# The Carbanionic Mechanism in the Prototropy of 1,3-Diphenylpropenes and 2-Methyl-1,3-diphenylpropenes

By **J. M. Figuera,* J. M. Gamboa,** and **J. Santos,** Instituto de Química Física 'Rocasolano', Serrano 119, Madrid 6, Spain

The base-catalysed isomerization of 1,3-diphenylpropenes and 2-methyl-1,3-diphenylpropenes has been studied. A detailed mechanism based on the intermediacy of carbanions is suggested. The effect of geometrical isomerism on carbanion stability has also been studied. The free energy of formation for the carbanions generated from 1,3-diphenylpropene decreases in the order *cis–cis* > *trans–cis* > *trans–trans* indicating that the [1,3] interaction across the top of the carbanion is dominant. The intramolecularity of the reaction has also been studied. It was found that the more stable the carbanion, the more intramolecular is the reaction. This result is explained by consideration of the particular structure of the carbanionic intermediates.

PROTOTROPY in low mobility systems (those that need a strongly basic catalyst in order to react) has been studied by Ingold [1] who suggested the B-$S_N2'$ mechanism (base-catalysed bimolecular electrophilic substitution with rearrangement). Cram [2] and his co-workers showed that this mechanism is unable to explain the partial intramolecularity of the reaction and other experimental details. They suggested a carbanionic mechanism that has been gradually refined.[2,3]

We have tried to detail the mechanism of the prototropy of 1,3-diphenylpropene and then to study the effect of some substituents on the carbanion stability and on the intramolecularity of the reaction. We have used a kinetic approach, utilizing $^{14}C$ and $^{3}H$ as tracers. We studied the mechanism of the reaction of 1,3-diphenylpropenes and then that of 2-methyl-1,3-diphenylpropenes for comparison purposes.

## EXPERIMENTAL

cis-1,3-*Diphenylpropene*.—This was prepared by the sodium borohydride reduction of 1,3-diphenylpropyne.[4] The main impurities, analysed by g.l.c., were the *trans*-isomer (1·2%) and 1,3-diphenylpropyne (0·3%).

trans-1,3-*Diphenylpropene*.—This compound was prepared following Stoermer and Thier.[4,5] The distilled product was 98% pure (g.l.c.).

trans-1,3-*Diphenyl*[1-$^{14}$C]*propene*.—Higgins's method [6] for substitution of a hydroxy- by a phenyl group in αβ-unsaturated alcohols was used. This method preserves the initial geometry of the double bond.[7] The compound employed in the kinetic runs was 97% pure (g.l.c.).

cis-2-*Methyl*-1,3-*diphenylpropene*.—This olefin was prepared in the same way as *trans*-1,3-diphenyl[1-$^{14}$C]propene. The sodium salt of *trans*-α-methylcinnamic acid (34 g), prepared previously by a Perkin condensation,[8] in water (350 ml) was photolysed using the full arc of an Osram HQA lamp (its outer glass cover removed). The equilibrium concentration, determined by n.m.r. spectroscopy, of the *cis*-isomer was 67%. The separation of the two isomers was accomplished by taking advantage of their different acid strength. The basic solution was acidified to pH 5, the precipitated *trans*-isomer was filtered off, and the solution was further acidified in order to precipitate the *cis*-form which then was filtered off and recrystallized, m.p. 91—92°, $\nu_{max.}$ (KBr) 2000—3500 (OH), 1680 (C=O), 1632 (C=C), 1245 and 1125 (C–O–H), 688, and 740 cm$^{-1}$ (aromatic monosubstitution), $\tau$ ($CDCl_3$) 2·72 (ArH), 3·17 (=CH), and 7·91 (Me). The acid was esterified with ethanol and then reduced to *cis*-α-methylcinnamyl alcohol with lithium aluminium hydride.[7] The yield of the two last steps was

---

[1] C. K. Ingold, 'Structure and Mechanism in Organic Chemistry,' Cornell Univ. Press, New York, 1953, p. 551.

[2] D. J. Cram, 'Fundamentals of Carbanion Chemistry,' Academic Press, New York, 1965, ch. V.

[3] See, for example (*a*) J. Almy and D. J. Cram, *J. Amer. Chem. Soc.*, 1969, **91**, 4459; (*b*) J. Almy, D. C. Garwood, and D. J. Cram, *ibid.*, 1970, **92**, 4321 and references therein.

[4] J. M. Gamboa, R. Pérez-Ossorio, and J. M. Figuera, *Anales de Quim.*, 1967, **63B**, 229.

[5] R. Stoermer and C. Thier, *Ber.*, 1925, **58**, 2611.

[6] G. M. C. Higgins, B. Saville, and M. B. Evans, *J. Chem. Soc.*, 1965, 702.

[7] J. M. Figuera, J. M. Gamboa, and J. Santos, *Anales de Quim.*, in the press.

[8] *Org. Reactions*, 1942, **1**, 251.

63%. The product had b.p. 101—102° at 0·6 mmHg, $\tau$ 3·71 (=CH), 2·86 (ArH), 5·79 $(=C{\cdot}CH_2{\cdot}O)$, and 8·11 (=C=Me).

*cis*-2-Methyl-1,3-diphenylpropene was obtained from the alcohol[6] and purified by preparative g.l.c. (Silicone Gum Rubber SE-52), $\nu_{max.}$ 1650 (C=C), 730 (=CH), 700, and 750 $cm^{-1}$ (aromatic monosubstitution), $\tau$ 2·81 and 2·84 (ArH), 3·52 (=CH), 6·44 $(CH_2)$, and 8·23 (Me).

*Kinetics.*—The catalytic solution was made from 60% dry ethanol, 40% anhydrous dioxan, and enough sodium metal to reach 1·3M.[9a] The olefin concentration in the solution was maintained at 0·3M.

The reaction tubes were refrigerated, filled with 10 µl of olefin and catalytic solution, degassed by the freeze–pump–thaw method, and then sealed in a dry nitrogen atmosphere. The tubes were then maintained in a thermostat regulating to ±0·05° (temperature stability was somewhat worse over long periods). The temperature at which most of the kinetics were measured, was chosen to minimize errors associated with the time to achieve thermal equilibrium.

Tritiated ethanol was prepared by an adaptation of a method for drying ethanol.[9b] A solution of tritiated water (0·1 ml) (5 Ci $ml^{-1}$; Radiochemical Centre, Amersham) in dry ethanol (25 ml) was prepared. This solution was dried by adding enough sodium ethoxide to consume the water. The solution was left overnight. After addition of ethyl formate (1 ml) a white precipitate of sodium formate was formed. The mixture was refluxed for 3 h and then the tritiated ethanol was distilled. The specific activity (scintillation counting) of the ethan[$^3$H]ol was 16·1 mCi $mol^{-1}$ (87% incorporation).

