TABLE IV

MELTING POINTS OF POLYSUBSTITUTED BENZOPHENONES

Substituents	Mp, °C Obsd	Mp, °C Found
m-Cl-*p'*-CH_3O[a]	72.0–72.5	...
m-Cl-*p'*-CH_3	97.0–98.0	97–98[b]
m,*p'*-Cl_2	112.5–113.5	113[c]
m,*m*-Cl_2-*p'*-CH_3O[d]	117.0–118.0	...
m,*m*-Cl_2-*p'*-CH_3[e]	49.5–50.0	...
m,*m*-Cl_2	66.5–67.5	65[f]
m,*m*,*p'*-Cl_3[g]	80.5–81.3	...

[a] *Anal.* Calcd for $C_{14}H_{11}O_2Cl$: C, 68.16; H, 4.50; Cl, 14.37. Found: C, 68.38; H, 4.51; Cl, 14.25. [b] W. E. Bachman and J. W. Ferguson, *J. Am. Chem. Soc.*, **56**, 2081 (1934). [c] H. L. Haller, P. D. Bartlett, N. L. Drake, M. S. Newman, S. J. Cristol, C. M. Eaker, R. A. Hayes, G. W. Kilmer, B. Magerlein, G. P. Mueller, A. Schneider, and W. Wheatley, *ibid.*, **67**, 1591 (1945). [d] *Anal.* Calcd for $C_{14}H_{10}O_2Cl_2$: C, 59.81; H, 3.59; Cl, 25.22. Found: C, 59.58; H, 3.46; Cl, 25.49. [e] Analyzed on benzhydrol; see Table V. [f] W. A. Waters, *J. Chem. Soc.*, 2106 (1929). [g] *Anal.* Calcd for $C_{13}H_7OCl_3$: C, 54.68; H, 2.47; Cl, 37.25. Found: C, 54.76; H, 2.31; Cl, 37.01.

TABLE V

PHYSICAL CONSTANTS OF POLYSUBSTITUTED BENZHYDROLS

Substituents	Mp, °C	Bp (mm), °C	$n^{20}D$
m-Cl-*p'*-CH_3O[a]	...	154–155 (0.6)	1.5991
m-Cl-*p'*-CH_3[b]	...	157–158 (1.1)	1.5933
m,*p'*-Cl_2[c]	...	147 (0.5)	1.6078
m,*m*-Cl_2-*p'*-CH_3O[d]	...	184–184.5 (1)	1.6064
m,*m*-Cl_2-*p'*-CH_3[e]	88.5–89.0	...	...
m,*m*-Cl_2[f]	45.5–46.0	149 (1.7)	...
m,*m*,*p'*-Cl_3[g]	103.5–104.0	...	...

[a] *Anal.* Calcd for $C_{14}H_{13}O_2Cl$: C, 67.61; H, 5.27; Cl, 14.26. Found: C, 67.60; H, 5.47; Cl, 14.40. [b] *Anal.* Calcd for $C_{14}H_{13}OCl$: C, 72.26; H, 5.63; Cl, 15.24. Found: C, 72.07; H, 5.66; Cl, 15.50. [c] *Anal.* Calcd for $C_{13}H_{10}OCl_2$: C, 61.68; H, 3.98; Cl, 28.01. Found: C, 61.73; H, 3.68; Cl, 28.20. [d] *Anal.* Calcd for $C_{14}H_{12}O_2Cl_2$: C, 59.38; H, 4.27; Cl, 25.04. Found: C, 59.46; H, 4.04; Cl, 25.25. [e] *Anal.* Calcd for $C_{14}H_{12}OCl_2$: C, 62.94; H, 4.53; Cl, 26.54. Found: C, 63.09; H, 4.75; Cl, 26.49. [f] Since the purification of this carbinol was troublesome, it was purified and analyzed on chloride. *Anal.* Calcd for $C_{13}H_9Cl_3$: C, 57.49; H, 3.34; Cl, 39.17. Found: C, 57.25; H, 3.14; Cl, 39.01. [g] *Anal.* Calcd for $C_{13}H_9OCl_3$: C, 54.29; H, 3.15; Cl, 36.99. Found: C, 54.25; H, 2.86; Cl, 37.01.

