Prototropy of 2-Methyl-1,3-diphenylpropenes. Stability of the Intermediary Carbanions

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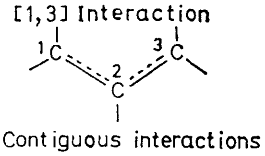
The prototropy of 2-methyl-1,3-diphenylpropenes under basic catalysis has been studied. The free energy of the carbanions generated from the substrate increases in the order *trans–trans* > *trans–cis*, indicating that the [1,2] interactions of the carbanion are dominant. This result is in contrast with the stability order found for related systems: the disagreement has been ascribed to the presence of the 2-methyl group.

In the prototropy *via* carbanionic intermediates [1,2] of 1,3-diphenylpropenes, a low mobility system, the stability of the intermediates is determined [3] by [1,3] interactions (Scheme 1). However, the introduction of a methyl group in C-2 alters the energy of the carbanion so much that it is to be expected that the stability will be determined by [1,2] contiguous interactions. In this work the prototropy of 2-methyl-1,3-diphenylpropenes has been studied in order to solve this problem. The substrates used were isotopically normal *trans*-2-methyl-1,3-diphenylpropene, and the *trans*-isomer labelled with ^{14}C in the 3-phenyl group.



SCHEME 1

EXPERIMENTAL

Isotopically normal and ^{14}C-labelled 2-methyl-1,3-diphenylpropenes were synthesized by the application of Higgins's method [4] for the substitution of a hydroxy- by a phenyl group in αβ-unsaturated alcohols to *trans*-α-methylcinnamoyl mesitoate (from *trans*-α-methylcinnamic acid [5-9]). This method maintains the initial geometry of the double bond. The ^{14}C-labelled phenyl group was introduced in the last step, substituting labelled bromobenzene for the unlabelled compound. The products were purified by preparative g.l.c. The i.r. spectra were identical to that reported by Gossauer *et al.*,[10] τ 2·81 (Ph), 3·67 (CH=C), 6·59 (CH_2), and 8·24 (CH_3C=). The products contained <1% of the *cis*-isomer. Radiochemical analysis (see below) showed that the product was labelled in the unconjugated ring, and the label in the other ring constituted 8·8, 10·4, and 12·6% for the three distillation fractions obtained.

Kinetics.—The catalytic solution was prepared from anhydrous ethanol–dioxan (3 : 2), and enough sodium metal to reach 1·3M.[11] The olefin concentration was 0·3M. The reaction tubes were refrigerated, filled with olefin (10 µl) and enough catalytic solution, degassed by the freeze-pump–thaw method, sealed under nitrogen, and finally introduced into a thermostat.

Analyses.—I.r. spectra were recorded on a Perkin-Elmer 125 spectrophotometer and n.m.r. spectra on a Perkin-Elmer R10 model. A Hewlett–Packard 5750 gas-chromatograph with a hot-wire detector was used for g.l.c. analysis. *trans*-2-Methyl-1,3-diphenylpropene was purified in a Perkin-Elmer F21 preparative gas chromatograph. *cis*- and *trans*-2-methyl-1,3-diphenylpropene were analysed by g.l.c. (8% butane-1,4-diol succinate on Chromosorb WHMDS; 200°; helium, 60 ml min^{-1}, as carrier gas).

In order to analyse the amount of ^{14}C label in the conjugated ring compared with the other ring, the propenes were ozonolysed and the ozonides decomposed with $LiAlH_4$. The resulting alcohols were analysed by radio-chromatography in a Cary ionization chamber coupled to the gas-chromatograph [20% silicone rubber (cyanoethylmethyl) on Chromosorb WAW; temperature programming 90—130°; helium, 115 ml min^{-1}, as carrier gas]. The chamber was maintained at *ca.* 200° and argon, 700 ml min^{-1}, was mixed up with the carrier to form the counting gas. The apparatus already described [12] was slightly modified, eliminating the combustion furnace. The ozonolysis was performed directly on the *cis–trans*-mixtures. Therefore, from the analysis of the resulting alcohols the total amount of isomers labelled in the conjugated ring ($t1C + c1C$) against those labelled in the unconjugated ring ($t3C + c3C$) was obtained (see Figure 1).

Integration of the Differential Equations.—The differential equations resulting from reacting systems of more than two substances ($A \rightleftharpoons B$) were integrated using a program described previously.[3]

RESULTS

The mechanism of the base-catalysed isomerization of allylic compounds, proposed by Cram,[13] can be written as in equation (1). In equation (1), the base, probably as an ion pair, abstracts a proton to form in one transition state, a carbanion hydrogen bonded to both terminal carbons of the allylic system. To provide the best geometry for this hydrogen bonding, the anionic sites should have hybridization between sp^2 and sp^3 and the C–C–C bond angle should

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

[2] (*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 therien.

[3] J. M. Figuera, J. M. Gamboa, and J. Santos, *J.C.S. Perkin II*, 1972, 1434.

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

[5] J. R. Johnson, *Org. Reactions*, 1942, **1**, 251.

[6] Liang Li and W. H. Elliot, *J. Amer. Chem. Soc.*, 1952, **74**, 4089.

