Tetrahedron Vol. 25, pp. 715 to 724. Pergamon Press 1969. Printed in Great Britain

CYCLIZATION OF THE ENOL ESTERS OF *o*-ACYLOXYPHENYL ALKYL KETONES—III

A CONTRIBUTION TO THE MECHANISM OF THE KOSTANECKI–ROBINSON ACYLATION[1,2]

T. SZÉLL, L. DÓZSAI, M. ZARÁNDY and K. MENYHÁRTH
Department of Applied Chemistry, University of Szeged, Szeged, Hungary

(*Received in the UK* 30 *July* 1968; *Accepted for publication* 5 *September* 1968)

Abstract—Re-examination of the mechanism of the Kostanecki–Robinson reaction has confirmed the scheme suggested by Baker,[3] and revealed that the reaction intermediates are enol esters which cyclize to γ-pyrones. Enol benzoate is probably the intermediate also in the Kuhn variant[14] of the Allan–Robinson reaction. The Kostanecki–Robinson acylations in non-aqueous media correspond to the cyclization of enol esters[2] in aqueous solvents. A kinetic study of the reaction has shown that the rate-determining step is the cyclization, the rate expression of which was found to be:

$$\text{d (chromone)}/dt = k\,[\text{enol acetate}]\,[CH_3COONa]$$
$$\text{and } d(CH_3COONa)/dt \approx 0$$

INTRODUCTION

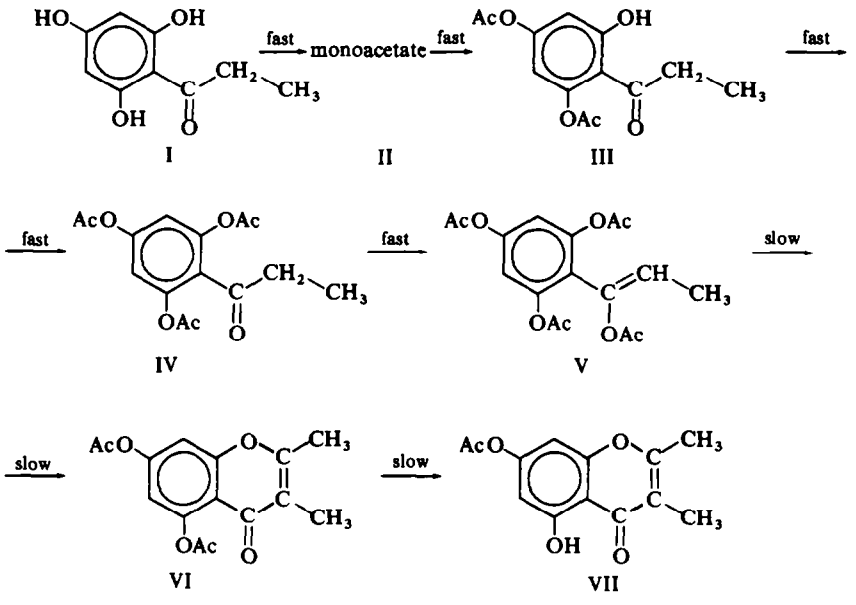
IN PART I[1], we reported that the enol esters of *o*-acyloxyphenyl alkyl ketones can be cyclized in the presence of bases in either aqueous or non aqueous media, to compounds containing the γ-pyrone ring. This process probably involves a reaction of the Baker–Venkataraman type.[1,3] Although there is a direct relationship between this cyclization and the Kostanecki acylation reaction,[4] we reported[1] that enol acetates are not intermediates of the Kostanecki–Robinson acylation. The supporting evidence for this assumption came from an experiment in which the enolacetate of 2,4,6-triacetoxypropiophenone (IV) apparently failed to give the expected end product—5,7-diacetoxy-2,3-dimethylchromone (V), even after heating for several hours under conditions of the Kostanecki–Robinson reaction. This conclusion was based on the m.p. of the product and recovery of some of the starting enol ester, but later it was found that the m.p. is unreliable in identifying the product and that IV is converted into V if sufficiently long reaction times are used. Therefore, the latter reaction is essentially a base-catalysed cyclization occurring in a non-aqueous medium, and is analogous to the cyclization reported recently.[1]