*Analyses.*—The i.r. spectra were recorded with a 125 Perkin-Elmer spectrophotometer and the n.m.r. spectra with a Perkin-Elmer R-10 model. A 5750 Hewlett–Packard gas chromatograph with a hot wire detector was used for g.l.c. The *cis*- and *trans*-1,3-diphenylpropenes were analysed by g.l.c. [20% silicone grease (cyanoethyl) on Chromosorb WAW at 210° and helium (60 ml $min^{-1}$) as carrier gas]. The tritiated olefins were analysed by radiochromatography in a Cary ionization chamber coupled to the gas chromatograph. The chamber was maintained at *ca.* 200° and argon (750 ml $min^{-1}$) was mixed with the carrier to form the counting gas. The apparatus already described[10] has been slightly modified by eliminating the combustion furnace. By this method of analysis the position of the tritium in the molecule is not determined. The system was calibrated with a sample of *trans*-1,3-diphenylpropene labelled with tritium (0·301 Ci $mol^{-1}$ as determined by liquid scintillation counting).

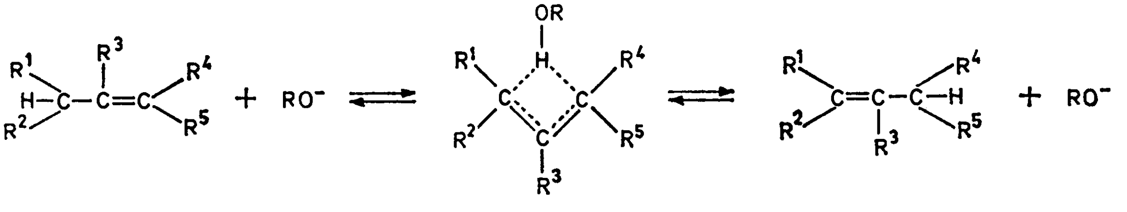
When carbon-14 was used, in order to analyse the amount of olefin labelled at C-1 against that labelled at C-3, the propenes were ozonolysed and the ozonides were decomposed by lithium aluminium hydride. The resulting alcohols were analysed following techniques previously described[10] although as in the tritium case the combustion furnace was eliminated.

The *cis*- and *trans*-2-methyl-1,3-diphenylpropenes were analysed by g.l.c. [8% butanediol succinate on Chromosorb WHMDS at 200° and helium (60 ml $min^{-1}$) as carrier gas].

*Integration of the Differential Equations.*—The differential equations resulting from reacting systems of more than two substances ($A \rightleftharpoons B$) were integrated numerically by the Runge–Kutta method.[11] The program, written in Fortran IV, is able to deal with up to 12 substances, interconverting mutually by first-order reactions. In the more complex system it is sometimes necessary to introduce an integration range so small that the computing time increases to a level that makes the program useless.

## RESULTS

*The Carbanionic Mechanism in the Prototropy of the 1,3-Diphenylpropenes.*—The mechanism of the base-catalysed isomerization of allylic compounds, suggested by Cram,[12] is given by equation (1). In the present case, with dioxan–ethanol as solvent, the carbanionic intermediates probably form a hydrogen-bonded ion pair although this point is beyond the scope of this work.



(1)

The reaction scheme (Figure 1) gives the proton transfer mechanism of 1,3-diphenylpropene in dioxan, ethan[$^3$H]ol, and sodium ethoxide. It has been deduced from the elementary steps of reaction (1) and taking into account the following limitations. (*a*) The allylic carbanionic intermediates maintain the geometry of their parent olefins[13,14] resisting rotation around their partial double bonds. A Hückel calculation of 1,3-diphenylallyl anion gives 27 kcal $mol^{-1}$ as the height of the rotational barrier.[15] (*b*) Each olefin isomer can form two different carbanions. The presence of a tritium atom in the methylene group raises this number to four. (*c*) Proton exchange involves rotation of the metal cation and its ligands within the ion pair.[16] (*d*) Each carbanion can yield two different products, which reduce to one if the carbanion is symmetric.

---

[9] (*a*) J. M. Figuera, Ph.D. Thesis, Madrid, 1965; (*b*) A. I. Vogel, 'Practical Organic Chemistry,' Longmans, London, 1948, p. 167.

[10] J. M. Gamboa, R. Pérez-Ossorio, and J. M. Figuera, *Anales de Quim.*, 1967, **63B**, 241.

[11] (*a*) H. Margenau and G. M. Murphy, 'Las Matemáticas de la Físcia y de la Química,' Ediciones y Publicaciones Españolas S.A., 1st edn., Madrid, 1962, p. 609; (*b*) K. B. Wiberg, 'Computing Programming for Chemists,' Benjamin, New York, 1965, pp. 128 and 151.

[12] Ref. 2, p. 180.

[13] W. S. Ela and D. J. Cram, *J. Amer. Chem. Soc.*, 1966, **88**, 5777.

[14] D. H. Hunter and D. J. Cram, *J. Amer. Chem. Soc.*, 1964, **86**, 5478.

[15] H. H. Freedman, V. R. Sandel, and B. P. Thill, *J. Amer. Chem. Soc.*, 1967, **89**, 1762.

[16] Ref. 2, pp. 176—179.

The rate constants have been grouped as follows. (*a*) Experimental rate constants which correspond to experimentally observable transformations. (*b*) Rate constants which correspond to elementary steps of the Cram mechanism. The collapse of the carbanions to give products is considered to be unimolecular but the carbanion exchange and formation are thought to be bimolecular in EtOH and EtO$^-$ respectively, although under the conditions employed they appear as pseudo-first order. This is obviously true when pure ethanol is used. In the case of ethan[$^3$H]ol it was found that the amount of tritium incorporated into the olefin did not exceed 0·1% of the total amount available in the solvent.

