Favorskii Rearrangements. VI. Formation of Indanone By-Products from α-Halodiphenyl- and α-Halotriphenylpropanones[1]

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Abstract: The diphenyl α-halopropanones $Ph_2CXCOCH_3$ (**1**) and $Ph_2CHCOCH_2X$ (**2**) react with 0.05 *M* NaOMe–MeOH to give essentially quantitative yields of ester $Ph_2CHCH_2CO_2Me$ (**5**). Under "inverse addition," however, where $[MeO^-] \cong 10^{-3}$ *M* the products from **1** (X = Cl) and from **2** (X = Cl or Br) are **5** and 1-phenyl-2-indanone (**9**) in a ratio of 1.6:1.0. These data point to a common intermediate from **1** and **2**; a dipolar ion is suggested. The rate-limiting step for the reaction of **1**, **2**, $Ph_2CXCOCH_2Ph$ (**3**), and $Ph_2CHCOCHXPh$ (**4**) with methoxide ion is proton abstraction. The principal product from the reactions of **3** and **4** with either low or high concentrations of methoxide ion is 1,3-diphenyl-2-indanone.

In previous papers in this series we have shown that Favorskii rearrangements of α-chloroarylpropanones and -arylbutanones fall into two mechanistic classes. On the one hand the systems $ArCHClCOCH_3$[3] and $ArCH_2COCH_2Cl$[4] react with NaOMe–MeOH by way of reversible carbanion (enolate ion) formation followed by rate-limiting halide release. On the other hand, for the systems $ArCH_2COCHXCH_3$, $PhCHXCOCH_2CH_3$, and $PhCH_2COCHXPh$ halide ion release is greatly accelerated and proton removal becomes rate limiting.[5] The latter systems show a strong tendency to form by-products attributable to solvolysis of intermediate enol allylic chlorides. The study has now been extended to the systems $Ph_2CXCOCH_3$ (**1**), $Ph_2CHCOCH_2X$ (**2**), $Ph_2CHCOCHXPh$ (**3**), and $Ph_2CXCOCH_2Ph$ (**4**). It was anticipated that the presence of the second or third phenyl group would accelerate loss of halide ion from the enolate ion (or enol) making this group of compounds fall into the second mechanistic class, *i.e.*, that proton removal would be rate limiting. This expectation has been realized and a new side reaction, indanone formation, has been discovered. Additional information concerning the mechanism of the Favorskii rearrangement has thus been obtained.

Results

Reactions of 1-Halo-1,1-diphenylpropanone (1). Reaction of **1** with 0.05 *M* NaOMe in MeOH at 0° gave 97% methyl 3,3-diphenylpropionate (**5**).[6] The isomeric chloro ketone **2** also gave an essentially quantitative yield of **5** under these conditions.[7] Rate data on systems **1** and **2** are compared with those from related systems in Table I.

Table I. Rates of Halide Release from α-Halo Ketones with Excess 0.05 *M* NaOMe–MeOH at 0°

Compound	k, M^{-1} sec^{-1} X = Cl	X = Br
$PhCHXCOCH_3$	$(4.0 \times 10^{-4})^a$	
$Ph_2CXCOCH_3$ (**1**)	2.5×10^{-2}	8.4×10^{-2}
$Ph_2CXCOCH_2Ph$	$\sim 1.4^b$	2.3^c
$PhCH_2COCH_2X$	$(2.6 \times 10^{-2})^d$	1.7^d
$Ph_2CHCOCH_2X$ (**2**)	6.6×10^{-1}	2.8
$Ph_2CHCOCHXPh$	$\sim 1.4^b$	1.5^c

[a] Corrected for yield of Favorskii product (see ref 2); k_{obsd} is 3.09×10^{-3}. [b] At 2.2°; a mixture of the isomeric chlorides was used. [c] At 2.9°. [d] From ref 3.

Reactions with **1** run in CH_3OD revealed only 11% of exchange at C-α′ with X = Cl and 6% with X = Br.

$$Ph_2CClCOCH_3 + NaOMe \xrightarrow{CH_3OD} Ph_2CHCH_2CO_2Me + NaCl$$
(contains 11% of D at C_α)

1 **5**

Dropwise addition of a 10% excess of a solution of 0.05 *M* NaOMe–MeOH over a 6-hr period to a dilute methanolic solution of **1** (X = Cl) gave 48% **5**, 17% 1-methoxy-1,1-diphenylacetone (**6**), and *ca.* 19% of a new ester **7**. The nmr spectrum of **7** revealed, beside the aromatic protons, only two singlet peaks (at δ 3.9 and 3.5) with relative intensities of 2:3 (relative to 10 for Ph). Treatment of **7** with aqueous sodium hydroxide gave a quantitative yield of a carboxylic acid, mp 131–132°, which had a neutralization equivalent of 245 and analyzed for $C_{15}H_{12}O_3$. Only a few structures fitting these data are possible and of these only one, *o*-benzoylphenylacetic acid, was probable from mechanistic considerations. This acid had the correct melting point

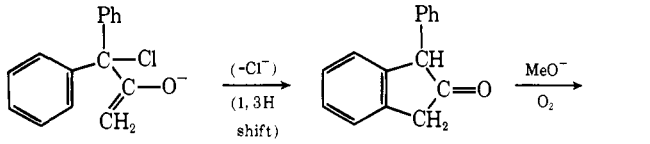
$$Ph_2CClCOCH_3 \xrightarrow[\text{(low conc)}]{NaOMe\text{–}MeOH} Ph_2CHCH_2CO_2Me + Ph_2C(OMe)COCH_3 + \text{(COPh, CH}_2\text{CO}_2\text{Me)}$$