Registry No.—Benzhydryl chloride, 90-99-3; *m*-chloro-*p'*-methyl benzhydryl chloride, 13389-44-1; *m*,*p'*-dichlorobenzhydryl chloride, 13389-45-2; *m*,*m*-dichlorobenzhydryl chloride, 13389-46-3; *m*,*m*-dichloro-*p'*-methylbenzhydryl chloride, 13389-47-4; *m*,*m*,*p'*-trichlorobenzhydryl chloride, 13389-48-5; *m*-chloro-*p'*-methoxybenzhydryl chloride, 13389-49-6; *m*,*m*-dichloro-*p'*-methoxybenzhydryl chloride, 13389-50-9; *m*-chloro-*p'*-methoxybenzophenone, 13389-51-0; *m*-chloro-*p'*-methylbenzophenone, 13395-60-3; *m*,*p'*-dichlorobenzophenone, 7498-66-0; *m*,*m*-dichloro-*p'*-methoxybenzophenone, 13395-62-5; *m*,*m*-dichloro-*p'*-methylbenzophenone, 13395-63-6; *m*,*m*-dichlorobenzophenone, 13395-64-7; *m*,*m*,*p'*-trichlorobenzophenone, 13395-65-8; *m*-chloro-*p'*-methoxybenzhydrol, 13395-66-9; *m*-chloro-*p'*-methylbenzhydrol, 13395-67-1; *m*,*p'*-dichlorobenzhydrol, 13421-95-9; *m*,*m*-dichloro-*p'*-methoxybenzhydrol, 13395-68-1; *m*,*m*-dichloro-*p'*-methylbenzhydrol, 13395-69-2; *m*,*m*-dichlorobenzhydrol, 13395-70-5; *m*,*m*,*p'*-trichlorobenzhydrol, 13421-96-0.

Acknowledgment.—The encouragement and support of Professor Herbert C. Brown during the course of the present work carried out in Purdue University are gratefully acknowledged.

Reactions of *o*-Halophenylazo Phenyl Sulfones and of (*o*-Chlorophenyl)triphenylphosphonium Iodide with Sodium Methoxide in Methanol[1]

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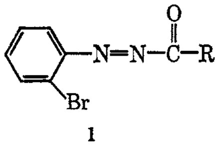
The reactions of *o*-halophenylazo phenyl sulfones with $NaOCH_3$ are essentially reactions of diazonium ions formed by ionic dissociation. In very dilute $NaOCH_3$, halobenzenes are produced by a radical mechanism; ordinary chlorobenzene (C_6H_5Cl) is formed in CH_3OD solution. In concentrated (2 *M*) $NaOCH_3$, halobenzenes arise *via* *o*-halophenyl anion intermediates; chlorobenzene-2-*d* is produced in CH_3OD solution. The action of $NaOCH_3$ on (*o*-chlorophenyl)triphenylphosphonium iodide affords chlorobenzene *via* the *o*-chlorophenyl anion intermediate, as shown by the formation of *o*-C_6H_4DCl in CH_3OD.

With the objective of finding new ways to generate *o*-halophenyl anions in methanol, we carried out the investigations now reported. New ways to generate these reactive intermediates were indeed found, but some of the phenomena encountered did not match our original expectations.

Reactions of *o*-Halophenylazo Phenyl Sulfones.[3]—Hoffmann[4] has reported that *o*-halophenylazo ketones (**1**) are cleaved by sodium ethoxide, forming esters ($RCOOC_2H_5$) and products which indicate the intermediacy of *o*-bromophenyl anions. Desiring a convenient source of *o*-bromoaryl anions,[5] and having found compounds of type **1** somewhat inconvenient to prepare, we investigated the action of methanolic sodium



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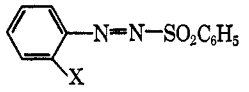

2a, X = Cl
b, X = Br

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(1) Financial support by the National Science Foundation is gratefully acknowledged.

(2) To whom correspondence should be addressed: University of California at Santa Cruz, Santa Cruz, Calif.