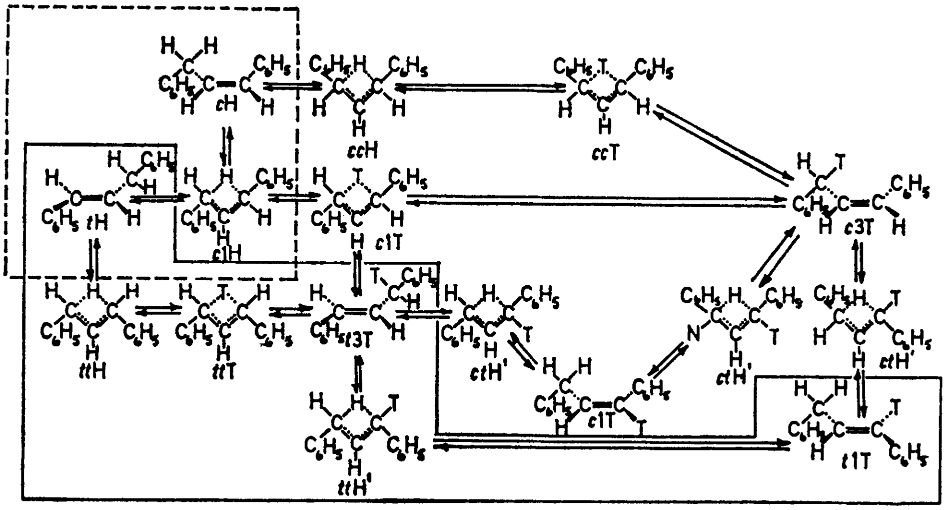
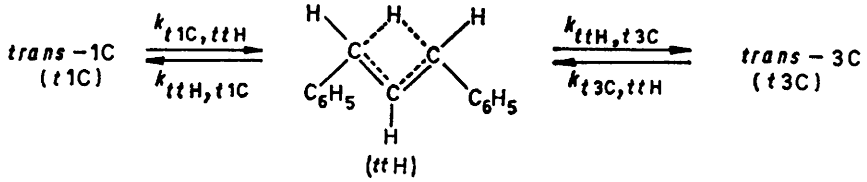


FIGURE 1 Reactions of 1,3-diphenylpropene in dioxan, ethan[$^3$H]ol, and sodium ethoxide. The full line encloses the kinetically significant reactions when the *trans*-isomer is the initial substrate. The broken line encloses the mechanism of *cis–trans* isomerization in the absence of tritium



(2)

Rate constants are identified by their subscripts, the first standing for the reactant, and the second for the product; in both cases the abbreviations of Figure 1 are used. Bimolecular constants are distinguished from their pseudo-first-order counterparts by the use of 2 as a superscript.

In order to find the values of the rate constants involved in Figure 1 we have chosen separate parts of it, susceptible to independent treatment, and evaluated their rate constants. When the values of these constants were introduced in the complete scheme, a satisfactory solution could be obtained. The procedure is self-explanatory. The steady-state condition has been applied to the carbanions and its range of application discussed.

The concentration of tritiated substrate was very small compared with the non-tritiated due to the relatively small rate of tritiation (the solution was 0·29 × 10$^{-3}$M in tritiated ethanol, which made the pseudo-first-order rate constant very small). These conditions made double tritiation negligible.

trans-1,3-*Diphenyl*[1-$^{14}$C]*propene* $\rightleftharpoons$ trans-1,3-*Diphenyl*-[3-$^{14}$C]*propene*.—From this reaction, assuming no secondary isotope effects, we can calculate the rate constants associated with the reaction *t*3T $\rightleftharpoons$ *t*1T of Figure 1.

The equilibrium constant favours the *trans*-isomer over the *cis*; consequently the reactions giving the final product are neglected. Figure 1 reduces to equation (2).

The [1,3] proton transfer proceeds through the *trans–trans* carbanion. Assuming that the steady-state is obtained, it follows that the reaction is kinetically equivalent to the direct transformation *t*1C $\rightleftharpoons$ *t*3C, in which the experimental rate constants are related to those of Figure 1 through equations (3) and (4).

$$k_{t1C,t3C} = k_{ttH,t3C}k_{t1C,ttH}(k_{ttH,t1C} + k_{ttH,t3C}) \qquad (3)$$

$$k_{t3C,t1C} = k_{t3C,ttH}k_{ttH,t1C}(k_{ttH,t1C} + k_{ttH,t3C}) \qquad (4)$$

The *tt*H carbanion should collapse toward one side or another with the same rate ($k_{ttH,t1C} = k_{ttH,t3C}$) and should be formed from both compounds also with identical rate ($k_{t1C,ttH} = k_{t3C,ttH}$), because ignoring the label, reactant and product are the same chemical entity. Therefore it is easily shown that equation (5) applies. Application of the

$$k_{t1C,t3C} = k_{tO3,t1C} = 1/2k_{t1C,ttH} = 1/2k_{t3O,ttH} \qquad (5)$$

rate law that corresponds to a first-order reversible reaction gives equation (6). Hence, the pseudo-first-order rate

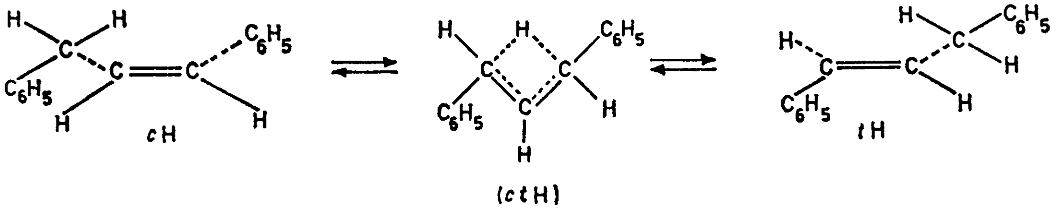
$$k_{t1O,t3O} = 0{\cdot}203 \pm 0{\cdot}013\ \mathrm{h^{-1}} \qquad (6)$$

constant of carbanion formation is $k_{tt,ttH} = 0{\cdot}406\ \mathrm{h^{-1}}$ and the corresponding bimolecular $^2k_{tH.ttH} = 0{\cdot}312\ \mathrm{l\ h^{-1}\ mol^{-1}}$.

The rate constants for carbanion collapse cancel in the kinetic expressions and are therefore unattainable by this method.

The range, for which the steady-state assumption holds has been investigated, the results obtained with and without this assumption being compared. It is necessary to assign arbitrary values to the rates of carbanion collapse. It has been found that if $k_{\text{collapse}}/k_{\text{formation}} \geqslant 100$ the errors are smaller than the experimental ones (for a carbanion whose free energy exceeds by 15 kcal mol$^{-1}$ that of the parent olefin, this value should be *ca.* $10^{10}$).

cis–trans-*Isomerization of* 1,3-*Diphenylpropene*.—In this case Figure 1 reduces to equation (7). The *cis–trans* carbanion *ct*H can collapse, once formed, toward the *cis*- or the *trans*-isomer. The *cis–cis* and *trans–trans* carbanions are not included because they are able to collapse only to the isomers from which they are formed.



(7)

This reaction represents the [1,3] proton transfer that produces a change of molecular geometry, the rest of the [1,3] proton migrations not being detectable.