The mechanism of the Kostanecki–Robinson reaction was the subject of fundamental and pioneering studies by Wittig,[5] but today, Baker's views[3] are generally accepted.[6]

RESULTS AND DISCUSSION

In order to obtain a detailed picture of the reaction mechanism, we applied TLC to several Kostanecki–Robinson acylations. The products obtained from phloropropiophenone at various stages of the reaction were identified by the analysis of samples taken at intervals. Each sample after decomposition with water, was ex-

tracted with ethyl acetate and chromatography of the extract revealed the presence of the following compounds:



The initial steps occur so rapidly that II and III were present in samples withdrawn at zero time.* A sample withdrawn after 5 minutes showed the presence IV and V, while VI could be detected after 15 minutes, and in less than 2 hours V and VI could be found in the mixture. A small quantity of VII only became apparent after 2 hours, and even after 4 hours, VI and only a small amount of VII were present. A qualitative analysis by TLC of the rates, using single pure intermediates as starting materials, revealed the cyclization of the enolacetate to be the slowest step in the reaction sequence. Starting from IV or V, it was established that V is a true intermediate, and not the product of some side equilibrium or a competitive reaction.

In the case of 2,4-dimethoxy-6-hydroxypropiophenone, attempts to synthesize the corresponding enolacetate were unsuccessful. Prof. W. D. Ollis suggested that enolacetate formation did occur, but that the intermediate was hydrolysed to the acetoxy ketone during treatment of the product with water. Indeed, if treatment with water was omitted, TLC of the reaction mixture revealed a spot not present in the previous experiments. Elution of this spot resulted in the isolation of crystalline 1-acetoxy-2(α-acetoxypropenyl)-3,5-dimethoxybenzene (VIII), a new compound the structure of which was determined by microanalysis and the IR spectrum. When spots of V and VIII were treated with a drop of alkali and development was continued, the product finally appeared at the position of the corresponding chromone, supporting our former observation[1] that these enolacetates undergo cyclization in the presence of alkali, to yield the chromone.

* Compound III was first synthesized during the present investigation.

Essentially the same base-catalysed cyclization occurs in the Kostanecki–Robinson reaction, although a non-aqueous solvent is used together with sodium acetate as the base. The cyclization can be effected with other bases. In our experiments, the least favourable results were obtained using pyridine. In some cases (e.g. phloropropiophenone, and 2,4-dihydroxydeoxybenzoin), this base promotes the reaction only to the stage of enolacetate formation, even after heating under reflux for 12 hr. Stronger bases, such as triethanolamine, triethylamine and guanidine gave better results, and the two latter may be used instead of sodium acetate, with the advantage that the reaction is performed in a homogeneous, instead of heterogeneous phase. At room temperature, the reactions practically stop at the enolacetate stage. When the Kostanecki reaction of I was carried out at 25°, the presence of IV was observed only after 8 hr, and that of V after 24 days, but the system contained only IV and V even after 210 days, the latter compound being slightly predominant. The reaction steps described have also been detected in the Kostanecki reaction of 2,4,6-trihydroxyacetophenone; in this case, however, the reaction product was 5,7-diacetoxy-2-methyl-3-acetylchromone, in agreement with former observations. The presence of diketones could not be detected in the course of Kostanecki acylations leading to chromones; as apparently the enolacetates undergo direct cyclization. In the conversion of phloroacetophenone into 3-acetylchromone, however, the presence of a yellowish, poorly separated spot of a product of unknown structure was detected. In accordance with Baker's assumption,[3] this would correspond to a diketone. The separation of the spots was unsatisfactory, and this prevented elucidation of the uncertainties and contradictions concerning this reaction and reported in the literature.[7–12] Owing to the difficulties, only one spot could be located. This according to its R_f value and UV spectrum was considered to be phloroacetophenone enolacetate (V). Further, it was ascertained that both the 3-acetylated and normal end-products were present, the former being predominent.

The enolacetate spot was also found in the analysis of the Kostanecki–Robinson reaction of 2-hydroxypropiophenone; and treatment of this spot with alkali resulted in cyclization to the chromone.

