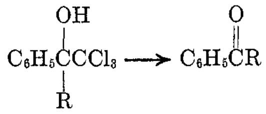
TABLE IV

HYDROLYSIS OF ALKYLPHENYLTRICHLOROMETHYLCARBINOLS



$$C_6H_5C(OH)(R)CCl_3 \longrightarrow C_6H_5C(=O)R$$

R	Reagent	Product	Yield, %
Cyclobutyl	H_2SO_4	Starting material	71
Cyclobutyl	K_2CO_3	Ketone	94
Cyclobutyl	ZnO	Starting material	98
Cyclobutyl	MgO	Starting material	98
Cyclobutyl	Pyridine	Starting material	95
Cyclobutyl	$AgNO_3$	Starting material + ketone	
Isopropyl	K_2CO_3	Ketone	83

phenyltrichloromethylcarbinols to the respective α-hydroxy acids. The results are shown in Table IV. In all cases studied, the only product formed was the parent ketone, arising from the elimination of chloroform. In the cases in which no ketone was formed, starting carbinol was nearly quantitatively recovered.

Oxidation of Glycolic Aldehydes. General Procedure. 2-Hydroxy-2-cyclobutylphenylacetic Acid (13).—To 2-hydroxy-2-cyclobutylphenylacetaldehyde (300 mg, 1.58 mmol) in dioxane (10 ml) at 10–15° was added potassium permanganate (250 mg) in water (10 ml). The solution was filtered to remove manganese dioxide and 5% sodium hydroxide was added to pH 10. The solution was extracted with ether (two 10-ml portions) to afford an oil (110 mg). The ir spectrum indicated the oil contained about 65% of cyclobutyl phenyl ketone and 35% of unreacted aldehyde. The aqueous basic solution was acidified with hydrochloric acid and extracted with ether (two 10-ml portions) to afford crude acid **13** which was recrystallized from chloroform to yield 140 mg (43%) of pure acid, mp 138–139° (lit.[9] mp 143–143.5°).

2-Hydroxy-2-cyclopropylphenylacetic Acid (14).—2-Hydroxy-2-cyclopropylphenylacetaldehyde (300 mg, 1.7 mmol) was oxidized with permanganate by the general procedure. The crude material was recrystallized from benzene–petroleum ether to yield 122 mg (37%) of pure product, mp 88.5–89.5° (lit.[9] mp 91–92°).

2-Hydroxy-2-cyclopentylphenylacetic Acid (15).—The glycolaldehyde **7** (300 mg, 1.47 mmol) was converted to the acid by the general procedure. The crude product was recrystallized from chloroform and gave 155 mg (48%) of pure acid, mp 146.5–147.5° (lit.[10] mp 147–148°).

2-Hydroxy-2-phenyl-3-methylbutanoic Acid (16). A.—2-Hydroxy-2-phenyl-3-methylbutyraldehyde (300 mg, 1.7 mmol) was oxidized with permanganate by the general procedure. The product was recrystallized from chloroform and amounted to 130 mg (40%), mp 148–149°.

Anal. Calcd for $C_{11}H_{14}O_3$: C, 68.02; H, 7.26. Found: C, 68.22; H, 7.55.

B.—To a cooled solution of 2-chloro-2-phenyl-3-methylbutyraldehyde (1.4 g, 71 mmol) in dioxane (110 ml) and concentrated HCl (6 ml) was added potassium permanganate (4.5 g, 28.5 mol) in water (55 ml). The solution was stirred in an ice bath for 45 min, at which time all potassium permanganate was consumed. The solution was filtered and extracted with chloroform (three 30-ml portions). The organic layer was dried ($MgSO_4$) and concentrated. The residue was dissolved in chloroform (5 ml) and petroleum ether (60 ml) and the solution was washed with saturated sodium bicarbonate solution (two 20-ml portions). The bicarbonate solution was acidified with HCl and filtered to yield 0.85 g (61%) of crude hydroxy acid **16**, mp 144–145°. A sample was recrystallized from chloroform and melted at 148–149°; the ir spectrum ($CHCl_3$) was identical with that of the material prepared above. The petroleum ether solution was dried and concentrated to yield 0.35 g of an oil which was shown by ir analysis to be predominantly unreacted α-chloroaldehyde.