5 (48%) **6** (17%) **7** (19%)

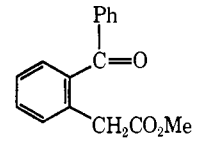
(1) For a preliminary report see F. G. Bordwell, R. G. Scamehorn, and A. C. Knipe, *J. Amer. Chem. Soc.*, **92**, 2172 (1970).
(2) National Institutes of Health Predoctoral Fellow, 1966–1968.
(3) F. G. Bordwell and R. G. Scamehorn, *J. Amer. Chem. Soc.*, **90**, 6751 (1968).
(4) F. G. Bordwell, R. G. Scamehorn, and W. R. Springer, *ibid.*, **91**, 2087 (1969).
(5) F. G. Bordwell and M. W. Carlson, *ibid.*, **92**, 3370, 3377 (1970).
(6) C. L. Stevens and A. E. Sherr (*J. Org. Chem.*, **17**, 1228 (1952)) report an 85% yield of ethyl 3,3-diphenylpropionate from **1** in refluxing 2.4 *M* NaOEt–EtOH.
(7) A 65% yield of ethyl 3,3-diphenylpropionate (plus 12% ethyl diphenylacetate) has been reported for the reaction of **2** (X = Cl) with refluxing 2.4 *M* NaOEt–EtOH.[6]
(8) L. Legrand and N. Locaih, *Bull. Soc. Chim. Fr.*, 73, 1787 (1964).

(128°,[8] 130–131°[9]) and spectral data. The corresponding methyl ester is also known,[10] and the infrared data agreed with that of the unknown ester.

The rationale used in deciding that the unknown ester might be **7** was the supposition that in dilute basic medium the enolate ion **8** (or the corresponding enol) derived from **1** might react intramolecularly to form 1-phenyl-2-indanone (**9**), which could react with oxygen in the presence of methoxide ion to form **7**.



8 **9**



7

This hypothesis was strengthened by the report of Smith and Wilson that **9** slowly dissolved in cold sodium hydroxide to form an unknown acid, mp 131°.[11] The hypothesis was confirmed by carrying out the "inverse addition" reaction of **1** with NaOMe in a nitrogen atmosphere. Under these conditions indanone **9**, identical with a synthetic sample, was isolated from the reaction mixture in place of **7**. Furthermore, **9** was found to be converted readily to **7** by reaction with oxygen in the presence of methanolic sodium methoxide.

Uncatalyzed methanolysis of **1** (X = Cl) for 6 hr gave 6% of **6**, showing that no more than *ca.* one-fourth of the amount of **6** formed during the inverse addition experiment could have arisen by uncatalyzed methanolysis. The major amount of **6** formed during the inverse addition experiment probably arises by way of methanolysis of an enol allylic chloride intermediate (see **1a** below). This route, in contrast to direct methanolysis of **1**, requires incorporation of one atom of deuterium into **6**. An inverse addition experiment carried out in MeOD did, indeed, lead to incorporation of *ca.* 1.5 deuterium atoms in the ketonic methyl group of **6**. In a control experiment **6** failed to exchange deuterium in 6 hr in 10^{-5} *M* NaOMe in MeOD (the approximate concentration present during inverse addition), although complete exchange did occur at a higher concentration (0.04 *M*). This supports the view that **6** arises from **1** *via* **1a** rather than by a direct methanolysis route.

Reactions of 3-Halo-1,1-diphenylpropanones (2). Reaction of the isomeric α-chloro ketone **2** under "inverse addition" gave essentially the same products as were formed from **1**, but in somewhat different proportions.

$$\underset{\mathbf{2}}{Ph_2CHCOCH_2Cl} \xrightarrow[\text{(low concn)}]{\text{NaOMe–MeOH}} \underset{\mathbf{5}\ (60\%)}{Ph_2CHCH_2CO_2Me} + Ph_2C(OMe)COCH_3 + \mathbf{7} + Ph_2CHCO_2Me$$

$$\mathbf{6}\ (2\%) \qquad (21\%) \qquad (1\%)$$

Essentially the same result was obtained with **2** (X = Br), the product distribution being **5** (61%), **6** (1.3%), and **7** (16%). (A comparable "inverse addition" experiment with **1** (X = Br) was precluded by the rapidity with which this compound undergoes uncatalyzed methanolysis.)

Since the product distribution from **1** and **2** at low methoxide concentrations was not the same (even after correcting for uncatalyzed methanolysis of **1**) it was clear that a common intermediate could not be giving rise to all three products. It seemed likely, however, that **5** and **7** might have their origin in a common intermediate. Further information on this point was obtained by repeating the reactions in a nitrogen atmosphere with rates of methoxide addition adjusted so as to take into account the relative reactivities of the two halo ketones. The product distribution of **5** and **9** was determined by nmr. The ratios of **5**:**9** determined in this way were 1.69 (from **1**, X = Cl), 1.64 (from **2**, X = Cl), and 1.66 (from **2**, X = Br).