[7] W. G. Brown, *Org. Reactions*, 1951, **6**, 486.

[8] J. A. Krinitsky, J. E. Johnson, and H. V. Carhart, *Analyt. Chem.*, 1948, **20**, 311.

[9] R. P. Barnes, *Org. Synth.*, 1941, **21**, 78.

[10] A. Gossauer, J. Morcillo, and R. Pérez-Ossorio, *Anales de Quim.*, 1963, **59B**, 198.

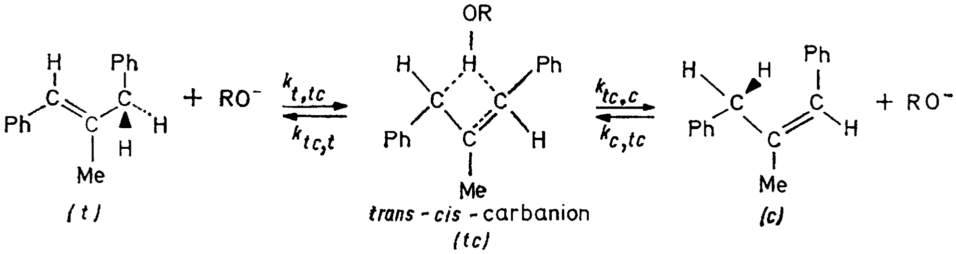
[11] J. M. Figuera, Ph.D. Thesis, Madrid, 1965.

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

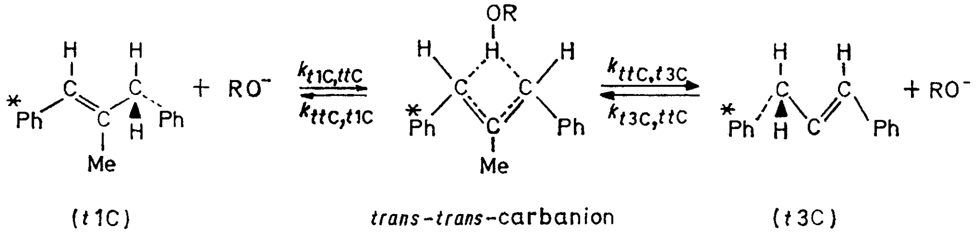
[13] Ref. 1, p. 180.

decrease to somewhat less than 120°. Collapse of this discrete intermediate to rearranged material provides an observable reaction, the *cis–trans*-isomerization.

In equation (1) we have supposed that the carbanion formed has one phenyl group *trans* (*i.e.* underneath the allylic system) and the other *cis* (*i.e.* above the allylic system). Accordingly, we call this the *trans–cis*-carbanion (*tc*C). However, if the base abstracts hydrogen from a different conformer of the substrate, a carbanion with different geometry could be formed [equation (2)]. We name this the *trans–trans*-carbanion. This particular carbanion has an interesting peculiarity: it is symmetric with respect to a vertical plane that bisects the allylic system. Collapse of this carbanion on either side reproduces the *trans*-isomer. Therefore, no observable reaction occurs. However, if we label one of the phenyl groups with ^{14}C, collapse of the carbanion to rearranged material yield the olefin with the labelled phenyl group in a different position and the reaction can be followed by the transposition of the tracer from one side of the double bond to the other.



(1)



(2)

There is another possible reaction *i.e.* exchange of the hydrogen bonded to the anionic sites of the carbanion with the solvent. However, this is not detectable in our system and can be neglected. Furthermore, this exchange is slower than collapse in closely related systems[3] and