Registry No.—**1**, 33483-07-7; **2**, 33483-08-8; **3**, 33483-09-9; **4**, 33483-10-2; **5**, 33483-11-3; **6**, 33483-12-4; **7**, 31142-50-4; **8**, 33483-14-6; **11**, 33487-50-2; **12**, 33487-51-3; **13**, 1460-47-5; **14**, 1460-46-4; **15**, 427-49-6; **16**, 15879-60-4.

Acknowledgment.—The authors wish to acknowledge Mr. James P. Lockhard for his valuable technical assistance.

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[9] S. B. Kadin and J. G. Cannon, *J. Org. Chem.*, **27**, 240 (1962).

[10] J. H. Biel, H. L. Friedman, H. A. Leiser, and E. P. Sprengler, *J. Amer. Chem. Soc.*, **74**, 1485 (1952).

Notes

Charge Distribution in the Addition of Dichlorocarbene to Olefins

ELLIS V. COUCH[1] AND JOHN A. LANDGREBE*

Department of Chemistry, University of Kansas, Lawrence, Kansas 66044

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Although numerous qualitative observations have demonstrated the electrophilic nature of dichlorocarbene in its addition to carbon–carbon double bonds,[2,3] quantitative measurements of the extent of charge development have been meager and are summarized in Table I. The addition of the carbene to styrenes[4] and α-methylstyrenes[5] was best correlated by σ^+, with the more reactive (more nucleophilic) α-methylstyrene system yielding the smaller ρ value. The order of magnitude of these ρ values reflects only modest charge development at the benzylic position in the transition state relative to the ground state in accord with expectations for a concerted but unsymmetrical addition passing through a transition state with unequal bond formation to the two carbon atoms of the double bond.[5-7]

In contrast to the above studies was a report by

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[1] Taken from the Ph.D. dissertation of E. V. Couch. Partial support from the Petroleum Research Fund is hereby acknowledged.

[2] W. Kirmse, "Carbene Chemistry," Academic Press, New York, N. Y., 1964, p 163.

[3] D. Bethell, *Advan. Phys. Org. Chem.*, **7**, 153 (1969).

[4] D. Seyferth, J. Y-P. Mui, and R. Damrauer, *J. Amer. Chem. Soc.*, **90**, 6182 (1968).

[5] I. H. Sadler, *J. Chem. Soc. B*, 1024 (1969).

[6] R. Hoffmann, *J. Amer. Chem. Soc.*, **90**, 1475 (1968).

[7] Such results do not clearly distinguish between the unsymmetrical concerted reaction or a two-step process involving a zwitterionic intermediate with a transition state which occurs early along the reaction coordinate.

TABLE I

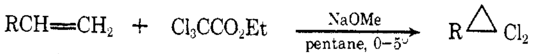
SUMMARY OF LFE CORRELATIONS FOR DICHLOROCARBENE ADDITIONS TO CARBON–CARBON DOUBLE BONDS

Olefin type	Method of $:CCl_2$ generation	Substituent constant	Reaction constant	Ref
$p\text{-}RC_6H_4CH{=}CH_2$	$PhHgCBrCl_2$	σ^+	-0.619 ± 0.045	4
$RC_6H_4(CH_3)C{=}CH_2$	$CHCl_3$ + KO-*tert*-Bu	σ^+	-0.378 ± 0.015	5
$R_1R_2C{=}CR_3R_4$		$\Sigma\sigma^*$	-4.3	8
$RCH{=}CH_2$	Cl_3CCO_2Et + NaOMe	σ^+	-0.74 ± 0.02	This work

Skell[8] that dichlorocarbene addition to a variety of simple aliphatic olefins could be correlated with the Taft σ^* parameter with $\rho^* \cong -4.3$, a value which seems unexpectedly negative. However, interpretation is complicated because the use of olefins with differing numbers of substituents led these authors to sum the substituent constants for all aliphatic groups on the double bond, a practice which is questionable in view of the well-known reactivity differences in 1,1- and 1,2-disubstituted olefins[2] each of which would possess the same $\Sigma\sigma^*$.

