Jarrousse,[6] from cyclohexanol and benzyl chloride in the presence of 55% sodium hydroxide and triethylamine at 50–55°. Yield of benzyl cyclohexyl ether, b.p. 164° (37 mm.), 141° (18 mm.), 132° (12 mm.), was 70%.

p-Xylyl bromide, b.p. 85–95° (4 mm.), m.p. 34–35° (needles from ethanol), was prepared in 44% yield by sunlight initiated bromination of *p*-xylene in carbon tetrachloride solution.

p-Xylyl cyclohexyl ether. Cyclohexanol (10.0 g., 0.1 mole) was added to a stirred mixture of 25 ml. of absolute ether and 3.9 g. (0.1 mole) of sodamide. Then 18.5 g. (0.1 mole) of *p*-xylyl bromide was added dropwise. The reaction was stirred in an oil bath at 70° for 21 hr. Then water was added to dissolve the sodium salt and the organic layer was extracted with ether. The ether layer was washed with water, dried with magnesium sulfate, and distilled. *p*-Xylyl cyclohexyl ether, b.p. 114° (4 mm.), was obtained in 44% yield.

Anal. Calcd. for $C_{14}H_{20}O$: C, 82.28; H, 9.87. Found: C, 79.92; H, 9.60.

4-Phenyl benzyl alcohol was made from 4-bromodiphenyl by the Grignard reaction.[7]

4-Chloromethyl diphenyl was made from the alcohol and thionyl chloride.[7]

p-Phenylbenzyl cyclohexyl ether, b.p. 160–167° (5 mm.), m.p. 84–86° (colorless plates from ethanol), was made by two methods. It was made from cyclohexanol and 4-chloromethyl diphenyl in 41% yield by the method described above for *p*-xylyl cyclohexyl ether: and it was made in 47% yield by the method of Jarrousse[6] described above for benzyl cyclohexyl ether.

1-Chloromethyl naphthalene was made by the method of Coles and Dodds.[8] *α-Naphthylmethanol* was made in 75% yield by hydrolysis of 1-chloromethylnaphthalene and in 45% yield by the Grignard reaction *via* alpha-bromonaphthalene according to Bourquelot and Bridel.[9] *α-Naphthylmethyl acetate*, b.p. 142–143° (4 mm.), 172–173° (13 mm.), was made in 24% yield by direct reaction of acetyl chloride with the alcohol. Acetic anhydride would not react with α-naphthylmethanol in the absence of a catalyst; and in the presence of sulfuric acid only polymeric products could be obtained.

Anal. Calcd. for $C_{13}H_{12}O_2$: C, 77.92; H, 6.04. Found: C, 76.94; H, 6.13.

α-Naphthylmethyl cyclohexyl ether was made in 27% yield from the chloride and cyclohexanol by the method of Jarrousse[4] described above for benzyl cyclohexyl ether. The compound is described in the literature[10] as a liquid, b.p. 165–166° (0.8 mm.). It was found in this work to be a solid, m.p. 40–41.5° (needles from ethanol), b.p. 176–177° (6 mm.).

Anal. Calcd. for $C_{17}H_{20}O$: C, 84.89; H, 8.39; M. W. 240.2. Found: C, 84.64; H, 8.21; M. W. 244.0.

---

(6) J. Jarrousse, *Compt. rend.*, 232, 1424 (1951).

(7) S. Goldschmidt, P. Modderman, and G. A. Overbeek, *Rec. trav. chim.*, 69, 1109 (1950).

(8) H. W. Coles and M. L. Dodds, *J. Am. Chem. Soc.*, 60, 853 (1938).

(9) E. Bourquelot and M. Bridel, *Compt. rend.*, 168, 323 (1919).

(10) W. Kruyt and H. Veldstra, *Landbouwk. Tijdschr.*, 63, 398 (1951); *Chem. Abstr.*, 55, 7287 (1951).

AMHERST, MASS.

