former is definitely in reasonable agreement with the experimental value while the latter is not.²⁶

The infrared spectrum of VII does not show any bands in solution which are not shown by the mull. Hence, a single fixed conformation, rather than an equilibrium, is indicated.

Chiurdoglu and co-workers⁹ have shown that the methylene deformation band in the 1450 cm.⁻¹ region can be of use as an indication of the minimum number of different kinds of methylenes which are to be found in a molecule. This region of the spectrum was examined for all the compounds discussed, and in each case the number of bands in this region was less than or equal to the number predicted from the different kinds of methylenes thought to be present. This criterion therefore is consistent with what has already been concluded, but yields no new information.

The conclusions drawn are that, as suggested earlier,⁴⁻¹³ cycloöctane ring in general appears to exist in a single conformation, that of a stretched crown. Ring substituents may be expected to take up various positions depending on their nature. A carbonyl group prefers to be at C-1, while its ketal prefers C-3.

Experimental

Cyclohexanone Ethylene Ketal (IV).—The preparation was carried out in the usual way.²⁷ The product was dis-

(25) J. W. Smith, "Electric Dipole Moments," Butterworths, London, 1955, p. 256.

(26) The possibility that the ketal is located at C-2 cannot be eliminated on the basis of the experimental facts, but it seems unlikely. Likewise, a skewed crown can be made to fit the facts.

(27) M. Sulzbacher, E. Bergmann, and E. R. Pariser, J. Am. Chem. Soc., 70, 2827 (1948). tilled through a spinning band column and the fraction distilling at $60-61^{\circ}$ (10 mm.) was collected, wt. 5.1 g., $n^{20}D$ 1.4580 (reported²⁷ b.p. 65° (10 mm.), $n^{21}D$ 1.4580).

Cycloöctanone Ethylene Ketal (VIII).—Five grams of cycloöctanone, 25 ml. of ethylene glycol, and 0.5 of ptoluenesulfonic acid monohydrate were refluxed in dry benzene for 80 hr. using a water separator. The reaction mixture was worked up as described for IV. The fraction distilling at 76–77° at 5 mm., 3.8 g., $n^{22}D$ 1.4755 was collected.

Anal. Calcd. for $C_{10}H_{18}O_2$: C, 70.52; H, 10.67. Found: C, 70.67; H, 10.65.

4-(*p*-Chlorophenyl)-cyclohexanone Ethylene Ketal (V).— The ketal was prepared from *p*-chlorophenylcyclohexanone^{23b} exactly as described for IV. The crude material was crystallized from pentane to give a 75% yield of product of m.p. $85-86.5^{\circ}$.

Anal. Calcd. for C₁₄H₁₇ClO₂: C, 66.49; H, 6.67. Found: C, 66.73; H, 6.89.

5-(p-Chlorophenyl)-cycloöctanone Ethylene Ketal (VII).— The ketal was prepared from 5-(p-chlorophenyl)-cycloöctanone⁷ exactly as described for the preparation of IV. The crude material (1.2 g.) was crystallized from pentane to give 1.0 g. (66%) of transparent crystals, m.p. 80–81°.

Anal. Calcd. for $C_{16}H_{21}ClO_2$: C, 68.41; H, 7.54. Found: C, 68.51; H, 7.66.

Dipole Moments.—The dipole moments of the various ketones were run at 25° in benzene solution and the data are given in Table I. The dipole moment apparatus has been described previously.²⁸ The moments were calculated by essentially the method of Halverstadt and Kumler.²⁹ utilizing an IBM 650 computer programmed as described earlier.³⁰ The molar refractivities were calculated from tables³¹; atomic polarization was neglected.

(29) I. F. Halverstadt and W. D. Kumler, J. Am. Chem. Soc., 64, 2988 (1942).

 (30) N. L. Allinger and J. Allinger, J. Org. Chem., 24, 1613 (1959).
 (31) A. I. Vogel, W. T. Cresswell, G. J. Jeffrey, and J. Leicester, Chem. Ind. (London), 358 (1950).

Cycloaddition of Diazo Compounds to Ethyleneboronic and Acetyleneboronio Esters¹

DONALD S. MATTESON

Department of Chemistry, Washington State University, Pullman, Washington

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Cycloadditions of ethyl diazoacetate and diphenyldiazomethane to dibutyl acetyleneboronate yield pyrazoleboronic acids. Dibutyl ethyleneboronate undergoes similar cycloadditions, but the initial adduct immediately undergoes boron migration from carbon to nitrogen followed by disproportionation to butyl borate and material which yields a 5-substituted 2-pyrazoline on alcoholysis. The rate of addition of ethyl diazoacetate to dibutyl ethyleneboronate is 0.3 times that to ethyl acrylate and is but slightly affected by solvents or changing from the *n*- to the *t*-butyl ester. The evidence supports a concerted mechanism for the cycloaddition. The reactivity of dibutyl ethyleneboronate correlates well with simple molecular orbital calculations if $\alpha_B \cong \alpha_C - 0.7\beta_{C-C}$.

On the basis of simple molecular orbital calculations, the prediction has been made that suitable nucleophilic reagents should attack the β -carbon atom of α,β -unsaturated boronic esters.² Diffi-

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culty in testing this prediction arises because the boron atom competes rapidly and efficiently for bases—for example, Grignard reagents react at boron.³ Nucleophilic attack at the β -carbon atom has now been verified with the cycloaddition of diazo compounds to dibutyl ethyleneboronate and

(3) D. S. Matteson, J. Org. Chem., 27, 275 (1962).

⁽²⁸⁾ N. L. Allinger, H. Blatter, M. A. DaRooge, and L. A. Freiberg. J. Org. Chem., 26, 2550 (1961).

⁽²⁾ D. S. Matteson, J. Am. Chem. Soc., 82, 4228 (1960).

acetyleneboronate, and kinetic measurements indicate that the boronic ester group is almost as effective as a carboxylic ester group in withdrawing electrons from the double bond.

Cycloaddition Products.—An equimolar mixture of ethyl diazoacetate and dibutyl ethyleneboronate at 25° does not evolve nitrogen⁴ but separates into two liquid phases. The colorless upper phase proved to be practically pure tributyl borate, representing 90% of the available butoxy groups. The viscous lower phase was freed of boron by treatment with ethanol and removal of ethyl borate under vacuum. Distillation yielded 45% of a liquid isomer (I) of the known 3-carbethoxy-2pyrazoline (II),⁵ followed by traces of the latter and considerable nonvolatile residue.

