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Formic Acid Reduction. XII.[1] Reductive Fission of Bridged Carbon-Carbon Bond of α,α'-Benzylidene- and α,α'-Methylene-bisketones

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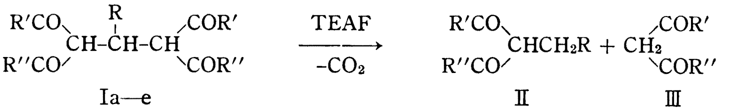
Reductive fission of one of the carbon-carbon bonds of the alkylidene- or arylmethylene-bond bridged between the two active carbons has been generalized in several examples by means of heating with the formate, triethylammonium formate which has been known as a distil lable liquid given by $5HCO_2H \cdot 2NEt_3$.

In a series of the previous papers dealing with the reactions of the formate reagents,[3] which have been known as distillable liquids composed of formic acid and trialkylamine, the reductive fission of one of the carbon-carbon bonds of the alkylidene- or arylmethylene-bond bridged between the two active carbons has been realized with a number of certain derivatives of barbituric acid[4] and of dimedone.[5] Since these recent works on this formate reaction are restricted within the reactions with such derivatives, we were tempted to investigate into the general applicability of this novel reductive fission reaction by extending to other compounds. The present study was undertaken to examine a program to develop the reaction to methylene- and benzylidene-bridged compounds of various active methylene.

Five α,α'-benzylidene- and α,α'-methylene-bis-β-diketones, Ia—e, shown in Table I were selected as substrates for the reaction. Using triethylammonium formate (TEAF) ($5HCO_2H \cdot 2NEt_3$) as a formate, these compounds were allowed to react on heating with this formate. Conditions and results are summerized in Table I. The reaction proceeded as expected in the following equation, with considerable emission of carbon dioxide, to give α-alkyl-substituted β-diketone (II) and β-diketone (III).



$$\begin{array}{l}R'CO \\ R''CO\end{array}\!\!>CH-\overset{\displaystyle R}{\overset{|}{C}}H-CH<\!\!\begin{array}{l}COR' \\ COR''\end{array} \xrightarrow[-CO_2]{TEAF} \begin{array}{l}R'CO \\ R''CO\end{array}\!\!>CHCH_2R + CH_2<\!\!\begin{array}{l}COR' \\ COR''\end{array}$$

Ia—e II III

From the previously reported formate reactions of barbituric acid[4] and dimedone,[5] there was considered a possibility that one of the product, β-diketone, III, undergoes successive methylation by reacting with the formate, but preliminary trials showed no methylation was occurred with these β-diketones.

Formation of equimolar amount of products II and III in theory were realized except runs 2 and 5 (see Table I). In run 2, as a secondary reaction product, acetophenone, formed through acid fission of 1,3-diphenyl-1,3-propanedione was obtained in 19% yield. In run

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[1] Part XI: K. Mori, H. Sugiyama and M. Sekiya, *Chem. Pharm. Bull.* (Tokyo), **19**, 1722 (1971).

[2] Location: *2-2-1 Oshika, Shizuoka.*

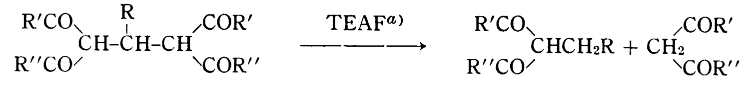
[3] The following formates composed of formic acid and trialkylamine have been known as constant boiling liquids possessing the given compositions. Triethylammonium formate (TEAF), bp 95° (15 mmHg), $5HCO_2H \cdot 2NEt_3$ [K. Ito, *Yakugaku Zasshi*, **86**, 1166 (1966)]. Trimethylammonium formate (TMAF), bp 91—92° (18 mmHg), $5HCO_2H \cdot 2NMe_3$; 1-Methylpiperidinium formate, bp 100.5° (20 mmHg), $5HCO_2H \cdot 2CH_3NC_5H_{10}$; 1-Methylmorphorinium formate, bp 89—90° (20 mmHg), $5HCO_2H \cdot 2CH_3NC_4H_8O$ [M. Sekiya and K. Ito, *Chem. Pharm. Bull.* (Tokyo), **12**, 677 (1964)].

