Acknowledgments.—To Dr. J. D. Stroupe for spectroscopic data and physical-chemical interpretation. To Dr. D. J. Cram for supplying infrared data for the phenylbutenes prior to their publication. To Mr. C. W. Nash and Mr. Thomas Callan, with their staffs, for analytical data reported.

Experimental

The Reaction of Secondary Amines, Formaldehyde and Olefinic Compounds.—The following general procedure was employed to prepare the compounds listed in Tables I, II and III. One mole of the amine was dissolved in 400 g. (6.6 moles) of acetic acid and 31.6 g. (1 mole, 95% assay) of paraformaldehyde was added. The mixture was heated until a clear solution was obtained and one mole of the olefinic compound was added. The mixture was stirred and refluxed for the length of time indicated. After cooling, the mixture was poured into 1.5 l. of water and extracted with benzene. The aqueous layer was made basic with excess sodium hydroxide solution. The amine was taken up in benzene, dried and distilled.

N,N,N′,N′-Tetramethyldiaminomethane was employed in some cases as the source of dimethylamine and one-half of the required formaldehyde. The addition of one equivalent of sulfuric acid or phosphoric acid per mole of amine before the olefin was added appeared to be advantageous with the less reactive systems. The more conveniently handled dimethylamine sulfate was successfully employed in several instances. These variations are indicated in the tables.

N,N-Dimethyl-3-phenylbutylamine.—Reduction of 75 g. of N,N-dimethyl-3-phenylbutenylamine (I) in 175 ml. of ethanol at 100 atm. and 100° using 7 g. of Raney nickel gave 59.5 g. (78%) of N,N-dimethyl-3-phenylbutylamine,[2] b.p. 110–113° (20 mm.), n^{25}D 1.4940.

Anal. Calcd. for $C_{12}H_{19}N$: C, 81.30; H, 10.80; N, 7.90. Found: C, 81.10; H, 10.85; N, 7.83.

N,N-Dimethyl-*p*-methoxycinnamylamine (II).—A mixture of 70 g. (0.28 mole, 76% assay) of technical dimethyl[5] amine sulfate solution, 13 g. (0.41 mole, 95% assay) of paraformaldehyde, 52 g. (0.39 mole) of *p*-methoxystyrene and 72 g. (1.2 moles) of acetic acid was stirred and refluxed for 18 hours. After cooling, the mixture was poured into 500 ml. of water and extracted with benzene. The aqueous layer was made basic with excess sodium hydroxide solution. The amine was taken up in benzene, dried and distilled to give 48 g. (64%), b.p. 110–135° (3 mm.). This was redistilled to give 22 g. (30%) of N,N-dimethyl-*p*-methoxycinnamylamine, b.p. 120–125° (3 mm.).

Anal. Calcd. for $C_{12}H_{17}NO$: C, 75.35; H, 8.96; N, 7.32. Found: C, 75.28; H, 9.29; N, 7.3.

N,N-Dimethyl-3,3-di-*p*-anisylallylamine (III).—A mixture of 9 g. (0.28 mole) of paraformaldehyde, 120 g. (2 moles) of acetic acid, 61.5 g. (0.25 mole) of dimethylamine sulfate (76% assay) was stirred and heated until a clear solution was obtained. Sixty grams (0.25 mole) of 1,1-bis-*p*-methoxyphenylethylene[6] was added. The mixture was stirred and refluxed 16 hr. The amine was isolated as in the previous examples and distilled to give 36 g. (12%) of N,N-dimethyl-3,3-di-*p*-anisylallylamine, b.p. 195–205° (2.2 mm.) n^{25}D 1.5853.

Anal. Calcd. for $C_{19}H_{23}NO_2$: C, 76.71; H, 7.79; N, 4.74. Found: C, 75.79; H, 7.47; N, 4.65.