The isomer (I) is 5-carbethoxy-2-pyrazoline. Like II,^{5a} I is readily oxidized with bromine to 3(5)-carbethoxypyrazole. In contrast to II, the ultraviolet spectrum of I closely resembles that of 2-pyrazoline and the infrared spectrum shows the carbonyl group to be unconjugated. Structure I has also been confirmed by n.m.r. (Varian Associates).



Unexpectedly, attempted preparation of an authentic sample of pyrazoline II from ethyl acrylate and diazomethane^{5b} yielded instead the third tautomer, long postulated to be an intermediate, 3-carbethoxy-1-pyrazoline (III), recognized by the absence of any N-H band in the infrared. This distillable liquid was readily tautomerized to crystalline II by warming with a catalytic amount of ethanol. Tautomerization of the less stable I to II via III might be expected in view of a recent report on the tautomerization of phenylhydrazones,⁶ but has been found to be very slow. Dibutyl ethyleneboronate and ethyl diazoacetate refluxed in ethanol for twenty-two hours yield about as much pyrazoline I as in the absence of solvent, plus 10%of tautomer II.

The pyrazoline I must result from the expected cycloaddition followed by migration of boron (instead of the customary hydrogen) from carbon to nitrogen, discussed below under Mechanism. There can be no doubt about the direction of the addition of ethyl diazoacetate to the double bond, since dibutyl 1-propene-1-boronate and propene-2-boronate yield, respectively, 4-methyl- and 3methyl-5-carbethoxy-2-pyrazoline as expected. These structures have been confirmed by infrared and ultraviolet spectra and oxidation to the corresponding pyrazoles.

In contrast to the above, the postulated initial adduct (IV) of dibutyl acetyleneboronate and ethyl diazoacetate does not permit boron migration, since it would result in a bent allenic carbon atom, but aromatizes via a normal proton shift, leading after hydrolysis to crystalline 5(3)-carbethoxypyrazole-3(5)-boronic acid (Va). The boronic acid



Va is sufficiently stable to permit alkaline hydrolysis of the carboxylic ester group to the acid, Vb. The structure of Va was proved by oxidation with hydrogen peroxide to 3-carbethoxy-2-pyrazol-5one (VI), identical with an authentic sample⁷ from hydrazine and diethyl oxalacetate.

Diphenyldiazomethane undergoes cycloadditions analogous to those of ethyl diazoacetate. With dibutyl ethyleneboronate, 5,5-diphenylpyrazoline (VII) results after alcoholysis. The postulated initial adduct (VIII) with dibutyl acetyleneboronate rearranges and the product isolated after hydrolysis is 4,5(3)-diphenylpyrazole-3(5)-boronic acid (IX). Structure IX is supported by alkaline



deboronation to 4,5(3)-diphenylpyrazole, by infrared and ultraviolet spectra, and by hydrogen peroxide deboronation to 3(5),4-diphenylpyrazol-5(3)one. Phenyl migrations in the pyrazole series have ample precedent.⁸

Diazomethane decomposes to polymethylene and nitrogen in a fraction of a second when poured into ethereal dibutyl acetyleneboronate, evidently because of the high Lewis acid strength of the latter. With dibutyl ethyleneboronate much polymethylene is also formed, but at -10° the color of the diazomethane persists about an hour, about half of the boronic ester is degraded to butyl borate, and 2-pyrazoline is formed in (at least) 5–10% yield after hydrolysis.

Kinetics.—Solutions initially contained 0.7-0.9% ethyl diazoacetate (redistilled at 1 mm.) and

⁽⁴⁾ Nitrogen evolution would not have been surprising in view of the familiar decomposition of diazomethane to nitrogen and polymethylene in the presence of borate esters [H. Meerwein and W. Burneleit, Ber., **61**, 1840 (1928)].

^{(5) (}a) K. von Auwers and E. Cauer, Ann., 470, 284 (1929).
(b) H. E. Carter, F. R. Van Abeele, and J. W. Rothrock, J. Biol. Chem., 178, 325 (1949).

⁽⁶⁾ R. O'Connor, J. Org. Chem., 26, 4375 (1961).

⁽⁷⁾ R. von Rothenburg, Ber., 25, 3441 (1892).

⁽⁸⁾ W. E. Parham and W. R. Hasek, J. Am. Chem. Soc., 76, 799 (1954).

SECOND-ORDER RATE CONSTANTS—ETHYL DIAZOACETATE ADDITIONS						
Reactant	Concentrationa	Solvent	10^5k_2 at $t_1{}^b$	$\log_{10} x_0/x_1^c$	10^5k_2 at t_2^d	$\log_{10} x_0/x_2^c$
$CH_2 = CHCO_2Et$	1.8 M	Dioxane	4.92	0.22	4.85	0.52
$CH_2 = CHCO_2Et$	1.0 M	Dioxane	4.97	.14	5.04	.23
$CH_2 = CHB(O-n-Bu)_2$	0,9 M	Dioxane	1.50	. 36	1.12	. 64
$CH_2 = CHB(O-n-Bu)_2$	0.5 M	Dioxane	1.42	. 20	1.08	.37
$CH_2 = CHB(O-n-Bu)_2$	0.2 M	Dioxane	0.79	.04	e	
$CH_2 = CHB(O-n-Bu)_2$	4.51~M	None	2.11	.25	2.07	. 43
$CH_2 = CHB(O-n-Bu)_2^f$	0.45~M	Abs. $ethanol^{f}$	1.33	.05	1.36	.11
$CH_2 = CHB(O-n-Bu)_2$	0.45 M	Dimethylformamide	1.49	.06	1.50	. 12
$CH_2 = CHB(O-n-Bu)_2$	0.45~M	Dimethylformamide (30.1°)	2,35	.09	2.14	.31
$CH_2 = CHB(O-n-Bu)_2$	0.15 M	Dimethylformamide (30.1°)	1.82	.02	1.57	.08
$CH_2 = CHB(O-n-Bu)_2$	0.45~M	Dimethylformamide (20.4°)	1.02	.04		
$HC = CB(O-n-Bu)_2$	0.9 M	Dioxane	0.19	.05	0.12	0.15

TABLE I Second-order Rate Constants—Ethyl Diazoacetate Additions

^a Rounded off; known to $\pm 0.5\%$. ^b In l. mole⁻¹ sec.⁻¹; at 25.05 $\pm 0.05^{\circ}$ unless otherwise indicated. ^c Rounded off; average deviation at different wave lengths $\pm 2\%$ except at very low values. ^d From t_0 to t_2 . ^c Optical density increased at t_2 . ^f Boronic ester largely transesterified.

