Tetrahedron, 1966, Vol. 22, pp. 407 to 413. Pergamon Press Ltd. Printed in Northern Ireland

REACTION OF OLEFINS WITH ACETYLACETONE IN THE PRESENCE OF THALLIC ACETATE

K. ICHIKAWA, S. UEMURA and T. SUGITA
Institute for Chemical Research, Kyoto University, Yoshida, Kyoto, Japan

(*Received* 25 *June* 1965; *in revised form* 7 *September* 1965)

Abstract—In acetic acid solution containing thallic acetate and perchloric acid, ethylene reacts with acetylacetone to give 3-acetyl-2- methyl-4,5-dihydrofuran as the major product. Similarly, styrene gives 3-acetyl-2- methyl-4-phenyl-4,5-dihydrofuran. Formation of these products can be explained by a mechanism through a reaction between olefin–thallic acetate addition compounds and active methylene of acetylacetone.

SIMILARITIES in chemical behavioı of mercuric, thallic and plumbic salts towards olefins have recently been pointed out.[1] These salts (in their higher valency states among possible ones) form addition compounds with olefins. For example, mercuric salt forms oxymercurials according to Eq. 1.[2] Thallic salt reacts similarly.[1,3] However,

$$\mathrm{RCH{=}CHR} + \mathrm{Hg(OAc)_2} \xrightarrow[\mathrm{R'OH}]{} \mathrm{RCH(OR')CHR{\cdot}HgOAc} + \mathrm{HOAc} \qquad 1.$$

$$(\mathrm{R} = \text{H, alkyl and aryl};\ \mathrm{R'} = \text{alkyl and acyl})$$

it is not always possible to isolate the oxythallates, because they react further to give oxidation products such as glycol derivatives and their rearranged products, depending on the structure of olefins and the reaction conditions.[1,3–5] Although no addition compound has been isolated as yet, in the case of lead tetraacetate, the oxidation

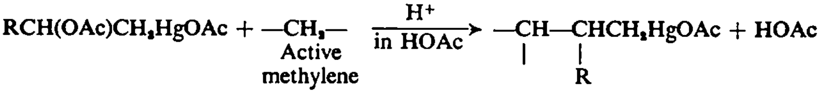
$$\mathrm{RCH{=}CH_2} + \mathrm{Tl(OAc)_3} \xrightarrow[\mathrm{R'OH}]{} \mathrm{RCH(OR')CH_2Tl(OAc)_2} + \mathrm{HOAc} \qquad 2.$$

$$(\mathrm{R} = \text{alkyl and aryl};\ \mathrm{R'} = \text{alkyl and acyl})$$

products are similar to those with mercuric and thallic salts. Further, experimental evidence to show the formation of adduct has been reported in the case of the reaction between lead tetraacetate and anethole in acetic acid.[6] It is clear, therefore, that the oxidation of olefins with these salts proceeds through common oxymetallation reaction.

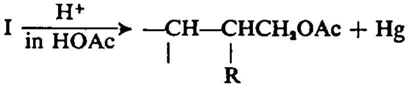
[1] H. J. Kabbe, *Liebig's Ann.* **656**, 204 (1962).
[2] See, for example, J. Chatt, *Chem. Revs.* **48**, 7 (1951).
[3] K. C. Paude and S. Winstein, *Tetrahedron Letters* 3393 (1964).
[4] R. R. Grinstead, *J. Org. Chem.* **26**, 238 (1961).
[5] C. B. Anderson and S. Winstein, *J. Org. Chem.* **28**, 605 (1963).
[6] K. Ichikawa and O. Itoh, *Bull. Inst. Chem. Res. Kyoto Univ.* **40**, 317 (1962).

Oxymercurials react with various active methylene and aromatic compounds according to Eqs 3 and 4.[7–10]

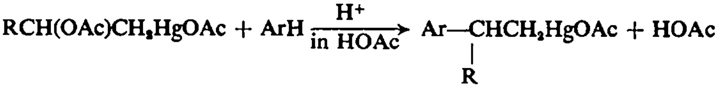


$$\mathrm{RCH(OAc)CH_2HgOAc} + \underset{\substack{\text{Active}\\ \text{methylene}}}{\mathrm{-CH_2-}} \xrightarrow[\text{in HOAc}]{H^+} \mathrm{-\underset{|}{C}H-\underset{\substack{|\\ R}}{C}HCH_2HgOAc} + \mathrm{HOAc} \qquad 3a.$$