The kinetic problem is identical to the previous one and therefore the steady-state assumption gives similar expressions. The difference arises in this case from lack of an *a priori* cause that can make the carbanion collapse in both ways at the same rate. However it was found experimentally that its tritiated analogue, the carbanion *ct*T, does collapse at the same rate to the *cis*- or *trans*-isomer. We assume that substitution of the tritium atom by hydrogen should not alter this behaviour. Applying the rate law that corresponds to a first order–first order reversible reaction we obtained the experimental and pseudo-first-order rate constants (8) and (9). The corresponding

$$k_{c\mathrm{H},t\mathrm{H}} = 1/2k_{c\mathrm{H},ct\mathrm{H}} = 0{\cdot}600 \pm 0{\cdot}018\ \mathrm{h}^{-1} \tag{8}$$

$$k_{t\mathrm{H},c\mathrm{H}} = 1/2k_{t\mathrm{H},ct\mathrm{H}} = 0{\cdot}135 \pm 0{\cdot}004\ \mathrm{h}^{-1} \tag{9}$$

bimolecular rate constants are given by equations (10) and (11).

$${}^{2}k_{c\mathrm{H},ct\mathrm{H}} = 0{\cdot}923\ \mathrm{l\ h^{-1}\ mol^{-1}} \tag{10}$$

$${}^{2}k_{t\mathrm{H},ct\mathrm{H}} = 0{\cdot}0208\ \mathrm{l\ h^{-1}\ mol^{-1}} \tag{11}$$

*Reaction of* trans-1,3-*Diphenylpropene in the Presence of Tritiated Ethanol*.—In this system the amounts of *c*H and *c*T found are very small with relation to *t*H and *t*T (*i.e.* within experimental error). Therefore we can neglect *trans* ⟶ *cis* reactions thus reducing the mechanism to that enclosed by the full line in Figure 1.

Assuming steady-state conditions for the carbanions *tt*H, *tt*T, and *tt*H′ we may deduce, in a way similar to that used in the Appendix, that the system is kinetically equivalent to (12) where the experimental rate constants are a function of the pseudo-first-order constants [equations (13) and (14)].

$$t\mathrm{H} \rightleftharpoons t3\mathrm{T} \rightleftharpoons t1\mathrm{T} \tag{12}$$

$$k_{t\mathrm{H},t3\mathrm{T}} = \frac{k_{t\mathrm{H},tt\mathrm{H}}k_{tt\mathrm{H},tt\mathrm{T}}k_{tt\mathrm{T},t3\mathrm{T}}}{k_{tt\mathrm{H},t\mathrm{H}}k_{tt\mathrm{T},tt\mathrm{H}} + k_{tt\mathrm{H},t\mathrm{H}}k_{tt\mathrm{T},t3\mathrm{T}} + k_{tt\mathrm{H},tt\mathrm{T}}k_{tt\mathrm{T},t3\mathrm{T}}} \tag{13}$$

$$k_{t3\mathrm{T},t\mathrm{H}} = \frac{k_{t3\mathrm{T},tt\mathrm{T}}k_{tt\mathrm{T},tt\mathrm{H}}k_{tt\mathrm{H},t\mathrm{H}}}{k_{tt\mathrm{H},t\mathrm{H}}k_{tt\mathrm{T},tt\mathrm{H}} + k_{tt\mathrm{H},t\mathrm{H}}k_{tt\mathrm{T},t3\mathrm{T}} + k_{tt\mathrm{H},tt\mathrm{T}}k_{tt\mathrm{T},t3\mathrm{N}}} \tag{14}$$

The expressions for the rate constants $k_{t3\mathrm{T},t1\mathrm{T}}$ and $k_{t1\mathrm{T},t3\mathrm{T}}$ are similar to those of the previous cases. If secondary isotope effects are neglected equation (15) is obtained, where the 1/2 factor corrects the statistically different availability of hydrogen in *t*3T.

In order to calculate the two unknown constants $k_{t\mathrm{H},t3\mathrm{T}}$ and $k_{t3\mathrm{T},t\mathrm{H}}$ we have proceeded as follows. We have started with a value for $k_{t\mathrm{H},t3\mathrm{T}}$ deduced from the initial slope of the curve of tritiated *trans*-concentration *vs.* time. Next, we found out by trial and error the rate constants which best

$$k_{t3\mathrm{C},t1\mathrm{C}} = k_{t1\mathrm{T},t3\mathrm{T}} = 1/2k_{t3\mathrm{T},t1\mathrm{T}} = 0{\cdot}203\ \mathrm{h}^{-1} \tag{15}$$

fitted the experimental data (Figure 2). These values are given by equations (16) and (17). In these calculations

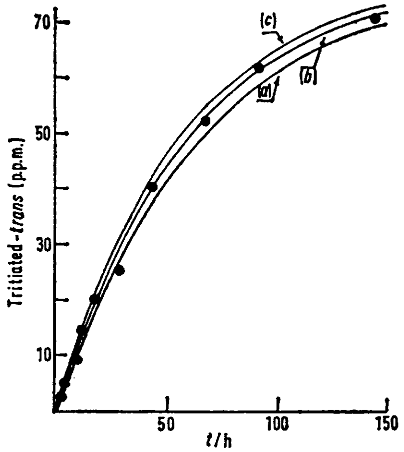


FIGURE 2 Reaction of *trans*-1,3-diphenylpropene in tritiated medium. Fitting of the curves to the experimental data gave the following values of $k_{t\mathrm{H},t3\mathrm{T}}$ and $k_{t3\mathrm{T},t\mathrm{H}}$: (a) $0{\cdot}121 \times 10^{-5}\ \mathrm{h}^{-1}$ and $0{\cdot}23 \times 10^{-1}\ \mathrm{h}^{-1}$, (b) $0{\cdot}13 \times 10^{-5}\ \mathrm{h}^{-1}$ and $0{\cdot}247 \times 10^{-1}\ \mathrm{h}^{-1}$, and (c) $0{\cdot}143 \times 10^{-5}\ \mathrm{h}^{-1}$ and $0{\cdot}27 \times 10^{-1}\ \mathrm{h}^{-1}$

$$k_{t\mathrm{H},t3\mathrm{T}} = 0{\cdot}13 \times 10^{-5}\ \mathrm{h}^{-1} \tag{16}$$

$$k_{t3\mathrm{T},t\mathrm{H}} = 0{\cdot}0247\ \mathrm{h}^{-1} \tag{17}$$

we have constrained the rate constants to obey the experimentally determined ratio (18). Equation (18) where $[t\mathrm{T}]_{\mathrm{e}}$

$$[t\mathrm{T}]_{\mathrm{e}}/3/2[t\mathrm{H}]_{\mathrm{e}} = k_{t\mathrm{H},t3\mathrm{T}}/k_{t3\mathrm{T},t\mathrm{H}} \tag{18}$$

and $[t\mathrm{H}]_{\mathrm{e}}$ are the experimental concentration of *t*1T + *t*3T and *t*H at equilibrium, respectively, is easily deduced from the equilibrium conditions.

