Catalytic Decomposition of Diphenyldiazomethane by Lewis Acids, Cyclopropanation Reactions of a Diphenylcarbenoid Species

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The first successful cyclopropanation reactions utilizing zinc chloride catalyzed decompositions of diphenyldiazomethane are reported. Various metal salts were surveyed for their relative activity toward diphenyldiazomethane decomposition and then several were chosen for cyclopropanation studies. Conjugated dienes and electron-rich olefins were found to be good cyclopropanation substrates. The diphenylcyclopropanation of cyclopentadiene was optimized by investigating changes of temperature, concentration, mode of addition, reaction time, the metal cation, and the anions. Mechanistic studies, including comparison with diphenylcarbene reactions, suggest that our results are best explained by a diphenylcarbenoid intermediate which reacts competitively with the olefin to produce a cyclopropane product and with diphenyldiazomethane to produce tetraphenylketazine and tetraphenylethylene.

The Lewis acid catalyzed decomposition of diphenyldiazomethane has been examined a number of times $^{2-4}$ using various catalysts, but only recently have good mechanistic studies on this reaction appeared.³ Furthermore, we know of no survey of Lewis acids that are effective in inducing diphenyldiazomethane decomposition. Although a number of catalyzed diphenylcyclopropanations have been attempted⁴ in analogy to the well-known studies⁵ on monoaryldiazomethane cyclopropanations, the only successful report involved two enamines in refluxing benzene⁶ with copper acetylacetonate. Gaspar's recent report^{4f} that this reaction does not proceed at room temperature suggests that the mechanism of this reaction is fundamentally different from that of the monoarylcyclopropanations, which is thought to involve reactive carbenoids.⁵ Although previous decomposition studies have shown little sign that a diphenylcarbenoid species thus generated would cyclopropanate olefins, a diphenylcarbenoid derived from dibromodiphenylmethane has been reported to cyclopropanate 2-butenes^{7a} and ethyl vinyl ether^{7b} in modest yields. A similar attempt with dichlorodiphenylmethane was unsuccessful.^{7c}

An extensive amount of work has been done on photolytically generated diphenylcarbene,⁸ but only recently have good studies of its cyclopropanation reactions appeared.⁹ Casey's recent report of diphenylcyclopropanation on ethyl vinyl ether by use of tungsten pentacarbonyl complex of diphenylcarbene¹⁰ and Gaspar's recent studies on catalyzed decomposition of diphenyldiazomethane^{4f} compel us to report our successful cyclopropanation reactions¹¹ using diphenylcarbenoid species generated by catalyzed decompositions of diphenyldiazomethane, our studies on the decomposition reaction, and some comparisons among diphenylcyclopropanation reactions.

Results and Discussion

Slow addition of ethereal diphenyldiazomethane (1) under nitrogen to a stirred anhydrous ethereal mixture of zinc chloride and a fivefold excess of cyclopentadiene at 25° with concentration and extraction followed by crystallization afforded a 35% yield of 6,6-diphenylbicyclo-[3.1.0]hex-2-ene (2) with tetraphenylketazine (3) and benzophenone (4) as the other principal products (cf. eq 1).



The relatively good yield, the ease of isolation, and the ease of scaling up compared with the carbene route¹² make this the preferred method for synthesizing 6,6-diarylbicyclo-[3.1.0]hex-2-enes. The most favorable reaction conditions were worked out using cyclopentadiene and were then applied to other olefins (cf. Table I). Conjugated cyclic dienes gave diminishing yields with increasing ring size; 1,3-cyclooctadiene did not react under these conditions. Although no reaction is seen with isoprene at 0°, results at 25 and 40° show a temperature-dependent regioselectivity for attack at the more electron-rich double bond. Use of the electron-rich ethyl vinyl ether in analogy to the previously mentioned enamines⁶ gave a gratifying 52% yield of 1-ethoxy-2,2-diphenylcyclopropane.