I

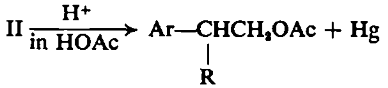


$$\mathrm{I} \xrightarrow[\text{in HOAc}]{H^+} \mathrm{-\underset{|}{C}H-\underset{\substack{|\\ R}}{C}HCH_2OAc} + \mathrm{Hg} \qquad 3b.$$



$$\mathrm{RCH(OAc)CH_2HgOAc} + \mathrm{ArH} \xrightarrow[\text{in HOAc}]{H^+} \mathrm{Ar-\underset{\substack{|\\ R}}{C}HCH_2HgOAc} + \mathrm{HOAc} \qquad 4a.$$

II



$$\mathrm{II} \xrightarrow[\text{in HOAc}]{H^+} \mathrm{Ar-\underset{\substack{|\\ R}}{C}HCH_2OAc} + \mathrm{Hg} \qquad 4b.$$

As a first attempt to use the oxythallation product for synthetic purpose other than oxidation, the reaction of ethylene and styrene with acetylacetone and anisole in the presence of thallic acetate has been studied to check whether or not the reactions similar to those of Eqs 3 and 4 with oxymercurials proceed.

For the present purpose, the thallic salt such that gives high concentration of the adduct and oxidizes olefin slowly is desirable. It has been reported that the anions in the reaction medium affect the rate of oxidation remarkably,[11] and that the oxidation of ethylene proceeds with thallic nitrate and sulfate at room temperature, but not with acetate.[4] This suggests that the thallic acetate is the most promising among the usual thallic salts. To reexamine these points, the reaction of thallic acetate with ethylene in acetic acid was investigated.

Thallic acetate reacted with ethylene very slowly in acetic acid as compared with the case of oxymercuration, but the decrease of trivalent thallium in the solution was actually observed. On perchloric acid treatment, ethylene glycol diacetate (III) was obtained in 95% yield based on the trivalent thallium consumed. On the other hand, only a trace of III was detected from the reaction mixture without perchloric acid treatment. These results show that the oxythallation of ethylene proceeds to some extent in acetic acid. The oxythallate remains unreacted in acetic acid and gives the oxidation product only after the addition of perchloric acid.

Considering the results mentioned above, the reaction of ethylene and styrene with acetylacetone in the presence of thallic acetate has been investigated as follows. Acetylacetone was added into a solution of thallic acetate dissolved in acetic acid and then ethylene was bubbled at 0°. The absorption was slow as in the case where acetylacetone was absent. A white precipitate formed gradually and the concentration of trivalent thallium decreased simultaneously. After 16 hr, the addition of ethylene was stopped and then 70% perchloric acid was introduced at 0–2° (ca. 1 molar). Upon

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[7] K. Ichikawa, S. Fukushima, H. Ouchi and M. Tsuchida, *J. Amer. Chem. Soc.* **80**, 6005 (1958).

[8] K. Ichikawa, S. Fukushima, H. Ouchi and M. Tsuchida, *J. Amer. Chem. Soc.* **81**, 3401 (1959).

[9] K. Ichikawa, H. Ouchi and S. Fukushima, *J. Org. Chem.* **24**, 1129 (1959).

[10] K. Ichikawa, O. Itoh, T. Kawamura, M. Fujiwara and T. Ueno, *J. Org. Chem.* in press.

[11] P. M. Henry, *J. Amer. Chem. Soc.*, **87**, 990 (1965).

addition of perchloric acid, a large amount of yellow precipitate formed instantaneously, which was analyzed as containing 13% of thallic salt as acetate. After 24 hr's duration, the concentration of trivalent thallium in the liquid phase was one tenth of the initial one. *3-Acetyl-2-methyl-4,5-dihydrofuran* (IV), whose structural proof will be described later, amounted to about 90% of the organic product. As minor products, III (ca. 4%), 1,1-diacetylcyclopropane (V; ca. 4%) and pentan-1-acetoxy-4-one (VI; ca. 2%) were obtained. The yield of IV was 10·2% on the basis of thallic salt consumed. Another experiment in the same manner as above except that perchloric acid was added to the initial reaction mixture (0·5 molar) and then ethylene was passed for 18 hr, also gave IV and traces of V and VI. The yield of IV was 22%, higher than that of the former. This improvement in the yield appears to have resulted from the following reason. In the former, the amount of the oxythallate which can react with acetylacetone is limited to that determined by the oxythallation equilibrium which is rather small in the case of ethylene. In the latter, oxythallate is formed as it is consumed. At 50°, the reaction in the latter procedure gave a mixture of III (7%), V (9%), VI (trace) and IV (83%), the yield of the last one being 20% on the basis of thallic salt consumed. As compared with the results at 0°, the relative ratio of III and V to IV was larger, while the total yield was almost the same.