The sensitivity of the curve fitting technique is shown in Figure 2 where the curves obtained for several pairs of values of $k_{t\mathrm{H},t3\mathrm{T}}$, $k_{t3\mathrm{T},t\mathrm{H}}$ that obey the above ratio are represented together with the experimental results.

We have also investigated the accuracy of the steady-state assumption, finding that it can be used for $k_{collapse}/k_{formation} \geqslant 1000$.

*Determination of the* $k_{exchange}/k_{collapse}$ *Ratio*.—Neglecting the isotope effects on the rate constants of carbanion formation and hydrogen–tritium exchange (*i.e.* accumulating those effects on the rates of carbanion collapse) we can deduce the expressions (19) and (20), in a way similar to

$$\frac{{}^{2}k_{ttH,ttT}}{k_{ttH.tH}} = \frac{k_{tH,t3T}}{({}^{2}k_{tH,ttH}[EtO^-] - k_{t3T,tH} - k_{tH,t3T})[EtOT]} \tag{19}$$

$$\frac{{}^{2}k_{ttT,ttH}}{k_{ttT,t3T}} = \frac{k_{t3T,tH}}{({}^{2}k_{t3T,ttT}[EtO^-] - k_{t3T,tH} - k_{tH,t3T})[EtOH]} \tag{20}$$

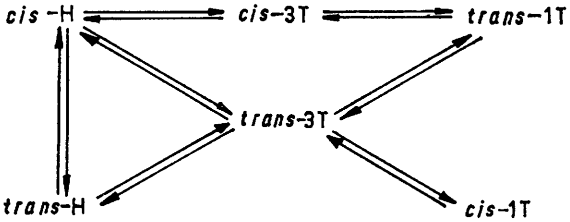
that used in the Appendix. Making ${}^{2}k_{tH,ttH} = 2\,{}^{2}k_{t3T,ttT}$ because of statistical reasons we find ${}^{2}k_{ttH.ttT}/k_{ttH.tH} = 1{\cdot}18 \times 10^{-2}$ and ${}^{2}k_{ttT.ttH}/k_{ttT,t3T} = 1{\cdot}54 \times 10^{-2}$ l mol$^{-1}$.

*Reaction of* cis-1,3-*Diphenylpropene in the Presence of Tritiated Ethanol*.—In order to estimate the rate constants corresponding to Figure 1 the following approximations and restrictions have been taken into account. (*a*) The *cis–cis* carbanions (*cc*H, *cc*T, and *cc*H′) have been omitted. The strong [1,3] interaction of the phenyl group should make them relatively unstable (see Discussion). (*b*) The steady-state assumption has been applied to all the carbanions involved (see previous cases and Appendix). Figure 1 reduces to Scheme 1. (*c*) The initial slopes of the curves relating the *c*T and *t*T concentration to time are equal (see Table 1), and therefore we assume that $k_{cH,c3T} = k_{cH,t3T}$ since according to the mechanism of Figure 1, all the initially formed tritiated *cis*- and *trans*-compounds are *c*3T and *t*3T respectively. (*d*) If the rates of production of *c*3T and *t*3T are equal, this reveals that the rate of collapse of the unique intermediate: the carbanion *ct*T, toward either of them is also the same. Generalizing this result to the *cc*H carbanion we can deduce equation (21), from the Appendix, which we may assume to be equal to the known

$$k_{c3T,cH}/k_{t3T,cH} = k_{c3T,ctT}/k_{t3T,ctT} \tag{21}$$

ratio $k_{cH,ctH}/k_{tH,ctH}$ provided that the isotope effects do not alter it. (*e*) It is easily shown that at equilibrium equation (22), holds $[tT]_e$ and $[cH]_e$ being the experimental concentration of $t1T + t3T$ and *c*H at equilibrium, respectively. The terms in the right side of equation (22) are known.

$$k_{cH,c3T}/k_{t3T,cH} = (k_{cH,tH}/6k_{cH,tH}) \times [tT]_e/[cH]_e \tag{22}$$



SCHEME 1

TABLE 1

Initial concentrations of *cis*- and *trans*-tritiated isomers formed in the prototropy of *cis*-1,3-diphenylpropene in a tritiated medium

| *t*/h | 0·167 | 0·333 | 0·50 | 0·75 | 1 |
|---|---|---|---|---|---|
| Tritiated-*trans* (p.p.m.) | 0·29 | 0·71 | 1·16 | 1·72 | 2·17 |
| Tritiated-*cis* (p.p.m.) | 0·31 | 0·76 | 1·07 | 1·55 | 1·84 |

The rate constants that, complying with the stated conditions, best fit the experimental results (Figure 3) are in Table 2.

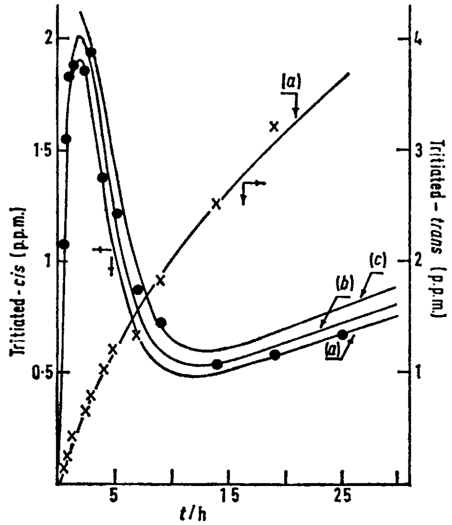


FIGURE 3 Reactions of *cis*-1,3-diphenylpropene in tritiated medium. Fitting of the curves to the experimental data for tritiated *cis*, ●, and *trans*, ×, gave $k_{cH,c3T} = 0{\cdot}28 \times 10^{-5}$ h$^{-1}$ and the following values of $k_{c3T,cH}$: (a) 0·20 h$^{-1}$, (b) 0·15 h$^{-1}$, and (c) 0·10 h$^{-1}$