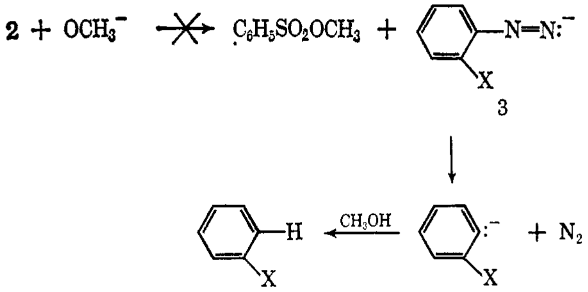
(3) Preliminary communication: J. F. Bunnett, D. A. R. Happer, and H. Takayama, *Chem. Commun.*, 367 (1966).

(4) R. W. Hoffmann, *Chem. Ber.*, **97**, 2763, 2772 (1964).

(5) J. F. Bunnett and D. A. R. Happer, *J. Org. Chem.*, **31**, 2369 (1966).

methoxide on *o*-halophenylazo phenyl sulfones of type **2**. Such azo sulfones are easily prepared and handled.

Our hope was that the azo sulfones would be cleaved by attack of methoxide ion on sulfur, forming methyl benzenesulfonate and (immediately) an *o*-haloaryldiimide ion (**3**) (*cf.* eq 1). The latter was expected to release N_2 and form an *o*-halophenyl anion which would then either take a proton from the solvent (forming a halobenzene) or lose halide ion (forming benzyne and eventually anisole).[4,5]

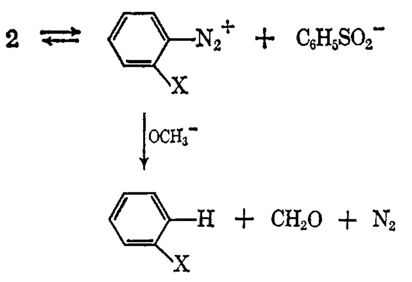


(1)

Chlorobenzene was indeed obtained, in 96% yield, on reaction of **2a** (0.001 mole) with sodium methoxide (0.001 mole) in methanol. When less than 1 mole of base was used per mole of **2a**, the yield was reduced. Thus only 28% of chlorobenzene was obtained from 1×10^{-3} mole of **2a** and 0.25×10^{-3} mole of $NaOCH_3$. Equation 1 as written would not consume base, but if the methyl benzenesulfonate quickly reacted with $NaOCH_3$, to form dimethyl ether and sodium benzenesulfonate, the observed stoichiometry would be accounted for.

However, several observations were inconsistent with this interpretation. If eq 1 were correct, thioanisole ought to be produced if the reaction were run in the presence of the strong nucleophile sodium thiophenoxide, but in fact no thioanisole was formed, although the yield of chlorobenzene was 67%. Also, reaction in methanol-O-*d* should afford chlorobenzene-2-*d*, but the chlorobenzene actually formed in the reaction of **2a** (0.001 mole) with $NaOCH_3$ (0.001 mole) in CH_3OD was virtually deuterium free, to judge from its infrared spectrum.[6]

A clue to the true character of the reaction was the fact that an acidified aqueous extract of a typical product mixture showed an ultraviolet spectrum identical with that of benzenesulfinic acid and different from that of benzenesulfonic acid. This suggested that the reaction should be formulated as in eq 2. It is known that azo sulfones in methanol dissociate reversibly into diazonium and sulfinate ions.[7] "Deamination" of diazonium salts in weakly alkaline methanol is also known.[8] Formaldehyde was established as a product by a Schiff color test and by isolation of its methone (dimedone) derivative.



(2)

Representation of the reaction by eq 2 was further substantiated by the fact that chlorobenzene formation was strongly repressed by sodium phenoxide in the reaction solution. Phenoxide ions couple with diazonium ions. The products of this reaction were colored orange-red. The visible–ultraviolet spectrum was identical with that of an authentic sample of 4-(*o*-chlorophenylazo)phenol under the same conditions.