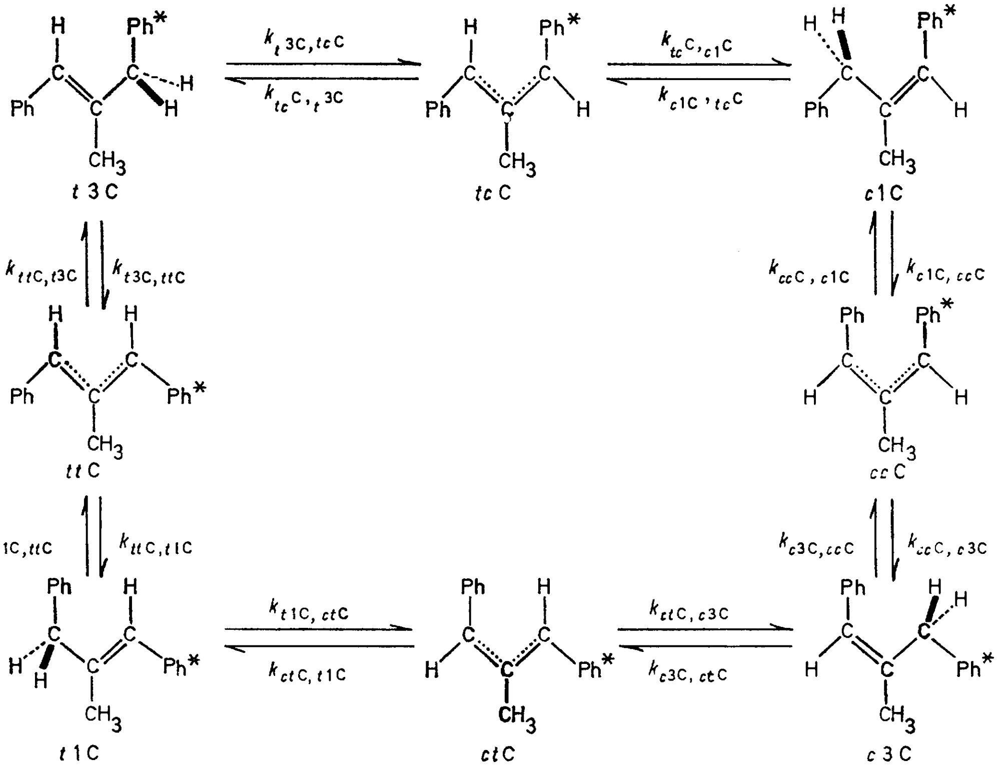


FIGURE 1 Reactions of [^{14}C]-2-methyl-1,3-diphenylpropene in dioxan, ethanol, and sodium ethoxide

therefore, equations (1) and (2) give an adequate representation of the reaction mechanism involved in our system. The above discussion assumes that the allylic carbanionic intermediates maintain the geometry of their parent olefin [14] as their partial double bonds cannot rotate.

Application of the ideas already described to the reactions of labelled *trans*-2-methyl-1,3-diphenylpropene in dioxan, ethanol, and sodium ethoxide yields the reaction scheme depicted in Figure 1. The abbreviations used in this Figure are as follows. In the olefins the first letter indicates the geometrical isomer ($t \equiv trans$ and $c \equiv cis$), the number indicates the carbon to which the labelled phenyl group is bonded, and the final C indicates that the molecule is ^{14}C-labelled. In the carbanions the first two letters indicate the geometrical distribution of the phenyl groups around the partial double bonds and the C that the carbanion is ^{14}C-labelled. Where abbreviations for unlabelled compounds are needed, the C is dropped.

The rate constants have been grouped as follows: (a) experimental rate constants which correspond to experimentally observable transformations (*i.e. cis–trans*-isomerization and transposition of the tracer); (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 carbanion formation is thought to be bimolecular (rate proportional to [EtO$^-$]), although under the conditions employed it appears as a pseudo-first-order reaction. Rate constants are identified by their subscripts, the first standing for the reactant, and the second for the products. Bimolecular constants are distinguished from their pseudo-first-order counterparts by the use of 2 as a superscript.

TABLE 1

Experimental rate constants for the *cis–trans*-isomerization of 2-methyl-1,3-diphenylpropene

	98·1°	106·5°	110·7°	120·6°	130·0°
$10k_{t,c}$/h^{-1}	0·208 ± 0·008	0·446 ± 0·021	0·67 ± 0·020	1·58 ± 0·05	3·06 ± 0·14
$10k_{c,t}$/h^{-1}	0·481 ± 0·018	1·020 ± 0·050	1·51 ± 0·045	3·56 ± 0·11	6·81 ± 0·31

In order to find the values of the rate constants involved in Figure 1 we have studied first the *trans–cis*-isomerization and evaluated the rate constants involved in this transformation. Introduction of these rate constants into the complete scheme can provide, at least in principle, its complete solution. The steady-state condition has been applied to the carbanions.

trans–cis-*Isomerization of the* 2-*Methyl*-1,3-*diphenylpropenes*.—Within the framework of Cram's mechanism the isomerization takes place as depicted in equation (1). The reaction was run at 98·1, 106·5, 110·7, 120·6, and 130·0°, starting with the *trans*-isomer. Application of the rate law that corresponds to a first order–first order reversible reaction gives eqnations (3) and (4) where c_0 and t_0 are the

$$c_e/(t_0 + c_0) \times \ln (c_e - c_0)/c_e - c) = k_{t,c}T \qquad (3)$$

$$k_{c,t} = k_{t,c} \times (t_0 + c_0 - c_e)/c_e \qquad (4)$$

initial concentrations of *cis*- and *trans*-isomers, c_e is the concentration of the *cis*-isomer at equilibrium, and c is the concentration of the *cis*-isomer at time T.

The rate constants are those of equation (1). In Figure 2 the expression $\log_{10}(c_e - c_0)/(c_e - c)$ has been plotted against time. The rate constant $k_{t,c}$ has been calculated by least squares from these data, and the reverse rate constant $k_{c,t}$ through equation (4). The calculated isomerization rate constants are in Table 1.