The isolation of 3-benzhydrylcyclohexa-1,4-diene (6) from the diphenylcarbene reaction with cyclohexadiene has analogy in the formation of 9-benzhydrylfluorene.^{2h} The benzhydryl radical produced by hydrogen abstraction can couple with the cyclohexadienyl radical to produce 6 competitively with self-coupling to produce 1,1,2,2-tetraphenylethane (7), and further hydrogen abstraction to produce diphenylmethane (8).¹³ The uv and NMR spectra were par-



ticularly useful in the structure elucidation of compound 6. The ultraviolet spectrum, 217 nm (ϵ 14,400) and 260 (962), is more reminiscent of that of diphenylmethane, 260 (501), than of 1,3-cyclohexadiene, 259 (10,000). The bisallylic and bisbenzylic methine ¹H NMR signals at δ 3.7 agree well with the methylene ¹H NMR signals of diphenylmethane at δ 4.0. The ¹H NMR absorption at δ 2.6 assigned to the bisallylic methylenes is much closer to those of 1,4-cyclohexadiene at δ 2.7 than to the methylenes of 1,3-cyclohexadiene at δ 2.1.

Our studies, summarized in Table I, indicate that anhydrous conditions, the correct mode of addition, 25° instead of 0°, zinc chloride instead of other Lewis acids, and extra reaction time all favor cyclopropanation. These conditions are too mild to induce a dipolar addition by diphenyldiazomethane, and no disappearance of diazo compound is seen without a Lewis acid. Tetraphenylketazine is a major product while tetraphenylethylene is usually quite minor and none of the tetraphenylethane characteristic of the diphen-

System ^a	Method	Temp, °C	Timeb	Cyclopropane	Ketazine I	Benzophenone	Otherd	
 CPD	ZnCl ₂	22	2 hr	35	24	29	Print	
CPD	$ZnCl_{2}$	22	9 hr	34.8	27	29		
CPD	$ZnCl_{2}$	22	10 min	23	28	25		
CPD	$ZnCl_2$	0-5	1 5 min	23 (28)	51	15		
CPD	ZnCl ₂	28	5 min	5 ^e	75			
CPD	$ZnCl_{2}$	05	45 min	0 ^{<i>f</i>}	91			
CPD	ZnI_2	0—5	10 min	(1.5)	76			
CPD	CuBr ₂	22	2 hr	0	28	50	15, TPY	
CPD	hv	0-5		19	1.2	25	36, TPE	
CHD	hv	05		18	7.9	6	35, TPE	
CHD	$ZnCl_2$	0-5	1 hr	0 (0)	43			
CHD	ZnCl ₂	25	11 min	2	34	39		
CHPD	ZnCl	22	15 min	0.4	25	52		
COD	ZnCl ₂	25	1 5 min	0 (0)	35	56		
ISOP	ZnCl ₂	0—5	15 hr	0 (0)	68			
ISOP	$ZnCl_2$	24	10 min	2.4 (≥5:1) ^s	34	16		
ISOP	$ZnCl_2$	40	20 min	5.5 (2.4:1) ^g	31	26		
ISOP	hv	24		73 (1.1:1) ^e	0		0	
EVE	$ZnCl_2$	25	2 hr	52	3.6	12	0	
EVE	$h\nu^h$			18.5	55.2	12	8.9, TPE	
EVE	$Ph_2CBr_2-MeLi^h$			4.8	0	16.5	20.6, TPY	
EVE	$W(CO)_5$ complex ⁱ	37	3 hr	65				

 Table I

 Reactions of Diphenylcarbene and Diphenylcarbenoid Species

^a CPD, cyclopentadiene; CHD, 1,3-cyclohexadiene; CHPD, 1,3-cycloheptadiene; COD, 1,3-cyclooctadiene; ISOP, isoprene; EVE, ethyl vinyl ether. ^b The time the reaction was stirred after addition was completed. ^c Isolated percentages of corresponding cyclopropane product, parentheses indicate HPLC yields determined against cumene internal standard. ^d TPY, 1,1,2,2-tetraphenylethylene; TPE, 1,1,2,2-tetraphenylethane; ketazine, tetraphenylketazine. ^e Undistilled ether used as solvent. ^f Stirring the reactants without catalyst for 1 hr at 0^o gave no reaction but nitrogen evolution was complete 15 min after addition of 0.1 mol % zinc chloride. ^g Ratio of disubstituted to monosubstituted double bond attack. ^h Reference 7b. ⁱ Reference 10.