As will be discussed later, these results show that the condensation of oxythallate with acetylacetone proceeds in the presence of perchloric acid. Rather low yields seem due to the oxidation of acetylacetone with thallic salt. Actually, thallic acetate was reduced almost completely by acetylacetone in acetic acid.

Similar experiments were carried out with styrene. The reactions proceeded in the same way as in the case of ethylene, and *3-acetyl-2-methyl-4-phenyl-4,5-dihydrofuran* (VII) was obtained as the only organic product detectable (69% yield based on the thallic salt consumed).

When the reaction times before and after the addition of perchloric acid were varied as 56 and 1, 1 and 46, and 0·5 and 1 hr with concentration of perchloric acid kept constant (0·5 molar), the yields of VII were 69, 57 and 50% respectively. These results show that the longer reaction time before the addition of the acid (for oxythallation), the better yields, and the condensation of oxythallate with acetylacetone proceeds rather rapidly.

With higher perchloric acid concentration (1·0 molar), the yield of VII was lower (51%) than that of the corresponding experiment (57%) with 0·5 molar perchloric acid. In this case, a considerable amount of styrene polymer and a small amount of α-phenylethyl acetate (VIII) were obtained.

Using methanol in place of acetic acid as the solvent, the same reaction with styrene was carried out at 0° and with 0·5 molar perchloric acid, the reaction times before and after the addition of perchloric acid being 1 and 26 hr. The product was a mixture of VII (91%) and 1,1-dimethoxy-2-phenylethane (IX, 9%), the latter being the oxidation product of styrene. The yield of VII was 59%, almost the same as that in acetic acid.

The structures of the dihydrofurans IV and VII were elucidated by analytical and spectral data. Elemental analyses showed that IV and VII should have formulae $C_7H_{10}O_2$ and $C_{13}H_{14}O_2$ respectively. The latter formed 2,4-dinitrophenylhydrazone, m.p. 160–163° and semicarbazone, m.p. 172–174°. However, IV formed neither hydrazone nor semicarbazone. IR spectrum of IV which showed strong absorptions at 1670, 1605 and 1230 cm^{-1} indicated the presence of α,β-unsaturated carbonyl group. UV absorption due to π–π^* transition of this group was found at 280 mμ (ε = 12200) in ethanol and at 270 mμ (ε = 13300) in hexane. The shift from the usual α,β-unsaturated carbonyl absorption can be explained by the substitution of alkyl and electronegative oxygen groups.[12] The absorption maximum due to n–π^* transition of carbonyl group was observed at 203 mμ (ε = 4300) in ethanol and at 190 mμ (ε = 6300) in hexane. By catalytic hydrogenation on Pd–$BaSO_4$, IV absorbed readily one mole of hydrogen at room temperature. The IR absorptions at 1670 and 1600 cm^{-1} disappeared and a new strong absorption of isolated carbonyl appeared at 1705 cm^{-1}. These results support that IV is 3-acetyl-2-methyl-4,5-dihydrofuran. NMR spectrum showed two multiplets centered at τ5·57 and 7·04 and a triplet at 7·79 with relative intensities of 2:2:6. At a glance, this seems inconsistent with the structure of IV, because four peaks with relative intensities of 2:2:3:3 are expected. Usually, acetyl protons and allylic methyl protons show signals at τ7·8–8·05 and 8·05–8·40 respectively.[13] In this case, it appears that the signal due to allylic methyl protons (a triplet, J = 1·5 c/s a long range coupling with C_4 protons) is shifted to lower magnetic field by the effect of negative oxygen and superimposed with the singlet of acetyl protons incidentally. Two multiplets at τ5·57 and 7·04 can be interpreted as the signals of C_4 and C_5 protons in A_2B_2 system.[14]