N,N-Dimethyl-3-anisyl-3-phenylbutylamine (IV).—Hydrogen chloride was passed into a solution of 87.5 g. (0.5 mole) of N,N-dimethyl-3-phenyl-3-butenylamine (I) in 216 g. (2 moles) of anisole with stirring and cooling to form the amine hydrochloride. The mixture was heated to 80° to effect solution of the amine salt and 70 g. of anhydrous zinc chloride was added slowly. An exothermic reaction took place and the temperature rose to 105°. Hydrogen chloride was passed into the solution for one hour, during which period the temperature rose to 110° and then fell to 80°. The mixture was then heated at 120° for 2 hours. After cooling, the mixture was mixed with 1 l. of water and 100 g. of concentrated hydrochloric acid. The unreacted anisole was separated from the aqueous layer which was then made basic with 500 ml. of 50% sodium hydroxide solution. The amine was taken up in benzene, dried, and distilled to give 103 g. (72%) of N,N-dimethyl-3-anisyl-3-phenylbutylamine, b.p. 185–195° (4.5 mm.), n^{25}D 1.5564.

Anal. Calcd. for $C_{19}H_{25}NO$: C, 80.52; H, 8.89; N, 4.94. Found: C, 80.26; H, 8.60; N, 4.95.

PHILADELPHIA, PA.

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(5) R. Quelet, *Bull. soc. chim.*, **7**, 196 (1940).

(6) R. Quelet and J. Allard, *ibid.*, **7**, 215 (1940).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, PENNSYLVANIA STATE UNIVERSITY]

The Stereochemistry of Radical–Olefin Addition Reactions. Reactions of *cis*- and *trans*-2-Butenes with Bromotrichloromethane

BY PHILIP S. SKELL AND ROBERT C. WOODWORTH[1]

RECEIVED JANUARY 3, 1955

The light-initiated free-radical chain reactions of *cis*- and *trans*-2-butene with bromotrichloromethane have been examined in detail to elucidate the relative rates of the successive reactions and the structure of the chain-carrying 3-trichloromethyl-2-butyl radical. The reaction of *cis*- or *trans*-2-butene with bromotrichloromethane produces a mixture of identical quantities of the two diastereomeric 1:1 addition products. These results indicate that the addition of a trichloromethyl radical to *cis*- or *trans*-2-butene produces the same mixture of diastereomeric 3-trichloromethyl-2-butyl radicals, CH_3—$CH(CCl_3)$—$\dot{C}H$—CH_3. There is no evidence in support of a three-atom ring structure for this radical. It seems likely that all aliphatic free radicals have the conventional open-chain structure. The addition of a $\cdot CCl_3$ radical to either of the 2-butenes proceeds at comparable rates: $k_c/k_t = 2.4$. The rate of interconversion of the diastereomeric 3-trichloromethyl-2-butyl radicals by rotation about the C_2–C_3 bond must be greater than the rate of reaction of these radicals with bromotrichloromethane. The rate of reaction of the diastereomeric radicals with bromotrichloromethane must be greater than the rate of dissociation of the radicals to $\cdot CCl_3$ and C_4H_8. A pyramidal structure for the trivalent carbon of the 3-trichloromethyl-2-butyl radical is suggested.

It is a well-known experimental fact that in polar media addition of bromine to olefins proceeds by a stereospecific course resulting in *trans* addition to the double bond. These facts have been explained by assuming a positively charged three-atom ring intermediate which formally derives from the placement of a Br^+ at a position approximately equidistant from the doubly bound atoms and above the plane of the double bond. This intermediate then acquires the equivalent of a Br^- which approaches from the free side of the double bond plane, thus resulting in the *trans* attachment of the two bromine atoms.

The experimental basis for a similar discussion of the addition of radicals to olefins has not lent itself

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[1] National Science Foundation Fellow.

to a consistent clear-cut decision regarding either the stereospecificity of this type of reaction or the structure of the intermediate radical–olefin adduct.

Mayo and Wilzbach[2] stated that copolymers of vinyl acetate and *cis*- or *trans*-dichloroethylene were stereochemically identical because they were dehalogenated with potassium iodide, liberating iodine at essentially the same rates even though the kinetics were complex. They thus were led to the conclusion that addition of a vinyl acetate radical to either of the dichloroethylenes produces the same radical or radical mixture. Mayo and Wilzbach concluded that the $\mathrm{R{-}CHCl{-}\dot{C}HCl}$ radicals have either a planar configuration or else a pyramidal configuration which inverts or racemizes faster than the radicals add to vinyl acetate.