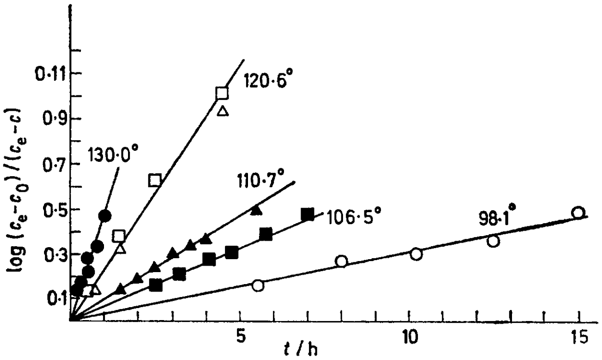


FIGURE 2 Kinetics of the *trans–cis*-isomerization of 2-methyl-1,3-diphenylpropene. Plot of log $(c_e - c_0)/(c_e - c)$ against time

The rate constants that correspond to elemental steps of Cram's mechanism [equation (1)] can be calculated as follows. The rate of disappearance of the *trans*-isomer (t) is given by equation (5) where T is the time, and the rate of formation of the carbanion tc is given by equation (6).

$$-\mathrm{d}[t]/\mathrm{d}T = k_{t,tc}[t] - k_{tc,c}[tc] \qquad (5)$$

$$\mathrm{d}[tc]/\mathrm{d}T = k_{t,tc}[t] + k_{c,tc}[c] - (k_{tc,t} + k_{tc,c})[tc] \qquad (6)$$

Application of the steady-state assumption to the carbanion tc gives equation (7). Then, the concentration of the

$$\mathrm{d}[tc]/\mathrm{d}T = 0 \qquad (7)$$

carbanion can be eliminated from equation (5) using equations (6) and (7). We thus obtain equation (8).

$$-\mathrm{d}[t]/\mathrm{d}T = \frac{k_{t,tc}k_{tc,c}}{k_{tc,t} + k_{tc,c}}[t] - \frac{k_{c,tc}k_{tc,t}}{k_{tc,t} + k_{tc,c}}[c] \qquad (8)$$

On the other hand, the directly observable *trans–cis*-isomerization may be represented by equation (9). For this

$$t \underset{k_{c,t}}{\overset{k_{t,c}}{\rightleftarrows}} c \qquad (9)$$

overall reaction the rate of disappearance of the *trans*-isomer is given by equation (10). If we compare equation

$$-\mathrm{d}[t]/\mathrm{d}T = k_{t,c}[t] - k_{c,t}[c] \qquad (10)$$

(10) with equation (8), they are equivalent if equations (11) and (12) apply. From these equations and assuming

$$k_{t,c} = k_{t,tc}k_{tc,c}/(k_{tc,t} + k_{tc,c}) \qquad (11)$$

$$k_{c,t} = k_{c,tc}k_{tc,t}/(k_{tc,t} + k_{tc,c}) \qquad (12)$$

that the *trans–cis*-carbanion collapses toward *cis*- and *trans*-isomers at the same rate ($k_{tc,t} = k_{tc,c}$), equations (13) and (14) are obtained.

$$k_{t,tc} = 2k_{t,c} \qquad (13)$$

$$k_{c,tc} = 2k_{c,t} \qquad (14)$$

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[14] (*a*) W. S. Ela and D. J. Cram, *J. Amer. Chem. Soc.*, 1966, **88**, 5777; (*b*) D. H. Hunter and D. J. Cram, *ibid.*, 1964, **86**, 5478.

The assumption of equal collapse rates holds in the prototropy of 1,3-diphenylpropene[3] where the structural differences between the isomers, as indicated by their difference in free energy, are larger than those found in the present case (see below). Thus, it is to be expected that the assumption will hold here.

From the experimental rate constants of isomerization $k_{t,c}$ and $k_{c,t}$ (see Table 1) the pseudo-first-order rate constants of carbanion formation from the *trans*-, $k_{t,tc}$, and from the *cis*-isomer, $k_{c,tc}$, are obtained through equations (13) and (14). Finally, as mentioned before, the rate constants of carbanion formation are thought to be bimolecular (rate proportional to [EtO$^-$]) and are deduced from their pseudo-first-order counterparts by equations (15) and (16). The calculated bimolecular rate constants ${}^2k_{i,j}$ are in Table 2.

$$k_{t,tc} = {}^2k_{t,tc}[\mathrm{EtO}^-] \qquad (15)$$

$$k_{c,tc} = {}^2k_{c,ct}[\mathrm{EtO}^-] \qquad (16)$$

Equilibrium Data.—The concentration of the two isomers at equilibrium were experimentally determined at 98·1,

$$\ln K = -\Delta H^0/RT + \Delta S^0/R \qquad (17)$$

106·5, 110·7, 120·6, and 130·0°. A least squares treatment of equation (17) gave the results in equation (18) for the differences in the enthalpy, entropy, and free energy of the

$$\begin{aligned} H^0_{cis} - H^0_{trans} &= 0{\cdot}35 \pm 0{\cdot}04 \text{ kcal mol}^{-1} \\ S^0_{cis} - S^0_{trans} &= -0{\cdot}18 \pm 0{\cdot}02 \text{ cal K}^{-1}\text{ mol}^{-1} \qquad (18) \\ G^0_{cis} - G^0_{trans} &= 0{\cdot}62 \pm 0{\cdot}09 \text{ kcal mol}^{-1} \end{aligned}$$

two isomers at 110 °C. In Figure 3 log K is plotted against the reciprocal temperature.