Results and Discussion

In the present study, dichlorocarbene generated by the method of Parham[9] was added to a series of monosubstituted olefins, **1**, in which the substituents were



1 **2**

a = $n\text{-}C_4H_9$ **d** = $PhCH_2CH_2$
b = CH_3OCH_2 **e** = $PhOCH_2$
c = $ClCH_2$

chosen so as to avoid undesirable side reactions, resonance effects, and differences in steric effects.[10] The exclusive product in each case was the expected dichlorocyclopropane (**2**) except for olefin **1b** which also resulted in a very small amount of 3-methoxy-4,4-dichloro-1-butene from insertion of the carbene into an allylic carbon–hydrogen bond. A suitable control experiment showed that under the reaction conditions the allylic chlorine atom of **1c** was not displaced by methoxide.

Values of ρ^* calculated for several pairs of olefins by use of eq 1 in which P_1, P_2, O_1, and O_2 represent the

$$\log\,[(P_1O_2)/(P_2O_1)] = \rho^*(\sigma_1^* - \sigma_2^*) \qquad (1)$$

relative amounts of product 1, product 2, initial olefin 1, and initial olefin 2, respectively, are in good agreement (Table II).

In order to ensure that the term (P_1O_2/P_2O_1) would be essentially equal to k_1/k_2, the ratio of total initial olefin to ethyl trichloroacetate was at least 10 for each competition.[4,11] The apparent molar product ratios determined by vapor phase chromatography were corrected from a detector sensitivity curve established from a series of known mixtures of products and an internal standard.

TABLE II

DICHLOROCARBENE COMPETITIONS IN ADDITIONS TO SELECTED MONOSUBSTITUTED OLEFINS

Substituent	σ^*	ρ^*
$n\text{-}C_4H_9$	-0.13	-0.71
CH_3OCH_2	0.52	-0.75
$ClCH_2$	1.05	
$PhCH_2CH_2$	0.08	-0.75
$PhOCH_2$	0.85	
	Av =	-0.74 ± 0.02

Although it is not possible to make a simple direct comparison of the values derived from σ^+ and σ^* correlations, respectively, the small negative values of the reaction constants listed in Table I suggest that the sensitivity of both styrenes and other monosubstituted olefins toward dichlorocarbene addition are comparable. The observed value of -0.74 in our study is similar to the values of -0.742 and -0.606 reported for the reaction of primary alkyl *p*-toluenesulfonates with ethanol (100°) and primary alkyl bromides with thiophenoxide in methanol (20°), respectively, neither of which would be expected to involve substantial charge separation in the transition state relative to the ground state.[12]

Experimental Section[13]

Methyl allyl ether was synthesized in 65% yield from allyl bromide (freshly distilled, dry) and sodium methoxide (commercial) according to the method of Bailey.[1] The product ether was separated from excess allyl bromide by fractional distillation (50-cm wire spiral column), bp 42° (lit.[14] bp 43°).

Attempted Reaction of Allyl Bromide with Sodium Methoxide under Conditions of Dichlorocarbene Generation.—Allyl bromide (6.05 g, 0.05 mol, freshly distilled, dry) was added to a cooled mixture of sodium methoxide (1.08 g, 0.02 mol, commercial) in pentane (20 ml) and stirred (2 hr, ice bath), followed by filtration, several water washes, and drying ($MgSO_4$). Careful distillation (50-cm wire spiral column) followed by observation of the nmr and ir spectra for the distillate with the same boiling range as methyl allyl ether showed no peaks attributable to it.