TABLE II

PSEUDO FIRST-ORDER RATE CONSTANTS-ETHYL DIAZOACETATE ADDITIONS

Reactant	$10^{5}k_{1}$ at t_{1}^{a}	$\log_{10} x_0/x_1^a$	$10^{t}k_1$ at t_2^{a}	$\log_{10} x_0/x_2$
$CH_2 = CHB(O-n-Bu)_2$	9.53	0.25	9.35	0.43
$CH_2 = CHB(O-n-Bu)_2$	9.16	.38	8.94	.55
$CH_2 = CHB(O-n-Bu)_4$	9.80	. 19	9.40	.42
$CH_2 = CHB(O-n-Bu)_2 (30.1^{\circ})$	13.50	.32	13.37	.71
$CH_2 = CHB(O-n-Bu)_2 (20.4^{\circ})$	6.11	.15	5.78	.45
$CH_2 = CHB(O-t-Bu)_2$	8.08	.46	7.78	. 55
$CH_2 = CHB(O-t-Bu)_2$	8.41	.13	7.80	.32
$HC = CB(O-n-Bu)_z$	1.22	.08	1.09	. 39
$CH_2 = CHSi(OEt)_3$	0.47	.03	0.35	.12
$CH_2 = C(CH_3)B(O-n-Bu)_2$.38	.03	0.17	. 06
$CH_2 = C(CH_3)B(O-n-Bu)_2^b$. 44	.05	0.32	. 10
CH ₃ CH=CHB(O-n-Bu) ₂ ^c	.069°	.024	0.067	.048

^a Pseudo first-order k in sec.⁻¹; see explanatory notes for Table I. ^b Redistilled. ^c Probably mixture of *cis* and *trans*; agreement of k values probably fortuitous, error may be 20%.

a large excess of the other reactant. The firstorder disappearance of ethyl diazoacetate (λ_{max} $380-385 \text{ m}\mu$) was followed by scanning the 420- $380\text{-m}\mu$ (and surrounding) region with a Cary Model 14 spectrophotometer at suitable time intervals. Values of log x_0/x at 420, 410, 400, and, where by-products did not make them inconsistent, 390 m μ and λ_{max} were averaged. The most serious source of error was the development of ultraviolet-absorbing and brownish by-products which caused the apparent k values to decrease with time, especially when the half-life of the diazoacetate was a day or more. The 0.01% phenothiazine present in the boronic ester samples as a radical inhibitor was only partly responsible, since redistillation of the dibutyl propene-2-boronate reduced but did not eliminate color formation. Dioxane (reagent grade)—the solvent most likely to permit radical side reactions-discolored very badly. However, dibutyl ethyleneboronate polymerized after two weeks in dioxane even with an inhibitor present, and the possible complications of removing or changing the inhibitor were not explored.

Table I lists k_2 's computed according to the assumed rate law

$$-\mathrm{d}x/\mathrm{d}t = k_2[x][y]$$

where x represents diazo and y olefinic compound. To provide an indication of the precision, the k found and the extent of reaction (as $\log x_0/x$) are tabulated for the first two measurements made. One or two additional points were usually taken and the apparent k invariably dropped somewhat, the magnitude of the decrease being similar to that of the disagreement between the first two points. Table II similarly lists pseudo first-order k_1 's for the reactions where the olefinic reactant served as solvent.

The three runs in dibutyl ethyleneboronate at 25° provide enough points (eight time values, 28 log x_0/x values at selected wave lengths) for a more complete treatment of the data. A least square fit yielded $k_1 = 9.02 \ (\pm 0.38 \text{ av. dev.}) \times 10^{-5} \text{ sec.}^{-1}$, while the average k_1 at the first point taken is 9.50 $(\pm 0.22) \times 10^{-5}$ and linear extrapolation of the k_1 's to t_0 leads to 9.9 $(\pm 0.2) \times 10^{-5}$. The first-order rate law has been checked to 82% completion, where the apparent over-all k dropped to 8.65 $\times 10^{-5}$.

In view of the above discussion, it is concluded that the apparent k at t_1 provides a satisfactory approximation to the true value.

It should be noted that the k_2 's for dibutyl ethyleneboronate obtained by dividing the pseudo



 k_1 's in Table II by the molarity of the pure boronic ester (4.55 M) are similar in magnitude to the k_2 's observed when the reaction was run in a solvent. Since the molar volumes of the various reactants listed in Table II differ by only a few per cent and solvent effects are small, direct comparison of the k_1 's is meaningful.

From the temperature dependence, $\Delta H^* = 15.0 \pm 1.9$ kcal./mole for ethyl diazoacetate and dibutyl ethyleneboronate without a solvent, 15.7 ± 1.2 in dimethylformamide. From the k_2 's at 25° , $\Delta S^* = -29.5$ and -28.0 e.u. (± 5), respectively.

The second-order rate constant for addition of diphenyldiazomethane in dimethylformamide at 25.1° to ethyl acrylate, 0.2 M, was found to be 2.97 (±0.1) × 10⁻³; to dibutyl ethyleneboronate, 0.5 M, 5.10 (±0.1) × 10⁻⁴; 1.0 M, 4.83 (±0.1) × 10⁻⁴.

In 1-octene (redistilled from sodium) at 25° the apparent pseudo first-order rate constant for the disappearance of ethyl diazoacetate was less than 1×10^{-7} , for diphenyldiazomethane, 1.7×10^{-6} ; in "spectro grade" 2,2,4-trimethylpentane, for diphenyldiazomethane, $1.0 \ (\pm 0.3) \times 10^{-6}$. Impurities in the 1-octene greatly accelerated the fading of both diazo compounds.

Mechanism.—The rate and product studies support the mechanism outlined in Chart I for the reaction of ethyl diazoacetate with dibutyl ethyleneboronate.