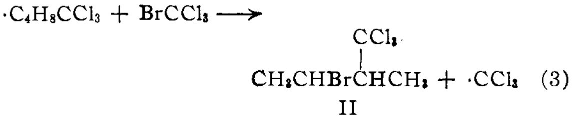
The isomerization of *cis*- and *trans*-dihalo-ethylenes by halogen atoms[3,4] has been studied in considerable detail with the conclusion that when the halogens are iodine or bromine, exchange of halogen atoms is a more rapid reaction than isomerization. These results are interpreted to indicate the existence of rotational isomers of structure $\mathrm{XH\dot{C}{-}CHX_2}$, and a barrier greater than 3 kcal./mole opposing the interconversion of these isomers by a rotation about the C–C bond.

The addition products obtained from the radical reaction of bromotrichloromethane with cyclic olefins were described by Kharasch and Friedlander.[5] Although these authors did not state specifically in the text that the Br and $\mathrm{CCl_3}$ groups were in *trans* relation to one another, their structural formulas are the conventional ones used to designate *trans* substituents. Fawcett[6] interpreted the base-affected elimination reactions, which these addition products undergo, as good evidence for the *trans* relationship of the Br and $\mathrm{CCl_3}$ groups and offered a simple steric explanation for the stereospecificity of this addition reaction in terms of the preferred approach of a $\mathrm{BrCCl_3}$ molecule to $\underset{/}{\mathrm{\dot{C}H}}{-}\underset{\backslash}{\mathrm{CH}}{-}\mathrm{CCl_3}$ being on the side of the molecule which is furthest from the $\mathrm{CCl_3}$ group. Goering, Abell and Aycock[7] also observed *trans* radical addition of HBr to cyclic olefins. However, from conformational considerations, the latter authors concluded that Fawcett's suggestion was not adequate for an explanation of their results and that a three-atom ring structure for the adduct of an olefin with a bromine atom, analogous to the bromonium ion, thereby is indicated.

To avoid the complications introduced by studying radical addition reactions to cyclic olefins, where rotation is restricted and it is necessary to employ complex conformational analysis for the interpretation of results, the addition of radicals to olefins such as the *cis*- and *trans*-2-butenes was undertaken. Bromotrichloromethane adds readily to either of the 2-butenes in a liquid phase light-initiated radical chain reaction in which the trichloromethyl radical and the trichloromethylbutyl radical I are the chain carriers.

$$\mathrm{Br{-}CCl_3} + h\nu \longrightarrow \mathrm{Br\cdot} + \mathrm{\cdot CCl_3} \qquad (1)$$

$$\mathrm{C_4H_8} + \mathrm{\cdot CCl_3} \longrightarrow \underset{\mathrm{I}}{\mathrm{\cdot C_4H_8CCl_3}} \qquad (2)$$



$$\mathrm{\cdot C_4H_8CCl_3} + \mathrm{BrCCl_3} \longrightarrow \underset{\mathrm{II}}{\mathrm{CH_3CHBr\overset{\displaystyle CCl_3}{\overset{|}{C}}HCH_3}} + \mathrm{\cdot CCl_3} \qquad (3)$$

With reaction conversions to II of 5–25% of theory at temperatures between 0 and 25° there is no detectable interconversion of *cis*- or *trans*-2-butene to its isomer. Samples of olefin taken from the reaction flask before and after illumination had infrared spectra which were identical between 2 and 15.5 μ. When the concentrations of reactants, temperature, and length of time and intensity of illumination are the same, comparable quantities of adduct II are obtained from either olefin when as little as 5–10% of the olefin is converted to II. The observation that *cis*- or *trans*-2-butene produces comparable quantities of adduct II in paired experiments under low conversion conditions precludes the possibility that only one of the olefins can add bromotrichloromethane and the other must isomerize to the reactive olefin in order to give the addition product. These results are consistent with the explanation that (a) both olefins react readily with the trichloromethyl radical, and (b) for both olefins the rate of reaction 3 is greater than the rate of the reverse of reaction 2.

The relative rates of addition of a trichloromethyl radical to *cis*- and *trans*-2-butene can be determined by a competition experiment if conditions are maintained which preclude isomerization of the olefins. A mixture of bromotrichloromethane and weighed quantities of *cis*- and *trans*-2-butene was allowed to react to 64% conversion of the olefins to II, and the reaction mixture was analyzed to determine the amount of unreacted *cis*- and *trans*-2-butene. The initial and final amounts of the olefins are shown in Table I.