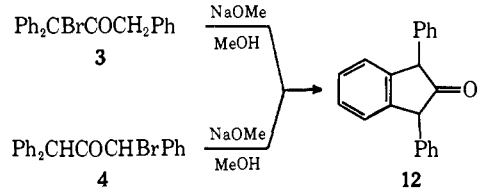
When **2** (X = Br) was refluxed in methanol solution containing 5–20% (v/v) of 2,6-lutidine, small amounts of isomeric methoxy ketones **6** and **11** were formed and the relative amounts of ester **5** and indanone **9** were reversed. Now the indanone was the major product (**5**:**9** ≅ 1.0:1.6). A similar result was obtained in an inverse addition reaction with methoxide under reflux.

$$\underset{\mathbf{2}}{Ph_2CHCOCH_2Br} \xrightarrow[\text{reflux}]{\text{Lut–MeOH}} \underset{\mathbf{6}}{Ph_2CCOCH_3}(OMe) + Ph_2CHCOCH_2OMe + \mathbf{5} + \mathbf{9}$$

11

When the experiment catalyzed by 2,6-lutidine was repeated, except that sufficient *p*-toluenesulfonic acid was added to neutralize one-half the lutidine, only the isomeric methoxy ketones **6** and **11** were obtained; **5** and **9** were not formed under these conditions.

Reactions of α-Halo-1,1,3-triphenylpropanones. The reaction of either $Ph_2CBrCOCH_2Ph$ (**3**) or $Ph_2CHCOCHBrPh$ (**4**) with 0.05 *M* sodium methoxide in methanol in a nitrogen atmosphere gave 1,3-diphenyl-2-indanone (**12**) in essentially quantitative yield. Similar results were obtained with concentrated (2 *M*) sodium methoxide.



12

In the absence of sodium methoxide, **3** underwent methanolysis ($t_{1/2} \cong 30$ min at 25°) giving **13**. No deuterium exchange occurred during this reaction, showing that it is the bromo ketone, itself, rather than the enol that is reacting. The isomeric bromide **4** was inert to uncatalyzed methanolysis at room temperature during 12 hr.

$$\underset{\mathbf{3}}{Ph_2CBrCOCH_2Ph} \xrightarrow[25°]{MeOH} [Ph_2\overset{+}{C}COCH_2Ph]Br^- \longrightarrow \underset{\mathbf{13}}{Ph_2CCOCH_2Ph}(OMe)$$

(9) M. Giliosal and D. N. Chandhury, *J. Indian Chem. Soc.*, **42**, 569 (1965).
(10) C. Collard-Charon and M. Renson, *Bull. Soc. Chim. Fr.*, 72, 443 (1963).
(11) A. C. B. Smith and W. Wilson, *J. Chem. Soc.*, 1342 (1955).

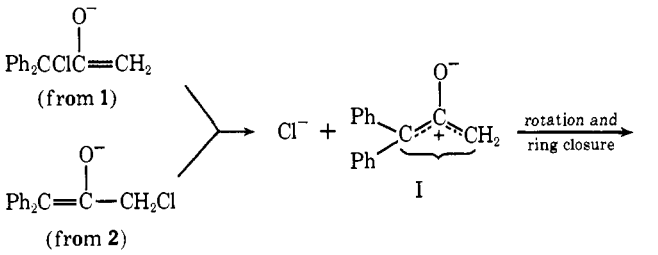
$$Ph_2CHCOCHBrPh \xrightarrow[25^\circ]{MeOH} \text{no reaction}$$
4

In the presence of 20% (v/v) 2,6-lutidine–MeOH, **3** gave 85% of indanone **12** in 30 min (43% conversion in 5 min). Under comparable conditions **4** remained unreactive, but on refluxing the solution for 8 hr 85% of **12** was formed. No deuterium exchange occurred with **4** under conditions where 22% exchange occurred with the parent ketone.

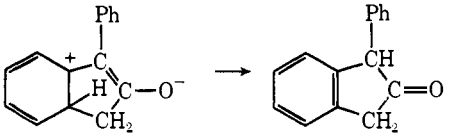
Discussion

Favorskii Rearrangement. Substitution of a phenyl group into the α position of $PhCHClCOCH_3$ giving $Ph_2CClCOCH_3$ (**1**) increases the yield of Favorskii rearrangement product obtained with 0.05 *M* NaOMe from 13 to 97%.[12] This is caused principally by a marked increase in the rate of chloride ion release from the enolate ion. This results in proton removal becoming essentially rate limiting (only 11% of deuterium exchange occurs with **1**, X = Cl, and only 6% with **1**, X = Br). For **1** (X = Cl) the rate of reaction to form Favorskii ester is about 625 times that for $PhCHCl-COCH_3$. This would be sufficient to increase the yield of Favorskii product to 89% even if the rate of epoxy ether formation remained constant in changing from $PhCHClCOCH_3$ to $Ph_2CClCOCH_3$. Since addition of methoxide ion to the carbonyl group is no doubt more hindered in **1**, epoxy ether formation must be slower for **1**, which accounts for the complete absence of this product. Inasmuch as α elimination is impossible for **1**, the rapidity with which it undergoes rearrangement is evidence against a carbene mechanism, which has also been excluded on other grounds.[4]

The 625-fold rate increase from $PhCHClCOCH_3$ to $Ph_2CClCOCH_3$ is expected on the basis of the dipolar-ion-like transition state envisioned for loss of halide ion from the enolate ion in these reactions,[3,4] since the presence of the second phenyl group should help to stabilize the developing positive charge.[13] The 625-fold figure is a *minimum* value since the observed rate for **1** relates to proton removal rather than to chloride ion release. The substitution of a phenyl group at the α' position ($Ph_2CHCOCH_2Cl$ *vs.* $PhCH_2COCH_2Cl$) causes a minimum of 25-fold rate increase for the same reason.[15] (The ρ values for chloride ion release in the $ArCHClCH_3$ and $ArCH_2COCH_2Cl$ systems are -2.4 and -5.0, respectively.[3,4]) In view of the low k_{Br}/k_{Cl} ratio for **2** (4.2/1.0) proton removal must be essentially rate limiting in this system. It is not unreasonable to expect ionization of chloride ion from the enolate ions of **1** and **2** to give rise to a common dipolar ion intermediate I.