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

Heterocyclic Vinyl Ethers. XIII. The Reaction of 2,5-Diphenyl-1,4-dithiadiene with *n*-Butyllithium and Dimethyl Sulfate[1]

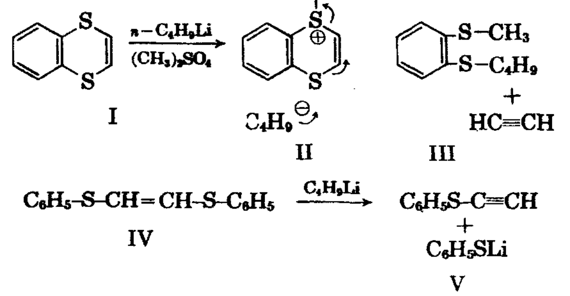
WILLIAM E. PARHAM AND MILLS T. KNELLER[2]

Received May 12, 1958

2,5-Diphenyl-1,4-dithiadiene (VI) does not react appreciably with *n*-butyllithium in ether at 0°; however, when dimethyl sulfate is present a substitution-elimination reaction occurs leading to phenylacetylene and the sulfides VIII and IX. VIII was shown to be a major component of the mixed sulfides, by alkaline hydrolysis of the corresponding crude sulfone to benzyl *n*-butyl sulfone (XII). It appears that the cleavage of the dithiadiene ring to acetylenes and alicyclic ethylenic sulfides is a general reaction, for both VI and benzo-1,4-dithiadiene (I) react similarly, and in a manner different from their open chain analogs.

The reaction of the ethylenic sulfides VIII and IX with phenyllithium was studied, and cleavage of the expected acetylenic sulfides to phenylacetylene was observed.

It has been previously shown that benzo-1,4-dithiadiene (I) does not undergo appreciable metalation by reaction with butyllithium in ether at 0°. However, when such reaction mixtures are treated with alkylating agents, a substitution-elimination reaction occurs (II), leading to the formation of acetylene and sulfides such as III. The open chain analogs of I, *cis* or *trans* bis-(phenylmercapto)-ethylene (IV), on the other hand, react rapidly with butyllithium in ether at 0° to give high yields of phenylmercaptoacetylene and lithium thiophenolate. The presence of dimethyl sulfate



$$C_6H_5{-}S{-}CH{=}CH{-}S{-}C_6H_5 \xrightarrow{C_4H_9Li} C_6H_5S{-}C{\equiv}CH + C_6H_5SLi$$

---

(1) This work was supported by the office of Ordnance Research, U. S. Army, Contract No. DA-11-022-Ord-2616.

(2) From the M.S. Thesis of M. T. Kneller, University of Minnesota, 1958.

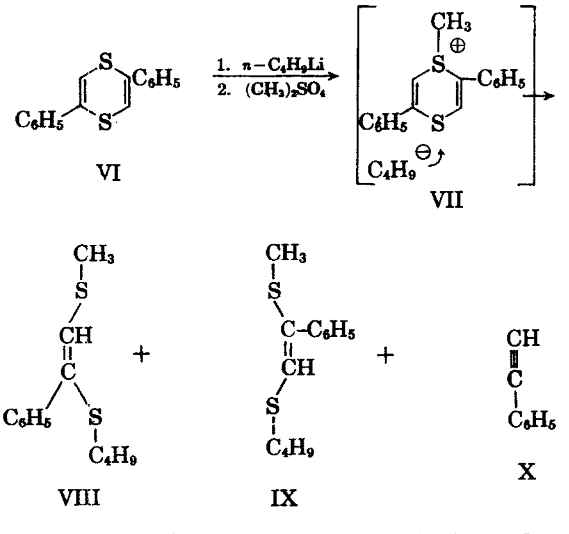
(3) W. E. Parham and Paul L. Stright, *J. Am. Chem. Soc.*, 78, 4783 (1956).

does not alter the course of this reaction, but does lead to methylated derivatives of phenylacetylene and thiophenol.

We were interested in extending our knowledge of the cleavage of dithiadienes, and their open chain analogs, and have accordingly completed a study of the reaction of 2,5-diphenyl-1,4-dithiadiene (VI), and products derived from VI, with organolithium derivatives. These reactions were studied both in the presence and absence of alkylating agents, and the results are described in this report.

The initial study concerned the reaction of 2,5-diphenyl-1,4-dithiadiene (VI) with *n*-butyllithium. The conditions employed were essentially identical to those previously reported for the conversion of IV to V. Only a small evolution of gas, presumably butane, was observed over a 2.5-hr. period. Water was then added to decompose the organometallic reagents, and the organic products were processed by chromatography and distillation. There was obtained an 87% recovery of 2,5-diphenyl-1,4-dithiadiene. The relatively small amount of butane liberated, together with the high recovery of 2,5-diphenyl-1,4-dithiadiene, suggested that very little reaction had occurred. Thus, under these conditions VI behaves in a manner analogous to I, but not to IV.

