

CLIII—*The Chemistry of the Glutaconic Acids. Part
XIX. A Consequence of Mobility.*

By JOHN PACKER and JOCELYN FIELD THORPE.

THE mobility of the hydrogen atom in the three-carbon system

$$\text{HC}\cdot\text{C}:\text{C} \rightleftharpoons \text{C}:\text{C}\cdot\text{CH},$$

so far as it has yet been investigated, reaches its maximum in glutaconic acid, causing this substance to exist in only one form, the postulated "normal" form to which has been ascribed the tentative constitution $\text{CO}_2\text{H}\cdot\text{CH}\cdot\text{CH}(\text{H})\cdot\text{CH}\cdot\text{CO}_2\text{H}$.

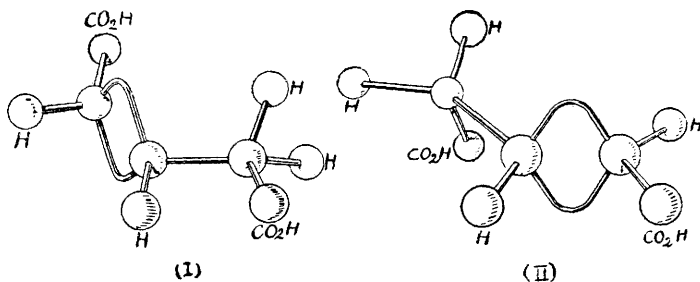
If the corresponding unsaturated formulæ be set up on the models, drawings of which are shown in Fig. 1, it will be found that this mobility may or may not involve a change from the hypothetical *cis*- (I) to the *trans*- (II) form and *vice versa*, depending on the spatial relationship of the methylene hydrogen atoms to the double bond at the time of change.

While this fact is, in itself, no argument for or against the "normal" form, yet it supplies certain explanations and deductions which are of fundamental importance in connexion with the chemistry of these substances.

It is certainly paradoxical that, whilst the two hydrogen atoms

of the methylene group are of equal value owing to the occurrence of free rotation about the single bond, they should have different values when used in bringing about the three-carbon change. But it must be remembered that the positions of the constituent atoms in space are determined by the tendency for like groups to take up positions as remote as possible from one another, a tendency which the molecule can satisfy owing to its power of free rotation about the single bond.

FIG. 1.



In the case of glutacnic acid, where it is immaterial on which side of the central carbon atom the double bond is placed, the tautomeric change would be expected, in the case of the *trans*-form to take place mainly without alteration in stereochemical configuration, and in the case of the *cis*-form to result mainly in conversion into the *trans*-form. In those derivatives of glutacnic acid in which substituting groups are attached to the α , β , or γ carbon atom and which may in consequence exist theoretically in more forms, the necessary alterations in the stable positions of the atoms in space may lead to differences in the tendency of the *cis*- and *trans*-forms to be converted into one another by the tautomeric change.

Certain deductions given below render it probable that valuable evidence will be obtainable on these lines regarding the existence or non-existence of the postulated "normal" form. Experiments on this point are now in hand, but it is thought desirable to publish this new point of view at once, because it offers an explanation as to why both forms of, for example, the β -methylglutaconic acids readily yield anhydrides.

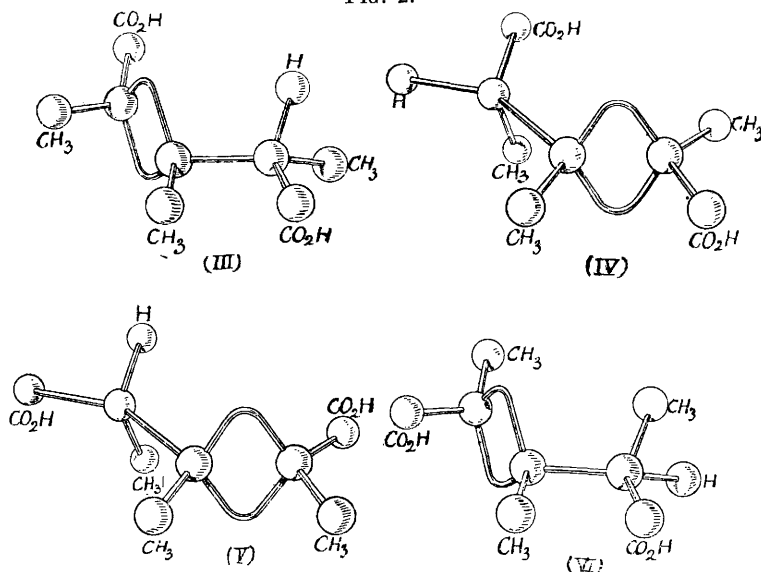
The argument has been used by us that the ready formation of the hydroxy-anhydride from both forms of β -methylglutaconic acid favours the assumption of the "normal" form rather than the *cis*- and *trans*-configuration, because in the analogous case of non-mobile systems, for example, $\alpha\alpha$ -dimethylglutaconic acid, $\text{CO}_2\text{H}\cdot\text{C}(\text{CH}_3)_2\text{:CH:CH}\cdot\text{CO}_2\text{H}$, the *trans*-form gives no anhydride. It is evident, however, from a study of the models, which are similar

to those for glutaconic acid, that the formation of the hydroxy-anhydride may be preceded by a change of configuration and hence the relative ease of formation of the anhydride from the *trans*- and *cis*-forms is seen to depend on the mobility of the tautomeric system under the conditions of dehydration.