ylcarbene is seen. Since changing the cation or its anions changes both the rate of decomposition (see below) and the amount of cyclopropanation, it is clear that the catalyst is involved in the decomposition reaction as well as the subsequent reactions. The best explanation for these results is a diphenylcarbenoid intermediate, and the overall mechanism (Chart I) follows the various modifications^{3a,4d} of Wittig's original suggestion¹⁴ about diazomethane decompositions.



The initial reaction of the Lewis acid with diphenyldiazomethane depends on the relative strength of the Lewis acid and the basic property of diphenyldiazomethane. Very strong Lewis acids like boron trifluoride etherate and aluminum chloride react very fast and tend to give larger amounts of tetraphenylethylene.²ⁱ Bethell argued^{3a} for the partitioned intermediate 10 based on a low degree of charge development on the diazo carbon, but this would not exclude the initial adduct 9 which could merely lose nitrogen on subsequent reaction.

Table II	
Relative Activity toward	
Diphenyldiazomethane Decomposition in	Air

Very fast ^a	$AlCl_3$, $TiCl_4$, $SnCl_4$, $BF_3 \cdot OEt_2$
Fast	$HgCl_2$, $Hg(NO_3)_2$, $CuBr_2$, $FeCl_3$, ZnI_2 , (<i>i</i> -
	$PrO)_{3}PCuI, CuCl[MeCN]^{b}$
Moderate	HgI_2 , $ZnCl_2$, $CuCl[ether]$, $CuCl_2 \cdot 2H_2O$,
	${ m SnCl_2} { m \cdot 2H_2O}, \ { m Hg_2Cl_2[MeCN]}$
Slow	CuCN, CrCl ₃ •6H ₂ O, AlCl ₃ •6H ₂ O
No reaction	$Hg_2Cl_2[ether], CdCl_2, Zn(CN)_2, Cr(OAc)_3$.
	$6H_2O$, NiCl ₂ • $6H_2O$, Co(NO ₃) ₂ • $6H_2O$,
	$CoCl_2 \cdot 6H_2O$, $MgCl_2 \cdot 6H_2O$, $CaCl_2$, LiCl,
	LiBr, NH_4Cl , tetraphenylethylene

^{*a*} Very fast, reacts completely in less than 1 min; fast, in less than 15 min; moderate, in less than 4 hr; and slow, reacts while standing for 24 hr. ^{*b*} Brackets indicate solvent where differences occurred.

Diphenyldiazomethane shows no reaction with lithium bromide at 25° (see below)^{5a} or with zinc chloride below -15° in ether, while phenyldiazomethane reacts with lithium bromide at 0° and with zinc chloride at -50° .^{4d} This decreased basicity can be attributed to inductive electron withdrawal and to the additional steric hindrance of the second phenyl ring.

The results of our qualitative survey of the reactivities of various metal salts toward diphenyldiazomethane in etherhexane and acetonitrile solution are listed in Table II. Since hydration does lower the reactivities, some of the strongly hydrated salts might change position if anhydrous samples were used, but within a series, the comparisons are probably sound. These relative values agree with published kinetic data for zinc chloride, zinc iodide, and cupric bromide.³

We note that salts of main groups I and II showed no

reaction and that salts of transition metals having stable lower oxidation states (Cr^{3+} , Fe^{3+} , and Cu^{2+}) reacted while others did not (Co^{2+} and Ni^{2+}). This supports Gaspar's suggestion^{4f} about initial electron transfer, and parallels Nozaki's observation that product distributions vary with the aqueous reduction potential for several salts.^{4e} The ligand effects on zinc(II) and mercury(II) decompositions correlate with their binding strengths to the metal ions. Thus the most tightly bound salts are least reactive. Hard-soft acid-base theory¹⁵ suggests that the soft iodide ion binds more strongly to mercury(II) than to zinc(II), so HgCl₂ reacts faster than HgI₂, while ZnI₂ reacts faster than ZnCl₂ even though the equilibrium acidities for zinc halides in ether are in the reverse order.¹⁶ Tighter binding could reduce reactivity because of lower solubility or because tighter ligands are less easily displaced during reaction.