It was difficult to follow the Allan–Robinson reaction,[13] since the TLC method on silicagel is less suitable for flavones than for chromones. For this reason a simple model was selected, and the Kuhn variant of the reaction was applied: The hydroxyketone was fused with benzoic anhydride in the presence of an organic base.[14] In the reaction of 2-hydroxyacetophenone (IX) in the presence of pyridine, triethanolamine, triethylamine, or guanidine, the first step was the formation of 2-benzoyloxyacetophenone (X) although the reaction was incomplete even after 24 hr. After the first step, benzoylation, a spot appeared which was eluted, but the product could not be crystallized. IR analysis showed that it consisted of the enolbenzoate of 2-benzoyloxyacetophenone (XI) and impurities. The next product was dibenzoylmethane (XII) indicating a Baker–Venkataraman conversion of the enolbenzoate. Finally, the two end-products of the reaction, i.e. flavone (XIII) and 3-benzoylflavone (XIV), appeared. The slowest step in the reaction sequence was the further conversion of the enolbenzoate.

Similar results were obtained in the Kostanecki acylation of deoxybenzoins yielding isoflavones. Owing to difficulties in the TLC method, preparative methods were used to check whether enol esters are again intermediates in the reaction. The

Up to a certain concentration (until the solution became saturated) the rate depended on the amount of sodium acetate present, but the use of greater quantities was ineffectual, and the overall reaction is approximately quasi-unimolecular. Values of $1{\cdot}7 \times 10^{-2}$ min^{-1} and 24 ± 3 kcal mole^{-1} grade^{-1} were found for the unimolecular rate constant (180°) and energy of activation, respectively (Fig. 1a). The reaction III → IV is so rapid that there is hardly any difference between the process III → V and IV → V. The rate constant of the reaction III → IV was estimated to be 10 times as high than that of IV → V.

EXPERIMENTAL

The TLC tests were made on 0·25–0·3 mm layers of Kiesel-gel-G (Merck) adsorbent; the plates coated with this layer were activated at 120° and stored over a drying agent ("Blaugel"). The solvent mixture consisted of benzene: $CHCl_3$: EtOH (50:48:2). Detection was made in UV light, spraying with 2N NaOH and with 15% $FeCl_3$ soln. The characteristics of the spots are shown in Table 1.

TABLE 1. BEHAVIOR OF TLC SPOTS

No.	Compound	R_f	Colour of the spot			
			× 100	In UV	Treated with NaOH in UV	$FeCl_3$
1	Phloropropiophenone	(I)	6·21	BR	DBR	BR
2	Phloroprophiophenone-monoacetate	(II)	25·48	BL	RBR	VBR
3	Phloropropiophenone-diacetate	(III)	52·54	BL	RBR	VBR
4	2,4,6-Triacetoxy-propiophenone	(IV)	36·92	DBL	DBR	—
5	2,4,6-Triacetoxy-propiophenone-enolacetate	(V)[1]	27·32	GBR	G	—
6	2,3-Dimethyl-5,7-diacetoxy-chromone	(VI)	30·54	G	BLG	—
7	2,3-Dimethyl-5-hydroxy-7-acetoxy-chromone	(VII)	45·61	BL	BL	—
8	2,3-Dimethyl-5,7-dihydroxy-chromone	[1]	15·20	LBR	DBL	B
9	2,4-Dimethoxy-6-hydroxy-propiophenone		68·30	BR	—	BR
10	2,4-Dimethoxy-6-acetoxy-propiophenone		52·10	—	G	—
11	2,4-Dimethoxy-6-acetoxy-propiophenone-enolacetate	(VIII)	57·80	BL	BLV	—
12	2,3-Dimethyl-5,7-dimetoxy-chromone		23·90	BL	BLG	—
13	2-Hydroxy-acetophenone	(IX)	66·80	BL	BLG	BR
14	2-Benzoyloxy-acetophenone	(X)	56·80	—	G	—
15	2-Benzoyloxy-acetophenone-enolbenzoate	(XI)	13·80	BL	BLV	—
16	2-Hydroxy-dibenzoyl-metán	(XII)	39·30	Y	DBR	—
17	Flavone	(XIII)	31·30	BL	DBL	BR
18	3-Benzoyl-flavone	(XIV)	67·60	G	BR	—
19	2-Hydroxy-propiophenone	[1]	71·20	BL	G	BR
20	2-Acetoxy-propiophenone	[23]	50·00	—	LBL	—
21	2-Acetoxy-propiophenone-enolacetate	[1]	49·20	BL	BLV	—
22	2,3-Dimethyl-chromone	[1]	30·20	—	DBL	—
23	Phloroacetophenone	[1,7]		RBR	YBR	BR