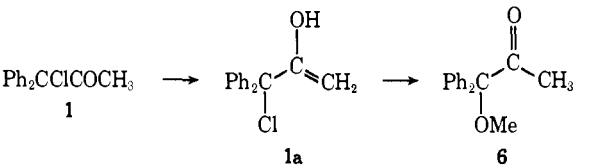


I


I′ 9

Bonding of the terminal side-chain carbon atom in I to one of the phenyl rings would give intermediate I′, which would be expected to tautomerize readily to **9**. This representation finds strong support in the observation that at low base concentration the ratio of ester **5** to indanone **9** is constant for **1** (X = Cl) and **2** (X = Cl, Br).

Appreciable formation of methoxy ketone **6** occurs from **1**, but not from **2**. If I is accepted as a common intermediate for indanone formation it cannot also serve as a source of **6** because **6** is obtained only from **1**. Some **6** is formed by methanolysis of **1**, but its main source is probably methanolysis of the corresponding enol allylic chloride (**1a**).[5] This is also no doubt the


1 1a 6

pathway by which **6** and **11** are formed from **2** (X = Br) and Lut–LutH$^+$ in MeOH.

Apparently, **1a** does not give rise to **9** or else the **5**:**9** ratio would not be the same for **1** as for **2**. The hypothesis that **9** arises from enolates corresponding to **1** and **2**, but not from the corresponding enols, is supported by the experiments with **2** (X = Br) and 2,6-lutidine in refluxing methanol. 2,6-Lutidine catalyzes the formation of methoxy ketones **6** and **11** and of ester **5** and indanone **9**, but addition of 0.5 mol of *p*-toluenesulfonic acid causes **5** and **9** to disappear. This can be explained if **6** and **11** arise from the enol whereas **5** and **9** arise from the enolate ion, since the concentration of the latter will be much lower in the buffered medium. The reversal of the **5**:**9** ratio appears to be a temperature effect since it was observed also in the inverse addition experiment with methoxide. This suggests that the reaction leading to indanone **9** has a higher activation energy than that leading to ester **5**.

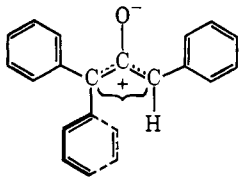
The observation that indanone **12** is the principal product from **3** or **4** with 2 *M* as well as with 0.05 *M* sodium methoxide shows that **12** is being formed from the corresponding enolate ion rather than the enol. Again a dipolar ion intermediate J is a reasonable precursor to the indanone **12**. The question arises, however, as to why J should be converted to **12** to a much larger extent than is I to **9** and why K forms no indanone whatsoever.

(12) The principal reaction with $PhCHClCOCH_3$ under these conditions is epoxy ether formation.[2] The yield of Favorskii ester from $PhCHClCOCH_3$ can be increased to 63%, however, by making the solution 2 *M* in $LiClO_4$ and increasing the temperature to 65°.[3]

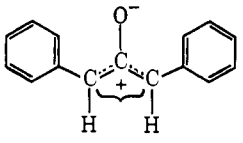
(13) For example, solvolysis of Ph_2CClCH_3 is 490,000 times faster than solvolysis of $PhCHClCH_3$ in 90% acetone–water at 25°.[14]

(14) H. C. Brown and T. Inukai, *J. Amer. Chem. Soc.*, **80**, 4964 (1958).

(15) The rate acceleration is not accompanied by an increase in yield because the yield with $PhCH_2COCH_2X$ is already nearly quantitative.[4] The 1% of Ph_2CHCO_2Me formed in the inverse addition reaction of 2 (X = Cl) presumably comes from addition of MeO^- to the carbonyl group and elimination of CH_2Cl^- in a haloform type reaction. At higher temperature (refluxing NaOEt–EtOH) a 12% yield of Ph_2CHCO_2Et is formed.[5]



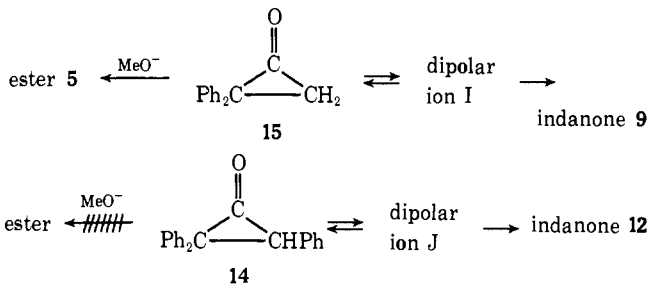
J



K

One would expect K to be of a stability comparable to J and to be more stable than I.[16] Reaction of 1-chloro-1,3-diphenylpropanone with 0.05 *M* NaOMe–MeOH gives 26% Favorskii ester, 36% α-methoxy ketone, and *ca.* 40% unidentified products.[5] (In 50% (v/v) H_2O–MeOH with 0.05 *M* base, 20% ester and 72% α-methoxy ketone are formed.[17]) K should give the same indanone **9** as is obtained from **1**, but neither **9** nor its oxidation product **7** was present. There is no obvious reason to expect K to be formed less readily than J. But K can undergo a disrotatory process readily to give a cyclopropane, the presumed intermediate leading to Favorskii ester, whereas disrotation for J will bring one of the electron-deficient carbon atoms in bonding distance to the ortho position on the phenyl ring making indanone formation highly probable. This is not the whole story, however, since the same is true for I, which is represented as forming **9** as the *minor* product.