The reaction of 2,5-diphenyl-1,4-dithiadiene with butyllithium was then carried out in the presence of dimethyl sulfate. The procedure used was similar to that previously described for I. As judged by spectral data, boiling points, and refractive index a number of products were formed in the reaction; however, two principal products were characterized.

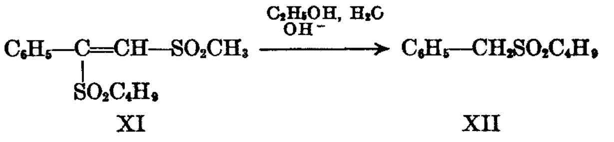


The infrared spectrum of the lower boiling liquids showed strong absorption at 3315 cm.$^{-1}$ and 2105 cm.$^{-1}$, typical of the terminal acetylenic group. The presence of phenylacetylene in these products was positively established by their conversion into mercury phenylacetylide. The product was identified by comparison of melting points, mixed melting points, and infrared spectrum of the derivative with authentic mercury phenylacetylide. The amount of derivative obtained corresponded to a 33% yield of phenylacetylene (X). In addition, small fractions with intermediate boiling points showed absorption at 2160 cm.$^{-1}$ typical of non-terminal acetylene. Although these products were not identified, they were most probably methylphenylacetylene and/or sulfides such as XIII.

The principal organic product, obtained in consistent yields of 60–71%, was a high boiling yellow oil (b.p. 114–115°/0.3 mm., n_D^{25} 1.6042). This material had the empirical formula $C_{13}H_{18}S_2$, which was consistent with the two probable sulfides VIII and IX.

The formation of VIII and/or IX, together with phenylacetylene, from 2,5-diphenyl-1,4-dithiadiene, established the general course of reaction to be that shown in the above equation. Thus, diaryldithiadienes react with *n*-butyllithium and dimethyl sulfate in a manner analogous to that previously observed for benzo-1,4-dithiadeine (I).

There remained the problem of determining the structure of the sulfide VIII and/or IX. It can be seen that the elimination of phenylacetylene from VII can occur in either of two ways, leading to VIII or IX. Distillation of various samples of this material gave relatively narrow ranges of boiling point and refractive index (n_D^{25} 1.6029–1.6059), and the infrared spectra of these samples were essentially identical. These results suggested that the product was homogeneous. However, the product failed to give a solid sulfone, or sulfilimine, and vapor phase chromatography suggested the possibility of four components. Assuming that no decomposition occurred during the chromatography, then the four components are considered to be the *cis* and *trans* isomers of VIII and IX.[4] That the crude sulfide was composed principally of VIII, (*cis* and/or *trans*) was shown by alkaline hydrolysis of the crude sulfone. *n*-Butyl benzyl sulfone (XII) was obtained in 51% yield. The yield of crude XII was 84%; there was no evidence for the presence of appreciable quantities of benzylmethyl sulfone, which would result from hydrolysis of the sulfone of IX.

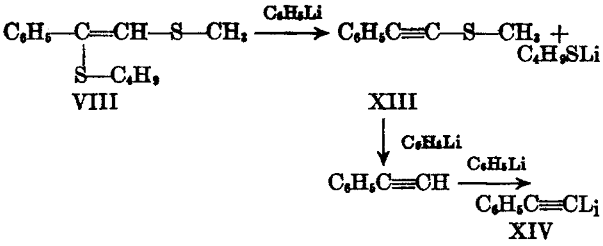


$$\underset{\text{XI}}{C_6H_5-\underset{\underset{SO_2C_4H_9}{|}}{C}=CH-SO_2CH_3} \xrightarrow[OH^-]{C_2H_5OH,\ H_2O} \underset{\text{XII}}{C_6H_5-CH_2SO_2C_4H_9}$$

---

[4] The *cis* isomers of VIII and/or IX should be formed in the reaction; however, the oils were processed by distillation. We have shown that partial or complete isomerization of related bis-sulfides occurs upon vacuum distillation [unpublished work, see also W. E. Truce and R. J. McManimie, *J. Am. Chem. Soc.*, **76**, 5745 (1954); W. E. Parham and I. Heberling, *J. Am. Chem. Soc.*, **77**, 1175 (1955)].