2a is also reduced to chlorobenzene when treated with concentrated (2 *M*) methanolic sodium methoxide. However, the reaction under these conditions is remarkably different in character, for the product in CH_3OD is now chlorobenzene-2-*d*, as shown by its infrared spectrum.[6] Thus the sought-for *o*-chlorophenyl anions were generated in 2 *M* $NaOCH_3$.

Evidence of a change of mechanism with change of base concentration was also found in reactions of the bromine analog, **2b**. *o*-Bromophenyl anion is known to partition, in methanol, between proton capture and bromide ion loss in such a way as to form about 11% of bromide ion.[4,5] The fact that 8% of bromide ion was liberated on treatment of **2b** with 2 *M* $NaOCH_3$ shows that most of the reaction goes *via* *o*-bromophenyl anion intermediates. On the other hand, only 1.1% of bromide ion was released on reaction of **2b** with an equimolar amount of base, although the yield of bromobenzene was 81%.

If **2b** is indeed functioning in these reactions as a source of *o*-bromobenzenediazonium ions, similar yields of bromobenzene and bromide ion should be obtained, at a given methoxide concentration, from *o*-bromobenzenediazonium fluoroborate. In the event, the results were nearly identical: 83% of bromobenzene and 8% of bromide ion in 2 *M* $NaOCH_3$; 86% of bromobenzene and 0.9% of bromide ion in very dilute base.

Our principal experimental results are summarized in Table I.

Reaction Mechanisms.—We have presented evidence that these reactions at all base concentrations occur *via* diazonium ions, and that *o*-halophenyl anions are intermediates in 2 *M* $NaOCH_3$ but not when only 1 equiv of base is provided.

As to the reactions in dilute base, all our observations are consistent with the intermediacy of *o*-halophenyl radicals. Such radicals would be expected to abstract hydrogen from the methyl of CH_3OD, rather than deuterium from the -OD function. A radical mechanism for deamination of diazonium salts in methanol has been proposed by DeTar and Turetzky.[8]

The *o*-halophenyl anions formed in 2 *M* $NaOCH_3$ doubtless stem from *o*-halophenyldiimide ions by loss of N_2. One possibility, sketched in a preliminary communication,[3] is that the aryldiimide ions are formed by attack of methoxide ions on azo ethers, $ArN{=}N\text{-}OCH_3$, formed by coordination of diazonium with methoxide ions. An E2 scission would afford methanol, formaldehyde, and aryldiimide ion. An alternative possibility, suggested by Dr. Christoph Rüchardt, is that the diazonium ion captures a hydride ion from

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[6] Recent work by Dr. H. Takayama, involving mass spectrometric analysis, has confirmed this result.

[7] C. D. Ritchie, J. D. Saltiel, and E. S. Lewis, *J. Am. Chem. Soc.*, **83**, 4601 (1961).

[8] D. F. DeTar and M. N. Turetzky, *ibid.*, **77**, 1745 (1955); **78**, 3925, 3928 (1956).

TABLE I

REACTIONS OF *o*-HALOPHENYLAZO SULFONES **2a** AND **2b** WITH METHANOLIC SODIUM METHOXIDE

Substrate	Substrate, mmoles	$NaOCH_3$, mmoles	Other substances, mmoles	CH_3OH, ml	C_6H_5X, %	Remarks
2a, X = Cl	1.0			25	5	
	1.0		*p*-$CH_3C_6H_4SO_3H$, 1.0	25	10	
	1.0	0.25		20	28	
	1.0	0.5		20	54	
	1.0	1.0		20	96	
	1.0	1.25		25	92	
	1.0		CH_3COONa, 1.25	25	31	
	1.0	1.25	C_6H_5SH, 1.0	25	67	No $C_6H_5SCH_3$ detected
	1.0	2.5	C_6H_5OH, 1.0	50	28	*o*-$ClC_6H_4N{=}NC_6H_4O^-$-*p* detected in H_2O layer by ultraviolet spectrum
	1.0	50.		25	71	
2b, X = Br	1.0	1.1		20	81	1.1% Br^- and 1% anisole formed
	1.0	40.		20	67	7.7% Br^- and 6.7% anisole formed
o-$C_6H_4BrN_2{}^+BF_4{}^-$	1.0	1.25		25	86	0.9% Br^- and 1% anisole formed
	1.0	50.		25	83	8.5% Br^- and 8.4% anisole formed