The concerted cycloaddition represented as the transition state X is supported by the rate law, the lack of solvent dependence, and the large negative entropy of activation. This reaction is thus entirely analogous to reactions of diazo compounds with unsaturated compounds in general, shown recently by Huisgen, *et al.*,⁹ to be concerted, not to

(9) R. Huisgen, H. Stangl, H. J. Sturm, and H. Wagenhofer, Angew. Chem., 73, 170 (1961).

involve the popularly written zwitterion intermediate.¹⁰ Closely paralleling the steric effects observed by Huisgen, *et al.*, a methyl substituent at the α -carbon of the double bond retards the cycloaddition by a factor of 20, at the β -carbon 100–150. There is not substantial bond formation with the boron atom in the transition state, since such bonding would require charge separation, ruled out above, together with alteration of the geometry about the boron, unlikely in view of the mere 12–15% reduction in rate when di-*tert*-butyl ethyleneboronate¹¹ is used in place of the *n*-butyl ester.

No intermediate preceding the tris(N-pyrazolinyl)boron XV has been detected. Infrared examination of the reaction mixture from the *tert*butyl ester, which does not separate into two phases until the reaction is over 80% complete, revealed no absorption bands except those of starting materials and products. Rapid disproportionation of the mixed borne ester-amide XIV would be expected.

It is concluded that the migration of boron from carbon to nitrogen in this system is much more facile than the analogous hydrogen tautomerization, even though the proton is activated by the adjacent carbethoxy group. As pointed out above, the latter rearrangement requires a catalyst, and it therefore must be an intermolecular process. For the former, the vacant p-orbital of boron makes possible an intramolecular migration as outlined in Chart I. This postulated mechanism amounts to nothing more unusual than attack by a neighboring group with an unshared electron pair on an electron deficient atom, boron, isoelectronic with a carbonium ion. to form a three-membered ring. Ordinarily, ring opening resulting in migration of the neighboring group with its electron pair may follow. In the present instance, the three-membered ring instead opens by carbon-boron bond rupture, directed by bond strengths and product stabilities, and the net result is migration of the $(BuO)_2B^+$ unit (though a high electron density is maintained on boron throughout the migration). Of course, this postulated intramolecular rearrangement is inaccessible to kinetic study in the present system and several possible intermolecular paths cannot be ruled out.

The essential electronic ingredients of the azo group which make the above boron migration possible (regardless of the detailed mechanism) are (a) an atom with an unshared pair of electrons and (b) an atom which can accept an electron pair so that the carbon-boron bond may break. Other boronic esters having α -substituents which fulfill these requirements should undergo similar deboronation.

Molecular Orbital Calculations.—The rates of reaction of dibutyl ethyleneboronate with diazo

⁽¹⁰⁾ E.g., see H. Zollinger, "Azo and Diazo Chemistry," Interscience Publishers, New York, N. Y., 1961, p. 107.

⁽¹¹⁾ Synthesis: D. S. Matteson, J. Org. Chem., 27, 3712 (1962). The esterification is very slow and cannot be done in a straightforward manner.

				TABLE]	III				
			Molecula	R ORBITAL	CALCULATIC	ONS			
				Free	Orbital	energy	Stab	ilization er	ergy ^c
		Charge (density	valence	Lowest	Highest	Radical	Anion	
Compound	$h_{\mathbf{B}}$	в	β-C	β-C	unfilled	filled	β-C	β-C	a-C
$CH_2 = CHCO_2H^a$			0.146	0.817	0.428	-1.000	0.202^{d}	0.70 ^d	-0.323
$CH_2 = CHB(OH)_2^b$	-0.50	-0.29	.147	.804	.487	-1.082	.163	.50	212
$CH_2 = CHB(OH)_2^b$	75	24	.115	.790	. 599	-1.059	. 140	.41	160
$CH_2 = CHB(OH)_2^b$	-1.00	21	.087	.777	.692	-1.039	.121	.33	113
^a Parameters: ha	$s = 2; h_{\phi}$	= 1; carbo	onyl group	$h_{\rm C} = +1$	$0.2; \beta_{\rm C=0} =$	$\beta_{\rm C-C} = 0.8$	βc_c; βc_o	$= \beta_{C-C}$.	Increasing

^a Parameters: $h_{\delta} = 2$; $h_{\delta} = 1$; carbonyl group, $h_{C} = +0.2$; $\beta_{C-O} = \beta_{C-C} = 0.8 \beta_{C-C}$; $\beta_{C-O} = \beta_{C-C}$. Increasing β_{C-C} to 1.1 β_{C-O} , β_{C-C} to 0.9 β_{C-O} , leaving other parameters (units β_{C-O}) unaltered (Streitwieser's values^{12a}), increases charge density to 0.157, free valence to 0.827, makes energies not directly comparable. ^b Parameters: $h_{\delta} = 2$; for C adjacent to B, $h_{C} = 0.1h_{B}$; $\beta_{B-O} = 0.6 \beta_{C-C}$; $\beta_{B-C} = 0.7 \beta_{C-C}$. ^c Localization energy compared with that of ethylene; defined in ref. 2. ^a Calculated with C—C double bond, C—O single bonds (the more favorable way).

compounds are surprisingly close to those of ethyl acrylate, the latter being favored by only a factor of three with ethyl diazoacetate in dioxane, six with diphenyldiazomethane in dimethylformamide. Simple molecular orbital calculations provide a satisfactory interpretation of these observations.

It has been shown⁹ that the rates of cycloadditions are highly sensitive to the electron-withdrawing character of the substituent in the vinyl compound, varying over several powers of ten. Accordingly, a "correct" set of heteroatom parameters should lead to calculation of some reactivity index associated with the qualitative concept of electronwithdrawing character-e.g., charge density at the β -carbon atom—to yield similar numerical values of the index for the boronic and acrylic esters. Unfortunately, it does not appear possible to demonstrate the validity of any particular index for this reaction on the basis of existing data. However, several different reactivity indices that are reasonable to associate with a concerted cycloaddition appear to correlate well with the observed rates, while the parameters suitable for boron seem to be confined to a narrow range. On the other hand, assumption of a zwitterion intermediate¹⁰ does not permit an internally consistent set of calculations.