[4] M. Sekiya and C. Yanaihara, *Chem. Pharm. Bull.* (Tokyo), **17**, 738 (1969); *idem, ibid.*, **17**, 752 (1969).

[5] M. Sekiya and K. Suzuki, *Chem. Pharm. Bull.* (Tokyo), **19**, 1531 (1971); *idem, ibid.*, **19**, 1540 (1971).

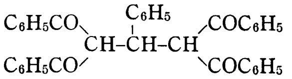
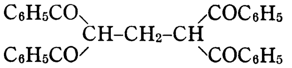
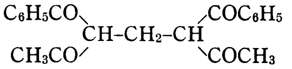
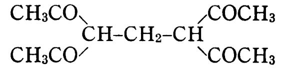
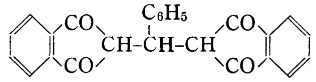
5, in addition to the product, II, two products, threads, IV, mp>350°, and prisms, V, mp 154°, were obtained. That these two compounds are secondary reaction products from 1,3-indandione, which should be formed, was confirmed by trial of the reaction of 1,3-indandione with TEAF, where the formations of IV and V in nearly similar proportion were realized. The product IV was identified as 5H-diindeno[1,2-*a*;1′,2′-*c*]fluorene-5,10,15-trione, which has been known[6] as the product obtained by treating 1,3-indandione with sulfuric acid or pyridine, by direct comparisons of its infrared (IR) and ultraviolet (UV) spectra with those of a synthetic authentic specimen. The product V was identified as [1,2′-diindan]-1′,3,3′-trione, reported previously,[7] by noting well correspondence of its physical and spectral data with its structure.

Table I. TEAF Reaction of α,α′-Benzylidene- and α,α′-Methylene-bis-β-diketones

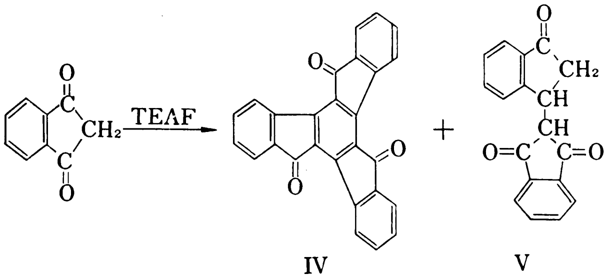


$(R'CO)(R''CO)CH\text{-}CH(R)\text{-}CH(COR')(COR'') \xrightarrow{TEAF^{a)}} (R'CO)(R''CO)CHCH_2R + CH_2(COR')(COR'')$

Ia—e II III

Run No.	Substrate	Compd. No.	Reaction Temp. °C	Reaction Time hr	% Yield of product II	% Yield of product III
1	 $(C_6H_5CO)_2CH\text{-}CH(C_6H_5)\text{-}CH(COC_6H_5)_2$	Ia	145—150	3.0	91	91
2	 $(C_6H_5CO)_2CH\text{-}CH_2\text{-}CH(COC_6H_5)_2$	Ib	145—150	8.0	92	75[b)]
3	 $(C_6H_5CO)(CH_3CO)CH\text{-}CH_2\text{-}CH(COC_6H_5)(COCH_3)$	Ic	145—150	2.5	36	34
4	 $(CH_3CO)_2CH\text{-}CH_2\text{-}CH(COCH_3)_2$	Id	145—150	1.5	10	10[c)]
5		Ie	120—125	2/3	68	0[d)]

a) Molar ratio of TEAF to substrate is 20: 1 (the former based on HCO_2H).
b) Acetophenone was obtained in 19% yield.
c) This product was isolated as 1-(*p*-nitrophenyl)-3,4,5-trimethylpyrazol.
d) 5H-diindeno-[1,2-*a*; 1′,2′-*c*]fluorene-5,10,15-trion (IV) and [1,2′-biindan]-1′,3,3′-trione (V) were obtained in 42% and 25% yields respectively.