The reaction of VIII[5] with one equivalent of phenyllithium was also investigated. It was hoped that the principal acetylenic sulfide that resulted



$$C_6H_5{-}\underset{\substack{|\\ S{-}C_4H_9}}{C}{=}CH{-}S{-}CH_3 \xrightarrow{C_6H_5Li} C_6H_5C{\equiv}C{-}S{-}CH_3 + C_4H_9SLi$$

VIII XIII

$$C_6H_5C{\equiv}C{-}S{-}CH_3 \xrightarrow{C_6H_5Li} C_6H_5C{\equiv}CH \xrightarrow{C_6H_5Li} C_6H_5C{\equiv}CLi$$

XIV

would establish whether the elimination reaction (IV–V or VIII–XIII) was occurring by: metalation with subsequent *beta* elimination of mercaptide, or metalation with subsequent α-elimination and rearrangement,[6] of the resulting carbene. There was obtained instead a 31% recovery of starting sulfide, a 35% yield of phenylacetylene, and only relatively small amounts of material boiling in an intermediate range. Some non-terminal acetylenes (infrared absorption at 2160 cm.$^{-1}$), presumably XIII and the corresponding butyl derivative, were present in the latter materials; however, they were present in such small amounts that their identification was considered to be of no significance. A 35% yield of phenylacetylene could account for 70% of the starting phenyllithium (VIII→XIV). It is probable, therefore, that the intermediate mercaptoacetylene (XIII) reacts at a comparable, or even faster, rate with phenyllithuim than does the starting sulfide VIII. These results suggest that the synthesis of substituted mercaptoacetylenes, by elimination of mercaptan from bis-substituted mercaptoethylenes, may prove generally unsatisfactory unless terminal acetylenes, such as V, result. The recent report by Truce, and his coworkers, of the cleavage of XV to XVI,[7] by reaction with *n*-butyllithium, suggest that there may be a considerable difference between butyllithium and phenyllithium in these reactions. This possibility will be the subject of further study.

$$\underset{XV}{(ArS)_2C{=}CHSAr} \xrightarrow{C_4H_9Li} \underset{XVI}{ArSC{\equiv}CSAr}$$

EXPERIMENTAL

The reaction of butyllithium with 2,5-diphenyl-1,4-dithiadiene in the absence of alkylating agent. 2,5-Diphenyl-1,4-dithiadiene[8] (5.36 g., 0.02 mole), in benzene (35 ml.), was added to a cold (−5°) solution of butyllithium[9] (from 1.07 g., 0.15 g.-atom of lithium) in ether (41 ml.). The mixture was stirred for 2.5 hr.; however, only a small evolution of gas was noted. Water (30 ml.) was added, and 7.8 g. of oil was isolated from the dry ($MgSO_4$) ethereal solution. This oil was chromatographed on a column of Alcoa alumina (300 g.), using petroleum ether and petroleum ether–benzene as eluant. There was recovered 4.68 g. of VI (m.p. 114–118°, 87% recovery); mixture melting point with authentic VI (m.p. 116–117°) was 114–117°.

The reaction of 2,5-diphenyl-1,4-dithiadiene (VI) *with butyllithium and dimethyl sulfate.* A solution of VI (13.8 g., 0.0052 mole), in dry benzene (120 ml.), was added dropwise to a solution of butyllithium[9] (from 35.4 g., 0.258 mole, of butyl bromide) in ether (155 ml.). An atmosphere of nitrogen was maintained, and the reaction temperature was maintained at −10°, with stirring, for 2 hr. Dimethyl sulfate (39 g., 0.31 mole), in ether (39 ml.), was added over a 23-min. period; the reaction temperature rose to 0°, even with external cooling. The resulting mixture was allowed to warm to room temperature (3.5 hr.), then water (210 ml.) was added. The ethereal solution was dried ($MgSO_4$), and concentrated and the resulting yellow-brown oil (19.2 g.) was distilled. The principal product 8.80 g. (71.5% yield) was collected at 117–121°/0.45 mm.; n_D^{26} 1.6059.

Anal. Calcd. for $C_{13}H_{18}S_2$: C, 65.49; H, 7.61; S, 26.90; M.W., 238.4. Found: C, 65.73; H, 7.56; S, 27.29; M.W. (freezing point, benzene), 223.

This procedure was repeated several times with minor variations; the yield of high boiling product varied between 64 and 71%.

Lower boiling fractions, collected between 25°/135 mm. and 77°/0.3 mm., contained terminal acetylene (infrared absorption at 3315 cm.$^{-1}$ and 2105 cm.$^{-1}$) and non-terminal acetylene (infrared absorption at 2180 cm.$^{-1}$).