TABLE I

COMPETITION BETWEEN *cis*- AND *trans*-2-BUTENES FOR BROMOTRICHLOROMETHANE

	Initial	Final
cis-2-Butene, g.	12.82	3.01
trans-2-Butene, g.	9.49	5.30
Bromotrichloromethane, g.	114.2	

Since the rate of dissociation of radical I is much

$$\underset{\mathrm{I}}{\mathrm{\cdot C_4H_8CCl_3}} \longrightarrow \mathrm{C_4H_8} + \mathrm{\cdot CCl_3}$$

smaller than the rate of reaction 3, the amount of each olefin which disappears during the reaction depends solely on the relative rates of reaction 2 for each of the isomeric olefins. The ratio of k_c/k_t can be calculated from the considerations

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[2] F. R. Mayo and K. E. Wilzbach, THIS JOURNAL, **71**, 1124 (1949).

[3] H. Steinmetz and R. M. Noyes, *ibid.*, **74**, 4141 (1952).

[4] R. M. Noyes, R. G. Dickinson and V. Schomaker, *ibid.*, **67**, 1319 (1945).

[5] M. S. Kharasch and H. N. Friedlander, *J. Org. Chem.*, **14**, 239 (1949).

[6] E. S. Fawcett, *Chem. Revs.*, **47**, 219 (1950).

[7] H. L. Goering, P. I. Abell and B. F. Aycock, THIS JOURNAL, **74**, 3588 (1952).

let $$cis\text{-2-butene} + \cdot CCl_3 \xrightarrow{k_c} \cdot C_4H_8CCl_3$$

$$trans\text{-2-butene} + \cdot CCl_3 \xrightarrow{k_t} \cdot C_4H_8CCl_3$$

$$C = \text{concentration of } cis\text{-2-butene}$$

$$T = \text{concentration of } trans\text{-2-butene}$$

then $$-\,\mathrm{d}C/\mathrm{d}t = k_cC(\cdot CCl_3)$$

$$-\,\mathrm{d}T/\mathrm{d}t = k_tT(\cdot CCl_3)$$

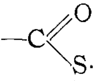
$$(\cdot CCl_3)\mathrm{d}t = \mathrm{d}T/k_tT = \mathrm{d}C/k_cC$$

$$\frac{1}{k_t}\int_{T_i}^{T_f}\frac{\mathrm{d}T}{T} = \frac{1}{k_c}\int_{C_i}^{C_f}\frac{\mathrm{d}C}{C}$$

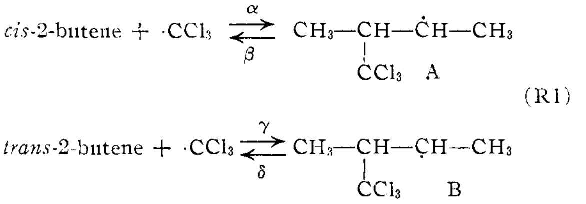
$$(1/k_t)\log(T_f/T_i) = (1/k_c)\log(C_f/C_i)$$

$$k_c/k_t = \log(C_f/C_i)/\log(T_f/T_i)$$

From the data cited above, the relative rates with which these isomeric olefins add a trichloromethyl radical to form I is $k_c/k_t = 2.4$.

Since it has been demonstrated that a trichloromethyl radical adds to *cis*- or *trans*-2-butene at comparable rates without concomitant isomerization of the unreacted olefin, it is possible to decide whether there is obtained (a) from each olefin a different diastereomeric radical or (b) from either olefin the same mixture of diastereomeric radicals. If (a) is correct then the adduct II from one olefin would be diastereomerically related to the product from the other olefin. If (b) is correct, an identical mixture of diastereomers of adduct II would be obtained from either olefin. In paired experiments the infrared spectrum of the product II from *cis*-2-butene is qualitatively and quantitatively indistinguishable from the spectrum of the product obtained from *trans*-2-butene. Since the infrared spectra of the two diastereomers are different,[8] these experiments indicate that (b) correctly describes the major substances produced when a trichloromethyl radical adds to either of the 2-butenes. The possibility that the intermediate radical I has a stable three-atom ring structure analogous to that postulated for the addition of a bromine atom to cyclic olefins[7] is precluded, for if the intermediate radical did have a stable cyclic structure, the radical produced from *cis*-2-butene would have the *meso*-configuration and that from the *trans*-2-butene the *d,l*-configuration, and the respective addition products II from these radicals would be diastereomerically related. These conclusions are consistent also with the results reported recently by Bordwell and Hewett[9] who added thioacetic acid to cyclic olefins by a radical reaction and obtained both diastereomeric thiolacetates, thus demonstrating that the radical  $CH_3{-}C(=O)S\cdot$ did not form a stable three-atom ring intermediate when it added to an olefin. While it is necessary to consider the possibility that a bromine atom is capable of forming a bridge structure with an olefin while a trichloromethyl radical or a thioacetate radical is not able to do so, conclusive evidence to support this contention is not apparent.[10]