1,1-Dichloro-2-*n*-butylcyclopropane (**2a**) was prepared by the method of Parham[9] except for the work-up. The reaction mixture was washed with water and dried ($MgSO_4$), washed with concentrated sulfuric acid followed by water, and dried ($MgSO_4$), followed by removal of the pentane and distillation to give product (4.1 g, 0.024 mol, 61.4%), bp 68° (10 mm) [lit.[11] bp 71.6–72° (20 mm)].

The nmr spectrum contained a large broad singlet at τ 8.45 and two peaks at 9.07 and 9.12 protruding from the multiplet which extends from 8 to 9.32. The ir spectrum (CCl_4) contains

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[8] P. S. Skell and M. S. Cholod, *J. Amer. Chem. Soc.*, **91**, 7131 (1969).

[9] W. E. Parham and E. E. Schweizer, *J. Org. Chem.*, **24**, 1773 (1959).

[10] R. A. Moss and A. Mamantov, *Tetrahedron Lett.*, 3425 (1968).

[11] W. von E. Doering and W. A. Henderson, Jr., *J. Amer. Chem. Soc.*, **80**, 5274 (1958).

[12] A. Streitwieser, Jr., *ibid.*, **78**, 4935 (1956).

[13] Elemental analyses were performed by the Department of Medicinal Chemistry at the University of Kansas or by the Galbraith Laboratories, Inc., Knoxville, Tenn., unless otherwise noted. Melting points and boiling points (capillary method) are uncorrected. Infrared spectra were obtained from a Beckman IR-8 instrument (sodium chloride optics) with a 1604 cm^{-1} (polystyrene *vs.* air) as a reference standard. Analyses of halides by vpc were performed with an F & M Model 700 instrument (thermal conductivity detector) and the following columns: 20% QF-1 on 30–60 Chromosorb P (15 ft × 0.25 in.); 20% Carbowax 20M on 30–60 Chromosorb P (12 ft × 0.25 in.); 20% tris(cyanoethoxy)propane on 30–60 Chromosorb P (12 ft × 0.25 in.); 15% SE-30 on 30–60 Chromosorb W (10 ft × 0.25 in.); and 10% OV-210 on 80–100 Gas Chrome Q (6 ft × $^1/_8$ in. glass column). Area measurements were performed with a Disc Integrator. A Varian A-60 or A-60-A spectrometer was used to determine nmr spectra of compounds as solutions in carbon tetrachloride containing 3–6% tetramethylsilane.

[14] W. J. Bailey and L. Nicholas, *J. Org. Chem.*, **21**, 648 (1956).

peaks at 2950 (s), 2870 (s), 2870 (s), 1425, 1375, 1218 (w), 1190 (w), 1118, 1040 (w), 1015 (w), 948 (w), 909, and 750 cm^{-1}.

1,1-Dichloro-2-(chloromethyl)cyclopropane (**2c**) was prepared in 25.1% overall yield from allyl chloride (freshly distilled, dry) *via* a method similar to the preparation of compound **2a**. The crude reaction mixture was washed and dried (MgSO$_4$) and the solvent removed. 1,1-Dichloro-2-(chloromethyl)cyclopropane was separated from the other components by preparative vpc (Aerograph Autoprep Model A-700, 15% Carbowax 20M). The observed boiling point was 162° [lit.[15] bp 56° (17 mm)].

The nmr spectrum shows a perturbed doublet with the smaller peak at τ 6.3, the larger at 6.42 (2 H, $J = 8$ Hz, Cl-CH$_2$) and also a multiplet from 7.6 to 8.8 (3 H, cyclopropyl). The ir spectrum (CS$_2$) contains peaks at 2950 (w), 1425, 1370, 1265, 1220 and 1201 (doublet), 1113 and 1096 (doublet), 1043, 1025, 965 (w), 948, 918, 871 (w), 809 (w), 775 (s, sh), 755 (s), and 714 cm^{-1} (s).