The amount of phenylacetylene present was estimated by the conversion of X, in the lower boiling fractions with boiling point close to that of phenylacetylene, to mercury phenylacetylide. The procedure used was that previously reported[10] by J. R. Johnson and W. L. McEwen; the yield of derivative (m.p. 126–127°) was 90% when authentic phenylacetylene was employed. The amount of mercury phenylacetylide (m.p. 125–126°, mixture m.p. 125–126°) obtained from the lower boiling fractions corresponded to 33% of the theoretical yield of phenylacetylene.

Oxidation of VIII *and/or* IX *with hydrogen peroxide. Alkaline hydrolysis of the product.* Hydrogen peroxide (30%, 13 ml.) was added in three portions, at 20-min. intervals, to a solution of VIII and/or IX (1.02 g., 0.0043 mole) in glacial acetic acid (16 ml.). The mixture was heated at the reflux temperature for 1 hr., and was then cooled and diluted with water (20 ml.). The *p*H of the solution was adjusted to 8 by the addition of solid sodium bicarbonate; the resulting solution was saturated with sodium chloride, extracted with ether (150 ml.), and then with methylene chloride (150 ml.). The combined organic extract was dried and concentrated, affording 0.95 g. of viscous oil.

The crude sulfone (0.95 g., 0.003 mole calcd. as XI) was dissolved in a solution prepared from ethanol (10 ml.) and 3*N* potassium hydroxide (10 ml.). The resulting mixture was heated for 5 hr. at the reflux temperature under a nitrogen atmosphere. The resulting mixture was cooled, and the resulting solid (0.47 g., 84% calcd. as XII) was collected and recrystallized from petroleum ether. There was obtained 0.34 g. (51% yield) of benzyl *n*-butyl sulfone melting at 96–

---

[5] VIII was obviously contaminated with IX; however, this fact does not obviate the ensuing argument.

[6] *Cf.* D. Y. Curtin, E. E. Harris, *J. Am. Chem. Soc.*, **73**, 2716, 4519 (1951); S. J. Cristol, R. F. Helmreich, *J. Am. Chem. Soc.*, **77**, 5034 (1955); A. Bothner-By, *J. Am. Chem. Soc.*, **77**, 3293 (1955), for discussion of related elimination reactions.

[7] W. E. Truce and R. Kassinger (paper presented before the Organic Division of the American Chemical Society, San Francisco, April 1958.

[8] R. H. Barker and C. Barkenbus, *J. Am. Chem. Soc.*, **58**, 262 (1936).

[9] H. Gilman and J. W. Morton, Jr., *Org. Reactions*, *VI*, 295 (1954).

[10] J. R. Johnson and W. L. McEwen, *J. Am. Chem. Soc.*, **48**, 474 (1926).

98° (mixture melting point with authentic[11] benzyl *n*-butyl sulfone, m.p. 94°, was 96–97°).

The reaction of VIII *and* IX *with phenyl lithium.* The apparatus employed was a 100-ml. three-necked flask, fitted with a condenser, nitrogen inlet, stirrer, and dropping funnel. The sulfide VIII and IX (5.04 g., 0.0211 mole) was added dropwise (15 min.) to a solution of phenyllithium, prepared[12] from bromobenzene (3.65 g., 0.0232 mole, and lithium, 0.34 g., 0.049 g.-atom) in ether (20 ml.). The mixture was stirred in a nitrogen atmosphere for 3 hr. at room temperature. The precipitated salts (containing the lithium salt of methyl and *n*-butyl mercaptans) were removed by filtration and discarded. The ether layer was acidified with dilute hydrochloric acid, washed with water, and dried over $MgSO_4$, and concentrated. The residual oil was distilled, and there was obtained a low boiling fraction (1.24 g.) and a high boiling fraction (1.60 g., b.p. 99–108°/0.06 mm., n_D^{25} 1.603). The higher boiling fraction was identified by physical properties, and by infrared spectra, as nearly pure starting sulfide (31.7% recovery).

The lower boiling fraction was a mixture containing phenylacetylene (infrared absorption at 3315 cm.$^{-1}$ and 2100 cm.$^{-1}$), non-terminal acetylene (infrared absorption at 2160 cm.$^{-1}$), and other products. An attempt to resolve this material by distillation was not successful since the quantities of each component present, other than phenylacetylene, was relatively small.

The amount of phenylacetylene present was estimated by its conversion into mercury phenylacetylide. The amount of derivative isolated (m.p. 125–126°, mixture m.p. 125–126°) corresponded to a 35.3% yield of phenylacetylene. This is a minimum quantity since some phenylacetylene was undoubtedly lost during the distillation.