IV V

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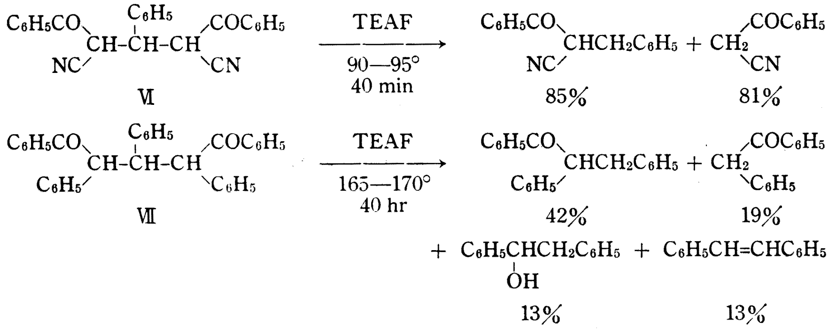
[6] J. Suszko and L. Wojcinski, *Ber.*, **69B**, 2452 (1936); M. Ionescu, *Ber.*, **60**, 1228 (1927); W.M. Fischer and A. Cirulis, *Ber.*, **65B**, 1852 (1932); J.N. Chatterjea, *J. Indian Chem. Soc.*, **36**, 69 (1959).

[7] G. Vanags and R. Zagats, *Latvijas PSR Zinatnu Acad. Vestes*, **1960**, 67 [*C. A.*, **55**, 12372 (1961)].

In the runs 3 and 4, low yields of the products II and III are considered to be due to side path of aldol condensation of such substrates possessing methylketones.

The formate reaction was further examined with benzylidene compounds bridged to monoketones, such as benzoylacetonitrile and deoxybenzoin. Under the reaction condition similar to the foregoing experiments, results obtained are shown in the following.



$$(C_6H_5CO)(NC)CH\text{-}CH(C_6H_5)\text{-}CH(COC_6H_5)(CN)\ \text{(VI)} \xrightarrow[\text{90—95°, 40 min}]{\text{TEAF}} (C_6H_5CO)(NC)CHCH_2C_6H_5\ (85\%) + CH_2(COC_6H_5)(CN)\ (81\%)$$

$$(C_6H_5CO)(C_6H_5)CH\text{-}CH(C_6H_5)\text{-}CH(COC_6H_5)(C_6H_5)\ \text{(VII)} \xrightarrow[\text{165—170°, 40 hr}]{\text{TEAF}} (C_6H_5CO)(C_6H_5)CHCH_2C_6H_5\ (42\%) + CH_2(COC_6H_5)(C_6H_5)\ (19\%) + C_6H_5CH(OH)CH_2C_6H_5\ (13\%) + C_6H_5CH{=}CHC_6H_5\ (13\%)$$

The result obtained in the run with VI shows that, in comparison with the run 1 in Table I, acceleration of the reaction by substitution of benzoyl group by nitrile group is excellent. However, as can be seen from the result obtained in the run with VII, substitution of benzoyl by phenyl restrained the reaction in great deal, where higher temperature and longer time were needed for the reaction. In this run, lower yield of deoxybenzoin product is due to its further conversion into 1,2-diphenylethanol and *trans*-stilbene.

Experimental

Preparation of α,α′-Benzylidene- and α,α′-Methylene-bisketones——As substrates for the TEAF reaction, were prepared seven α,α′-benzylidene- and α,α′-metylene-bisketones, Ia, Ib, Ic (mp 80—81°), Id (mp 33—35°), Ie (mp 162—164°), VI and VII (mp 216—218°), from corresponding ketone and aldehyde. Among these compounds Ia, Ib and VI were best prepared by the following method using boron trioxide as a dehydrating agent, previously reported[5] in this laboratory for the preparation of analogous dimedone derivatives. To a solution of 0.04 mole of the corresponding ketone (1,3-diphenyl-1,3-propanedione or benzoylacetonitrile), 0.02 mole of aldehyde (benzaldehyde or paraformaldehyde) and piperidine (0.012 mole) dissolved in 60 ml of benzene was suspended 0.03 mole of granular boron trioxide and the mixture was refluxed with stirring. After filtration of the warm mixture, the filtrate was treated by usual isolation procedures. Reaction time, yield and identification of the products are described in the following.