TABLE 2

Calculated rate constants (h$^{-1}$) for the kinetically significant processes of Figure 1

| | | | | | |
|---|---|---|---|---|---|
| $k_{cH,c3T}$<br>$k_{cH,t3T}$ | $k_{c3T,cH}$ | $k_{t3T,cH}$ | | $k_{cH,tH}$<br>$k_{c1T,t3T}$ | $k_{tH,cH}$<br>$k_{t1T,c3T}$ |
| $0{\cdot}28 \times 10^{-5}$ | 0·20 | $0{\cdot}45 \times 10^{-2}$ | | 0·60 | $0{\cdot}135 \times 10^{-1}$ |
| $k_{tH,t3T}$ | $k_{t3T,tH}$ | $k_{t1T.t3T}$ | $k_{t3T,t1T}$ | $k_{t3T,c1T}$ | $k_{c3T,t1T}$ |
| $0{\cdot}19 \times 10^{-5}$ | $0{\cdot}361 \times 10^{-1}$ | 0·203 | 0·1015 | $0{\cdot}675 \times 10^{-2}$ | 0·30 |

For the direct process a range of $k_{cH,c3T}$ between 0·30 and $0{\cdot}26 \times 10^{-5}$ h$^{-1}$ permits a good fit with the experimental data. For the reverse process the curve fitting technique is less discriminating (see Figure 3) but the relationship (22) reduces the acceptable values of $k_{c3T,cH}$ to the range 0·19—0·22 h$^{-1}$.

The variation of the rate constant $k_{tH,t3T}$ from the previously obtained value (see preceding case) is probably due to long range temperature stability problems. In any case, this rate constant begins to affect the results only when practically all the *cis*-products are near to equilibrium concentrations, reducing the system to the one previously studied.

*Determination of the* $k_{exchange}/k_{collapse}$ *Ratio*.—Experimental evidence (see above) indicates that the *cis–trans* carbanion collapses at the same rate towards the *cis*- or *trans*-olefin, *i.e.* $k_{ctT,c3T} = k_{ctT,t3T}$ and $k_{ctH,cH} = k_{ctH,tH}$. Furthermore, neglecting the isotope effects on the rate constants of carbanion formation and hydrogen–tritium exchange, we may apply the equations (37) and (38) (see Appendix), obtaining ${}^{2}k_{ctH.ctT}/k_{ctH.cH} = 0{\cdot}0483$ and ${}^{2}k_{ctT,ctH}/k_{ctT,c3T} = 0{\cdot}222$ l mol$^{-1}$.

The two ratios would be equal if the previous assumptions had held; the disparity gives a rough idea of the errors involved in the calculation.

cis-trans-*Isomerization of the* 2-*Methyl*-1,3-*diphenylpro-*

*penes.*—The method of approach is the same as that used previously for the isomerization of 1,3-diphenylpropenes. The reaction was run at different temperatures and the resulting bimolecular rate constants for carbanion formation are in Table 3.

TABLE 3

Bimolecular rate constants of carbanion formation in the 2-methyl-1,3-diphenylpropenes

| | Temperature | | |
|---|---|---|---|
| | 111 °C | 121·6 °C | 130·5 °C |
| $^{2}k_{c\mathrm{H},ct\mathrm{H}}$/l mol$^{-1}$ h$^{-1}$ | 0·215 ± 0·024 | 0·615 ± 0·025 | 1·054 ± 0·018 |
| $^{2}k_{t\mathrm{H},ct\mathrm{H}}$/l mol$^{-1}$ h$^{-1}$ | (0·954 ± 0·11) × 10$^{-1}$ | 0·283 ± 0·011 | 0·457 ± 0·080 |

*Activation Parameters.*[17]—The Arrhenius plots corresponding to formation of the *cis–trans* carbanion *ct*H from the *cis-* and *trans*-2-methyl-1,3-diphenylpropenes and 1,3-diphenylpropenes, are given in Figure 4 along with that corresponding to *trans–trans* carbanion formation from *trans*-1,3-diphenylpropene. The values for the diphenylpropanes have been calculated from previous work.[10] The Arrhenius parameters, together with the entropy, enthalpy, and free energy of activation at 85° are given in Table 4.

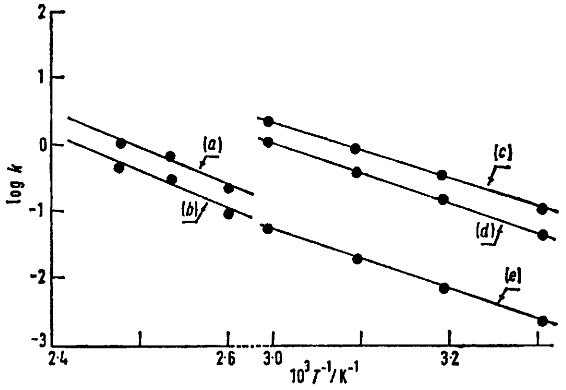


FIGURE 4 Arrhenius plot: (a) and (b) reactions $c\mathrm{H} \longrightarrow ct\mathrm{H}$ and $t\mathrm{H} \longrightarrow ct\mathrm{H}$ for 2-methyl-1,3-diphenylpropene; (c), (d), and (e) reactions $c\mathrm{H} \longrightarrow ct\mathrm{H}$, $t\mathrm{H} \longrightarrow tt\mathrm{H}$, and $t\mathrm{H} \longrightarrow ct\mathrm{H}$ for 1,3-diphenylpropene respectively

TABLE 4

Kinetic parameters for the formation of *cis–trans* carbanion from *cis-* and *trans*-1,3-diphenylpropenes and 2-methyl-1,3-diphenylpropenes and for the formation of the *trans–trans* carbanion from *trans*-1,3-diphenylpropene

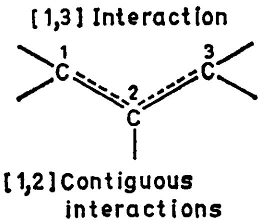
| Substrate | Reaction | *A*<br>l mol$^{-1}$ h$^{-1}$ | $E_{\mathrm{act.}}$<br>kcal mol$^{-1}$ | $\Delta S^{\ddagger}$<br>cal mol$^{-1}$ K$^{-1}$ | $\Delta H^{\ddagger}$<br>kcal mol$^{-1}$ | $\Delta G^{\ddagger}$<br>kcal mol$^{-1}$ |
|---|---|---|---|---|---|---|
| 1,3-Diphenylpropene | $c\mathrm{H} \longrightarrow ct\mathrm{H}$ | 7·11 × 10$^{12}$ | 19·1 | −18·35 | 18·4 | 25 |
| 1,3-Diphenylpropene | $t\mathrm{H} \longrightarrow ct\mathrm{H}$ | 1·45 × 10$^{12}$ | 20·5 | −21·61 | 19·8 | 27·5 |
| 1,3-Diphenylpropene | $t\mathrm{H} \longrightarrow tt\mathrm{H}$ | 2·06 × 10$^{13}$ | 20·3 | −16·08 | 19·6 | 25·4 |
| 2-Methyl-1,3-diphenylpropene | $c\mathrm{H} \longrightarrow ct\mathrm{H}$ | 8·59 × 10$^{13}$ | 25·6 | −13·26 | 24·9 | 29·6 |
| 2-Methyl-1,3-diphenylpropene | $t\mathrm{H} \longrightarrow ct\mathrm{H}$ | 3·42 × 10$^{13}$ | 25·5 | −15·5 | 24·8 | 30·2 |

## DISCUSSION

In this particular work a system of six interconverting substances have been fully analysed by computer and the particular rate constants calculated. The agreement of the calculated curves (Figure 3) with the experimental data is good evidence that the prototropy follows the proposed carbanionic mechanism of Figure 1. From this base, we have been able to evaluate the qualitative dependence of the carbanion stability on its geometrical isomerism, and get some insight in the factors affecting the intramolecularity of these reactions.