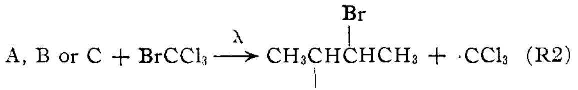
Our interpretation of the bromotrichloromethane-2-butene reaction system is summarized in the following equations and energy diagram.



$$cis\text{-2-butene} + \cdot CCl_3 \underset{\beta}{\overset{\alpha}{\rightleftarrows}} CH_3{-}CH(CCl_3){-}\dot{C}H{-}CH_3 \quad \text{A}$$

$$trans\text{-2-butene} + \cdot CCl_3 \underset{\delta}{\overset{\gamma}{\rightleftarrows}} CH_3{-}CH(CCl_3){-}\dot{C}H{-}CH_3 \quad \text{B} \qquad \text{(R1)}$$

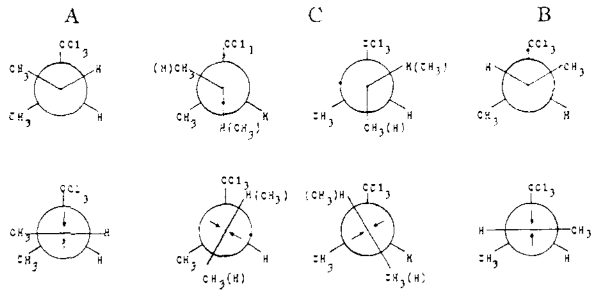
$$\text{A} \underset{\epsilon'}{\overset{\epsilon}{\rightleftarrows}} \text{C} \underset{\epsilon'''}{\overset{\epsilon''}{\rightleftarrows}} \text{B}$$



$$\text{A, B or C} + BrCCl_3 \xrightarrow{\lambda} CH_3CH(CCl_3)CHBrCH_3 + \cdot CCl_3 \quad \text{(R2)}$$

II

The relative rates of reaction are ϵ's $> \alpha = 2.4\,\gamma \approx \lambda > \beta, \delta$



From a consideration of (1) bond energies, (2) the fact that bromotrichloromethane reacts with many polymerizable olefins to produce 1:1 addition products, (3) the absence of *cis–trans* isomerization in the reactions of bromotrichloromethane with the 2-butenes, and (4) the exothermicity of bromotrichloromethane–olefin addition reactions, it appears that both (R1) and (R2) are moderately exothermic (10–20 kcal./mole for each step).

Since the 3-trichloromethyl-2-butyl radicals do not have cyclic structures, open-chain structures which have either a planar or pyramidal trivalent carbon are indicated.[11] For the pyramidal structures all of the possible non-eclipsed rotational isomers (enantiomorphs not included) of the two diastereomeric radicals are represented.[12] In the case of the planar structures all the non-eclipsed ro-

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(8) In connection with a research project not related to the subject considered in this paper, the study of the composition of the diastereomeric mixture of II is being continued. A partial resolution of this mixture has served to demonstrate that the infrared spectra of the two diastereomers are different in the 7–12μ region.

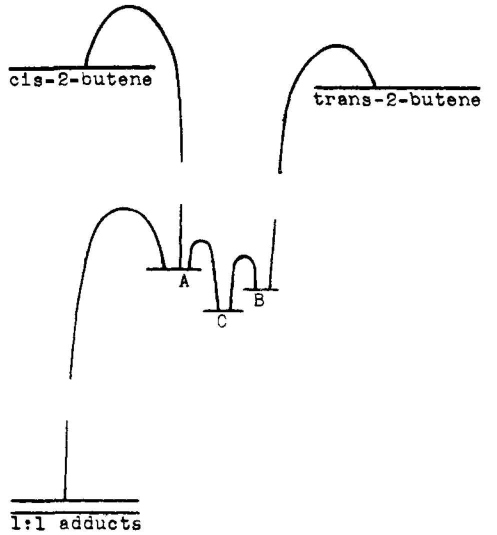
(9) F. G. Bordwell and W. A. Hewett, Abstracts of papers presented at the 126th Meeting of the American Chemical Society, p. 6-O, September 13, 1954.