2,4-Dibenzoyl-1,3,5-triphenyl-1,5-pentanedione (Ia): Refluxing for 8 hr. Yield, 27%. Needles (from EtOH) which showed mp 175—178° different from that of reported previously[8] (mp 157—158°). *Anal.* Calcd. for $C_{37}H_{28}O_4$: C, 82.81; H, 5.26. Found: C, 82.86; H, 5.38. IR $\nu_{\max}^{\text{KBr}}$ cm^{-1}: 1670, 1688 (C=O). UV $\lambda_{\max}^{\text{MeOH}}$ mμ (log ε): 252 (4.67).

2,4-Dibenzoyl-1,5-diphenyl-1,5-pentanedione (Ib): Refluxing for 2 hr. Yield, 99%. Needles (from EtOH), mp 176—177° (lit.,[9] mp 175.5—176°). *Anal.* Calcd. for $C_{31}H_{24}O_4$: C, 80.85; H, 5.25. Found: C, 80.91; H, 5.25. IR $\nu_{\max}^{\text{KBr}}$ cm^{-1}: 1669, 1685 (C=O). UV $\lambda_{\max}^{\text{KBr}}$ mμ (log ε): 250 (4.70), 282 (3.73, shoulder), 328 (2.91).

2,4-Dibenzoyl-3-phenylglutaronitrile (VI): Refluxing for 2 hr. Yield, 99%. Needles (from EtOH), mp 102—102.5° (lit.[10] mp 114°). *Anal.* Calcd. for $C_{25}H_{18}O_2N_2$: C, 79.35; H, 4.79; N, 7.40. Found: C, 79.18; H, 4.85; N, 7.46. IR $\nu_{\max}^{\text{KBr}}$ cm^{-1}: 2224 (C≡N), 1621 (C=O). UV $\lambda_{\max}^{\text{MeOH}}$ mμ (log ε): 233 (4.22, shoulder), 245 (4.27), 308 (4.36).

TEAF Reaction of α,α′-Benzylidene- and α,α′-Methylene-bisketones. General Procedure for the Reaction——Seven α,α′-benzylidene- and α,α′-methylene-bisketones, Ia—e, VI and VII were subjected to the

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[8] I.L. Finar, *J. Chem. Soc.*, **1961**, 674.

[9] S.V. Liberman and E.C. Wagner, *J. Org. Chem.*, **14**, 1001 (1949); H. Hellman and D. Dieterich, *Ann.*, **632**, 73 (1960).

[10] M. Ruccia, A. Arcoles and S. Cusmano, *Atti Accad. Sci., Lettetre Arti Palermo*, Pt I **23**, 184 (1964) [*C. A.*, **62**, 13138 (1965)].

formate reaction by the following general procedure. A mixture of the substrate and TEAF in 1: 20 (based on HCO_2H) molar proportion was heated with stirring, while a constant stream of dry air free from CO_2 or nitrogen was introduced in order to check transfer of emission of CO_2 by $Ba(OH)_2$ solution. The mixture was heated until emission of CO_2 was almost ceased. Reaction conditions, treatment of the reaction mixture and identification of the products are given in the following.

Reaction of 2,4-Dibenzoyl-1,3,5-triphenyl-1,5-pentanedione (Ia) with TEAF——A mixture of 10.7 g (0.02 mole) of Ia and 34.6 g (0.40 mole based on HCO_2H) of TEAF was heated at 145—150° for 3 hr. The mixture was concentrated under reduced pressure to remove triethylamine and excess of TEAF. The resulting residue was subjected to distillation *in vacuo* to give 1,3-diphenyl-1,3-propanedione as a solid distillate, bp 125—130° (0.017 mmHg). Yield, 4.1 g (91%). Prisms (from MeOH), mp 76—79°. Identity of the product was made by comparisons of its IR and UV spectra with those of an authentic sample and mixed melting point test. The foregoing solid distillation residue was recrystallized from EtOH gave needles, mp 99—103°, which was identified as 2-benzyl-1,3-diphenyl-1,3-propanedione by comparisons of its IR and UV spectra with those of an authentic specimen obtained by the previously reported method[11] and mixed melting point test. Yield, 5.7 g (91%). *Anal.* Calcd. for $C_{22}H_{18}O_2$: C, 84.05; H, 5.77. Found: C, 83.93; H, 5.83. IR $\nu_{\max}^{\mathrm{KBr}}$ cm^{-1}: 1662, 1692 (C=O). UV $\lambda_{\max}^{\mathrm{MeOH}}$ $\mathrm{m}\mu$ ($\log \varepsilon$): 249 (4.37), 321 (2.52, shoulder).