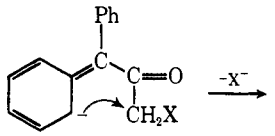
Another question posed by the results is the role methoxide ion concentration plays. Indanone **9** is formed only at low methoxide ion concentrations whereas indanone **12** is formed at either low or high methoxide ion concentrations. It would seem that competition from the alternative pathway, ester formation, has been eliminated in the latter instance. One way to accommodate these observations is to assume that a rapid equilibrium is set up between dipolar ions I and J and the corresponding cyclopropanones **15** and **14**.[18]



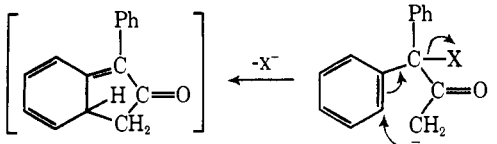
With **15**, the rate–equilibrium balance is apparently such that formation of **5** and **9** is competitive.[19] A change in solvent from methanol to 50% (v/v) H_2O–MeOH caused an increase in the amount of indanone **9** relative to ester **5**. This is consistent with a shift in the equilibrium toward dipolar ion, which would be expected to be more effectively solvated by water than by methanol.

The exclusive formation of indanone **12** from **3** or **4**, even at high methoxide concentrations, is explicable if we assume either that (a) the cyclopropanone **14** ⇄ dipolar ion J equilibrium strongly favors J, or that (b) the rate of formation of indanone **12** from J is much faster than the rate of formation of the ester by attack of methoxide ion on **14**, or its hemiketal.[19]

The constancy of the ratio **5**:**9** at low methoxide ion concentrations is difficult to rationalize by mechanisms which do not invoke a common intermediate. For example, it is conceivable that the intermediate (I′) leading to indanone **9** might be formed as follows.



enolate ion from **2**



I′

enolate ion from **1**

This mechanism is highly unlikely since it would require that this process compete with the accompanying Favorskii rearrangement to the same degree for the enolate ion derived from **1** (X = Cl) as for that derived from **2** (X = Cl or Br). This is, in essence, an extension of the π-participation mechanism suggested in earlier papers.[3,4] Here the possibility of π overlap over the whole system in the transition state would appear to be particularly favorable because of the absence of strain. The data indicate, however, that π participation by remote atoms (C-1 and C-5) is unimportant, which raises doubts about the importance of this effect in other systems as well.[20]

Conclusions

Our conclusion is that loss of halide ion from carbanion intermediates in these and other Favorskii rearrangements proceeds without appreciable 1,3-π participation to form a dipolar ion as a primary intermediate. This dipolar ion can undergo a disrotatory process to form a cyclopropanone, which reacts with alkoxide ion and solvent to form the Favorskii ester. Indanones may either be formed from dipolar ions in lieu of cyclopropanones (in properly substituted systems), or may be formed from phenyl-substituted cyclopropanones with which they are in equilibrium.[18]

Experimental Section

1-Chloro-1,1-diphenylacetone (1, X = Cl). Sulfuryl chloride (6.50 g; 48.2 mmol) in 10 ml of carbon tetrachloride was added rapidly at 25° to 10.0 g (47.6 mmol) of 1,1-diphenylacetone in 30 ml of carbon tetrachloride. After refluxing for 8 hr, the solvent was removed and nmr analysis showed only about 60% conversion had occurred. The proper amount of sulfuryl chloride was added and

(16) For steric reasons the third phenyl group in J cannot be coplanar with the allylic system and the other two phenyl groups. For this reason J is probably not much more stable than K. Also, for steric reasons, K is probably more stable than I.

(17) M. W. Carlson, Ph.D. Dissertation, Northwestern University, Aug 1969.

(18) Recent calculations by R. Hoffmann (*J. Amer. Chem. Soc.*, **90**, 1475 (1968)) indicate that the dipolar ion ("oxyallyl") would be favored at equilibrium relative to either cyclopropanone or allene oxide.

(19) N. J. Turro and W. B. Hammond (*ibid.*, **87**, 3258 (1965)) have presented evidence, using tetramethylcyclopropanone and its hemiketal, which suggests that the cyclopropanone, hemiketal, and dipolar ion are all in equilibrium in methanol solution. The hemiketal is the principal species present, and it is converted almost quantitatively to the Favorskii ester.

(20) It is of interest in this connection that R. H. Griffin and J. G. Jewett (*ibid.*, **92**, 1104 (1970)) have concluded on the basis of secondary deuterium isotope effects that solvolytic transition states leading to allylic cations reflect but little 1,3-π interaction.

refluxing was continued for 15 hr. The solvent was removed and the orange solid which resulted was dissolved in chloroform and filtered through 200 g of silica gel to remove the tars and color. Crystallization of the product from pentane afforded 7.5 g (30.7 mmol; 64%) of 1-chloro-1,1-diphenylacetone: mp 63–64° (lit.[6] mp 65–66°); λ_{max}^{KBr} 5.82 (C=O), 6.70, 6.90, 7.38, 8.41, 8.53, and 12.03 μ; $\delta_{TMS}^{CDCl_3}$ 7.32 (s, 10, Ph) and 2.36 (s, 3, CH_3).