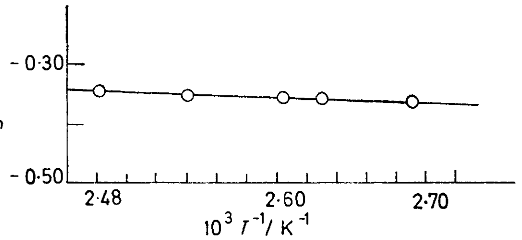

FIGURE 3 Van't Hoff representation of the change of equilibrium constant of the *trans–cis*-isomerization of 2-methyl-1,3-diphenylpropene with temperature

Reactions of Labelled trans-*2-Methyl-1,3-diphenylpropene.*—Application of Cram's mechanism to the reactions of labelled *trans*-2-methyl-1,3-diphenylpropene in dioxan, ethanol, and sodium ethoxide gives the scheme in Figure 1. The introduction of the label allows the reaction steps that go through 'symmetrical' carbanions to be followed. These steps do not produce any observable geometrical isomerization but the reaction can be followed by the transposition of the label from one side of the double bond to the other.

Figure 1 is complicated and some simplifications must be made in order to calculate the rate constants involved. Let equation (19) represent a reaction in which two substances X and Y interconvert through an intermediate C (this scheme corresponds to any individual transformation depicted in Figure 1). Assuming a steady-state concentration of C, equation (20) is obtained, following the

$$\begin{tikzcd} \mathrm{X} \arrow[r, shift left, "k_{\mathrm{x,c}}"] & \mathrm{C} \arrow[l, shift left, "k_{\mathrm{c,x}}"] \arrow[r, shift left, "k_{\mathrm{c,x}}"] & \mathrm{Y} \arrow[l, shift left, "k_{\mathrm{y,c}}"] \end{tikzcd} \qquad (19)$$

$$k_{\mathrm{x,y}} = k_{\mathrm{x,c}}k_{\mathrm{c,y}}/(k_{\mathrm{c,x}} + k_{\mathrm{c,y}}) \qquad (20)$$

procedure used to obtain equations (11) and (12). If the rate constants for formation of X and Y from the intermediate C are equal ($k_{\mathrm{c,x}} = k_{\mathrm{c,y}}$) equation (20) reduces to equation (21).

$$k_{\mathrm{x,y}} = 1/2k_{\mathrm{x,c}} \qquad (21)$$

Applying equation (20) to the different transformations in Figure 1 that are of the form (19) we obtain equation (22). This scheme is kinetically equivalent to that of Figure 1 as long as the steady-state approximation holds; results obtained in similar cases[3] indicate that this should be the case.

TABLE 2

Bimolecular rate constants ($10^{-1}k$/l mol^{-1} h^{-1}) for the formation of the *cis–trans*-carbanion from 2-methyl-1,3-diphenylpropenes at different temperatures

Reaction	98·1°	106·5°	110·7°	120·6°	130·0°
t–tc	0·320 ± 0·012	0·686 ± 0·032	1·03 ± 0·03	2·43 ± 0·15	4·71 ± 0·21
c–tc	0·74 ± 0·28	1·57 ± 0·08	2·32 ± 0·07	5·47 ± 0·34	10·05 ± 0·05

A least squares procedure was used with the usual standard errors.

$$\begin{tikzcd} t3\mathrm{C} \arrow[r, shift left, "k_{t3\mathrm{C},c1\mathrm{C}}"] \arrow[d, shift left, "k_{t3\mathrm{C},t1\mathrm{C}}"] & c1\mathrm{C} \arrow[l, shift left, "k_{c1\mathrm{C},t3\mathrm{C}}"] \arrow[d, shift left, "k_{c1\mathrm{C},c3\mathrm{C}}"] \\ t1\mathrm{C} \arrow[u, shift left, "k_{t1\mathrm{C},t3\mathrm{C}}"] \arrow[r, shift left, "k_{t1\mathrm{C},c3\mathrm{C}}"] & c3\mathrm{C} \arrow[l, shift left, "k_{c3\mathrm{C},t1\mathrm{C}}"] \arrow[u, shift left, "k_{c3\mathrm{C},c1\mathrm{C}}"] \end{tikzcd} \qquad (22)$$

If we neglect isotope effects the number of different rate constants in equation (22) is reduced to four. One represents the *cis–cis*-transformation ($k_{c3\mathrm{C},c1\mathrm{C}}$ and $k_{c1\mathrm{C},c3\mathrm{C}}$), the second corresponds to the *trans–trans*-reaction ($k_{t3\mathrm{C},t1\mathrm{C}}$ and $k_{t1\mathrm{C},t3\mathrm{C}}$). The third, corresponding to the *cis–trans*-transformation ($k_{c1\mathrm{C},t3\mathrm{C}}$ and $k_{c3\mathrm{C},t1\mathrm{C}}$) and the fourth, corresponding to the *trans–cis* ($k_{t1\mathrm{C},c3\mathrm{C}}$ and $k_{t3\mathrm{C},c1\mathrm{C}}$) have been previously evaluated. Therefore, only four rate constants are unknown in equation (22).