Reaction of 2,4-Dibenzoyl-1,5-diphenyl-1,5-pentanedione (Ib) with TEAF——A mixture of 9.2 g (0.02 mole) of Ib and 34.6 g (0.40 mole based on HCO_2H) of TEAF was heated at 145—150° for 8 hr. The reaction solution was concentrated under reduced pressure to remove triethylamine and excess of TEAF. Vaccum distillation of the residue gave a solid distillate, bp 139—148° (0.03 mmHg) which was composed of 1,3-diphenyl-1,3-propanedione and 2-methyl-1,3-diphenyl-1,3-propanedione. Separation of these was carried out by silica gel column chromatography using benzene as an eluent. Evaporation of the first eluent gave crystals of 1,3-diphenyl-1,3-propanedione. Prisms (from MeOH), mp 78—80°. Yield, 3.4 g (75%). Identity of the product was made by comparisons of its IR and UV spectra with those of the authentic sample. Evaporation of the second eluent gave crystals of 2-methyl-1,3-diphenyl-1,3-propanedione. Prisms (from MeOH), mp 81°. (lit.,[12] mp 83—84°). Yield, 4.4 g (92%). *Anal.* Calcd. for $C_{16}H_{14}O_2$: C, 80.64; H, 5.92. Found: C, 81.02; H, 6.12. IR $\nu_{\max}^{\mathrm{KBr}}$ cm^{-1}: 1662, 1685 (C=O) (lit.,[12a] IR $\nu_{\max}$ cm^{-1}: 1667, 1689). UV $\lambda_{\max}^{\mathrm{MeOH}}$ $\mathrm{m}\mu$ ($\log \varepsilon$): 246 (4.09), 279 (3.07) [lit.,[13] UV $\lambda_{\max}^{\mathrm{EtOH}}$ $\mathrm{m}\mu$ ($\log \varepsilon$): 246 (4.37), 282 (3.30)]. MNR (15% solution in $CDCl_3$) τ[14]: 8.42 (3H, doublet, $J=7.5$ cps, $-C\underline{H}_3$), 4.70 (1H, quartet, $J=7.5$ cps, $>C\underline{H}-$), 2.75—1.80 (10H, multiplet, aromatic protons).

The foregoing TEAF distillate was diluted with water and excess of KOH was added on cool. The liberated triethylamine layer was separated and dried over $MgSO_4$. Evaporation of the triethylamine and distillation of the residue gave oily material which was identified as acetophenone. Yield, 0.45 g (19%).

Reaction of 3,5-Dibenzoyl-2,6-heptanedione (Ic) with TEAF——A mixture of 13.5 g (0.04 mole) of Ic and 69.2 g (0.80 mole based on HCO_2H) of TEAF was heated at 145—150° for 2.5 hr. The reaction solution was concentrated under reduced pressure to remove triethylamine and excess of TEAF. The fractional distillation of the resulting residue gave an oily distillate, bp 77—80° (0.1 mmHg), and a solid distillate, bp 123—127° (0.1 mmHg). The former was identified as 2-methyl-1-phenyl-1,3-butanedione [lit.,[15] bp 104—105° (5 mmHg)]. Yield, 2.5 g (36%). *Anal.* Calcd. for $C_{11}H_{12}O_2$: C, 74.97; H, 6.86. Found: C, 74.85; H, 7.18. n_{D}^{26} 1.5230. IR $\nu_{\max}^{\mathrm{liq}}$ cm^{-1}: 1672, 1709 (C=O). UV $\lambda_{\max}^{\mathrm{MeOH}}$ $\mathrm{m}\mu$ ($\log \varepsilon$): 246.5 (3.84), 281.5 (2.97), 320 (2.56, shoulder). NMR (12% solution in $CDCl_3$) τ[14]: 8.59 (3H, doublet, $J=7.5$ cps, $-C\underline{H}_3$), 7.80 (3H, singlet, $-COC\underline{H}_3$), 5.18 (1H, quartet, $J=7.5$ cps, $>C\underline{H}-$), 2.70—1.55 (5H, multiplet, aromatic protons). The latter distillate was identified as 1-phenyl-1,3-butanedione. Prisms (from MeOH), mp 53—55°. Yield, 2.2 g (34%). This product was identified by comparisons of its IR and UV spectra with those of an authentic sample and mixed melting point test.