(3)

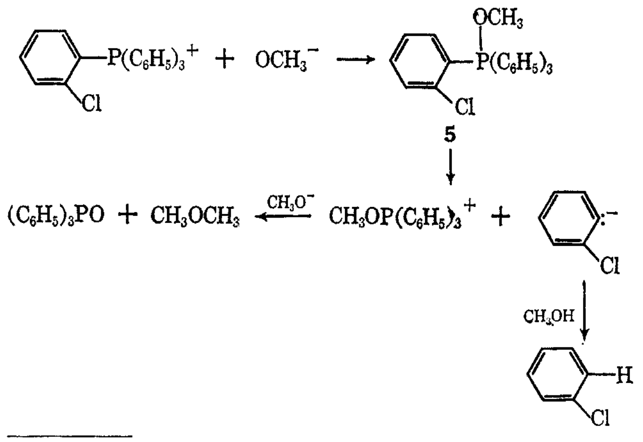
methoxide ion (eq 3) and that the resulting aryldiimide loses a proton to the strong base present. Preliminary kinetic experiments by Dr. Hiroaki Takayama support the Rüchardt mechanism.

Reactions of (*o*-Chlorophenyl)triphenylphosphonium Iodide.—On the basis of indications in the literature,[9-11] we anticipated that methoxide ion would attack the phosphorus atom of (*o*-chlorophenyl)triphenylphosphonium ion (**4**), with subsequent release of *o*-chlorophenyl anion. Proton capture from the solvent would then form chlorobenzene.

In fact, chlorobenzene was formed in high (93%) yield on treatment of **4** with sodium methoxide for 5 min in boiling methanol. No benzene was detectable as a cleavage product. From a cleavage conducted in methanol-O-*d* solution, the chlorobenzene obtained was mainly deuterated in the 2 position, as shown by the excellent match of its infrared spectrum to that of the best sample of chlorobenzene-2-*d* prepared by Zoltewicz and Bunnett.[12] Thus *o*-chlorophenyl anions were indeed intermediates in the reaction.

A possible mechanism for the cleavage is presented in Scheme I. This resembles a mechanism proposed, for ethoxide cleavage of *p*-nitrobenzyltriphenylphosphonium ion, by Grayson and Keough.[10]

SCHEME I



An alternative mechanism, disfavored by Grayson and Keough, was suggested by Aksnes and Songstad;[11] it involves rate-limiting attack of alkoxide ion on alkyl carbon of a species such as **5**, forming a dialkyl ether and an anionic fragment which then separates into a carbanion and a tertiary phosphine oxide. The latter mechanism would seem to be called for by the third-order kinetics claimed by Aksnes and Songstad. However, these authors did not present compelling evidence that the cleavages by ethoxide ion in absolute ethanol have a third-order rate law.

In either case, the facility of the cleavage and the fact that an *o*-chlorophenyl rather than an unsubstituted phenyl anion is released as an intermediate are associated with the special stabilizing effect of *o*-halogen substituents on phenyl anions.[13]

Efforts to prepare *o*-bromophenyltriphenylphosphonium iodide by the method of Horner and Hoffmann[14] were unsuccessful.

Experimental Section

Azo Sulfones 2a and 2b.—Into 600 ml of a chilled water solution of the appropriate diazonium salt (from 0.1 mole of amine), a solution of sodium benzenesulfinate was slowly added with efficient stirring. The precipitated azo sulfone was collected and recrystallized from methanol or ethanol, care being taken not to prolong heating of the solution. *o*-Chlorophenylazo phenyl sulfone (**2a**) was obtained as orange needles, mp 103–104° (lit.[15] 98°). *o*-Bromophenylazo phenyl sulfone, mp 85.5–86°, was also obtained as orange needles.

Anal. Calcd for $C_{12}H_9BrN_2O_2S$: C, 44.31; H, 2.79; N, 8.62. Found: C, 44.51; H, 2.64; N, 8.59.

General Experimental Procedure.—All of the reactions were carried out under essentially the same conditions.