Integration of the differential equations that correspond to equation (22) should allow, by trial and error and comparison with the experimental results, the determination of the unknown experimental rate constants.

Unfortunately, the analytical curves are very insensitive to the value of the rate of *cis–cis*-reaction [it should be remembered that our experimental data are the sum of $c1\mathrm{C} + t1\mathrm{C}$ against $c3\mathrm{C} + t3\mathrm{C}$ (see Experimental section)]. When we tried to find the rate constants which best fitted the experimental data, we found that practically any value of the rate was compatible with the data. We therefore decided to evaluate the rate constant for *trans–trans*-transformation for two extreme cases: (a) instantaneous *cis–cis*-conversion, and (b) no *cis–cis*-conversion.

The reaction was run at 106·5, 110·7, 120·6, and 130·0°. The analytical curves that best fitted the experimental results, for the two extreme cases cited, are plotted together with the experimental points in Figure 4.

Activation Parameters.—The Arrhenius representations of the rate constants for formation of *trans–cis*-carbanion from the *cis*- and *trans*-isomers (Table 2) and for formation of *trans–trans*-carbanion from the *trans*-isomer (Table 3) are in Figure 5. Least-squares fitting of these data gave the results in Table 4. The thermodynamic parameters have been calculated from the Arrhenius parameters by the usual equations.[15]

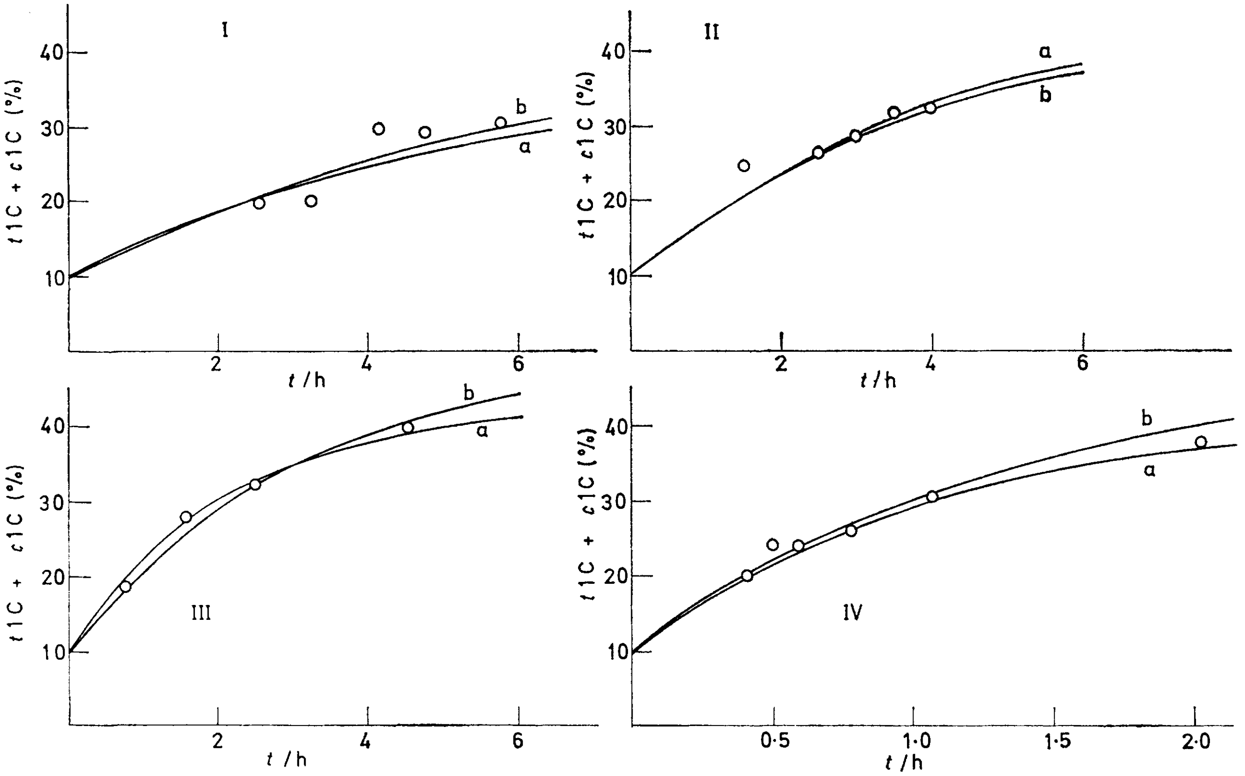

FIGURE 4 Kinetics of the isomerization of *trans*-2-methyl-1,3-diphenylpropene in dioxan, ethanol, and sodium ethoxide. Fitting of the analytical curves to the experimental data for the two extreme cases studied: I, temperature 106·5°; curve a, $k_{t,t}$ = 0·015 h^{-1} for $k_{c,c}$ = 0; curve b $k_{t,t}$ = 0·035 h^{-1} for $k_{c,c}$ = ∞; II, 110·7°; a, $k_{t,t}$ = 0·040 h^{-1} for $k_{c,c}$ = 0; b, $k_{t,t}$ = 0·068 h^{-1} for $k_{c,c}$ = ∞; III, 120·6°; a, $k_{t,t}$ = 0·050 h^{-1} for $k_{c,c}$ = 0; b, $k_{t,t}$ = 0·090 h^{-1} for $k_{c,c}$ = ∞; IV, 130·0°; a, $k_{t,t}$ = 0·080 h^{-1} for $k_{c,c}$ = 0; b, $k_{t,t}$ = 0·20 h^{-1} for $k_{c,c}$ = ∞