TABLE 1—*continued*

No	Compound	R_f	Colour of the spot			
			× 100	In UV	Treated with NaOH in UV	$FeCl^3$
24	Phloroacetophenone-monoacetate		—	BL	BR	BR
25	Phloroacetophenone-diacetate		—	BL	BR	BR
26	2,4,6-Triacetoxy-acetophenone	21	—	BL	RBR	—
27	2,4,6-Triacetoxy-acetophenone-enolacetate		—	BL	BLV	—
28	2-, Ethyl-3-acetyl-5,7-diacetoxy-chromone	7	—	LBL	G	—
29	2,4,6-Triacetoxydeoxybenzoin		60·0	BL	BLG	—
30	2,4,6-Triacetoxydeoxybenzoin enol-acetate		79·0	BLG	Y	—

B = black; BL = blue, BLG = bluish-green; BLV = bluish violet; BR = brown; DBL = dark blue; DBR = dark brown; G = green; GBR = greenish brown; LBL = light blue; LBR = light brown; RBR = reddish brown; VBR = violet brown; Y = yellow; YBR = yellowish brown; — = non visible.

Kostanecki–Robinson reactions were carried out with 8–11 mmoles (usually 1·5 g) of the hydroxyketone and 1·8 g of the base or NaOAc in Ac_2O (30 ml), by heating the mixture under reflux in an oil bath at 180°.

In the Allan–Robinson reactions, 5 g of the base (pyridine or triethylamine) and 9 g benzoic anhydride were used for 1·5 g of the hydroxyketone. The samples were withdrawn after 0, 5, 10, 15, 30, 60, 120, 240 and 480 min and then after 12, 18, 24 and 36 hr. The samples were run on plates which also contained the pure standards, previously synthesized as individual spots and in admixture with one another. The

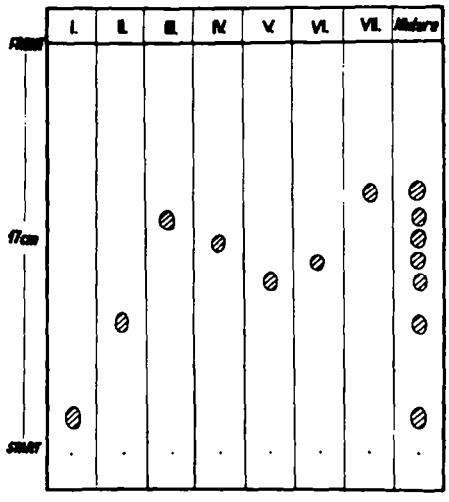


FIG. 2 TLC spots obtained at the Kostanecki–Robinson acetylation of phloropropiophenone.

distribution of the spots is shown for I in Fig. 2. The standards were prepared according to the references indicated in Table 1; the cases not mentioned are described below.

Phloropropiophenone monoacetate (II)

A soln of phloropropiophenone (0·47 g; 2·5 mmoles) in 2N NaOH (2·5 ml) was mixed with crushed ice (1·7 g), and then vigorously shaken with Ac_2O (0·5 ml) for 5 min. The mixture was quickly extracted with ether (2 × 10 ml), the ether soln washed with water (2 × 5 ml), and the solvent evaporated *in vacuo*. The residual oil was dissolved in EtOH (3 ml) and water was added in drops until the appearance of turbidity. The soln was allowed to stand overnight in a refrigerator, and later the crystals were filtered off. The mother liquor gave a second crop on standing; this was twice recrystallised from 20% EtOH. The product, m.p. 130–131°, gave a dark violet colour reaction with $FeCl_3$. (Found: C, 58·8; H, 5·4; O, 35·6; MeCO, 19·7. $C_{11}H_{12}O_5$ (224·2) requires: C, 58·9; H, 5·4; O, 35·7; MeCO, 19·2%).