The authors do not wish to call into question the existence of the "normal" form, which is supported by a number of experimental facts, but they desire to point out that :

A. Assuming glutaconic acid to be the stable *trans*-form, it follows that the formation of the hydroxy-anhydride must take

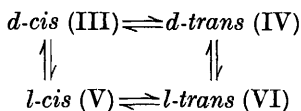
FIG. 2.



place through the *cis*-modification, the inability to isolate the *cis*-form of the acid by hydration of the hydroxy-anhydride being due to the mobility of the system. The existence of two forms of β -methylglutaconic acid, each giving the same hydroxy-anhydride with equal readiness, is due to the same mechanism, but in this case the order of mobility is lower and hence the *cis*-modification can be isolated by hydrating the hydroxy-anhydride under special conditions.

B. In such cases as the $\alpha\gamma$ -dimethyl- and $\alpha\beta\gamma$ -trimethyl-glutaconic acids, the theoretically possible *cis*- and *trans*-forms should be capable of resolution into optically active forms, so that, for example, the four forms of the $\alpha\beta\gamma$ -trimethylglutaconic acids depicted in Fig. 2 should be capable of existence as well as the "normal" form

$\text{CO}_2\text{H}\cdot\text{C}(\text{CH}_3)\cdot\text{C}(\text{CH}_3)(\text{H})\cdot\text{C}(\text{CH}_3)\cdot\text{CO}_2\text{H}$. It will be seen that the tautomeric changes may result in the following transformations



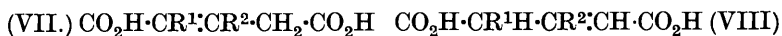
but when the tendency of like groups to take up positions as far apart as possible is also considered the following deductions can be made :

(i) The two enantiomorphous *cis*-forms (III) and (V) will tend to pass into the correspondingly active *trans*-forms (IV) and (VI) rather than into each other, unless the change is arrested at the intermediate "normal" form.

(ii) The two enantiomorphous *trans*-forms (IV) and (VI) will show a greater tendency to interconversion (racemisation) than in the case of the *cis*-forms, and this change may take place to the practical exclusion of transformation into the *cis*-forms.

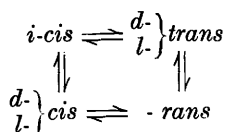
(iii) If the stable form of the acid is the *trans*-form, it will be capable of resolution into optically active forms which will be distinct from the active forms of the *cis*- (labile) acid ; inability to resolve the stable form would be evidence for the "normal" constitution.

C. In the case of α - and $\alpha\beta$ -substituted glutaconic acids the structural isomerides (VII) and (VIII) are theoretically possible as well as the "normal" form



and each may exist in *cis*- and *trans*-forms. The two forms of (VII) will be incapable of resolution into optically active forms, whilst the two forms of (VIII) will be capable of such resolution under conditions not leading to tautomeric mobility. This should afford an experimental means of determining the position of the double bond in these unsaturated forms.

These isomeric forms are theoretically interconvertible by tautomeric change according to the scheme :



and a study of the models in these cases leads to the following conclusions :

(i) Where R^1 and R^2 are positive groups, the *trans*-forms will be more stable than the *cis*-forms.

(ii) Where R^2 is a negative group (*e.g.*, C_6H_5), the relative stability of the *cis*-forms will be increased.

D. The reduction in mobility of the glutaconic system brought about by the substitution of various groups for hydrogen atoms, and the consequent increase in stability of the labile unsaturated forms, can be explained by an application of Thorpe and Ingold's theory of the influence of attached groups on the carbon tetrahedral angle; for the effect of such groups is obviously to reduce the strain in the double bond or two-carbon ring.

The effect of a group in the β -position will be to stabilise both the $\alpha\beta$ - and $\beta\gamma$ -unsaturated forms, whilst the effect of a group in the α -position will be greater in stabilising the $\alpha\beta$ - than the $\beta\gamma$ -unsaturated form, so that in general a group in the β -position will have a greater effect in retarding the mobility of the system than will the same group in the α -position. Hence in the case of α - and $\alpha\beta$ -substituted acids, the $\alpha\beta$ -unsaturated forms (VII) should be more stable than the $\beta\gamma$ -unsaturated forms (VIII).

In the case of β -phenyl- α -methylglutaconic acid one stable and three labile forms are known. To the *cis*- and *trans*-labile forms of Thorpe and Wood have been assigned the $\alpha\beta$ -, and to the labile form of Feist the $\beta\gamma$ -unsaturated structure. If these constitutions are correct, the above considerations favour the "normal" structure for the stable form of the acid, since the only other possible structure is that of the $\beta\gamma$ -unsaturated *trans*-form, which would be expected to be relatively unstable.

An examination of these acids from the above points of view has been commenced in the hope of thus throwing further light on their constitutions.

IMPERIAL COLLEGE OF SCIENCE AND TECHNOLOGY,
SOUTH KENSINGTON.

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