The azo sulfone (10^{-3} mole) was placed in a flask immersed in a constant-temperature bath (61°) and a solution of sodium methoxide in methanol of suitable strength (0.06 or 2 *M* usually) was placed in another flask in the bath. After thermal equilibrium was reached, 20 or 25 ml of the methoxide–methanol solution was pipetted into the flask containing the azo sulfone. When reaction was complete, 10 ml of benzene containing a small amount of either bromobenzene or chlorobenzene (whichever was not expected as a reaction product) as an internal standard

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[9] L. Horner, H. Hoffmann, H. G. Wippel, and G. Hassel, *Chem. Ber.*, **91**, 52 (1958).

[10] M. Grayson and P. T. Keough, *J. Am. Chem. Soc.*, **82**, 3919 (1960).

[11] G. Aksnes and J. Songstad, *Acta Chem. Scand.*, **16**, 1426 (1962).

[12] J. A. Zoltewicz and J. F. Bunnett, *J. Am. Chem. Soc.*, **87**, 2640 (1965).

[13] J. F. Bunnett, *J. Chem. Educ.*, **38**, 278 (1961); J. F. Bunnett and B. F. Hrutfiord, *J. Org. Chem.*, **27**, 4152 (1962).

[14] L. Horner and H. Hoffmann, *Chem. Ber.*, **91**, 45 (1958).

[15] H. C. Freeman, R. J. W. LeFevre, J. Northcott, and I. Youhotsky, *J. Chem. Soc.*, 3381 (1952).

was added and, after thorough mixing, the solution was poured into water. The two layers were separated. The benzene layer was dried over anhydrous magnesium sulfate and analyzed by gas-liquid partition chromatography.

The aqueous layer contained any halide ions formed, and these could be titrated potentiometrically with standard silver nitrate solution.

The procedure was modified according to the needs of the reaction. For acid-base titrations the whole of the contents of the reaction was titrated with standard acid, and the benzene was not added. For identification of benzenesulfinic acid ether was used instead of benzene, and the aqueous layer was diluted to a suitable concentration and examined in an ultraviolet spectrophotometer. The experimental procedure for the experiments in CH_3OD differed in that pentane was used instead of benzene. The pentane solution was passed through a short alumina column (*ca.* 2 cm), the pentane was cautiously evaporated under reduced pressure, and the infrared spectrum of the residue was examined.

The results of a number of experiments are summarized in Table I. No anisole was ever obtained as a product from **2a**.

Identification of Certain Products.—From a reaction of **2a** in the presence of phenol (Table I), the products were partitioned between benzene and water. The ultraviolet-visible spectrum of the aqueous layer showed an absorption maximum at 423 mμ, identical with that of an alkaline solution of 4-(*o*-chlorophenylazo)phenol.

From a reaction of 0.001 mole of **2a** with 25 ml of 0.05 *M* sodium methoxide, the product was poured into water, made slightly alkaline, and extracted with ether. The water layer was acidified and extracted thrice again with ether. The ultraviolet spectrum showed a band at 245–275 mμ with fine structure maxima at 259, 265, and 272 mμ. The spectrum was identical with that of an authentic sample of benzenesulfinic acid and different from that of an authentic sample of benzenesulfonic acid.

From the reaction of 0.001 mole of **2a** with 5 ml of 0.2 *M* sodium methoxide, the volatile products were distilled (heating with boiling-water bath) and collected. The presence of formaldehyde was estalished by a positive color test using a modified Schiff reagent.[16] The remainder of the distillate was dissolved in 20 ml of methanol, combined with a solution of methone (dimedone) in methanol, heated 30 min on the steam bath, and chilled overnight. White needles (28 mg) of the methone derivative of formaldehyde were obtained, mp 190.2° (lit.[16] 191.4°).