Mixing a fivefold excess of cyclopentadiene with ethereal diphenyldiazomethane at 0° gave no reaction, but addition of 0.1 mol % zinc chloride quickly gave 91% tetraphenylketazine (3) with no trace of cyclopropane (2). Clearly the competition between olefin and excess diazo compound for the carbenoid greatly favors the more polarizable diazo compound. Previous workers⁴ found no cyclopropanation because they used unreactive olefins. Apparently diene reactivity is determined by both electron density and by planarity, or the ability to attain a planar conformation. A planar conformation would facilitate the formation of an allylic carbonium ion on the diene residue after electrophilic attack. This type of intermediate, 13 or 14, allows one to pre-



dict stereochemical results for closure of unsymmetrical carbenoids.¹⁷ Initial work with unsymmetrically substituted diphenyldiazomethanes suggests that the syn-anti selectivities are the same for both the phenylarylcarbene and the phenylarylcarbenoid cyclopropanation reactions.¹⁸ This will be discussed in a subsequent publication.

For cyclopropanation Zn(II) is much better than Cu(II) or Hg(II) and the more tightly bound zinc chloride promotes cyclopropanation better than zinc iodide. This correlates with the tendency to rearrange to the α -halo metal halide intermediate. Mercury(II) is known to form these derivatives readily and they are not particularly reactive toward cyclopropanation at or below 25°.¹⁹ Furthermore, both chlorodiphenylmethylmercuric chloride^{2c} and iodofluorenylzinc iodide^{3a} have been isolated.

Our interest in the source of benzophenone oxygen led to separate ether extraction of the reaction mixture both before and after aqueous hydrolysis. Less than 10% of the benzophenone was present in the extract before hydrolysis, and this small amount could come from a small amount of water in the commercial anhydrous ether used for extraction. Perhaps the α -chloro zinc chloride (11) or some similar intermediate produces benzophenone during hydrolysis.

With the very reactive olefin ethyl vinyl ether, the diphenylcyclopropanation reactions appear to be dependent more on temperature than on the nature of the specific reagent. At -20° the methyllithium reaction with dibromodiphenylmethane gave only 4.8% cyclopropanation,^{7b} while the zinc chloride catalyzed reaction with diphenyldiazomethane gave 52% at 25°, and the tungsten pentacarbonyl complex gave 65% at 37°.¹⁰ However, on the less reactive 2-butenes, the methyllithium reaction gave 10-15% cyclopropanation at -20° ^{7a} when the tungsten complex¹⁰ gave only a trace at 50°. In agreement with previous work,^{7c} we

found no cyclopropanation reaction with 1,3-cyclohexadiene using Olofson's method^{5b} with chlorodiphenylmethane. Apparently the 2-butenes show some real reactivity differences that ethyl vinyl ether does not show. Furthermore, cyclopentadiene would be a better substrate for future reactivity comparisons.

The similarity of the cyclopropanation yields for diphenylcarbene reacting with cyclopentadiene, cyclohexadiene, and ethyl vinyl ether is probably caused by the competition with hydrogen abstraction that occurs in all three cases. The ratio of cyclopropanation to abstraction varies in the direction predicted by steric effects:^{9a} ethyl vinyl ether (2: 1); cyclopentadiene (1:2); and cyclohexadiene (1:3.4).

The regioselectivity of attack on isoprene was obtained by integrating the vinyl region of the ¹H NMR spectra for the cyclopropane products. The zinc chloride carbenoid gave a 5:1 preference at 24° and a 2.4:1 preference at 40° for the more electron-rich disubstituted double bond. Diphenylcarbene showed little selectivity.

The best explanation for the isoprene results is that the less reactive diphenylcarbenoid must rely more on electron density to promote complexation with the olefin than the more energetic diphenylcarbene does. We are continuing our work on the nature of cyclopropanation transition states.