Reaction of 3,5-Diacetyl-2,6-heptanedione (Id) with TEAF——A mixture of 10.6 g (0.05 mole) of Id and 86.5 g (1.0 mole based on HCO_2H) of TEAF was heated at 145—150° for 1 hr in the stream of N_2 (stream of air is not preferable for this reaction). The reaction solution was distilled under reduced pressure. The first distillate trapped in a receiver cooled in a dry ice-acetone bath was redistilled to give 2,4-pentanedione, bp 137—140°, which was identified by comparisons of its IR and UV spectra with those of an authentic sample. Yield, 0.5 g (10%). Content of 3-methyl-2,4-pentanedione in the second formate distillate was isolated by the following procedures. To the distillate, 7.7 g (0.05 mole) of *p*-nitrophenylhydrazine was added and the mixture was heated at 100° for 1 hr. After removal of TEAF by evaporation under reduced pressure,

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[11] M. Sekiya and K. Suzuki, *Chem. Pharm. Bull.* (Tokyo), **18**, 1530 (1970).

[12] *a*) A.A. Scala, N.B. Bikales and E.I. Becker, *J. Org. Chem.*, **30**, 303 (1965); *b*) H.E. Zaugg, R.J. Michaels and E.J. Baker, *J. Am. Chem. Soc.*, **90**, 3800 (1968); C.R. Hauser, B.I. Ringler, F.W. Swamer and D.F. Thompson, *J. Am. Chem. Soc.*, **69**, 2649 (1947).

[13] A.S. Dreiding and J.A. Hartman, *J. Am. Chem. Soc.*, **75**, 3723 (1953).

[14] Tetramethylsilane (TMS) was used as an internal standard.

[15] L.I. Smith and J.R. Holum, *J. Am. Chem. Soc.*, **78**, 3417 (1956); C. Weygand and H. Forkel, *J. Pract. Chem.*, [2] **116**, 297 (1927).

the resulting crystalline residue was extracted with benzene. Evaporation of benzene and recrystallization of the residue from EtOH gave crystals of 1-(*p*-nitrophenyl)-3,4,5-trimethylpyrazol, mp 116—117° (lit.,[16] mp 116—117°), weighing 1.2 g (10% as 3-methyl-2,4-pentanedione), which was identified by comparisons of its IR spectrum with that of an authentic specimen preparded from 3-methyl-2,4-pentanedione and *p*-nitrophenylhydrazine in TEAF. A preliminary experiment showed that nearly quantitative yield of the product was gained by this pyrazol formation reaction in TEAF.