The monoacetate structure was confirmed by IR analysis, but the position of the acetyl group (which is probably *para*) could not be unequivocally decided.

Phloropropiophenone di- (III) *and triacetate* (IV)

A mixture of 2,4,6-trihydroxypropiophenone (1·37 g; 7·5 mmoles), Ac_2O (15 ml) and pyridine (1·4 ml) was heated on a water bath at 95° for 2 hr, kept for 1 hr at room temp, and then poured into ice-water (25 ml). After keeping the temp below 0° for several hr, cold water (25 ml) was added gradually to give an emulsion which solidified after 4 hrs below 0°. The product was filtered off, washed with ice-cold water (2 × 25 ml), and dried at room temp (1·4 g; 60%). Recrystallization from light petroleum (b.p. 70–90°) and EtOH gave the triacetate (IV) as needles, m.p. 55–56·5°. (Found: C, 58·5; H, 5·3; MeCO, 42·3. $C_{15}H_{16}O_7$ (308·3) requires: C, 58·4; H, 5·2; MeCO, 41·9%).

The mother liquor of the above product (about 75 ml) after standing 5–6 days in a refrigerator, deposited 0·14 g (7%) of crystalline III, which was recrystallized from 65% EtOH, m.p. 69–70°. The structure as that of 2,4-diacetoxy-6-hydroxypropiophenone was supported by the IR analysis and by the dark violet colour with $FeCl_3$. (Found: C, 58·9; H, 5·2; MeCO, 32·4. $C_{13}H_{14}O_6$ (266·1) requires: C, 58·65; H, 5·3; MeCO, 32·3%).

4,6-*Dimethoxy*-2-*hydroxypropiophenone* was prepared from phloropropiophenone and a calculated amount of Me_2SO_4 in acetone in the presence of K_2CO_3 as suggested personally by Prof. K. Venkataraman's group, m.p. 113–114°.

1-*Acetoxy*-2(α-*acetoxypropenyl*)-3,5-*dimethoxybenzene* (VIII)

Samples withdrawn after 24 hr from a Kostanecki–Robinson reaction mixture of 4,6-dimethoxy-2-hydroxypropiophenone were run on 10 chromatographic plates (20 × 20 cm). The spots of adsorbent containing the enolacetate were removed from the plates, and extracted with $CHCl_3$. Any AcOH in the extract was neutralized with K_2CO_3, and, after filtration, the solvent was evaporated. The remaining colourless viscous oil was dissolved in pet. ether and stored in a refrigerator yielding VIII as white plates, m.p. 81–82°; the $FeCl_3$ colour test was negative. (Found: C, 61·1; H, 6·2. $C_{15}H_{18}O_6$ (294·0) requires: C, 61·2; H, 6·1%). The IR spectrum was consistent with the expected structure. Under the conditions of the cyclization of enol esters in aqueous medium,[1] VIII undergoes ring closure to yield 5,7-dimethoxy-2,3-dimethylchromone only in 3–4% yield; however, this conversion can be achieved on the silica gel layer by treatment of the spot with a drop of 2N NaOH and rapid drying in hot air. Cyclization was also effected by triethylamine under the conditions of the Baker–Venkataraman reaction of enol esters in non-aqueous medium.[2]

2-*Benzoyloxyacetophenone enolbenzoate* (XI)

The preparation of pure XI, in a manner analogous to that described for VIII, has so far been unsuccessful —an oily product being obtained. The lack of a ketone band in the IR spectrum indicated that the product is mainly enolbenzoate.

3-*Benzoylflavone* (XIV)

Similarly, as described, the unidentified spot of R_f 0·676 was isolated and extracted to yield a crystalline substance, m.p. 117–118° (from EtOH), whose analysis was consistent with the 3-benzoylflavone[20] structure. (Found: C, 80·8; H, 4·4. $C_{22}H_{14}O_3$ (326·3) requires: C, 81·0; H, 4·3%). On repetition the m.p. was 128–130°.