A useful set of heteroatom parameters has been assembled by Streitwieser.^{12a} Values consistent with this set have been chosen for heteroatom parameters in the present calculations. These are referred to $\beta_{C=C}$ for ethylene, assumed to be about 1.1 times the unit $\beta_{\rm CC}$ for benzene used in Streitwieser's table. Although the bond integrals β_{B-C} and β_{B-O} should be similar in magnitude to β_{C-N} and β_{C-F} , respectively, boron does not contribute any electron to the π -bond system along with its p-orbital and therefore its coulomb integral, $\alpha_{\rm B}$, cannot be extrapolated precisely from those of other elements which do. Table III lists results calculated for several possibly pertinent reactivity indices as $h_{\rm B}$, defined by $h_{\rm X} = (\alpha_{\rm X} - \alpha_{\rm C})/\beta$, is varied from -1.0 to -0.5.¹⁸

From Table III it can be seen that $h_{\rm B} \cong -0.8$ to -0.6 yields suitably close values for the charge

densities (as well as the possibly relevant free valences) at the β -carbon atoms of the boronic and acrylic esters, slightly favoring the latter. This correlation amounts to assumption that the cycloaddition step is exothermic and the transition state is structurally similar to the starting materials in accord with Hammond's postulate.14 A better model for the transition state might be a chargetransfer complex in which the vinyl compound acts as the acceptor. The lower the energy of the lowest unoccupied orbital of the vinyl compound, the closer it approaches the energy of the highest occupied orbital of the diazo compound and the greater the binding energy between the two becomes. This model is consistent with the orbital symmetries and appears to correlate in at least qualitative fashion with observed reactivities, including the enhanced activity of strained double bonds noted by Huisgen⁹; it applies equally to dienophiles in the Diels-Alder reaction. Reasonable values for this reactivity index are also found when $h_{\rm B}$ is near -0.7; the energy level spacings remain consistent with the ultraviolet spectra.

Simple localization energies do not correlate well with the observed reactivities. For example, the bond or (in this case identical) α -carbon localization energy varies in the wrong direction and would by itself require ethylene to be a better dienophile than any substituted ethylene, obviously absurd. However, as a small term in the transition state energy that is often in opposition to the reactivity trends, the bond localization energy fits in well with the transition state model in which the β -carbon is more strongly bound than the α -carbon, a model that has been reviewed and discussed for the Diels-Alder reaction by Streitwieser.^{12b} The stabilization energy for addition of a radical to the β -carbon atom of the ethyleneboronic ester seems somewhat unfavorable within the reasonable range of boron parameters unless a favorable term attributed to partial binding at the α -carbon is qualitatively considered, which makes the correlation again appear reasonable if $h_{\rm B} \cong -1$ to -0.5. Insufficient data are available to justify any quantitative calculations of energies of assumed transition state models.

⁽¹²⁾⁽a) A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists," Wiley, New York, N. Y., 1961, p. 135; (b) p. 437.

⁽¹³⁾ These calculations were done with an IBM 709 computer by the Washington State University Computing Center.

⁽¹⁴⁾ G. S. Hammond, J. Am. Chem. Soc., 77, 334 (1955).

Addition of an anion to the double bond of an ethyleneboronate should be extremely difficult, inasmuch as the anion stabilization energies shown in Table III place the boron compound closer to butadiene (0.36β , simplest model) than to ethyl acrylate; the relative position of the boron compound becomes less favorable when the increase in negative charge concentrated on the boron atom is considered, not to mention the competing direct attack by the base on the boron atom. Thus, the rapid cycloaddition reactions of the boronic ester with diazo compounds provide independent evidence against the formerly postulated two-step mechanism with an intermediate zwitterion¹⁰ and in favor of Huisgen's⁹ concerted process.

The heteroatom parameters adopted above represent some revision of those used to correlate previous work.^{2,3} Revision of $h_{\rm B}$ upward from -1 to the presently suggested -0.7 seems to provide improved correlation of both the present and previous results. The calculated results are relatively insensitive to any reasonable parameter changes for oxygen. It may be noted that when appropriate correction for electronegativity of attached atoms is made, the presently assigned $h_{\rm B}$ is equivalent to that used by Good and Ritter, -1.0, for excellent correlation of the properties of vinylboranes.¹⁶

One report appears at first sight to contradict the parameters assigned above to boron. From spectra of charge-transfer complexes of tetracyanoethylene with borazaro compounds, Dewar and Rogers¹⁶ have estimated that $h_{\rm B} = -1.59$, a value which does not appear to correlate with the present and previous^{2,3} experimental results. However, Dewar and Rogers used an approximate perturbation treatment which has turned out to involve a linear extrapolation beyond the region of linearity. Solution of the secular determinants¹³ reveals that the slope $\partial E/\partial \alpha_{\rm B}$ actually falls off rapidly as $h_{\rm B}$ approaches the region of interest, making the calculated energies relatively insensitive to the value assigned to $h_{\rm B}$. Two of the listed¹⁶ compounds agree well with calculations whether $h_{\rm B}$ is chosen as -0.9 or as -1.59 while the other two are both off by 0.18 β at $h_{\rm B}=-0.9$, by 0.12 and 0.23 β at $h_{\rm B}=$ -1.59, where the average deviation for hydrocarbons is 0.033β . A satisfactory correlation of these spectra with simple molecular orbital calculations does not now appear possible,¹⁷ and the results cast doubt on the present calculations only insofar as they tend to undermine simple calculations involving heteroatoms in general.

In summary, the known properties of dibutyl ethyleneboronate correlate well with simple molecular orbital calculations when $h_{\rm B} = -0.7$ and $\beta_{\rm B_C} = 0.7\beta_{\rm C=C}$. While selection of heteroatom param-

(17) M. J. S. Dewar, private communication. Prof. Dewar has suggested that the Hückel method may not be valid for molecules containing heteroatoms. eters is necessarily subject to considerable uncertainty, there appear to be no data in the literature which would require grossly different parameters for satisfactory correlation. These parameters represent substantial delocalization of electrons into the vacant p-orbital of boron and associated qualitatively large chemical effects.