The bimolecular rate constant for *trans–trans*-carbanion formation can be obtained as follows. In this particular case the carbanion should collapse toward reactant and product at the same rate, as they are the same *trans*-isomer (neglecting isotope effects). Therefore, equation (21) can be used to obtain the pseudo-first-order rate constant for *trans–trans*-carbanion formation, and from that constant the bimolecular value is found by equation (23). The results are in Table 3.

TABLE 3

Bimolecular rate constants for the formation of the *trans–trans*-carbanion from *trans*-2-methyl-1,3-diphenylpropene at different temperatures for two limiting cases, $k_{c,cc}$ = 0 or ∞

Temperature	106·5°	110·7°	120·6°	130°
$10\ {}^2k_{t,tt}$/l mol^{-1} h^{-1} ($k_{c,c}$ = 0)	0·23	0·61	0·76	1·23
$10\ {}^2k_{t,tt}$/l mol^{-1} h^{-1} ($k_{c,c}$ = ∞)	0·54	1·05	1·38	3·1

$$k_{t,tt} = {}^2k_{t,tt}[\mathrm{EtO^-}] \qquad (23)$$

The free energies of activation calculated at the reaction temperatures are in Table 5. For the formation of the *trans–cis*-carbanion the Arrhenius parameters of Table 4 were used, and for the formation of *trans–trans*-carbanion

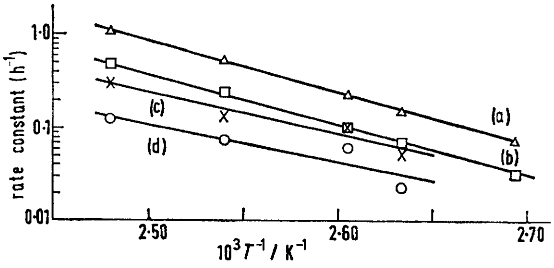

FIGURE 5 Arrhenius plots: (a) reaction *c–tc*, △ experimental data; (b) reaction *t–tc*, ☐ experimental data; (c) reaction *t–tt*, assuming $k_{c,c}$ = ∞, × experimental data; (d) reaction *t–tt*, assuming $k_{c,c}$ = 0, ○ experimental data

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[15] A. Weissberger, 'Technique of Organic Chemistry, vol. VIII, Part 1, Investigation of Rates and Mechanisms of Reactions,' Interscience, New York, 2nd edn., 1961, p. 199.

equation (24) was used, where the symbols have their usual meaning and k_{rate} is the rate constant.

$$\Delta G^{\ddagger}_{T} = RT\,(\ln k/h + \ln T - \ln k_{\text{rate}}) \qquad (24)$$

DISCUSSION

The substitution of a methyl group for the hydrogen atom at C-2 in 1,3-diphenylpropenes must alter the stability of the molecules and of the corresponding carbanions. The overall effect of this substitution on the reaction mechanism and reaction rate will be determined by the balance of the effects mentioned above.

TABLE 4

Kinetic parameters, calculated at 85°, for the formation of the *trans–cis*-carbanion from *cis*- and *trans*-2-methyl-1,3-diphenylpropene and for the formation of the *trans–trans*-carbanion from *trans*-2-methyl-1,3-diphenylpropene

Reaction	$\ln(A/\text{l mol}^{-1}\,\text{h}^{-1})$	$E_a/\text{kcal mol}^{-1}$	$\Delta S^{\ddagger}/\text{cal mol}^{-1}\,\text{K}^{-1}$	$\Delta H^{\ddagger}/\text{kcal mol}^{-1}$	$\Delta G^{\ddagger}/\text{kcal mol}^{-1}$
t–tc	31·07 ± 0·96(31·16) [a]	25·4 ± 0·7(25·5)	−15·42(−15·5)	24·7(24·8)	30·2(30·2)
c–tc	31·45 ± 0·95(32·08)	25·1 ± 0·7(25·6)	−14·67(−13·3)	24·4(24·9)	29·6(29·6)
t–tt($k_{c,c} = 0$) [b]	21·1 ± 5·2	18 ± 4	−35	18	30·4
t–tt($k_{c,c} = \infty$) [b]	24·0 ± 3·3	20 ± 2	−29	19	30·0

[a] Values in parentheses are from ref. 3 and have been calculated starting from the *cis*-isomer and are in good accord with the values calculated in this work starting from the *trans*-isomer. [b] The kinetic parameters for formation of the *trans–trans*-carbanion have been calculated for the two cases explained in the text.