1-Bromo-1,1-diphenylacetone (1, X = Br) was prepared by the procedure of Stevens and Lenk.[21]

Favorskii Reaction of 1 (X = Cl). A 1.00-g (4.1 mmol) sample of **1** (X = Cl) was added in one portion to 150 ml of 0.05 *M* sodium methoxide in methanol at 0°. After stirring for 2 hr, the solution was poured into saturated brine and extracted with ether (three 50-ml portions). The combined organic phases were washed with dilute sodium bicarbonate solution and with water, and dried over magnesium sulfate. The solvent was removed and the resulting oil was adsorbed onto a 50-g silica gel column. Elution with 5% ether in hexane afforded 961 mg (4.0 mmol; 98%) of methyl 3,3-diphenylpropionate: mp 45–46° (lit. mp 43–45°,[22] 48°[23]); λ_{max}^{KBr} 5.75 (C=O), 6.68, 6.87, 6.97, 7.97, and 8.58 μ; $\delta_{TMS}^{CDCl_3}$ 7.22 (s, 10, Ph), 4.57 (t, 1, J = 7 Hz), 3.49 (s, 3, OCH_3), and 3.02 (d, 2, J = 7 Hz, CH_2).

Reaction of 1 (X = Cl) with Sodium Methoxide in Methanol-*O-d*. Sodium (145 mg; 6.31 mg-atoms) was dissolved in 50 ml of methanol-*O-d* and the solution was cooled to 0°. 1-Chloro-1,1-diphenylacetone (500 mg; 2.05 mmol) was added in one lot. After stirring for 15 min (6 half-lives), the solution was acidified with dilute nitric acid and poured into water and ether. The aqueous layer was extracted with ether (two 50-ml portions) and the combined organic layers were washed with water, dried over magnesium sulfate, and concentrated. Chromatography on silica gel gave 454 mg (1.89 mmol; 92%) of methyl 3,3-diphenylpropionate, mp 45–46°. Nmr analysis showed only 0.23 D at α-C or only 11.5% exchange prior to rearrangement.

Reaction of 1 (X = Br) with Sodium Methoxide in Methanol-*O-d*. The same procedure as for **1** (X = Cl) was used for the reaction of 550 mg (1.91 mmol) of **1** (X = Br) and 127 mg (5.52 mg-atoms) of sodium in 50 ml of methanol-*O-d*. The reaction was terminated after 6 min and chromatography on silica gel afforded 413 mg (1.72 mmol; 90%) of methyl 3,3-diphenylpropionate, mp 45–46°. Nmr analysis showed only 0.12 D at α-C, or *ca.* 6% exchange prior to rearrangement.

Solvolysis of 1 (X = Cl) in Methanol. A 10^{-3} *M* solution of **1** (X = Cl) in methanol was prepared and allowed to stand at 25°. After 5 hr, only 6.4% reaction had occurred as determined by halide titration. After 17 hr, 23% of the chloride was present as free ions. The same method of analysis was used as with the kinetic titrations.

The Inverse Addition Procedure for the Reaction of 1 (X = Cl) with Sodium Methoxide in Methanol. A 2.00-g (8.2 mmol) sample of **1** (X = Cl) was dissolved in 100 ml of methanol. To this solution was added, over 6.5 hr, 180 ml of 0.05 *M* sodium methoxide solution (25°). The reaction gradually turned very dark during the addition, and after stirring for 1.5 additional hr the solution was neutralized with acetic acid. The bulk of the methanol was removed and the residue was taken up in water and ether. The aqueous layer was washed with ether and the combined organic fractions were washed with dilute sodium bicarbonate solution and with water, and dried over magnesium sulfate. The solvent was removed and the residue was adsorbed onto a 70-g silica gel column and eluted with 1 l. of 3%, 1 l. of 6%, 0.5 l. of 15%, 0.5 l. of 25%, 1 l. of 30%, and 0.5 l. of 50% ether in hexane. The 250-ml cuts numbered 3–7 contained 1268 mg of a mixture of 1-methoxy-1,1-diphenylacetone and methyl 3,3-diphenylpropionate. The mixture was analyzed by glc and nmr and contained 935 mg (3.9 mmol; 48%) of Favorskii ester and 333 mg (1.39 mmol; 17%) of methoxy ketone, identified by comparison with an authentic sample[21] (glc peak enhancement, and mixture nmr analysis). Fractions numbered 9–14 contained 376 mg (1.57 mmol; 19%) of a yellow oil, identified as methyl *o*-benzoylphenylacetate: λ_{max}^{film} 5.75 (C=O), 6.01 (ArCO), 7.85, and 8.55 μ [lit.[10] 5.78 (C=O) and 6.01 (ArCO)]; $\delta_{TMS}^{CDCl_3}$ 7.2–8.0 (m, 9, Ar), 4.04 (s, 2, CH_2), and 3.63 (s, 3, OCH_3).

Treatment of the ester with methanolic sodium hydroxide afforded *o*-benzoylphenylacetic acid: mp 131–132° (lit.[9] 130–131°); neut equiv 245; λ_{max}^{KBr} 2.8–4.1 (broad), 5.87, 6.03, 7.70, 7.82, 8.02, 10.56, and 12.91 μ; $\delta_{TMS}^{CDCl_3}$ 11.77 (s, 1, CO_2H), 7.5–8.3 (m, 9, Ar), and 4.00 (s, 2, CH_2).

Anal. Calcd for $C_{15}H_{12}O_3$: C, 74.99; H, 5.04. Found: C, 74.82; H, 5.06.

Cuts numbered 17–21 contained 110 mg of dark red viscous tar which gave only very broad peaks in the nmr. The bicarbonate washes above were acidified and extracted with ether. About 90 mg of red tar was also obtained from these acid fractions.