(10) The bromine and iodine atom induced exchange and isomerization of the dibromo- and diiodoethylenes[2,3] are not explained readily by three atom ring intermediates involving halogen atoms. Also, if a three atom ring intermediate was important in chlorine atom additions to olefins we would not expect to find among the benzene hexachloride isomers structures such as these ascribed to the δ- and ϵ-isomers (three adjacent chlorine atoms on the same side of the ring), unless 1,4-dichlorocyclohexadiene-2,5 also was postulated as a reaction intermediate. R. Reimenschneider [*Monatsh. Chem.*, **85**, 1133 (1954)] observed in the light initiated addition of bromine to α-3,4,5,6-tetrachlorocyclohexane-1 both *cis* and *trans* radical addition of bromine.

(11) The term diastereomeric radicals is reserved for the two families of rotational isomers which can be interconverted only by an inversion of the pyramid.

(12) M. S. Newman, Abstracts of papers presented at the 126th Meeting of the American Chemical Society, p. 10-F, September 15, 1954.

tational isomers (enantiomorphs not included) are shown.



It is evident that equilibration of radicals A, B and C is achieved by a rotation about the C_2–C_3 axis. For the pyramidal radical, interconversion of the two diastereomeric forms is achieved by an inversion of the trivalent group. With the planar structures, additions of a bromine atom from above the plane of the radical will produce one of the diastereomeric 1:1 adducts and addition from below will produce the other. Since the same mixture of diastereomeric addition products II is obtained from *cis*- or *trans*-2-butene, it follows that either the complete equilibration of A, B and C is more rapid than the reaction of these radicals with bromotrichloromethane, or one of the isomeric radicals reacts much more rapidly than the others.

From a consideration of the operation of a van der Waals-type of force law between non-bonded atoms it is possible to estimate the relative energies of the various isomeric radicals and the size of the barriers opposing rotation about the C_2–C_3 axis.[13] In the planar radical the CH_3 and H substituents of the trivalent carbon (C_2) cannot occupy simultaneously positions relative to the substituents of C_3 which correspond to potential minima. In the pyramidal radical the CH_3 and H substituents of C_2 can occupy simultaneously the positions corresponding to potential minima. Consideration of the van der Waals repulsions alone indicate that the pyramidal radical is 3–10 kcal./mole more stable than the planar radical. It also follows that the barriers to rotation about the C_2–C_3 axis are 3–6 kcal./mole for the pyramidal radicals, and considerably less for the planar radicals.

Bonding forces make the pyramidal ammonia molecule more stable than the planar ammonia molecule,[14] although repulsions between non-bonded atoms favor the planar structure. If these same bonding forces operate in carbon radicals, the combination of these forces and the repulsions between non-bonded atoms indicate a pyramidal structure for the 3-trichloromethyl-2-butyl radical.

Experimental

Materials.—Bromotrichloromethane (Dow Chemical Co.) was distilled in the dark through a 3-foot helices packed column at 180 mm. pressure to obtain material distilling at a constant temperature of 61.0°, $n^{25}D$ 1.5030. The isomeric 2-butenes (*trans*-low boiling, *cis*-high boiling), obtained from Phillips Petroleum Co., were Pure Grade (99 mole % minimum purity).

Analysis.—The *cis*- and *trans*-2-butenes were identified by comparison of gas infrared spectra of the samples with the spectra of the pure olefins. A 10.0-cm. cell, fitted with NaCl optics, and a Perkin–Elmer model 21 double beam infrared spectrometer were used. For quantitative work the 14.90 μ band was used for the *cis*-olefin and the 7.64 μ band for the *trans*. At these wave lengths corrections for the presence of the isomeric olefin were not necessary and the optical density was a linear function of the pressure up to 100 mm.