Experimental

5-Carbethoxy-2-pyrazoline (I).—An equimolar mixture of dibutyl ethyleneboronate² (9.2 g.) and ethyl diazoacetate (5.7 g.) was kept at 20-25° under nitrogen in a stoppered flask. The flask was kept in a water bath at first; otherwise, after a few minutes the reaction mixture became hot and decomposed. The only evidence of pressure increase was the tendency of the well greased stopper to loosen if not clamped down. Separation into two liquid phases began after a few hours. After 12 days the reaction mixture was cooled to -15° and the phases were separated. The upper phase, 7.16 g. (93% based on butoxy groups available). was shown to be tributyl borate by its infrared spectrum, the only evidence of impurity being a weak ester band at 5.77 μ , easily removed by distillation. The viscous yellow lower layer was washed with ligroin and treated with 15 ml. of absolute ethanol. After removal of the ethanol and (presumably) ethyl borate with the water pump, distillation yielded 3.16 g. (44%) of 5-carbethoxy-2-pyrazoline (I), b.p. 65-70° ($\overline{0.1}$ mm.), a trace of the 3-carbethoxy isomer (II), and considerable nonvolatile residue. The analytical sample was redistilled through a short column, b.p. 60-65° (0.1 mm.).

Anal. Calcd. for $C_8H_{10}N_2O_2$: C, 50.69; H, 7.09; N, 19.71. Found¹⁸: C, 50.62; H, 7.19; N, 19.84.

5(3)-Carbethoxypyrazole-3(5)-boronic acid (Va) was prepared from dibutyl acetyleneboronate¹⁹ (9.1 g.) and ethyl diazoacetate (5.7 g.) by the above procedure. After 12 days the partially crystallized reaction mixture solidified on cooling to -15° but recrystallization proved impractical. The product was treated with 50 ml. of water and the butanol-water azeotrope was removed by distillation at 20 mm. After thorough washing with water 6.97 g. (75%) of the crystallized twice from water (30 ml./g.), 75% recovery, m.p. 195-201° to a glass.

Anal. Calcd. for $C_4H_9BN_9O_4$: C, 39.17; H, 4.93; B, 5.88; N, 15.23. Found: C, 39.04; H, 4.97; B, 5.99; N, 15.06.

5(3)-Carboxypyrazole-3(5)-boronic acid (Vb) was prepared by boiling 1.84 g. of the ethyl ester Va in 20 ml. of 5% aqueous sodium hydroxide for 30 sec., cooling, and precipitating with 2.5 ml. of hydrochloric acid, yield 1.45 g. (93%), m.p. 195–196° dec. The analytical sample was recrystallized from water (140 ml./g.), m.p. 196.5–197.5° dec.

Anal. Caled. for $C_4H_5BN_2O_4$: C, 30.80; H, 3.26; B, 6.94; N, 17.97. Found: C, 30.59; H, 3.25; B, 6.74; N, 18.00.

Other Ethyl Diazoacetate Additions.—With dibutyl ethyleneboronate in ethanol (0.05 mole in 60 ml.) refluxed 22 hr. there resulted 5-carbethoxy-2-pyrazoline (I) in 42% yield and crude 3-carbethoxy-2-pyrazoline (II) in 11% yield, b.p. $90-100^{\circ}$ (0.1 mm.), mushy solid but shown to have only a few per cent of impurities by infrared. With di-tertbutyl ethyleneboronate¹¹ at $20-25^{\circ}$ phase separation occurred after approximately 24 hr.; after 9 days there was obtained a 90% yield of tert-butyl borate and a 40% yield of 5-carbethoxy-2-pyrazoline (I). With dibutyl 1-propene-1-boronate² 9 days at $20-25^{\circ}$ and 1 day on the steam bath

⁽¹⁵⁾ C. D. Good and D. M. Ritter, J. Am. Chem. Soc., 84, 1162 (1962).

⁽¹⁶⁾ M. J. S. Dewar and H. Rogers, *ibid.*, 84, 395 (1962).

⁽¹⁸⁾ Microanalyses by Galbraith Laboratories, Knoxville, Tenn.
(19) D. S. Matteson and K. Peacock, J. Am. Chem. Soc., 82, 5759 (1960).

no phase separation occurred; after alcoholysis there was obtained a 22% yield of 4-methyl-5-carbethoxy-2-pyrazoline, b.p. 55-60° (0.02 mm.).

Anal. Caled. for C7H12N2O2: C, 53.83; H, 7.75; N, 17.94. Found: C, 53.87; H, 7.87; N, 17.70.

With dibutyl propene-2-boronate² under the above conditions there resulted 3-methyl-5-carbethoxy-2-pyrazoline, b.p. 55-60° (0.02 mm.), in 35% yield.

Anal. Found: C, 53.72; H, 7.80; N, 17.81.

With vinyltriethoxysilane (redistilled) at 52° for 40 hr. a mixture of isomers resulted in 50% yield after molecular distillation at 50-65° (0.02 mm.). The infrared spectrum suggests that the lower boiling isomer (after removal of forerun, low in nitrogen) is 3-carbethoxy-5-triethoxysilyl-1-pyrazoline. The higher boiling material contains an N-H group and its formation is accelerated by ethanol, but structural assignment must await further evidence.

Anal. Caled. for C12H24N2O5Si: C, 47.34; H, 7.94; N, 9.20; Si, 9.22. Lower boiling, found: C, 47.47; H, 7.91; N, 9.13; Si, 9.10. Higher boiling, found: C, 47.14; H, 8.01; N, 9.21; Si, 9.13.

5,5-Diphenyl-2-pyrazoline (VII).-A solution of 3.68 g. of dibutyl ethyleneboronate and 4.2 g. of crude diphenyldiazomethane²⁰ in 10 ml. of ether was allowed to stand under nitrogen. The reaction was slightly exothermic at first and it appeared that some nitrogen was evolved, making use of a closed system impractical. After 24 hr., 25 ml. of ethanol was added and then distilled under reduced pressure. Hydrolysis of the distillate yielded 0.92 g. (75%) of boric acid, m.p. 177-179°. The residue was recrystallized from approximately 25 ml. of ether to yield 2.86 g. (64%) of 5.5-diphenvl-2-pyrazoline (VII), m.p. 67-77°. This material was very unstable to air, making purification difficult. The analytical sample was recrystallized several times from ether and from alcohol–water, m.p. 72–78.5°

Anal. Calcd. for $C_{15}H_{14}N_2$: C, 81.05; H, 6.35; N, 12.61. Found: C, 80.86; H, 6.55; N, 12.60.