The Inverse Addition Reaction of 1 (X = Cl) under Nitrogen. A 0.05 *M* sodium methoxide in methanol solution (90 ml) was added dropwise over a 6-hr period to 1.00 g (4.1 mmol) of **1** (X = Cl) in 50 ml of methanol (25°). The system had been evacuated and filled with nitrogen prior to the start of the reaction. After stirring for an additional hour, the solution (which remained yellow throughout the reaction) was neutralized with acetic acid and worked up as previously described. The crude product was adsorbed onto a silica gel column (70 g) and eluted with 1 l. of 3% and 1.5 l. of 6% ether in hexane. Fraction (250 ml) number 3 contained 46 mg of 1-methoxy-1,1-diphenylacetone (with spectral properties identical with those of an authentic sample): λ_{max}^{film} 5.82 (C=O), 6.90, 9.12, and 9.27 μ; $\delta_{TMS}^{CDCl_3}$ 7.36 (m, 10, Ph), 3.08 (s, 3, OCH_3), and 2.21 (s, 3, CH_3). Fraction 4 contained 321 mg of a mixture of methoxy ketone (30%) and methyl 3,3-diphenylpropionate (70%) as determined by both glc and nmr analysis. Fraction 5 contained 361 mg of a mixture of ester (66%) and 1-phenyl-2-indanone (34%). Fraction 6 contained 106 mg of a mixture which was 63% indanone and 37% ester. Fractions 5, 6, and 7 were dissolved in 95% ethanol and treated with 2,4-dinitrophenylhydrazine reagent. A yellow precipitate formed immediately and after two recrystallizations from ethanol–chloroform had mp 197° dec. A mixture melting point with the DNP derivative obtained from authentic 1-phenyl-2-indanone had mp 196–197° dec. The total yields were: 1-methoxy-1,1-diphenylacetone, 142 mg (0.59 mmol; 14%); methyl 3,3-diphenylpropionate, 474 mg (1.98 mmol; 48%); and 1-phenyl-2-indanone, 188 mg (0.90 mmol; 22%). The nmr spectra of the ester–indanone mixtures were identical with those of mixtures prepared from authentic samples.

In another experiment the yields were 125 mg (0.52 mmol; 13%) of methoxy ketone, 509 mg (2.12 mmol; 52%) of ester, and 207 mg (1.00 mmol; 24%) of indanone.

1-Phenyl-2-indanone (9) was prepared by the method of Smith and Wilson.[11] Distillation afforded 2.5 g (12.0 mmol; 70%) of 1-phenyl-2-indanone which solidified on standing. Crystallization from hexane gave large prisms: mp 47–49° (lit.[11] mp 51–53°); bp 139–142° (0.5 mm); λ_{max}^{KB} 5.72 (C=O), 6.69, 6.89, 8.78, 13.43, and 14.26 μ; $\delta_{TMS}^{CCl_4}$ 6.9–7.4 (m, 9, Ar), 4.58 (s, 1, CH), 3.53 (s, 2, CH_2).

The 2,4-dinitrophenylhydrazone derivative had mp 193–195° dec (lit.[11] mp 199°).

The Reaction of 1-Phenyl-2-indanone (9) with Sodium Methoxide in Methanol (O_2 Present). A 300-mg (1.44 mmol) sample of **9** was added in one portion to 25 ml of 0.05 *M* sodium methoxide solution. The solution soon started to turn dark and after 2 hr no starting material could be detected. The solution was neutralized with acetic acid and the methanol was removed. The residue was taken up in ether and water and the aqueous phase was washed again with ether. The combined organic fractions were washed with water, dried over magnesium sulfate, and concentrated. The resulting oil (335 mg) was evaporatively distilled to give 231 mg (0.91 mmol; 63%) of methyl *o*-benzoylacetate, bp 150° at 0.5 mm, with spectral properties identical with those previously described.

3-Chloro- and 3-Bromo-1,1-diphenylacetone (2). The preparation of **2** (X = Cl) was carried out as described by Stevens and Sherr:[6] mp 68.5–69.5° (lit. mp 66–67°); $\delta_{TMS}^{CCl_4}$ 7.30 (s, 10, Ph), 5.42 (s, 1, CH), and 4.18 (s, 2, CH_2).

2 (X = Br) was prepared by Robert Frame by the method of Stevens and Lenk;[21] mp 68° (lit. 68.5–69.5°).

Favorskii Reaction of 2 (X = Cl). A 1.00-g (4.1 mmol) sample of **2** (X = Cl) was added in one portion to 200 ml of 0.05 *M* sodium methoxide at 0°. After stirring for 2 hr, the solution was processed as in the procedure with **1**. The dry organic fraction was concentrated and gave a light yellow oil (1.050 g). Nmr analysis of the crude product showed methyl 3,3-diphenylpropionate as the only discernible product. Chromatography afforded 975 mg (4.06 mmol; 99%) of the ester, mp 41–44°.

Quantitative Analysis of the Inverse Addition Reaction Products. A. Reaction of 1 (X = Cl). A 1.00-g (4.1 mmol) sample of **1** (X = Cl) was dissolved in 50 ml of methanol. Sodium methoxide solution (180 ml; 0.025 *M*) was added during 16 hr. The work-up was as previously described. The reaction product was dissolved in

(21) C. L. Stevens and C. T. Lenk, *J. Org. Chem.*, **19**, 538 (1954).
(22) W. G. Dauben, C. F. Hiskey, and M. A. Muhs, *J. Amer. Chem. Soc.*, **74**, 2082 (1952).
(23) D. Vorlander, E. Rack, and W. Leister, *Ber.*, **56**, 1131 (1923).

deuteriochloroform and the product ratios were determined from the nmr spectrum using successive integrations. The ratio of ester to indanone was 1.69:1.0; 100 μl (1.408 mmol) of dimethyl sulfoxide was added to the nmr tube and the spectrum was integrated again. The yield of methyl 3,3-diphenylpropionate was 1.11 mmol (27%). The yield of 1-phenyl-2-indanone was 0.657 mmol (16%), and there was 1.63 mmol (40%) of 1-methoxy-1,1-diphenylacetone.