Typical examples for the preparation of *deoxybenzoin phenol- and enolacetates* are given below.

2,4-*Diacetoxydeoxybenzoin* (XV)

2,4-Dihydroxydeoxybenzoin was heated in Ac_2O without any condensing agent, as described by Chapman *et al.*[18,17] yielding XV, m.p. 136° (from EtOH).

The enolacetate (XVI) was prepared from XV (0·23 g; 1 mmole) by heating under reflux in a mixture of Ac_2O (1 ml) and pyridine (0·5 ml) for 45 min. The solvent was removed *in vacuo* and the only brown residue dissolved in EtOH was left in a refrigerator yielding XVI, as white crystals (0·23 g; 61·6%), m.p. 120–122°. The m.p. rose to 123–125° on repeated recrystallizations; shiny needles (from EtOH). In the presence of pyridine, only XVI was obtained, even after heating under reflux for 9 hr. The IR and NMR spectra were consistent with the 2,4-diacetoxydeoxybenzoin enolacetate structure. (Found: C, 67·8; H, 5·1. $C_{20}H_{18}O_6$ (354·3) requires: C, 67·7; H, 5·1%). M.p. was the same as obtained by V. Szabó.[17]

The Kostanecki–Robinson reaction of XV

Compound XV (0·24 g; 1 mmole) was heated under reflux in Ac_2O in the presence of fused NaOAc (0·01 g) for 45 min. After the addition of water (5 ml), the mixture was left in a refrigerator until the separated oily material solidified. This recrystallized from EtOH to a product melting at 122–124° (no depression on admixture with XVI). According to TLC, it consisted of XVI containing some XV and a small quantity of XVII. If the reaction was continued for 10 hr, only XVII was obtained, m.p. 162–163° (lit.[19] m.p. 162°).

Hydrolysis of XV *and* XVI

Compound XV (0·1 g; 0·4 mmole) and, in a parallel experiment, XVI (0·11 g; 0·4 mmole) was dissolved in EtOH (10 ml) and to each soln 2N NaOH (5 ml) was added. After heating under reflux for 5 min and acidifying the mixture with 5N HCl, 7-hydroxy-2-methylisoflavone (0·02 g; 25% and 0·036 g; 51‰ respectively), m.p. 240–242° (lit.[19] m.p. 240°) was obtained.

The same method was applied to 2,4,6-*trihydroxy-* and 2,4-*dihyrdoxy-4'-methoxydeoxybenzoin* always allowing 1 hr heating under reflux for the preparation of both phenol- and enolacetates. The products were recrystallized three times. The m.ps of the *phenol acetates* were – 129–130° (Found: C, 65·2; H, 4·8. $C_{20}H_{18}O_7$ (370·3) requires: C, 64·9; H, 4·9%); and 109–110°[16] (Found: C, 66·9; H, 5·0. $C_{19}H_{18}O_6$ (342·3) requires: C, 66·7; H, 5·3%); and those of the corresponding *enolacetates* obtained from the phenolacetates as above 120–121° (Found: C, 64·3; H, 4·6. $C_{22}H_{20}O_8$ (412·3) requires: C, 64·1; H, 4·9%); and 127–128° (Found: C, 65·9; H, 5·0. $C_{21}H_{20}O_7$ (384·4) requires: C, 65·6; H, 5·2%) respectively. These compounds were identified by C—H, NMR and IR analysis. Prolonged heating under reflux of the trihydroxy compound in the presence of Ac_2O and pyridine resulted in the formation of the corresponding isoflavone.