Experimental Section

General. All melting points were determined on a hot stage apparatus and are corrected. Unless otherwise noted, magnesium sulfate was employed as a drying agent. The ir spectra were determined on a Beckman IR-5A or Acculab 1. NMR spectra were recorded on a Varian A-60A or EM-360. All diazo reactions were run under a nitrogen atmosphere. All HPLC work was done on a Waters ALC-202 with 1000 psig pump and 254-nm uv detector. Analytical determinations were done on a 6 ft \times 0.125 in. Corasil C-18 (27-50 μ) reversed phase column using 1:1 acetonitrile-water eluent with cumene as an internal standard. Ether solvent was dried over lithium aluminum hydride or sodium benzophenone ketyl and then distilled before use. Ultraviolet spectra were determined on a Cary 14 spectrophotometer.

General Conditions for Carbenoid Reaction of Diphenyldiazomethane with Olefins. All reactions involved slow addition (ca. 10 mmol/hr) of an ethereal diphenyldiazomethane²⁰ solution (5-30 mmol, 0.1-0.5 M) to a stirred ethereal suspension or solution of the metal salt (5-30 mmol, nominally 0.5-2 M) and the olefin (fivefold excess, ca. 1.7 M) in a one-necked flask equipped with constant-pressure addition funnel, magnetic stirring bar, nitrogen line for initial flushing, a burette for monitoring nitrogen evolution, and an external temperature bath with thermometer. After the addition was complete (100-200 ml of nitrogen evolved per 10 mmol), the reaction mixture was stirred (10 min-9 hr) before the ether and excess olefin were removed in vacuo. The crude reaction mixture was slurried with 100 ml of ether to remove the ether-soluble material. The residue was partitioned between 100 ml of ether and 10 ml of water in a separatory funnel and any insoluble material was removed by filtration before the water layer was drawn off. The insoluble material generally included some tetraphenylketazine, mp 160-163° (lit. mp 163-164°),²¹ identified by melting point, ir, and TLC; variable amounts of tetraphenylethylene, mp 224 (lit.²² mp 223-224°); and a white solid, mp 205-250°. The ether layer was then washed twice more with 10-ml portions of water.

Generally, the two ether solutions were combined, dried, and concentrated (additional ketazine often crystallized out). HPLC aliquots were removed. The residue was dissolved in a minimum amount of benzene and was then chromatographed on a slurry packed Florisil column (ca. 1×53 cm). Elution with hexane gave residual olefin and the cyclopropane product, 10% ether-hexane gave benzophenone and some ketazine, and elution with up to 50% ether-hexane gave the remainder of the ketazine and some slowmoving tars. The results are listed in Table I and individual experimental details are listed below for some experiments.

Control Run with Reactants Mixed. A 3.88-g (20 mmol) sample of diphenyldiazomethane in 20 ml of dry ether was mixed with 6.60 g (8.3 ml, 100 mmol) of freshly distilled cyclopentadiene. Stirring for 1 hr at 0-5° gave no evolution of nitrogen and no observable diminution of color. After adding 2.56 ml of 0.8 M ethereal

ZnCl₂ solution, nitrogen began evolving. After an additional 45 min of stirring the reaction mixture was worked up to give 3.30 g (91%) of tetraphenylketazine crystals, mp 161-162°

Temperature Control Run. A 6.60-g (100 mmol) sample of cyclopentadiene and 25.6 ml (20 mmol, 0.8 M) of ethereal zinc chloride were mixed with 50 ml of dry ether as before. After cooling to -40° (internal temperature), slow addition of a 3.88-g (20 mmol) sample of diphenyldiazomethane in 200 ml of dry ether was begun but the temperature continued to drop to -50° . No nitrogen evolution or fading of the color was observed, so addition was stopped and the flask was allowed to warm up. At -15° , but not before, both diminution of color and nitrogen evolution were observed. The temperature stabilized at about 3° during the reaction. Products were not isolated for this reaction.