4,5(3)-Diphenylpyrazole-3(5)-boronic Acid (IX).-A solution of 3.64 g. of dibutyl acetyleneboronate and 4.2 g. of diphenyldiazomethane in 10 ml. of ether evolved a little gas but did not warm noticeably. After 4 days the ether was removed under vacuum and the residue was treated with approximately 50 ml. of ethanol and 5 ml. of water. The crude precipitated solid (5.0 g.) was recrystallized from ethanol, yielding 3.40 g. (55%) of 4,5(3)-diphenylpyrazole-3(5)-boronic acid (IX) crystallized with 1 mole of ethanol, loses alcohol, 77°, m.p. 155-160°. Absolute ethanol was used for further recrystallizations since the solubility in 95%ethanol was inconveniently low. The first analytical sample, m.p. 170-174°, was dried 24 hr. at 25°, 0.02 mm.; the second, m.p. 183-200° dec., was dried 20 hr. at 65°, 4 hr. at 100°, 0.02 mm., drastic treatment for a boronic acid.

Anal. Caled. for C15H13BN2O2 C2H6O: C, 65.83; H, 6.18; B, 3.49; N, 9.04. Found: C, 66.05; H, 5.93; B, 3.69; N, 9.24. Calcd. for C₁₅H₁₃BN₂O₂: C, 68.22; H, 4.96; B, 4.10; N, 10.62. Found: C, 68.58; H, 4.76; B, 4.25; N, 10.55.

3-Carbethoxy-1-pyrazoline (III).-A cooled solution of diazomethane²¹ from 3.0 g. of nitrosomethylurea in 60 ml. of anhydrous ether was carefully decanted from the aqueous alkali used for its preparation and, without drying, added to an ethereal solution of 2.5 g. of ethyl acrylate. Standing overnight, far longer than necessary for complete reaction of the diazomethane, did not affect the result. (Carter, et al.,^{5b} used excess diazomethane, but it appears likely that something else not deducible from the experimental description was the adventitious tautomerization catalyst.) Vacuum distillation at 0.1 mm. yielded 2.3 g. of 3-carbethoxy-1-pyrazoline (III). The analytical sample was redistilled through a short column, b.p. 49-51° (0.1 mm.). Heating 0.45 g, of III with 0.05 g, of ethanol on the steam bath 0.5 hr. yielded, after two recrystallizations, 0.19 g. of 3-carbethoxy-2-pyrazoline (II), m.p. 69-75°. The infrared spectrum of III (neat) lacked the N-H band near 3 μ and the strong bands in the $11-15-\mu$ region characteristic of 2-pyrazolines; the unconjugated C=O band appeared at 5.83 μ and the N=N band at 6.42 μ .

Anal. Calcd. for C6H10N2O2: C, 50.69; H, 7.09; N, 19.71. Found: C, 50.41; H, 7.09; N, 19.75.

Diazomethane and Dibutyl Ethyleneboronate.-Diazomethane from 2.1 g. of nitrosomethylurea in 45 ml. of ether cooled in an ice salt bath reacted with 1.84 g. of dibutyl ethyleneboronate in about 1.5 hr. Some polymethylene was formed. Distillation yielded 0.16 g. of a solution containing $35 \pm 10\%$ pyrazoline in butanol, established by infrared comparison in the 11–15- μ region with solutions of authentic pyrazoline, prepared in 13% yield from hydrazine hydrate and acrolein.²² The higher boiling fraction (0.90 g.) was found by infrared to be approximately a 1:1 mixture of dibutyl ethyleneboronate and butyl borate.

Diazomethane and Dibutyl Acetyleneboronate.-Diazomethane from 5.0 g. of nitrosomethylurea in 100 ml. of ether added to 6.1 g. of dibutyl acetyleneboronate in 25 ml. of ether at 5° vigorously evolved nitrogen on contact, precipitating 0.50 g. of polymethylene. Distillation of the liquid after addition of a little butanol yielded 3.5 g. of dibutyl acetyleneboronate, 1.7 g. of butyl borate (possibly an artifact from traces of base and hydroxylic materials, which rapidly decompose acetyleneboronates), and 0.1 g. of residue.

Spectra of 2-Pyrazolines.-Ultraviolet spectra taken in absolute ethanol are tabulated in Table IV, together with the C=N infrared band taken on the pure liquid except where otherwise indicated. Other infrared spectral data relevant to the structures of the new 2-pyrazolines include the C=O band at 5.75–5.77 μ for 5-carbethoxy-2-pyrazoline (I) (neat or in chloroform) and the methyl-substituted homologs (neat) but shifted to 5.82-5.85 μ for the conjugated 3-carbethoxy-2-pyrazoline (II) (chloroform). A weak but distinct band attributed to C-H stretching of the N=C-H unit appears at 3.25-3.29 μ in the spectra of 2pyrazoline and its above mentioned 5- and 4,5-substituted derivatives, but is absent from the 3-methyl-5-carbethoxy and 3-carbethoxy derivatives. 2-Pyrazoline (neat) showed the strongest absorption centered at 13.2 μ with subsidiary bands at 11.55, 12.0, and 15.6 µ. 5-Carbethoxy-2-pyrazoline showed the corresponding bands at 11.4, 11.8, 12.6, 13.4 (strongest of group), and 15.1 μ ; the methyl homologs showed similar but somewhat shifted bands.

TABLE IV

Spectra of 2-Pyrazolines

Substituent(s)	Ultraviolet $\lambda_{max}, m\mu$	¢max	Infrared: $C = N, \mu$
None	230	3750	6.27^{a}
			6.18
5-Carbethoxy-	225	3220	6.23^{b}
4-Methyl-5-carbethoxy-	227	3210	6.24
3-Methyl-5-carbethoxy-	220	4120	6.11
3-Carbethoxy-	292	8930	6.35^{c}

^a Stronger of doublet. ^b Not shifted by chloroform. ^c In chloroform.

Deboronations.-Treatment of 0.09 g. of 5(3)-carbethoxy-3(5)-boronic acid (Va) in 1 ml. of ethanol with 0.24 ml. of 30% hydrogen peroxide for 7 days, addition of 0.5 ml. of water to crystallize the product, and sublimation yielded $0.03\,$ g. of 3-carbethoxy-2-pyrazol-5-one (VI), m.p. 175-181.5°, shown by infrared (of 2% chloroform solution) and mixture m.p. to be the same as an authentic sample⁸ pre-

⁽²⁰⁾ L. I. Smith and K. L. Howard, "Organic Syntheses," Coll. Vol III, John Wiley & Sons, Inc., New York, N. Y., 1955, p. 351.
 (21) F. Arndt, *ibid.*, Coll. Vol. II, John Wiley & Sons, Inc., New

York, N. Y., 1943, p. 165.

