls are axial and two are equatorial in each conformation, and the conformations are in fact superimposable. For isomer E, again there are two conformations which are superimposable, each contains two axial and two equatorial methyl groups.



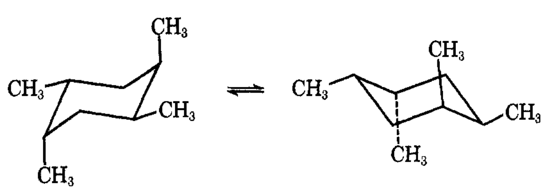
A



B



C



D

---

[1] Paper LXXV: N. L. Allinger and J. C. Graham, *J. Org. Chem.*, **36**, 1688 (1971).

[2] Supported in part by Grant GP-15263 from the National Science Foundation.

[3] Abstracted from the Ph.D. dissertation of N.A.P., submitted to Wayne State University, May 1970.

[4] Correspondence concerning this paper should be addressed to this author at the University of Georgia, Athens, Ga. 30601.

[5] E. L. Eliel, N. L. Allinger, S. J. Angyal, and G. A. Morrison, "Conformational Analysis," Interscience–Wiley, New York, N. Y., 1965.

[6] C. J. Egan and W. C. Buss, *J. Phys. Chem.*, **63**, 1887 (1959).