Large-Scale Preparation of 6,6-Diphenylbicyclo[3.1.0]hex-2-ene. Following the general procedure, an ethereal solution of 19.0 g (100 mmol) of diphenyldiazomethane in 50 ml was added to 41 ml (33 g, 500 mmol) of freshly distilled cyclopentadiene and 20.4 g (100 mmol) of fused zinc chloride in 60 ml of ether at 25° over 1 hr. After stirring for an additional 1 hr at 25°, the ethereal solution was decanted and concentrated in vacuo, and the resulting oil was extracted with hot hexane. Crystallization of the concentrated hexane solution gave 6.10 g (26.2%) of 6,6-diphenylbicyclo[3.1.0]hex-2-ene, mp 80-81° (lit.¹² mp 80-81°).

Zinc Chloride-Diphenyldiazomethane Reaction with 1.3-Cycloheptadiene. Following the general procedure an ethereal solution of 3.72 g (19 mmol) of diphenyldiazomethane in 25 ml of dry ether was added to 4.71 g (50 mmol) of 1,3-cycloheptadiene and 2.6 g (20 mmol) of fused zinc chloride in 25 ml of ether at 25° and then stirred for an additional 10 min. After concentration in vacuo, partitioning between ether and water gave 2.32 g of insoluble solid, mp 190-250°. After crystallizing out 883 mg of ketazine, mp 163-164°, from the ether-soluble fraction, the remaining 1.93 g of ether-soluble material was then chromatographed on a Florisil column to give 1.90 g of benzophenone (52%) and 20.9 mg (0.45%) of 8,8-diphenylbicyclo[5.1.0]oct-2-ene as a clear oil: NMR (CCl₄) δ 7.27 (5 H s, ArH), 7.05 (5 H s, ArH), 5.87 (1 H d with further splitting, vinyl CH), 5.6-5.1 (1 H m, vinyl CH), 2.85-0.8 (10 H envelope); ir (thin film) 3050, 3020, 2920, 2880, 1600, 1590, 1440, 1175, 1140, 1070, 1030, 745, 690 $\rm cm^{-1}$

Anal. Calcd for C₂₀H₂₀: C, 92.26; H, 7.74. Found: C, 91.87; H, 7.94.

An ether-insoluble solid, 419 mg, mp 240-250°, was isolated by filtration of the initial ether-water wash. Such material was isolated from nearly every reaction in varying yield, with mp 205-250°. TLC analysis shows a trace of tetraphenylketazine but the major component moves somewhat slower with chloroform eluent; NMR (CDCl₃) § 7.5 (ArH, s); ir (mull) 3360, 3320 (OH), 3090, 3060 (ArCH), 1595, 1565, 1445, 1390, 1230, 860, 690 cm⁻¹. Although elemental analyses on different samples varied, they indicated a probable C₂₆H₂₀N₂Cl₂Zn·2H₂O formula. Although this is formally a hydrated 1:1 complex of zinc chloride and tetraphenylketazine, it was not formed when ketazine was mixed with ethereal zinc chloride. The exact structure is still under investigation.

Diphenylcarbene Reaction with Cyclopentadiene. A Pyrex tube containing 1.94 g (10 mmol) of diphenyldiazomethane and 25 ml of freshly distilled cyclopentadiene was immersed in an ice bath alongside a 450-W Hanovia well and irradiated for 4 hr at 0-5°. After concentration and collection of 529 mg of tetraphenylethane, mp 208-211° (lit.²³ mp 211°), and 72 mg of tetraphenylketazine, mp 164-165°, the residue was chromatographed on a Florisil column packed with hexane to give 2.25 g of cyclopentadiene dimer, 652 mg of semisolid containing product, 296 mg of tetraphenylethane, and 457 mg of semisolid identified as benzophenone (25%) by ir and TLC. Crystallization afforded 456 mg (19.6%) of 6,6-diphenylbicyclo[3.1.0]hex-2-ene, mp 80-81°. The total tetraphenylethane yield was 36.4%.