Reaction of 2,2′-Benzylidenebis-1,3-indandione (Ie) with TEAF——A mixture of 7.6 g (0.02 mole) of Ie and 34.6 g (0.40 mole based on HCO_2H) of TEAF was heated at 120—125° for 40 min. Yellow crystals were deposited in the reaction mixture in the course of the reaction. On cooling, the crystals which may be refered as 5H-diindeno[1,2-*a*;1′,2′-*c*]fluorene-5,10,15-trione were collected by filtration and recrystallized from $CHCl_3$. Yellow threads, mp>350° (lit.,[6] mp >360°), weighing 1.1 g (42%). *Anal.* Calcd. for $C_{27}H_{12}O_3$: C, 84.31; H, 3.15. Found: C, 84.21; H, 3.16. IR ν_{max}^{KBr} cm^{-1}: 1713 (C=O); 1603 (phenyl); 1208, 744 (disubstituted phenyl). UV λ_{max}^{MeOH} mμ (log ε): 303.5 (4.83), 323.5 (4.78). The filtrate was concentrated under high reduced pressure to remove triethylamine and excess of TEAF. The resulting residue was subjected to distillation *in vacuo* to give a solid distillate, bp 145—163° (0.04 mmHg), which was recrystallized from EtOH to give yellow prisms of 2-benzyl-1,3-indandione, mp 97—98°. Yield, 3.2 g (68%). Identity of this product was made by comparisons of its IR and UV spectra with those of an authentic specimen obtained by the previously reported method[11] and mixed melting point test. IR ν_{max}^{KBr} cm^{-1}: 1713, 1745 (C=O). UV λ_{max}^{MeOH} mμ (log ε): 225.5 (4.62), 248 (4.07). NMR (10% solution in dimethylsulfoxide-d_6)τ[14]: 6.78 (2H, doublet, J=6 cps, $-CH_2-$), 6.20 (1H, triplet, J=6 cps, $>C\underline{H}-$), 2.85 (5H, singlet, aromatic protons), 2.10 (4H, singlet, aromatic protons). The foregoing distillation residue was extracted with MeOH several times. After decolorization with charcoal and evaporation of MeOH, the resulting residue was recrystallized from MeOH to give prisms of [1,2′-diindan]-1′,3,3′-trione, mp 154° (lit.,[7] mp 155—156°). Yield, 0.7 g (25%). *Anal.* Calcd. for $C_{18}H_{12}O_3$: C, 78.25; H, 4.38. Found: C, 78.19; H, 4.42. IR ν_{max}^{KBr} cm^{-1}: 1711, 1749 (C=O). UV λ_{max}^{MeOH} mμ (log ε): 227 (4.68), 245 (4.32), 292.5 (3.43). NMR (15% solution in CF_3CO_2H) τ[14]: 6.72—6.87 (2H, quartet, C_2-$\underline{H}_2$), 5.91—5.97 (1H, doublet, C_2'-$\underline{H}$), 5.27—5.55 (1H, multiplet, C_1-$\underline{H}$), 1.70—2.70 (8H, multiplet, aromatic protons).

Reaction of 2,4-Dibenzoyl-3-phenylglutaronitrile (VI) with TEAF ——A mixture of 7.8 g (0.02 mole) of VI and 34.6 g (0.40 mole based on HCO_2H) of TEAF was heated at 90—95° for 40 min. The reaction solution was concentrated *in vacuo* to remove triethylamine and excess of TEAF. Vaccum distillation of the resulting residue gave a solid distillate, bp 107—153° (0.06 mmHg) which was composed of α-benzoylhydrocinnamonitrile and benzoylacetonitrile. Separation of these was carried out by silica gel column chromatography using benzene as an eluent. Evaporation of the first eluent gave crystals of α-benzoylhydrocinnamonitrile, prisms (from iso-Pr ether), mp 79—80° (lit.,[17] mp 79—80°). Yield, 4.0 g (85%). *Anal.* Calcd. for $C_{16}H_{13}ON$: C, 81.68; H, 5.57; N, 5.95. Found: C, 81.71; H, 5.56; N, 5.92. IR ν_{max}^{KBr} cm^{-1}: 2238 (C≡N), 1699 (C=O). UV λ_{max}^{MeOH} mμ (logε): 249 (4.09), 284 (3.41, shoulder). NMR (15% solution in $CDCl_3$)τ[14]: 6.75 (1H, doublet, J=9 cps, methylene proton), 6.73 (1H, doublet, J=6 cps. methylene proton), 5.45 (1H, quartet, J=6 and 9 cps, $>C\underline{H}-$), 2.00—2.75 (10 H, multiplet, aromatic protons). Mass Spectrum *m/e* (relative intensity): 235 (P, 12), 105 ($C_6H_5CO^+$, 100), 91 ($C_7H_7^+$, 10), 77 ($C_6H_5^+$, 38); metastable peak, 56.4 [$C_6H_5CO^+(105) \rightarrow C_6H_5^+(77) + CO$, Calcd., 56.5]. Removal of the second eluent gave crystals of benzoylacetonitrile which was identified by comparisons of its IR and UV spectra with those of an authentic sample prepared by the previously reported method.[18] Prisms (from iso-Pr ether), mp 80—81°. Yield, 2.6 g (81%).