Procedure.—Reactions were carried out in heavy walled soft-glass pressure bottles or ordinary Pyrex flasks. The gaseous olefin was condensed on a weighed portion of bromotrichloromethane and the weight increase represented the weight of olefin. The reaction mixtures were placed in a water-bath and then irradiated by a 200 watt tungsten filament lamp at distances of 6 to 12″. After suitable reaction periods a sample of the unreacted olefin was taken into the evacuated gas infrared cell for analysis. The addition product was isolated by distillation, through a 6″ Vigreux column, of the unreacted material at 160 mm. and of the residue at 20 mm. pressure.

Reaction of *cis*-2-Butene with Bromotrichloromethane.—In a typical experiment 16.9 g. of *cis*-2-butene and 51.9 g. of bromotrichloromethane were irradiated for 4.5 hours at a temperature of 10–20°. The infrared spectrum of the unreacted olefin at 100 mm. pressure was indistinguishable from the spectrum of the original olefin. Distillation of the reaction mixture separated starting materials from 5.8 g. of addition product, b.p. 100–100.5° (20 mm.). No other reaction products were evident.

Reaction of *trans*-2-Butene with Bromotrichloromethane. In an experiment identically paired with the above, 16.5 g. of *trans*-2-butene and 51.0 g. of bromotrichloromethane were mixed. After irradiation the infrared spectrum of the unreacted olefin at 100 mm. pressure was indistinguishable from the spectrum of the original olefin. Distillation separated 3.4 g. of addition product, b.p. 100–100.5° (20 mm.). No other products were evident.

The ratio of the weights of addition product obtained in other paired experiments were not identical with that reported in the above experiments. The differences were moderate and erratic, and in one instance more addition product was obtained from the *trans*-olefin than from the *cis*. In all instances there was no evidence of isomerization of the unreacted olefin. The differences may be explained by the presence of small variable amounts of an inhibitor, possibly oxygen.

Comparison of Addition Products (II) from *cis*- and *trans*-2-Butenes.—The infrared spectra of all addition products obtained from the light-catalyzed reactions, at temperatures between 10 and 20°, regardless of the composition of reacting olefin, were qualitatively and quantitatively identical when compared neat in a 0.025-mm. cell. *In vacuo* fractional distillation of this addition product achieved partial separation of the diastereomers, so that it was possible to recognize absorption bands at 7.67, 7.79, 8.76, 9.46, 10.64, 11.94 μ characteristic of one isomer, and bands at 7.62, 7.74, 8.71, 9.23, 9.64, 10.78, 12.17 μ characteristic of the other isomer.

Competition between *cis*-2-Butene and *trans*-2-Butene for Bromotrichloromethane.—A mixture of 12.82 g. of *cis*-2-butene, 9.49 g. of *trans*-2-butene and 114.2 g. of bromotrichloromethane was irradiated for 27.5 hours at 0°. The partial pressures of the unreacted olefins in the gas phase which was in equilibrium with the reaction mixture were calculated from the total pressure of gas above the reaction mixture and the composition of the gas as determined by infrared analysis. An empirical curve, for each of the pure olefins, relating the weight of olefin dissolved to its partial pressure above the solution (solvent: bromotrichlorometh-

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[13] J. O. Hirschfelder and J. W. Linnett, *J. Chem. Phys.*, **18**, 130 (1950); E. A. Mason, *ibid.*, **23**, 49 (1955); J. G. Aston, *Discussions Faraday Soc.*, **10**, 73 (1951).

[14] Transition state for the pyramid inversion.

ane and addition product) was obtained. With these solubility data, the partial pressures of the olefins above the reaction mixture could be converted to the weight of dissolved unreacted olefins: 3.01 g. of *cis*-2-butene and 5.30 g. of *trans*-2-butene. Distillation of the reaction mixture separated 63 g. of addition product. Since there is a volume decrease during the reaction, the final concentration of olefin was arbitrarily corrected for a 5% volume decrease, resulting in a 4% decrease of k_c/k_t.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE A. AND M. COLLEGE OF TEXAS]

Equilibrium Constants of Substituted Benzophenones in the Meerwein–Ponndorf Reaction[1]

BY DON E. PICKART[2] AND C. KINNEY HANCOCK

RECEIVED FEBRUARY 1, 1955

Equilibrium constants in toluene at 100° for benzophenone and seven *p*-substituted benzophenones in the Meerwein–Ponndorf reaction have been determined. log $K^{100°}$ values show a good linear relationship with Hammett's σ-values, the σ-values being additive for disubstituted derivatives. Statistical treatment of the data yields the following results: (1) equation of the regression line, log $K^{100°} = 1.296\ \sigma - 0.355$, where 1.296 is the reaction constant ρ; (2) standard deviation from the regression line, 0.0605; (3) correlation coefficient, 0.992. The positive sign of ρ supports a mechanism previously proposed by others for the reaction.