Diphenylcarbene Reaction with 1,3-Cyclohexadiene. A 1.00-g (5.15 mmol) sample of diphenyldiazomethane dissolved in 10 ml of 1,3-cyclohexadiene was irradiated as before for 3 hr at 0-5°. After concentration 174 mg of tetraphenylethane was isolated and the residue was chromatographed on a Florisil column with hexane to give 64 mg of cyclohexadiene residue, 141 mg of diphenylmethane (16.2%), a mixture of the cyclopropane product plus an isomer, 19 mg of crystals, mp 83-84°, 1.2% of benzophenone, a total of 35.2% of tetraphenylethane, and 7.9% ketazine. The product mixture was rechromatographed to give 228 mg of clear oil identified as 7,7-diphenylbicyclo[4.1.0]hept-2-ene (18%) which afforded clear crystals: mp 49-50°; NMR (CCl₄) & 7.26 (5 H s, ArH) 7.09 (5 H s, ArH), 6.35-6.0 (1 H m, vinyl H), 5.55-5.2 (1 H m, vinyl

H), 2.35–1.15 (6 H m); uv (95% ethanol) λ_{max} (ϵ) 276 (634), 268 (1090), 226 (14,300), 260 (shoulder, 1400; ir (mull) 3040, 3020, 2910, 2850, 1600, 1490, 1440, 1060, 1020, 745, 680 cm⁻¹

Anal. Calcd for C19H18: C, 92.63; H, 7.36. Found: C, 92.65; H, 7.42.

The following fractions afforded 145 mg of crystals, mp 83-89° (11.5%), identified as 3-benzhydrylcyclohexa-1,4-diene. Recrystallization gave mp 101-102° with NMR (CCl₄) & 7.25 (10 H s, ArH), 5.58 (4 H d of d with overlapping inner peaks and satellites ± 14 Hz and smaller coupling ca. 2 Hz visible, vinyl H's), 3.70 (2 H m, bisallylic methines), 2.60 (2 H m, bisallylic methylenes); uv (95% ethanol) λ_{max} (ϵ) 268 (736), 260 (962), 255 (800), 217 (shoulder, 14,400); ir (Nujol, fluorolube) 3030, 2090, 1600, 1490, 1450, 1410, 1090, 1030, 950, 900, 750, and 690 cm⁻¹.

Anal. Calcd for C₁₉H₁₈: C, 92.63; H, 7.36. Found: C, 92.61; H, 7.46

Decomposition Studies. All reactions were run in air with 0.1 mmol of diphenyldiazomethane dissolved in 3.0 ml of commercial grade solvent. Approximately 50 mg of the metal salt was added and decomposition was followed by disappearance of color. Times for disappearance are listed in Table II. No attempt was made to dry the solvents or the salts.

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Arylsulfonoxylation of Aromatic Compounds. VI. Decomposition of m-Trifluoromethylbenzenesulfonyl Peroxide in the Absence of Solvent and in the Presence of Ethylbenzene and Cumene^{1a,b}

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m-Trifluoromethylbenzenesulfonyl peroxide (1) has been synthesized and found to be slightly more stable than the nitrobenzenesulfonyl peroxides. The thermal decomposition of 1 in ethylbenzene and cumene gives exclusively nuclear substitution with no side-chain products characteristic of a homolytic reaction. The stability and heterolytic dissociation of sulfonyl peroxides substituted with electron-withdrawing groups (NO_2 , CF_3) therefore are inherent and do not require the presence of a radical trap (e.g., a nitro group). Competitive m-trifluoromethylbenzenesulfonoxylations gave K_{Ar}/K_B : ethylbenzene, 14.8; cumene, 12.1. The ortho, meta, and para orientations (partial rate factors) are: ethylbenzene, 33.3, 5.8, 60.9% (14.8, 2.6, 54.2); cumene, 28.5, 7.8, 63.7% (10.3, 2.8, 46.1). The reactions of 1 with these two alkylbenzenes in ethyl acetate solution are first order with respect to the arenes and the enthalpies (entropies) of activation are: ethylbenzene, 16.7 (-17.4); cumene, 16.6 (-18.2). The reaction of 1 with benzene is first order with respect to the arene in methylene chloride, but in ethyl acetate an overall order of 0.66 is due to a competition to the reaction first order with respect to benzene (ΔH^{\ddagger} , 18; ΔS^{\ddagger} , -20) by a reaction zero order with respect to benzene (ΔH^{\ddagger} , 30; ΔS^{\ddagger} , 22). The ΔS^{\ddagger} for the zero-order reaction corresponds to a homolytic mechanism. The thermal decomposition of neat 1 (1.00 mol) and treatment of the reaction mixture with ethanol produced m-trifluoromethylbenzenesulfonic acid (0.538), 2-hydroxy-4-trifluoromethylbenzenesulfonic acid (0.617), ethyl m-trifluoromethylbenzenesulfonate (0.159), m-trifluoromethylphenyl m-trifluoromethylbenzenesulfonate (0.261), and m-trifluoromethylphenol (0.04). These products can be explained by a series of ionic intermediates.