⁽²²⁾ T. Curtius and F. Wirsing, J. prakt. Chem., 50, 531 (1894).

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Substituent(s), 2-pyrazoline	Substituent(s), pyrazole	Yield (purified), %	M.p.,°C.	Lit., ²³ ° m.p., °C.
5-Carbethoxy-	3(5)-Carbethoxy-	40	160-162) a	
-	· · ·		Ş	160
3-Carbethoxy-	3(5)-Carbethoxy-	30	157-160	
4-Methyl-5-carbethoxy-	4-Methyl-3(5)-carbethoxy-	25	8083	82-83
3-Methyl-5-carbethoxy-	5(3)-Methyl-3(5)-carbethoxy-	25	158 - 159.5	156 - 158
5,5-Diphenyl-	1,3-Diphenyl- ^b	80	84-86	84-85
^{<i>a</i>} Identity confirmed by infra	red. ^b Infrared shows no N—H.			

TABLE V

Pyrazoles from 2-Pyrazolines

pared from hydrazine hydrate, the sodium salt of diethyl oxalacetate, and acetic acid in ethanol. Treatment of 0.31 g. of 4,5(3)-diphenylpyrazole-3(5)-boronic acid (IX) in 10 ml. of boiling ethanol with 0.25 ml. of 30% hydrogen peroxide for 5 min. and three crystallizations from ethanolwater yielded 0.11 g. of 3(5),4-diphenylpyrazol-5(3)-one, m.p. 232-237°.

Anal. Caled. for $C_{15}H_{12}N_2O$: C, 76.25; H, 5.12; N, 11.86. Found: C, 76.38; H, 5.38; N, 11.85.

Heating 0.10 g. of 4,5(3)-diphenylpyrazole-3(5)-boronic acid (IX) with 4 ml. of 10% aqueous potassium hydroxide dissolved the boronic acid, then led immediately to crystallization of 4,5(3)-diphenylpyrazole, completed by boiling about 3 min., yield 0.06 g. (85%), m.p. 155-157.5° (lit.

(23)(a) "Beilstein's Handbuch der Organischen Chemie," 4th ed., vol. 23, 1st supp., Julius Springer, Berlin, 1936, p. 67; (b) *ibid.*, vol. 23, p. 253; (e) *ibid.*, vol. 23, p. 178; vol. 25, pp. 116, 117, 120. m.p. 154-155°^{23a}; 3,5-diphenylpyrazole, m.p. 199-200°,^{23b} is excluded). The first attempt at preparation of the boronic acid IX, in which the boronic ester was hydrolyzed with water and methanol and solutions were allowed to stand for prolonged periods, yielded 0.7 g. of 4,5(3)-diphenylpyrazole as a by-product. The ultraviolet spectrum of 4,5(3)-diphenylpyrazole, $\lambda_{max} 252 \text{ m}\mu$, $\epsilon 1.19 \times 10^4$, $\lambda_{max} 227 \text{ m}\mu$, $\epsilon 1.94 \times 10^4$, ϵ rising steeply below 218 m μ (not taken below 210 m μ), closely resembled that of the boronic acid IX, which had plateaus at 250 m μ , $\epsilon 2.23 \times 10^4$, and 224 m μ , $\epsilon 3.38 \times 10^4$, $\lambda_{max} 202 \text{ m}\mu$, $\epsilon 6.98 \times 10^4$ (in abs. ethanol).

Pyrazoles for structure proof of pyrazolines were obtained by oxidizing the pyrazoline in ether with an equimolar amount of pyridine hydrobromide-bromine complex in water, neutralizing with sodium bicarbonate, extracting with ether, and recrystallizing or subliming the product as necessary. Results are tabulated in Table V. The infrared spectrum was consistent with the assigned structure in each case.

Reaction of the Silver Salt of Phenylnitroacetonitrile with Triphenylmethyl Chloride¹

DAVID Y. CURTIN, ROBERT J. CRAWFORD, AND DONALD K. WEDEGAERTNER²

Noyes Chemical Laboratory, University of Illinois, Urbana, Illinois

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The product II from the reaction of the silver salt I of phenylnitroacetonitrile with triphenylmethyl chloride, originally reported⁵ to be tetraphenyldiazoethane (B) has now been found to be α, α' -bis(triphenylmethaneazo)stilbene (D). More detailed aspects of the structure such as stereochemistry and the possibility of valence tautomerism remain to be investigated. The substance II has been reduced with lithium aluminum hydride, phenyllithium, or phenylmagnesium bromide to benzilbis(triphenylmethylhydrazone) (V) which can be reoxidized to II with silver oxide. The bisazoethylene II, when heated, is converted to diphenylacetylene, nitrogen, and triphenylmethyl radicals which are found as triphenylmethyl peroxide. With mild acid treatment bisazoethylene II is converted to 1-triphenylmethylamino-4,5-diphenyltriazole (VII) which reacts with benzoyl chloride to give the known 1-benzoylamino-4,5-diphenyltriazole. Attempts to carry out Diels-Alder reactions with II were unsuccessful.

The reactions of the silver salt I of phenylnitroacetonitrile with halides such as methyl iodide,⁸ benzyl chloride,⁸ or benzhydryl bromide⁴ generally lead to the nitronic ester (A) produced by alkylation on an oxygen atom or to secondary products resulting from further reaction of the nitronic ester.

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This work is described principally in the Ph.D. thesis submitted by Donald Keith Wedegaerther to the University of Illinois, 1962. Preliminary results are described in the Ph.D. thesis of Robert James Crawford, University of Illinois, 1956. Both will be available on microfilm from University Microfilms, Ann Arbor, Mich.

(2) Allied Chemical Fellow, 1959-60; Charles Pfizer Fellow, Summer, 1960; Union Carbide Plastics Fellow, 1960-61.

(3) J. T. Thurston and R. L. Shriner, J. Org. Chem., 2, 183 (1937).
(4) R. L. Shriner and G. B. Brown, *ibid.*, 2, 560 (1938).

Triphenylmethyl chloride has been shown to be unique, however.⁵ It reacts with the silver salt I



(5) H. Wieland and A. Höchtlen, Ann., 505, 237 (1933).