IR spectrum of VII showed strong absorptions at 1676, 1600 and 1230 cm^{-1}, and those of the usual mono-substituted phenyl compound. UV absorption showed maxima at 205 mμ (ε = 16600) and 280 mμ (ε = 13300) in ethanol and at 192·5 mμ (ε = 35500) and 270 mμ (ε = 11500) in hexane. The hydrogenation product of VII showed a new strong absorption at 1700 cm^{-1} in place of those at 1676 and 1600 cm^{-1} of the parent compound. All these data fully substantiated the structure of VII as in the case of IV. NMR spectrum of VII showed signals centered at τ2·74, a multiplet at 5·22–5·87, a doublet (J = 1 c/s) centered at 7·66 and a singlet at 8·10 with relative intensities of 5:3:3:3. These signals can be assigned to phenyl protons, three protons attached to C_4 and C_5 (in AB_2 system[14]), methyl protons attached to C_2 (doublet by long range coupling with C_4 proton) and methyl protons of acetyl group. The value of methyl protons here is also lower than the usual. Thus the NMR data also support the structure of VII.

The other products were identified by comparing with authentic samples by gas chromatography.

The fact that ethylene and its oxidation products such as ethylene glycol or its diacetate did not react with acetylacetone under the conditions used in the condensation, appears to show that the reaction proceeds through the formation of oxythallates of ethylene and styrene. Since the intermediate thallium compounds could not be isolated, detailed discussion of the mechanisms might be speculative. However, it is most likely that reaction 5 analogous to reaction 3a with an oxymercurial, takes

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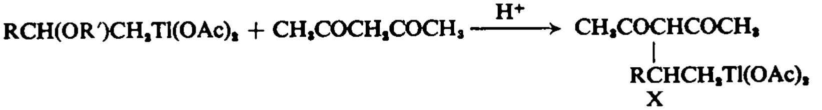
[12] A. E. Gillam and E. S. Stern, *Electronic Absorption Spectroscopy* p. 103. E. Arnold, London (1960).

[13] See, for example, L. M. Jackman, *Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry* p. 57. Pergamon Press, London (1959).

[14] See, for example, J. A. Pople, W. G. Schneider and H. J. Bernstein, *High Resolution Nuclear Magnetic Resonance* pp. 123, 142. McGraw-Hill, New York (1959).

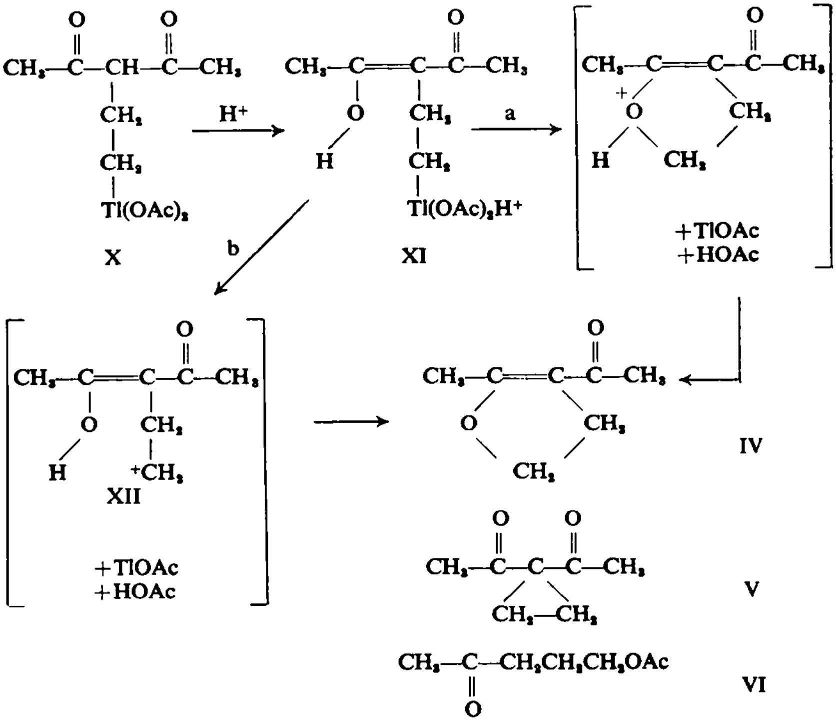
place and the organothallium compound (X) formed reacts to give the final products.

$$RCH{=}CH_2 + Tl(OAc)_3 \xrightarrow[R'OH]{} RCH(OR')CH_2Tl(OAc)_2$$



$$RCH(OR')CH_2Tl(OAc)_2 + CH_3COCH_2COCH_3 \xrightarrow{H^+} \underset{\underset{X}{RCHCH_2Tl(OAc)_2}}{CH_3CO\overset{}{C}HCOCH_3} \qquad 5.$$

The oxymercurial of ethylene also gave the same products, IV, V and VI, in the condensation reaction with acetylacetone, although the relative ratio of the products was different.[10] Thus, the similar mechanisms may operate in both the reactions with thallium and mercury compounds.