Of all the arylsulfonyl peroxides reported up to this time (benzene-, p-toluene-, p-chlorobenzene-, p-bromobenzene-, 3,4-dichlorobenzene-, and o-, m-, and p-nitrobenzenesulfonyl peroxides),^{2,3} only the nitro derivatives are sufficiently stable at room temperature for routine laboratory use. The nitrobenzenesulfonyl peroxides have been found to undergo a heterolytic scission in the presence of aromatic substrates leading to an electrophilic substitution.

$$(O_2NC_6H_4SO_3)_2 + C_6H_5X \longrightarrow O_2NC_6H_4SO_3C_6H_4X + O_2NC_6H_4SO_3H (1)$$

There are two possible reasons for the stability of the nitrobenzenesulfonyl peroxides. First, the electron-withdrawing effect of the nitro group, by reducing the electron density on the peroxidic oxygens, may suppress any tendency for homolytic scission, similar to the stabilizing influence previously observed in the nitrobenzoyl peroxides.⁴ Second, all sulfonyl peroxides may be inherently susceptible to an induced homolytic decomposition and the stabilizing effect of the nitro group could be due to its ability to interrupt such a chain reaction by acting as a radical trap. $^{5-8}$

In the present work it was planned to synthesize *m*-trifluoromethylbenzenesulfonyl peroxide (1) and study its stability and some of its reactions. The m-trifluoromethyl group in its electron-withdrawing ability (σ 0.42) is similar to the *m*-nitro group (σ 0.71) but it is not a radical trap; therefore any unusual stability or reactions of 1 must be attributed specifically to the inductive effect of the trifluoromethyl group.

Results and Discussion

Synthesis of 1 was successfully accomplished by established methods⁹ and it was found to be sufficiently stable at room temperature for routine laboratory use. Its high stability in contrast to that of most of the other arylsulfonyl peroxides can be due only to the inductive effect of the trifluoromethyl group, and the stability of the nitrobenzenesulfonyl peroxides now can similarly be attributed to the inductive effect of the nitro group.

Thermal decomposition of 1 in ethyl acetate solutions of alkylbenzenes was undertaken next. The nitrobenzenesulfonyl peroxides have been found to react in high yields with these hydrocarbons exclusively by an electrophilic substitution of the nucleus. The absence of any sidechain attack products characteristic of a homolytic dissociation of these peroxides conceivably could be attributed again to the nitro group acting as a radical trap. It has now been found that the reaction of 1 with ethylbenzene and cumene gives only nuclear substitution (Table I), although yields of as little as 1% of 2,3-diphenyl-2,3-dimethylbutane-(the expected side-chain attack products) could have been detected. The result with cumene is particularly significant, for this hydrocarbon undergoes side-chain hydrogen abstraction readily with a variety of free-radical reagents.¹⁰⁻¹² Therefore, the tendency of the arylsulfonyl peroxides to undergo heterolytic scission in the presence of aromatic substrates is inherent and not dependent on the presence of a trapping agent for free radicals to prevent an induced decomposition from becoming predominant.

The relative reactivities with respect to benzene and the orientations of substitution of ethylbenzene and cumene using 1 (Table II) are characteristic of an electrophilic substitution and are similar to those obtained using o- and mnitrobenzenesulfonyl peroxides. The greatest differences are the slightly greater ortho substitutions obtained with 1.

The kinetic orders of the reactions with respect to arene