Methyl 2,2-dichlorocyclopropylcarbinyl ether (**2b**) was prepared from methyl allyl ether in 7.45% yield by the procedure described for compound **2a**. The crude reaction mixture was washed and the solvent removed. The residue was stirred and kept at reflux for 3 hr with sodium hydroxide solution (a volume excess, 20% by weight). The basic solution was extracted with pentane; the pentane layer was washed and dried (MgSO$_4$); and the pentane was removed. The residual liquid was distilled to give colorless product, bp 155°, 73° (37 mm).

The nmr spectrum displays a doublet centered at τ 6.5 (2 H, $J = 6$ Hz, OCH$_2$CH), a singlet at 6.66 (3 H, CH$_3$O–), and a multiplet from 7.82 to 8.98 (3 H, cyclopropyl). The ir spectrum contains peaks at 2990 (w), 2920, 2880, 2820, 1430, 1400, 1220 (w), 1195, 1142, 1100 (s), 1052 (w), 1032 (w), 1009 (w), 985 (w), 915 (w), and 747 cm^{-1} (s).

Anal. Calcd for C$_5$H$_8$OCl$_2$: C, 38.74; H, 5.20. Found: C, 38.61; H, 4.96.

4,4-Dichloro-3-methoxy-1-butene is apparently formed as a minor (*ca.* 5%) product resulting from dichlorocarbene insertion into an allylic carbon–hydrogen bond during the formation of methyl 2,2-dichlorocyclopropylcarbinyl ether. A few drops of this insertion product were obtained by preparative vpc (F & M Model 700, 15% QF-1). The nmr spectrum shows a doublet centered at τ 4.4 ($J = 5$ Hz, –CCl$_2$H) superimposed upon a multiplet absorbing from 3.82 to 4.9 (total area 4 H) which resembles an ABC splitting pattern (–CH=CH$_2$). Additionally the spectrum contains a poorly resolved triplet at 6.16 (1 H, $J = 6$ Hz, –OCHCH=CH$_2$) and a sharp singlet at 6.6 (3 H, CH$_3$O–). The ir spectrum (CS$_2$) has peaks at 1180 (w), 1100, 980 (w), and 932 in common with those of methyl allyl ether, as well as a major peak at 778 cm^{-1} (CCl$_2$), some 35 cm^{-1} removed from the corresponding peak in the spectrum of the expected carbene addition product **2b**.

1,1-Dichloro-2-(2-phenylethyl)cyclopropane (**2d**), bp 69° (0.15 mm) [lit.[16] bp 96° (4 mm)], was obtained in 10% yield from 4-phenyl-1-butene (freshly distilled, Aldrich) *via* the process described for compound **2a**. The nmr spectrum contains a singlet at τ 2.82 (5 H, aryl), a triplet centered at 7.2 (2 H, $J = 8$ Hz, benzyl), and a multiplet from 8.0 to 9.1 (5 H, CH$_2$–cyclopropyl). The ir spectrum coincides with that reported.[16]

Phenyl 2,2-dichlorocyclopropylcarbinyl ether (**2e**) was synthesized from allyl phenyl ether in 12.1% yield according to the procedure described previously, bp 79° (0.28 mm). The nmr spectrum consisted of a complex multiplet from τ 2.55 to 3.3 (5 H, aryl), a doublet centered at 5.97 (2 H, $J = 6$ Hz, –OCH$_2$–), and a multiplet from 7.66 to 8.89 (3 H, cyclopropyl). The ir spectrum (CS$_2$) shows peaks at 3032 (w), 2934 (w), 2875 (w), 1592 (s), 1398, 1330 (w), 1298, 1237 (s), 1218 (s), 1168, 1112, 1077, 1041 (s), 884 (w), 800, 748 (s), and 687 cm^{-1} (s).

Anal. Calcd for C$_{10}$H$_{10}$OCl$_2$: C, 55.32; H, 4.64. Found: C, 55.59; H, 4.81.