*Effect of the Substituents on the Carbanion Stability.*—Two types of substituent interaction can be distinguished in the studied carbanions: [1,3] interaction across the top of the molecule and a [1,2] interaction between contiguous substituents along the bottom of the molecule (Scheme 2). Each of these interactions will be analysed separately. The free energy of formation of each carbanion should not be very different from the free energy of the activated complex from which it is formed; accordingly we have taken the last one, following Hammond postulate,[18] as a measure of the relative stability of the carbanion.

[1,3] *Interactions.*—The free energy of activation, $\Delta G^{\ddagger}$, for the reactions leading to *cis–trans* and *trans–trans* carbanions from *trans*-1,3-diphenylpropene are 27·5 and 25·4 kcal mol$^{-1}$ respectively. Accordingly, substitution of a [1,3] hydrogen–hydrogen by a [1,3] hydrogen–phenyl interaction increases the carbanion free energy by 2 kcal mol$^{-1}$. Under the present experimental conditions it has not been possible to obtain numerical data for the [1,3] phenyl–phenyl interaction. The carbanion to which it corresponds is formed at a relatively low rate; assuming this rate constant to be nil a good fit to experimental results was found. Additional data concerning the reaction *cis*-1,3-diphenyl[3-$^{14}$C]propene $\longrightarrow$ *cis*-1,3-diphenyl[1-$^{14}$C]propene supports this assumption.[7] We may conclude that the order of carbanion stability is *trans–trans* > *trans–cis* > *cis–cis* in the same order as the [1,3] steric interactions. Ela and Cram[13] obtained similar results for a different substrate.



SCHEME 2

[1,2] *Contiguous Interactions.*—The free energy of the carbanion relative to the initial compounds is higher in

---

[17] A. Weissberger, ' Technique of Organic Chemistry,' Interscience, New York, vol. VIII, Part I, Investigation of Rates Mechanisms of Reactions, 2nd ed., p. 199.

[18] G. S. Hammond, *J. Amer. Chem. Soc.*, 1955, **77**, 334.

the 2-methyl-1,3-diphenylpropenes than in the 1,3-diphenylpropenes (4·6 or 2·7 kcal mol$^{-1}$ depending on the isomer taken as reference). This increment may be ascribed to the growing-in of a [1,2] methyl–phenyl interaction. This interaction might alter the order of stability in the 2-methyl substituted carbanion. Preliminary data on the *trans*-2-methyl-1,3-diphenyl[1-$^{14}$C]-propene prototropy has shown that rate constant of carbanion *trans–cis* formation is greater than that of the *trans–trans*.[19]

*Intramolecularity*.—The experimental ratios $k_{\text{exchange}}/k_{\text{collapse}}$ are given in Table 5. The data dispersion arises from the accumulation of the isotope effects on the exchange step, due to the necessary approximations used (see Results). This discrepancy may give an estimation of the errors involved in those approximations. In any case the following trends appear clearly. (*a*) The reaction is predominantly intramolecular. (*b*) The rate of exchange is influenced by thermodynamic stability ($\Delta G$) of the carbanion. The more stable the carbanion is, the more bonded the bridge hydrogen atom, and therefore the less easily exchanged. The *trans–trans* carbanion, more stable by *ca*. 2 kcal mol$^{-1}$ than the *cis–trans*, exchanges hydrogen at a rate 10 times smaller.

TABLE 5

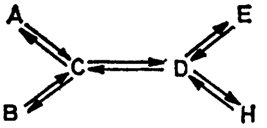
The $k_{\text{exchange}}/k_{\text{collapse}}$ ratio for the *trans–trans* and *cis–trans* carbanions

| | *trans–trans* | *cis–trans* |
|---|---|---|
| $k_{\text{exchange}}/k_{\text{collapse}}$ | $1{\cdot}18 \times 10^{-2}$ and<br>$1{\cdot}54 \times 10^{-2}$ | 0·048 and 0·22 |

In this argument we have emphasized the influences on the rate of exchange, although the experimental data are referred to ratios of rates and therefore, the trends can be due to variations of the rate constants for collapse. This does not seem to be the case since the rates of collapse show little sensitivity to structural factors; we have shown above that the *cis–trans* carbanion collapses to *cis*- or *trans*-compound at the same rate.

## APPENDIX

*The Steady-state Assumption*.—The most complex system to which the steady-state condition has been applied is one of five reversible and simultaneous reactions (Scheme 3).



SCHEME 3

Assuming a steady-state for C and D, then the rate of disappearance of A is given by equation (23) and the rates of

$$-\mathrm{d}[\mathrm{A}]/\mathrm{d}t = k_{\mathrm{AC}}[\mathrm{A}] - k_{\mathrm{CA}}[\mathrm{C}] \qquad (23)$$

formation of C and D by equations (24) and (25). Applications of the steady-state assumption to C and D gives equation (26). Then, the concentration of C may be

$$\mathrm{d}[\mathrm{C}]/\mathrm{d}t = k_{\mathrm{AC}}[\mathrm{A}] + k_{\mathrm{DC}}[\mathrm{D}] + k_{\mathrm{BC}}[\mathrm{B}] - [\mathrm{C}](k_{\mathrm{CA}} + k_{\mathrm{CB}} + k_{\mathrm{CD}}) \qquad (24)$$