MINNEAPOLIS 14, MINN.

---

(11) J. Buchi, M. Prost, H. Eichenberger, and R. Liberherr, *Helv. Chim. Acta*, **35**, 1527 (1952).

(12) G. Wittig, *Newer Methods of Preparative Organic Chemistry*, Interscience Publishers, Inc., New York, N. Y., 1948, p. 576.

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

Formation of Carbenes from α-Haloesters[1]

WILLIAM E. PARHAM AND FREDERIC C. LOEW[2]

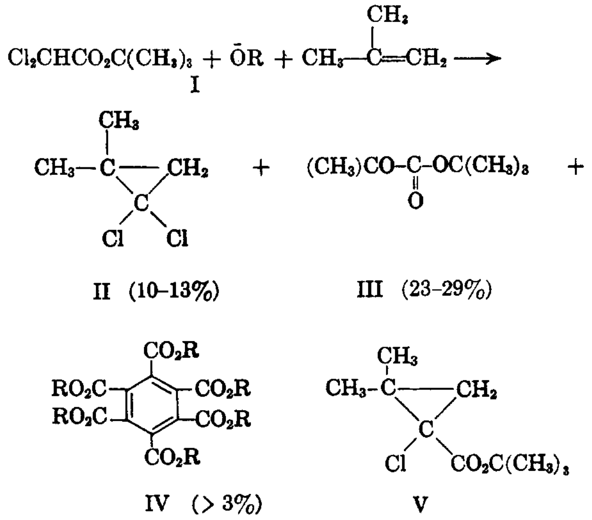
Received May 19, 1958

The reaction of butylate ion with the *t*-butyl esters of chloroacetic, dichloroacetic and trichloroacetic acid has been studied, and it has been shown that carbene intermediates result from the di- and tri-chloro esters. The reaction of *t*-butyl dichloroacetate with butylate ion, in the presence of isobutylene, results in the formation of 1,1-dichloro-2,2-dimethylcyclopropane (II), di-*t*-butyl carbonate (III) and hexa-*t*-butyl mellitate (IVa). The reaction of the trichloro ester, under similar conditions, affords di-*t*-butyl carbonate (III) and the cyclopropane II. Thus, under the conditions employed, both of these esters are converted into dichlorocarbene.

In a previous communication[3] we suggested that the reaction between esters of dichloroacetic acid and base might lead to carbenes. However, when indene was used as the carbene acceptor no products were obtained which could have been derived from chlorocarbalkoxy carbene. We have now made a study of the action of the *t*-butylate ion upon the *t*-butyl esters of chloroacetic, dichloroacetic, and trichloroacetic acid and have found that carbenes result from the last two.

The reaction of *t*-butyl dichloroacetate with *t*-butylate ion in the presence of isobutylene was first studied, and the products isolated were 1,1-dichloro-2,2-dimethylcyclopropane (II), *t*-butyl carbonate (III) and a neutral ester which has been shown to be hexa-*t*-butyl mellitate (IVa).

The isolation of 1,1-dichloro-2,2-dimethylcyclopropane (II) from the above reaction is convincing evidence for the formation of dichlorocarbene (VII) as an intermediate.[3–6] The formation of this car-



I

II (10–13%)

III (23–29%)

IV (> 3%)

V

(a) R = —$C(CH_3)_3$
(b) R = H
(c) RO = Cl
(d) R = CH_3

---

(1) This work was supported by a grant (NSF-G2163) from the National Science Foundation.

(2) Sinclair Refining Company Fellow, 1956–1957.

(3) W. E. Parham and R. R. Twelves, *J. Org. Chem.*, **22**, 730 (1957).

(4) (a) J. Hine, *J. Am. Chem. Soc.*, **72**, 2438 (1950); (b) J. Hine and A. M. Dowell, Jr., *J. Am. Chem. Soc.*, **76**, 2688 (1954); (c) J. Hine, P. C. Peek, Jr., and B. D. Oakes, *J. Am. Chem. Soc.*, **76**, 6162 (1954); (d) J. Hine, A. M. Dowell, Jr., and J. E. Singley, Jr., *J. Am. Chem. Soc.*, **78**, 479 (1956).

(5) (a) W. von E. Doering and A. K. Hoffmann, *J. Am. Chem. Soc.*, **76**, 6162 (1954); (b) W. von E. Doering and P. LaFlamme, *J. Am. Chem. Soc.*, **78**, 5448 (1956).