The organothallium compound (X) formed by the reaction of oxythallate of ethylene with acetylacetone is protonated to give XI. For the process that XI forms IV, two pathways are possible. Nucleophilic substitution by hydroxy oxygen on the carbon attached to thallium forms the dihydrofuran (IV) via path a. In an alternative mechanism, XI splits AcOH and TlOAc to produce the primary carbonium ion (XII) via path b. This carbonium ion formation was postulated by Kabbe in the case of oxidation of olefin with thallic salt.[1] Subsequent electrophilic attack of the carbonium ion (XII) on the enolate oxygen gives the dihydrofuran (IV). At the present stage of investigation, it is difficult to decide which is correct of these two mechanisms. The fact that neither 1-methoxy-4-pentanone nor 3,3-diacetyl-1-ethoxypropane was obtained by the reaction pursued in methanol solution, seems to favor path a of these two. However, it is difficult to explain the formation of V and VI in acetic acid via path a. It is most probable that the carbonium ion (XII) reacts with enol double bond to form V (intramolecular alkylation) or with the solvent, acetic acid, to form 3,3-diacetylpropyl acetate which splits acetyl group to give VI in the presence of perchloric acid. At higher reaction temperature the proportion of V and VI in products is larger than that at lower temperature. This suggests that the path b is not completely deleted. The reaction might proceed through both mechanisms concurrently.

The possibility of the reaction of oxythallate with aromatic compound analogous to reaction 4 has been studied using ethylene and anisole as the substrates. The major product was the oxidation product of ethylene (III) and the expected product, anisylethyl acetate was obtained in a yield of only 3%. This shows that the reaction of oxythallate to give III proceeds much faster than the condensation with anisole. However, it is demonstrated that the reaction of oxythallate analogous to reaction 4 can proceed under the similar condition.

EXPERIMENTAL

Materials. Thallic acetate was prepared by the method proposed by Grinstead,[4] and dried over P_2O_5. The purity was more than 97% (by iodometry). Acetic acid, styrene and acetylacetone were used after distillation. Commercial ethylene was used without purification.

Oxidation of ethylene. Ethylene was bubbled into a solution of thallic acetate (25 g; 65·5 m-mole) in 50 ml acetic acid at 60°. As ethylene was introduced, a yellow precipitate was gradually formed. After 10 hr, the concentration of trivalent Tl in the liquid phase decreased to three quarters of the initial one (by iodometry). No more decrease of trivalent Tl was observed after the additional introduction for 10 hr. After cooling to room temp, 25 ml portion (containing 21·4 m-mole of thallic acetate) was taken out of the liquid layer, and was mixed with 9·3 g 70% perchloric acid. The reaction mixture was kept at room temp for 10 hr, diluted with water and extracted with benzene. The benzene solution was washed with sat. $NaHCO_3$ aq, dried over Na_2SO_4 and distilled. There was obtained 1·02 g of III, b.p. 60–61°/4·5 mm, saponification value 74·8. In the aqueous solution of benzene extraction 14·1 m-mole thallic acetate remained unreacted. Analysis by iodometry showed that 28% of the yellow precipitate were thallic salt as acetate. However, it is not clear what the precipitate consists of, because the physical properties such as m.p. and solubilities are different from both thallium triacetate and monoacetate. Another 25 ml portion of the reaction mixture was treated by the same method as mentioned above without perchloric acid. Only a trace of III detected in the product by gas chromatography.