From reaction of 0.001 mole of **2a** with 0.001 mole of $NaOCH_3$ in 5 ml of CH_3OD, the chlorobenzene (isolated as described above) had an infrared spectrum resembling that of ordinary chlorobenzene and lacking bands characteristic of chlorobenzene-2-*d*. From the reaction of 0.002 mole of **2a** in 10 ml of 2 *M* $NaOCH_3$ in CH_3OD, the chlorobenzene obtained matched in infrared spectrum the best sample of chlorobenzene-2-*d* prepared by Zoltewicz and Bunnett.[12]

Action of Sodium Methoxide on Phosphonium Salt 4.—*o*-Chlorophenyltriphenylphosphonium iodide (**4**), mp 242° (lit.[14] 242-244°), was prepared by the method of Horner and Hoffmann.[14]

A mixture of **4** (0.5 mmole) and sodium methoxide (0.6 mmole) in 10 ml of methanol was boiled 5 min under reflux. The mixture was steam distilled, and the distillate was extracted with benzene. A known amount of bromobenzene was added to the extract which was then analyzed by gas-liquid partition chromatography. The yield of chlorobenzene was 93%. A similar experiment was performed but with methylene chloride as extraction solvent; chlorobenzene was again obtained, but there was no indication of benzene or anisole in the gas-liquid chromatogram.

To a solution of 0.004 mole of sodium methoxide in 5 ml of methanol-O-*d*, 834 mg (1.67 × 10^{-3} mole) of **4** was added. The resulting amber solution was heated 10 min at reflux. The product mixture was steam distilled, and the distillate was extracted with pentane. The pentane extract was dried over anhydrous magnesium sulfate, and the pentane was evaporated. The infrared spectrum of the residue was very similar to that of chlorobenzene-2-*d*[12] and different from that of ordinary chlorobenzene.

Registry No.—**2a**, 13389-62-3; **2b**, 13389-63-4; (*o*-chlorophenyl)triphenylphosphonium iodide, 13389-64-5; sodium methoxide, 124-41-4; methanol, 67-56-1.

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[16] J. F. Walker, "Formaldehyde," Reinhold Publishing Corp., New York, N. Y., 1953, p 367.

Further Studies on the Mechanism of Diphenylketene Cycloaddition[1]

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Received April 24, 1967

Diphenylketene undergoes 1,2 cycloaddition with cyclopentadiene, 1,3-butadiene, isoprene, and chloroprene to give substituted cyclobutanones. Cyclopentadiene is 240 times as reactive as 1,3-butadiene. In the cycloaddition of diphenylketene and isoprene, there is a predominance of the 1,2-cycloaddition product over the 3,4-cycloadduct. The cycloaddition of diphenylketene and chloroprene also produced both isomers, but the 3,4 cycloadduct predominated. These results are regarded as consistent with the near-concerted mechanism previously described.

Ketenes generally undergo 1,2-cycloaddition reactions with olefinic compounds to form substituted cyclobutanones.[2] While this characteristic reaction of ketenes has been known for many years, it has received relatively little attention from a mechanistic point of view. A very striking feature of this reaction is that only one of the two possible orientation isomers is produced with essentially all of the olefins and dienes that have been studied. However, this is the isomer that would be predicted on the basis of the diradical mechanism, dipolar mechanism, or a concerted process considering only bond polarizations. Another interesting feature of this cycloaddition reaction is that only 1,2 adducts are produced with dienes; no substituted cyclohexenones have been reported.[3]

Huisgen, Feiler, and Binsch have investigated the cycloaddition of diphenylketene and dimethylketene with both *cis*- and *trans*-propenyl propyl ether.[4] In both cases it was reported that the *cis* form reacted faster than the *trans* form. It was also reported that each of the two geometrically isomeric ethers had retained their original configurations in the cycloadduct. This stereoselective *cis* addition was interpreted as being strong evidence for a one-stage multicentered cycloaddition.

We have recently reported on the kinetics and mecha-

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[1] This work was supported by a Faculty Research Grant, North Texas State University, Denton, Texas.

[2] R. N. Lacey, "The Chemistry of Alkenes," S. Patai, Ed., Interscience Publishers, Inc., New York, N. Y., 1964, p 1197.

[3] J. C. Martin, P. G. Gott, V. W. Goodlett, and R. H. Hasek, *J. Org. Chem.*, **30**, 4175 (1965).

[4] R. Huisgen, L. Feiler, and G. Binsch, *Angew. Chem. Intern. Ed. Engl.*, **3**, 753 (1964).