Kinetical measurements

The reaction components were measured and heated in sealed ampoules of 10 ml in a bath of given temp, each phial containing 2 ml soln. After determined periods of time, one of the ampoules was removed from the bath, opened, and its contents mixed with water (15 ml). The concentrations of III and IV varied between 0·05 and 0·20 mole l^{-1}, and that of NaOAc between 0·0035 and 0·14 g/s ml. The temp of the bath was usually 160°, 170°, or 180°, but measurements were also made at 138° and 115°. The reaction mixture was allowed to stand in a refrigerator for 2 days, the ppt filtered off, dissolved with EtOH and the solns diluted to a constant volume. The extinctions of the solns were measured at different wave lengths between 220 and 300 mμ. The solubilities of the substances in aqueous AcOH were determined and the results of the measurements were corrected with these factors, although the latter were very small. The Beer–Lambert law was valid for the systems. The measurements were made with a Beckmann Spectrophotometer.* As the reaction progressed, the colour of the soln became brown, but this did not appreciably interfere with the measurement at the wave lengths used. Neither did the presence of a small amount of VII, formed in the reaction, significantly disturb the measurement, particularly if it was made at 300 mμ. Uncertainties in following the conversion of III into V were due to the fact that the extinctions of III and IV are very near to each other.

Acknowledgement—The authors take pleasure in expressing their gratitude to Professor W. D. Ollis (University of Sheffield) for discussions and to Professors R. Bognár and V. Szabó (University of Debrecen) for communicating some of their experimental findings on deoxybenzoin enol esters. Gifts of starting materials from Professor L. Farkas, Dr. M. Nógrádi and Dr. J. Váradi (Techn. University, Budapest) and

* The method of calculation is to be published in *Acta Phys. et Chem. Acta Univ. Szeged.*

Professor T. R. Seshadri (University of Delhi) are acknowledged. Thanks are due to Dr. P. Sohär for the JR and NMR spectra. The grant of the Hungarian Ministry of Education is gratefully acknowledged.

REFERENCES

[1] Part I: T. Széll, *J. Chem. Soc.* C. 2041 (1967).
[2] Part II: *Tetrahedron* 25, 707 (1969).
[3] W. Baker, *J. Chem. Soc.* 1381 (1933).
[4] St. von Kostanecki and Lloyd, *Ber. Dtsch. Chem. Ges.* **34**, 102 and 2942 (1901).
[5] G. Wittig, Fr. Bangert and H. E. Richter, *Liebigs Ann.* **446**, 155 (1925).
[6] E. H. Rodd, *Chemistry of Carbon Compounds* Vol. 4; p. 890. Elsevier, New York (1959).
[7] F. W. Canter, F. H. Curd and A. Robertson, *J. Chem. Soc.* 1255 (1931).
[8] K. C. Gulati, S. R. Seth and K. Venkataraman, *Ibid.* 1765 (1934).
[9] F. D. Chattaway and H. Irving, *Ibid.* 2492 (1931).
[10] A. Sonn and W. Bülow, *Ber. Dtsch. Chem. Ges.* **58**, 1691 (1925).
[11] M. Davies and H. J. Smith, *Chem. & Ind.* 1597 (1965).
[12] V. B. Whalley, *J. Am. Chem. Soc.* **74**, 5795 (1952).
[13] J. Allan and R. Robinson, *J. Chem. Soc.* 2192 (1924).
[14] R. Kuhn and I. Löw, *Ber. Dtsch. Chem. Ges.* **77**, 196 (1944).
[15] A. C. Mehta and T. R. Seshadri, *J. Chem. Soc.* 3823 (1954).
[16] V. N. Gupta and T. R. Seshadri, *J. Sci. Ind. Res.* **16B**, 116 (1957).
[17] Personal Communication from V. Szabó (University, Debrecen).
[18] E. Chapman and H. Stephen, *J. Chem. Soc.* 404 (1923).
[19] W. Baker and R. Robinson, *Ibid.* **127**, 1984 (1925).
[20] A. T. M. Dunne, J. E. Gowan, J. Keane, B. M. O'Kelly, D. O'Sullivan, M. M. Roche, P. M. Ryan and T. S. Wheeler, *J. Chem. Soc.* 1252 (1950).
[21] D. H. R. Barton and T. Bruun, *Ibid.* 603 (1953).
[22] W. Baker, *Ibid.* 1351 (1953).
[23] Y. Tahara, *Ber. Dtsch. Chem. Ges.* **25**, 1309 (1892).