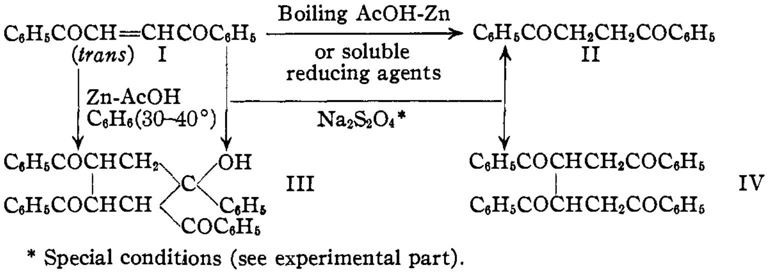
[CONTRIBUTION FROM THE COBB CHEMICAL LABORATORY, UNIVERSITY OF VIRGINIA]

The Reductions of Unsaturated 1,4-Diketones with Zinc Combinations. The Formation of the Cyclic Dimolecular Products

BY ROBERT E. LUTZ, LOWRY LOVE, JR., AND FRED S. PALMER

The reduction of unsaturated 1,4-diketones in homogeneous solution with soluble reducing agents leads exclusively to monomolecular products, the saturated 1,4-diketones or the corresponding furans. The mechanism undoubtedly involves initially the 1,6-addition of hydrogens or their equivalent at the oxygen atoms at the ends of the conjugated system, with oxidation–reduction potential a measure of the driving force in the reaction. The reduction with metal combinations, however, presents a more complex picture. *Trans*-dibenzoylethylene, which is reduced chiefly to dibenzoylethane (II) by zinc dust in hot glacial acetic acid, gives on slower reduction in the cold smaller amounts of II and very considerable yields of the dimolecular product, *cyclo*-bis-dibenzoylethane-A (III), the structure of which has been elucidated in the preceding paper. With zinc and benzene–glacial acetic acid mixtures at 30–35° (conditions most favorable to dimolecular reduction), there is produced largely the dimolecular product III and very little dibenzoylethane. In this type of reduction, therefore, dibenzoylethylene behaves to some extent like a simple α,β-unsaturated ketone.

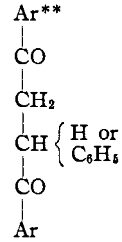


* Special conditions (see experimental part).

Of the various unsaturated 1,4-diketones, *trans*-dibenzoylethylene is the one most prone to give dimolecular reduction products. Using zinc and glacial acetic acid at room temperature (typical conditions under which *trans*-dibenzoylethylene gives largely the dimolecular product) only monomolecular products are obtained from the following

V	*Cis*-$C_6H_5COCH{=}CHCOC_6H_5$
VI	*Cis*- and *trans*-$ClC_6H_4COCH{=}CHCOC_6H_4Cl$
VII	*Trans*-$CH_3C_6H_4COCH{=}CHCOC_6H_4CH_3$
VIII	*Trans*-$(CH_3)_3C_6H_2COCH{=}CHCOC_6H_2(CH_3)_3$
IX	*Cis*-$C_6H_5COCBr{=}CBrCOC_6H_5$
X	*Cis*-$C_6H_5COCH{=}C(C_6H_5)COC_6H_5$***
XI	*Cis*-$C_6H_5COCBr{=}C(C_6H_5)COC_6H_5$
XII	$C_6H_5COCH_2CHX^*COC_6H_5$
XIII	*dl*- or *meso*-$C_6H_5COCHX^*CHXCOC_6H_5$

$\xrightarrow{\text{Zn AcOH}}$



$Ar^{**}-CO-CH_2-CH\{H \text{ or } C_6H_5\}-CO-Ar$

XIV

*X = Cl or Br. **Ar = Corresponding aromatic group. *** Gave mainly the corresponding furan.

Other examples have been described in earlier papers.[1]

It is a striking fact that in reductions with zinc and glacial acetic acid at room temperature *trans*-dibenzoylethylene gives largely *cyclo*-bis-dibenzoylethane-A (III) whereas the *cis* isomer gives a nearly quantitative yield of the monomolecular product II (although other conditions were found under which the *cis* isomer also gave III in considerable amounts).