Introduction

The history and nature of the Meerwein–Ponndorf reaction have been reviewed by Wilds.[3] The generally accepted mechanism,[4] shown in Fig. 1, involves the formation of a coördination complex A which assumes the cyclic transition state B and facilitates the direct transfer of the hydride ion, leading to C, which breaks down to yield acetone and the aluminum alkoxide product.

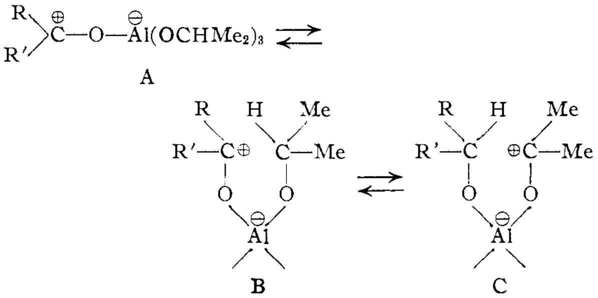

Fig. 1.—Mechanism of the Meerwein–Ponndorf reaction.

Baker and Adkins[5] determined polarographically the equilibrium positions and relative oxidation–reduction potentials of various alcohol–ketone systems. They also developed a method for synthesizing the aluminum alkoxide reductant *in situ* by the use of aluminum *t*-butoxide.

Brockman and Pearson[6] found a linear relationship between half-wave potentials of substituted benzophenones and Hammett's[7] substituent constants which indicates that electron-withdrawing groups favor reduction at the dropping mercury electrode.

The present study was undertaken with the objects of studying the effect of structure on equilibrium constants of substituted benzophenones in the Meerwein–Ponndorf reaction and of applying the results to a further consideration of the reaction mechanism.

Experimental

Materials.—The materials used in this work either were synthesized by well known methods or procured commercially. Physical constants of the purified materials were in good agreement with values reported in the literature.

Apparatus.—A Sargent model XXI polarograph was used. The 10-ml. electrolysis vessel was of the Heyrovsky–Erlenmeyer style (Sargent No. S-29370). Reaction mixtures were equilibrated at 100 ± 0.1° in an oven (Precision No. 504).

Determination of Equilibrium Constants.—The experimental procedure was similar to that of Cox and Adkins.[8] In some cases, diethyl ketone, diethylcarbinol, a substituted benzophenone, and the correspondingly substituted benzhydrol were equilibrated. In the remaining cases, only diethylcarbinol and a substituted benzophenone were used. Experiments proved that either method gave satisfactory results, but mixtures of the latter type required more time to reach equilibrium.

The solutions were made 0.05 *M* in total ketone and 0.05 *M* in total carbinol with toluene used as solvent. The reaction mixture contained 10 ml. of the above solution along with 1 ml. of catalyst (0.70 *M* solution of aluminum *t*-butoxide in toluene). Immediately after adding the catalyst and mixing, four 2-ml. aliquots were removed. The first of these was diluted with 10 ml. of 92% isopropyl alcohol to hydrolyze the catalyst and give a sample at zero time which was used for the polarographic standard. Three other aliquots were pipetted into constricted, nitrogen-filled, Pyrex test-tubes which then were sealed off and placed in the oven at 100°. At the specified times, the tubes were opened, and the contents diluted with 10 ml. of 92% isopropyl alcohol.

Polarographic cells were made of standard and test samples alike by diluting 2 ml. of the clear liquid with an equal volume of isopropyl alcohol and 1 ml. of 0.84 *N* tetramethylammonium hydroxide.

When all four components were originally present in the reaction mixture, the first tube was analyzed after one week. The second tube was analyzed one week later and, if identical analyses were obtained, the mixture was assumed to have reached equilibrium. When only two components were originally present, tubes were analyzed after three and four weeks. In all cases, equilibrium was attained after these periods.

Polarograms were run at 35 ± 0.01°. The equilibrium concentration of aryl ketone, determined from the polarogram by the Borcherdt[9] "b" method, was sufficient to de-

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