B. Reaction of 2 (X = Cl). Using the same procedure for analysis as described in A, 500 mg (2.05 mmol) of **2** (X = Cl) when treated with 45 ml of 0.05 *M* sodium methoxide solution during 7 hr afforded 1.10 mmol (54%) of methyl 3,3-diphenylpropionate, 0.667 mmol (31%) of 1-phenyl-2-indanone, and about 0.07 mmol (3%) of 1-methoxy-1,1-diphenyl-2-propanone. The ratio of Favorskii ester to indanone is 1.64:1.

C. Reaction of 2 (X = Br). The reaction of 500 mg (1.73 mmol) of **2** (X = Br) and 40 ml of 0.05 *M* sodium methoxide added over 7 hr was carried out as described above. Nmr analysis showed 0.97 mmol (56%) of methyl 3,3-diphenylpropionate, 0.584 mmol (34%) of 1-phenyl-2-indanone, and 0.036 mmol (2%) of 1-methoxy-1,1-diphenylacetone. The ratio of Favorskii ester to indanone is 1.66:1.

D. Method of Analysis. The nmr spectrum of the mixture of these products contained an ester triplet at 4.57 ppm and an indanone singlet at the same place. The ester OCH_3 singlet and the indanone CH_2 singlet at 3.49 and 3.53 also overlapped. The ester doublet at 3.02 and the methoxy ketone OCH_3 singlet at 3.08 ppm were integrated together but the area due to methoxy ketone could be subtracted since the methoxy ketone α-methyl peak at 2.21 ppm could be easily integrated. The area due to the ester CH_2 group was thus determined, and from this the relative amount of indanone could be determined from either of the other sets of peaks (*i.e.* at 4.57 and 3.49 ppm).

1-Bromo-1,1,3-triphenylpropanone (3). To 10 g (0.035 mol) of 1,1,3-triphenylacetone[24] in 50 ml of carbon tetrachloride there was added 6.08 g (0.038 mol) of bromine at $-10°$ (reaction initiated by adding a few drops of bromine at room temperature). The residue obtained was found by nmr analysis to consist of a mixture of *ca.* 40% **3** and 60% **4**. Crystallization from hexane gave 2.5 g (12%) of **3**: mp 102°; $\delta_{TMS}^{CCl_4}$ 7.1 (s, 5), 7.25 (s, 10), 3.95 (s, 2).

Anal. Calcd for $C_{21}H_{17}BrO$: C, 69.04; H, 4.69. Found: C, 69.09; H, 4.82.

3-Bromo-1,1,3-triphenylpropanone (4). The bromination of 1,1,3-triphenylpropanone was repeated, and then 5 ml of ether was added to the reaction mixture. After 30 min at room temperature the solvent was evaporated and the residue crystallized from cyclohexane giving 10.2 g (80%) of 3-bromo-1,1,3-triphenylacetone (**4**): mp 35°; $\delta_{TMS}^{CCl_4}$ 7.2 (m, 15), 5.45 (s, 1), 5.38 (s, 1).

Anal. Calcd for $C_{21}H_{17}BrO$: C, 69.04; H, 4.69. Found: C, 69.14; H, 4.81.

Isomerization of **3** to **4** under hydrogen bromide catalysis was also effected in a separate experiment with **3** in CCl_4–Et_2O; no reaction occurred in the absence of ether.

1,3-Diphenyl-2-indanone (12) from 3 or 4. To 60 ml of 0.5 *M* NaOMe—MeOH saturated with nitrogen was added 3.65 g (0.01 mol) of either **3** or **4** in 20 ml of chloroform. After 30 min at room temperature, the solution was neutralized with dilute hydrochloric acid, evaporated (at 40°) to a volume of 15 ml, and extracted with chloroform. The extract was washed with water, dried, and evaporated to yield 2.8 g (97%) of **12**, mp 169° dec; lit.[25] mp 169° dec. A similar, but small scale reaction in 2 *M* NaOMe–MeOH gave (by nmr analysis) *ca.* 70% **12** and 30% unidentified material (decomposition products of **12**). Identification of **12** followed from its melting point, nmr ($\delta_{TMS}^{CDCl_3}$ 7.0–7.4 (m, 14), 4.79 (s, 2)), and elemental analysis.

Anal. Calcd for $C_{21}H_{16}O$: C, 88.72; H, 5.67. Found: C, 88.78; H, 5.88.

A solution of 3.65 g (0.01 mol) of **3** in 20 ml of chloroform was added to 10 ml of 2,6-lutidine and 40 ml of methanol. After 60 min at room temperature, the solution was diluted with 100 ml of water and extracted with three 150-ml portions of chloroform. The extract was washed with water, 2 *N* hydrochloric acid, and again with water. After drying and evaporation there was obtained 80% of 1,3-diphenylindanone (**12**).

Treatment of **4** (0.2 g) as described above gave no reaction. When repeated under reflux for 8 hr there was obtained 85% of 1,3-diphenylindanone (**12**).

Reaction of 12 with Oxygen in Sodium Methoxide. Addition of 1 *M* NaOMe–MeOH to a solution of **12** in methanol caused the immediate development of a high intensity at 305 nm. During an hour the intensity of this peak decreased and a new band at 253 nm developed. This behavior is qualitatively similar to that observed with 1-phenyl-2-indanone, and the rates are of a comparable order of magnitude. The kinetics were erratic, however, and no quantitative measurements were achieved. The product(s) of this oxidation were not identified.

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