Reaction of 1,2,3,4,5-Pentaphenyl-1,5-pentanedione (VII) with TEAF——A mixture of 9.6 g (0.02 mole) of VII and 34.6 g (0.40 mole based on HCO_2H) of TEAF was heated at 165—170° for 40 hr. The reaction was followed by checking TLC (silica gel-benzene) of the reaction mixture, because of emission of CO_2 owing to gradual decomposition of TEAF was observed at this high temperature. Crystals deposited in the reaction mixture on cool were collected as recovery of the starting VII. The filtrate was concentrated under reduced pressure to remove triethylamine and excess of TEAF, and the residue was extracted with benzene. Additional recovery of VII was obtained as insoluble material. Total recovery , 21%. Evaporation of the extract and distillation of the residue under reduced pressure gave a semisolid distillate, bp 130—165° (5 mmHg). The distillate was subjected to silica gel column chromatography using benzene as an eluent. Evaporation of the first eluent and washing the resulting residue with petr. ether gave crystals of *trans*-stilbene, plates (from petr. ether), mp 121—122°. Yield, 0.2 g (5.6%). *Anal.* Calcd. for $C_{14}H_{12}$: C, 93.29; H, 6.71. Found: C, 93.32; H, 6.78. IR ν_{max}^{KBr} cm^{-1}: 1494, 1598 (phenyl); 960.3 (*trans* -CH=CH-); 763 (phenyl). UV λ_{max}^{MeOH} mμ (log ε): 228.5 (4.24), 295 (4.48), 307 (4.46). NMR (10% solution in $CDCl_3$) τ[14]: 2.90 (2H, singlet, $-C\underline{H}=C\underline{H}-$), 2.80—2.35 (10H, multiplet, aromatic protons). Evaporation of the second eluent and washing theresulting residue with petr. ether gave crystals of 1,2-diphenylethanol. Prisms (from petr. ether), mp 60—65°. Yield,

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0.5 g (13%). *Anal.* Calcd. for $C_{14}H_{14}O$: C, 84.81; H, 7.12. Found: C, 84.31; H, 7.00. IR ν_{max}^{KBr} cm^{-1}: 3286 (OH); 1609, 1501, 763, 744, 700 (phenyl). NMR (10% solution in $CDCl_3$) τ14): 8.05 (1H, singlet, -OH), 7.00 (2H, doublet, $J=7$ cps, $-CH_2-$), 5.10 (1H, triplet, $J=7$ cps, $>CH-$), 2.74 (5H, singlet, aromatic protons), 2.65 (5H, singlet, aromatic protons). Deoxybenzoin was obtained by evaporation of the third eluent and recrystallized from MeOH. Prisms, mp 55—56°. Yield, 1.5 g (19%). Identity of this product was made by comparisons of its IR and UV spectra with those of an authentic sample prepared by the previously reported method19) and mixed melting point test.

The solid distillation residue obtained by the foregoing distillation of the benzene solution was recrystallized from EtOH to give needles of 1,2,3-triphenylpropanone, mp 114—116°. Yield, 2.4 g (42 %). Identity of this product was made by comparisons of its IR and UV spectra with those of an authentic specimen obtained by the previously reported method11) and mixed melting point test.

The foregoing TEAF distillate was diluted with water and added excess of KOH on cooling. After drying the liberated triethylamine layer over $MgSO_4$, evaporation gave additional *trans*-stilbene, weighing 0.3 g. Total yield, 0.5 g (13%).

Reaction of 1,3-Indandione with TEAF——A mixture of 7.3 g (0.05 mole) of 1,3-indandione and 86.5 g (1.0 mole based on HCO_2H) of TEAF was heated at 120—125° for 40 min. In the beginning, the reaction mixture became homogeneous liquid, but soon after yellow crystals were deposited. On cooling, the crystals were collected by filtration. Recrystallization from $CHCl_3$ gave yellow threads of 5H-diindeno[1,2-*a*;1',2'-*c*]fluorene-5,10,15-trione, mp>350°. Yield, 2.8 g (44%). Identity of the product was made by comparisons of its IR and UV spectra with those of the authentic specimen. The foregoing TEAF filtrate was concentrated under high reduced pressure to remove excess of TEAF. The resulting residue was triturated with MeOH to give fine crystals. Recrystallization of this material from MeOH gave prisms of [1,2'-diindan]-1',3,3'-trione, mp 153—154°, which was identified by comparisons of its IR and UV spectra with those of an authentic specimen. Yield, 2.4 g (35%).

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19) *Org. Syn.*, Coll. Vol. 2, P 156.