The Mechanism of Dimolecular Reduction.—The fact that *cyclo*-bis-dibenzoylethane-A is obtained under reducing conditions under which the open chain isomers are stable, definitely excludes the possibility that the ethylene linkage alone is involved, and indicates that a conjugate reaction occurs with cyclization taking place through the intermediate enolic groups. The results therefore furnish positive evidence for the generally accepted hypothesis that the reduction of α,β-unsaturated ketones by metal combinations involves a conjugate mechanism with the reaction beginning on oxygen.

The usual 1,4-dimolecular reduction mechanism might seem to find support from the fact that under comparable conditions the *trans* isomer in

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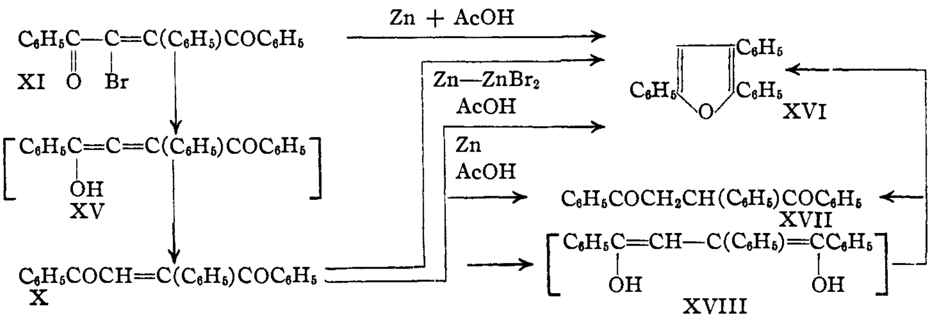
[1] (a) Lutz, THIS JOURNAL, **51**, 3008 (1929); (b) Lutz and Taylor, *ibid.*, **55**, 1593 (1933); (c) Lutz and Wilder, *ibid.*, **56**, 2065 (1934).

contrast with the *cis* gives chiefly the dimolecular product, although both stereoisomers are reduced with comparable ease.[2] The stereochemical factor, however, may be without significance in view of the fact that *trans*-dibenzoylethylene with respect to tendency to undergo dimolecular reduction is unique among the unsaturated 1,4-diketones including *cis*-dibenzoylethylene. In consideration of this fact and in view of the known reactivity of enolic intermediates, an alternative and equally plausible mechanism is 1,6-reduction followed by condensation between the resulting enol or enolate and the reactive conjugated system of another molecule of unreacted dibenzoylethylene.

The zinc–glacial acetic acid reduction of dibenzoylphenylbromoethylene XI is of interest in connection with the catalytic effect of zinc bromide which is generated during the reduction.[3] The furan XVI is the chief product of this reaction. It is produced in much smaller yield in the reduction of dibenzoylphenylethylene X, but becomes the major product when zinc bromide is added to the reagents. The fact that dibenzoylphenylethane XVII and triphenylbromofuran are stable under the reaction conditions shows that the loss of bromine and the dehydrations to the furan XVI occur at some intermediate stage, and indicates that in both reductions there is formed in the final step the same intermediate dienol or dienolate (XVIII). The elimination of bromine from XI undoubtedly takes place through 1,4-reduction of the α-bromo ketone to the allenic enol or enolate XV.[4]



The zinc–acetone reductions of *dl*- and *meso*-dibenzoyldibromoethanes XIX are of interest because, in contrast with the dibenzoyldichloro- and monohalogeno-ethanes (XIII and XII), considerable yields of *cyclo*-bis-dibenzoylethane-A are obtained. *Trans*-dibenzoylethylene does not react under these conditions but does so when zinc bromide is added to the reagent, the products being the same as those obtained in the reduction of the dibromides where the zinc bromide is generated during the reaction.[5] Dibenzoylbromoethylene is not reducible by the Zn–ZnBr$_2$–acetone reagent. These facts suggest that the reduction of the dibromides under these conditions proceeds partly at least through elimination of bromine with the intermediate formation of dibenzoylethylene, followed by competing mono- and dimolecular reduction.