In Figure 1 the conformations of the *cis*- and *trans*-2-methyl-1,3-diphenylpropenes and of the possible derived carbanions are shown. These conformations have been deduced by the use of molecular models. It has been assumed that their fundamental characteristics are not altered by the presence of a methyl group compared with those of the 1,3-diphenylpropenes. This assumption does not affect the qualitative conclusions.

TABLE 5

Free energies of activation ($\Delta G^{\ddagger}/\text{kcal mol}^{-1}$) at several temperatures for formation of the *trans–cis*-carbanion from *trans*- and *cis*-2-methyl-1,3-diphenylpropene and the *trans–trans*-carbanion from *trans*-2-methyl-1,3-diphenylpropene

Reaction	$\Delta G^{\ddagger}_{106\cdot5\,°\text{C}}$	$\Delta G^{\ddagger}_{110\cdot7\,°\text{C}}$	$\Delta G^{\ddagger}_{120\cdot6\,°\text{C}}$	$\Delta G^{\ddagger}_{130\,°\text{C}}$
c–tc [a]	29·96	30·02	30·17	30·31
t–tc [a]	30·54	30·61	30·76	30·91
t–tt ($k_{c,c} = \infty$) [b]	30·8	30·63	31·22	31·34
t–tt ($k_{c,c} = 0$) [b]	31·43	31·04	31·69	32·08

[a] Calculated from the Arrhenius parameters. [b] Calculated from the rate constants.

Effect of the Methyl Group on Isomer Stability.—The difference in free energy ΔG at 85 °C between *cis*- and *trans*-1,3-diphenylpropenes is 2·5 kcal mol^{-1}.[3] The substitution of a methyl group for the hydrogen atom at C-2 reduces this difference to 0·6 kcal mol^{-1} (see Table 4).

This result may be rationalized as follows. In the 1,3-diphenylpropenes the different stability of the isomers may be ascribed to the phenyl–benzyl interaction; this is obviously greater in the *cis*-isomer. On the other hand, in the methyl-substituted olefins molecular models suggest that the methyl–phenyl interaction, along the lower part of the molecule, should predominate and over-run other possible interactions. These interactions are present in both isomers. In the *trans*-isomer the methyl interacts with the 1-phenyl group attached; in the *cis*-isomer the methyl interacts with the 3-phenyl group. In the latter case the different bond angle involved ($\text{Ph–}\widehat{\text{C}}\text{–C}_{sp_3}$ *ca.* 109° in *cis vs.* $\text{Ph–}\widehat{\text{C}}\text{–C}_{sp_2}$ *ca.* 120° in *trans*) should force the phenyl to stay slightly closer to the methyl group. This explains both the similar stability of the isomers and their relative stability. This discussion is based on the conformations of the isomers depicted in Figure 1; molecular models show that other possible conformations can be neglected.

Effect of Methyl Substitution on Carbanion Stability.—The rate constant for formation of the *trans–trans* carbanion from the *trans*-2-methyl-1,3-diphenylpropene is slower at every temperature studied, than the rate constant for formation of the *trans–cis*-carbanion (see Tables 2 and 3). This result contrasts with the behaviour of the unsubstituted olefin where the formation of the *trans–trans*-carbanion is faster than that of the *trans–cis*.[3] In explaining this, we follow the Hammond postulate[16] and take the free energy of the activated complex as a measure of the relative stability of the carbanion formed from this complex. The data on free energy in Table 5 show that the *trans–trans*-carbanion is slightly less stable than the *trans–cis* over the range of temperatures studied. This result indicates that [1,2] contiguous interactions predominate over [1,3] interactions.

Exactly the opposite was obtained in the unsubstituted 1,3-diphenylpropenes,[3] and other cases of carbanions with similar structures[14a,17] where the *trans–trans*-carbanion was the more stable. The preponderance of the [1,2] interactions in the present case should be ascribed to the involvement of the relatively bulky methyl group.

The analysis of the interactions shows a delicate balance between opposite effects (see Table 4). The reduced [1,3] interactions in the *trans–trans*-carbanion make it more stable than the *trans–cis* by an enthalpy difference of *ca.* 8 kcal mol^{-1}. This indicates that the absence of bulky groups on top of the carbanion, allows a proton to be strongly bonded to the carbanion, while

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

[17] (*a*) R. D. Guthrie, D. A. Jaeger, W. Meister, and D. J. Cram, *J. Amer. Chem. Soc.*, 1971, **93**, 5137; (*b*) D. A. Jaeger and D. J. Cram, *ibid.*, p. 5153.

the presence of a phenyl group in the *trans–cis*-carbanion forces the proton to stay in a less favourable position for bonding. However, the loss of ' freedom,' that may be ascribed to the [1,2] interactions, sufficiently decreases the entropy of the *trans–trans*-carbanion relative to the *cis–trans* such that the effect of the enthalpy is overcome at every temperature at which the reaction was followed.

The enthalpy increase of the *trans–cis*-carbanion relative to the *trans–trans* is not observed in the 1,3-diphenylpropenes, where the absence of the methyl group increases the C–C–C angle thus allowing more favourable bonding of the proton.

One of us (C. S.) thanks Ministerio de Educación y Ciencia for a studentship.

[3/084 *Received, 15th January, 1973*]