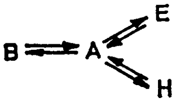
$$\mathrm{d}[\mathrm{D}]/\mathrm{d}t = k_{\mathrm{ED}}[\mathrm{E}] + k_{\mathrm{HD}}[\mathrm{H}] + k_{\mathrm{CD}}[\mathrm{C}] - [\mathrm{D}](k_{\mathrm{DC}} + k_{\mathrm{DE}} + k_{\mathrm{DH}}) \qquad (25)$$

$$\mathrm{d}[\mathrm{C}]/\mathrm{d}t = \mathrm{d}[\mathrm{D}]/\mathrm{d}t = 0 \qquad (26)$$

eliminated from equation (23) by solution of the simultaneous equations (24) and (25). We have on reduction equation (27) where DEN is equal to $k_{\mathrm{CA}}(k_{\mathrm{DC}} + k_{\mathrm{DE}} + k_{\mathrm{DH}}) + k_{\mathrm{CB}}(k_{\mathrm{DC}} + k_{\mathrm{DE}} + k_{\mathrm{DH}}) + k_{\mathrm{CD}}(k_{\mathrm{DE}} + k_{\mathrm{DH}})$.

$$-\frac{\mathrm{d}[\mathrm{A}]}{\mathrm{d}t} = \frac{k_{\mathrm{AC}}k_{\mathrm{CB}}(k_{\mathrm{DC}} + k_{\mathrm{DE}} + k_{\mathrm{DH}})}{\mathrm{DEN}}[\mathrm{A}] - \frac{k_{\mathrm{CA}}k_{\mathrm{BC}}(k_{\mathrm{DC}} + k_{\mathrm{DF}} + k_{\mathrm{DH}})}{\mathrm{DEN}}[\mathrm{B}] + \frac{k_{\mathrm{AC}}k_{\mathrm{CD}}k_{\mathrm{DE}}}{\mathrm{DEN}}[\mathrm{A}] - \frac{k_{\mathrm{ED}}k_{\mathrm{DC}}k_{\mathrm{CA}}}{\mathrm{DEN}}[\mathrm{E}] + \frac{k_{\mathrm{AC}}k_{\mathrm{CD}}k_{\mathrm{DH}}}{\mathrm{DEN}}[\mathrm{A}] - \frac{k_{\mathrm{HD}}k_{\mathrm{DC}}k_{\mathrm{CA}}}{\mathrm{DEN}}[\mathrm{H}] \qquad (27)$$

For Scheme 4 the rate of disappearance of A is given by equation (28) where we use primes as superscripts to distinguish these rate constants from those of Scheme 3.



SCHEME 4

$$-\frac{\mathrm{d}[\mathrm{A}]}{\mathrm{d}t} = k'_{\mathrm{AB}}[\mathrm{A}] - k'_{\mathrm{BA}}[\mathrm{B}] + k'_{\mathrm{AE}}[\mathrm{A}] - k'_{\mathrm{EA}}[\mathrm{E}] + k'_{\mathrm{AH}}[\mathrm{A}] - k'_{\mathrm{HA}}[\mathrm{H}] \qquad (28)$$

If we compare equation (28) with equation (27) they are equivalent if equations (29)—(34) apply. Therefore, we

$$k'_{\mathrm{AB}} = k_{\mathrm{AC}}k_{\mathrm{CB}}(k_{\mathrm{DC}} + k_{\mathrm{DE}} + k_{\mathrm{DH}})/\mathrm{DEN} \qquad (29)$$

$$k'_{\mathrm{AE}} = k_{\mathrm{AC}}k_{\mathrm{CD}}k_{\mathrm{DE}}/\mathrm{DEN} \qquad (30)$$

$$k'_{\mathrm{AH}} = k_{\mathrm{AC}}k_{\mathrm{CD}}k_{\mathrm{DH}}/\mathrm{DEN} \qquad (31)$$

$$k'_{\mathrm{BA}} = k_{\mathrm{CA}}k_{\mathrm{BC}}(k_{\mathrm{DC}} + k_{\mathrm{DE}} + k_{\mathrm{DH}})/\mathrm{DEN} \qquad (32)$$

$$k'_{\mathrm{EA}} = k_{\mathrm{ED}}k_{\mathrm{DC}}k_{\mathrm{CA}}/\mathrm{DEN} \qquad (33)$$

$$k'_{\mathrm{HA}} = k_{\mathrm{HD}}k_{\mathrm{DC}}k_{\mathrm{CA}}/\mathrm{DEN} \qquad (34)$$

have reduced the six compounds system to one of four, kinetically equivalent. No assumption has been made about A, B, E, and H; so that they can be intermediates of a more complex reaction.

In order to find an expression for the ratios $k_{\mathrm{CD}}/k_{\mathrm{CA}}$ and $k_{\mathrm{DC}}/k_{\mathrm{DE}}$ we make $k_{\mathrm{CD}} = k_{\mathrm{DC}}$, $k_{\mathrm{DE}} = k_{\mathrm{DH}}$, and $k_{\mathrm{CA}} = k_{\mathrm{CB}}$. Thus, equation (35) is obtained. Dividing equation (30)

$$k'_{\mathrm{AE}} = \frac{k_{\mathrm{CD}}k_{\mathrm{AC}}k_{\mathrm{DE}}}{2k_{\mathrm{CD}}(k_{\mathrm{CA}} + k_{\mathrm{DE}}) + 4k_{\mathrm{CA}}k_{\mathrm{DE}}} \qquad (35)$$

by (33), and supposing $k_{\mathrm{CD}} = k_{\mathrm{DC}}$ and $k_{\mathrm{AC}} = k_{\mathrm{ED}}$, gives equation (36) which when introduced into equation (35) leads to (37).

$$k_{\mathrm{DE}} = (k_{\mathrm{CA}}k'_{\mathrm{AE}})/k'_{\mathrm{EA}} \qquad (36)$$

$$\frac{k_{\mathrm{CD}}}{k_{\mathrm{CA}}} = \frac{4k'_{\mathrm{AE}}}{k_{\mathrm{ED}} - 2k'_{\mathrm{EA}} - 2k'_{\mathrm{AE}}} \qquad (37)$$

By a similar treatment we may obtain equation (38).

$$\frac{k_{\mathrm{DC}}}{k_{\mathrm{DE}}} = \frac{4k'_{\mathrm{EA}}}{k_{\mathrm{ED}} - 2k'_{\mathrm{EA}} - 2k'_{\mathrm{AE}}} \qquad (38)$$

---

[19] C. Sáa, Ph.D. Thesis, Madrid, 1971.

We thank Dr. A. Grau of Junta de Energia Nuclear (Madrid) (J.E.N.) for the liquid scintillation measurements, Dr. M. Rico of our Institute for recording and interpreting the n.m.r. spectra, Centro de Cálculo Electronico of Consejo Superior de Investigaciones Contificas (C.S.I.C.) for the computing facilities, and Instituto de Estudios Nucleares of J.E.N. for financial assistance. One of us (J. S.) thanks Instituto de Cultura Hispánica and C.S.I.C. for studentships.

[2/061 *Received, 11th January, 1972*]