Reaction of ethylene with acetylacetone. The following example shows the typical experimental procedure. Acetylacetone (20 g) was added to a solution of 25 g thallic acetate in 55 ml acetic acid. The mixture was cooled to 0° and mixed with 7·5 g 70% perchloric acid (0·5 molar). Ethylene was bubbled into this solution under stirring at 0–2° for 18 hr. The reaction mixture was filtered to remove 8·9 g precipitate. Analysis of the precipitate by iodometry showed that 13% of thallic salt as acetate were contained. The whole distillate after removing benzene was analyzed by gas chromatography. The product was almost pure IV with traces of V and VI. Redistillation gave 1·66 g (22% based on the thallic salt consumed) of pure IV, b.p. 65–67°/4 mm, n_D^{20} 1·5007. (Found: C, 66·61; H, 8·31. $C_7H_{10}O_2$ requires: C, 66·64; H, 7·99%.) IR maxima of IV (KBr, liq.): 2950 (m), 2900 (m), 1735 (w), 1670 (s), 1605 (s), 1482 (w), 1425 (m), 1387 (s), 1372 (sh), 1360 (sh), 1265 (sh), 1230 (s), 624 (m), 603 (w), 472 (w).

Compound IV (138·7 mg) in 50 ml MeOH was hydrogenated over Pd-$BaSO_4$ in a shaking apparatus and absorbed 23·1 ml (15°) H_2, equivalent to one double bond.

Reaction of styrene with acetylacetone. The following example shows the typical experimental procedure. To a solution of 25 g thallic acetate in 55 ml acetic acid were added 20 g styrene and 20 g acetylacetone. The mixture was kept at −5° under stirring for 11 hr, and then 9 g 70% perchloric acid (0·5 molar) was added slowly during 1 hr. The stirring was continued for 28 hr at room temp. The reaction mixture was filtered from the precipitate formed (14 g) and worked up as in the case of ethylene. There were obtained 7·75 g (69% yield based on the thallic salt consumed) of VII, b.p. 135–136°/3 mm, n_D^{20} 1·5557. (Found: C, 76·95; H, 7·22. $C_{13}H_{14}O_2$ requires: C, 77·20; H, 6·98%.)

2,4-Dinitophenylhydrazone, m.p. 160–163°. (Found: C, 59·74; H, 5·02; N, 14·57. $C_{19}H_{18}O_5N_4$ requires: C, 59·68; H, 4·75; N, 14·65%.) Semicarbazone, m.p. 172–174°. IR maxima of VII (KBr, liq.): 3050 (w), 2970 (w), 2870 (w), 1750 (w), 1676 (s), 1620 (sh), 1600 (s), 1504 (w), 1460 (w), 1430 (w), 1390 (s), 1380 (sh), 1325 (w), 1230 (s), 1207 (m), 1135 (w), 1085 (w), 1035 (w), 1000 (m), 970 (w), 943 (m), 920 (m), 775 (m), 710 (s), 680 (w), 650 (w), 630 (m), 620 (w), 550 (w).

Compound VII (240·7 mg) in 50 ml MeOH was hydrogenated over Pt catalyst, and absorbed 26·0 ml (15°) H_2, equivalent to one double bond.

Reaction of ethylene with anisole. To a mixture of thallic acetate (25 g) and anisole (28 g) in acetic acid (50 ml), ethylene was introduced for 10 hr with stirring at 50°, and then 15 g 70% perchloric acid was mixed and ethylene was introduced for another 10 hr. At the end of this duration, no more trivalent Tl existed in the solution. The precipitate (12·2 g) formed was filtered off, and the filtrate was distilled under red. press. giving a mixture, b.p. 56–120°/4 mm, yield 2·25 g, which consisted of III (78%) and anisylethyl acetate (18%) by gas chromatography.

Authentic samples of gas chromatography. Compound III was prepared by the reaction of ethylene glycol with acetic acid in the presence of small amount of H_2SO_4, b.p. 64–68°/5 mm, n_D^{20} 1·4151. The preparation of V and VI will be reported in a separate paper.[10] Compound IX was prepared by the method reported by Kabbe,[1] b.p. 65–68°/3 mm, n_D^{20} 1·4990; VIII was prepared by the reaction of α-phenylethyl alcohol with acetic acid in the presence of H_2SO_4, b.p. 100–120°/13 mm.

Spectral measurements. IR and UV absorption spectra were obtained by JASCO IR-S and HITACHI EPS-2U respectively. NMR spectra were determined by Varian 60 using tetramethylsilane as the internal standard.

Acknowledgments—The authors are indebted to Dr. T. Singu, Department of Pharmacy, for determining n.m.r. spectra, and to Professors M. Ohno and Y. Inouye of this Institute for giving convenience in the hydrogenation experiments.