Competitive Addition of Dichlorocarbene to Olefins.—To a magnetically stirred mixture of pentane (30 ml, dry, alkene free) and sodium methoxide (1.62 g, 0.03 mol, commercial) cooled in an ice bath were added, by syringe through a rubber septum, equimolar quantities (0.125 mol) of each olefin. The syringe cap was quickly replaced by a pressure compensated addition funnel containing ethyl trichloroacetate (4.78 g, 0.025 mol) and the system was held tightly closed by rubber bands. The ester was added dropwise (*ca.* 1.5 hr) and the reaction mixture left stirring an additional 1.5 hr. The reaction mixture was gravity filtered, the residual sodium methoxide rinsed with pentane (two 15-ml portions), and this washing combined with the filtrate. The solution was washed (four 30-ml portions) and dried (MgSO$_4$) and the solvent removed under vacuum at room temperature. Vpc analysis of the distillate indicated complete absence of any dichlorocyclopropyl product.

For olefins with an aryl substituent the reaction mixture was filtered, washed twice (two 20-ml portions), and dried (MgSO$_4$). The pentane was removed and the product mixture partially distilled under vacuum (50-cm wire spiral column). Methyl ethyl carbonate distilled from the mixture at room temperature (0.1 mm). Most of the excess olefin likewise distilled at a bath temperature of 75° (0.1 mm). The head temperature was not permitted to rise above 30° (0.1 mm). Vpc analysis of the distillate indicated complete absence of any dichlorocyclopropyl product.

Weighed portions (*ca.* 27 μl) of the product mixture were thoroughly mixed with weighed amounts (*ca.* 3 μl) of internal standard in small screw cap vials sealed with a square of polyethylene sheet. 7,7-Dichloronorcarane was used as the internal standard for all the olefin competitions except that of phenyl allyl ether *vs.* 4-phenyl-1-butene for which 1,1-dichloro-2-benzylcyclopropane was used. Several aliquots (*ca.* 1 μl) were withdrawn from each of the vials by a syringe (Hamilton, 10 μl) and injected directly into the vpc. Each column used was calibrated by injecting solutions containing internal standard in known and varied quantities of the carbene adduct products in order to provide an experimental correlation of peak area ratios with compound mole fractions. The observed peak area ratios were corrected to actual mole fractions by reference to this sensitivity calibration curve.

Registry No.—**2a**, 3722-08-5; **2b**, 33707-14-1; **2c**, 3722-05-2; **2d**, 20849-80-3; **2e**, 33666-40-9; dichlorocarbene, 1605-72-7; 4,4-dichloro-3-methoxy-1-butene, 33712-31-1.

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[15] W. M. Wagner, H. Kloosterziel, and S. Van der Ven, *Recl. Trav. Chim. Pays-Bas*, **80**, 740 (1961).

[16] V. S. Aksenov, I. A. Dyakonov, and R. R. Ksotokov, *Zh. Org. Khim.*, **4**, 1680 (1968).

Palladium-Catalyzed Reactions of Allene with Diolefins

D. Robert Coulson

Contribution No. 1852 from the Central Research Department, Experimental Station, E. I. du Pont de Nemours and Company, Wilmington, Delaware 19898

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Several examples of transition metal catalyzed oligomerizations of allenes have been reported.[1] However, such reactions of allenes with other olefins are relatively rare.[2] In this regard we wish to report two novel examples of catalyzed reactions of allene with diolefins.

When a mixture of allene, butadiene, and a catalytic amount of bis(triphenylphosphine)(maleic anhydride)palladium[3] was heated to 120°, a 39% yield of a 3:1 mixture of *trans*- and *cis*-2-methyl-3-methylene-1,5,7-octatriene (**1**), respectively, was obtained. Hydrogenation of **1** over 5% Pd on charcoal yielded 2,3-dimethyloctane.

During the preparation of **1**, concurrent dimerizations of the butadiene to a mixture of 4-vinylcyclo-

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[3] S. Takahashi, T. Sibano, and N. Hagihara, *Bull. Chem. Soc. Jap.*, **41**, 454 (1968).