$$\underset{\text{XIX}\quad dl\text{ or }meso}{C_6H_5COCHBrCHBrCOC_6H_5} \longrightarrow \left[\underset{trans}{C_6H_5COCH{=}CHCOC_6H_5}\right] \longrightarrow \text{I} + \text{II}$$

This mechanism is consistent with the following facts: (a) the yield of *cyclo*-bis-dibenzoylethane-A is much higher in the reduction of dibenzoylethylene than in the case of the dibromides, as would be expected in view of the necessarily higher concentration of dibenzoylethylene during the reaction; (b) the monomolecular product predominates when *trans*-dibenzoylethylene is added slowly to the Zn–ZnBr$_2$–acetone mixture over a period of several hours so that the concentration during reaction is very low, thus simulating conditions involved in the reduction of the dibromides; and (c) dibenzoylbromoethane (XII) which could not

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(2) Conant and Lutz, This Journal, **45**, 1047 (1923). In homogeneous solution where the configuration is without appreciable effect, both carbonyl groups of either *cis* or *trans* isomers are surrounded by reductant ions and may be supposed to react practically simultaneously. In the reduction of the *cis* compound by metal combinations, the spatially proximate carbonyl groups also should be able to react in quick succession or simultaneously at the metal surface, whereas the reaction with the *trans* compound, initiated at one carbonyl oxygen with the other spatially removed from the immediate source of hydrogen, could hardly be completed as easily and would afford the maximum opportunity for the dimolecular coupling to become a competing or even the dominant reaction.

(3) Lutz, Tyson, Sanders and Fink, This Journal, **56**, 2679 (1934).

(4) Such a hypothesis has been suggested in an earlier paper (Refs. 1c, 3). *Cf.* the formation of the allenic halogenomagnesium enolate by the action of the Grignard reagent on α-bromo-β-phenylbenzalacetophenone [Kohler and Tishler, This Journal, **57**, 217 (1935)], and also the reactions between the Grignard reagent or magnesium [Fisher, *ibid.*, **57**, 381 (1935)] and α-halogeno ketones.

(5) Probably the effective reducing agent is a Zn–ZnBr$_2$ combination analogous to the Mg–MgI$_2$ reagent of Gomberg and Bachmann [This Journal, **49**, 237 (1927)].

form dibenzoylethylene or its equivalent in an intermediate step, does not undergo dimolecular reduction.

Cis-dibenzoylethylene in contrast with the *trans* isomer is reduced by the Zn–$ZnBr_2$–acetone reagent to a mixture in which the monomolecular product predominates. From this fact, if the mechanism of reduction of the *dl* and *meso* dibromides suggested above is correct, it would follow that the *trans* isomer and not the *cis* is involved as intermediate, and that the elimination of halogen from the *dl* and *meso* dibromides does not take place in a consistent stereochemical sense.[6]

Experimental Part

Separation of the mixtures obtained in reductions where the dimolecular products are formed is exceedingly difficult and involves laborious fractional crystallizations. Mixtures of dibenzoylethane and *cyclo*-bis-dibenzoylethane-A were usually partly separated by taking advantage of the higher solubility and higher rate of solution, and also the more rapid rate of crystallization (despite its greater solubility) of the monomolecular product. Such mixtures were usually digested for a very short time with boiling ethanol and filtered quickly; the residue consisted chiefly of the dimolecular compound, and the first fraction crystallizing quickly from solution was largely dibenzoylethane. The last fractions of crystals thrown out from the alcohol solution by dilution with water, on similar digestion with hot alcohol, at times yielded the cyclic dimolecular isomers -B and -C when these were present in small amounts. The following method was used in the separation of some of the mixtures resulting from the sodium hydrosulfite reductions. The crude product was precipitated by diluting the reaction mixture with water, the aqueous solution containing the bisulfite addition compound XIX being worked up as described separately below. This crude residue was digested for a short time with boiling ethanol. The insoluble residue was filtered off quickly, and digested with hot benzene, again leaving an insoluble residue consisting largely of *cyclo*-bis-dibenzoylethane-C (which was purified by recrystallization from chlorobenzene). The benzene filtrate gave a crystalline product which on fractionally crystallizing from benzene or chloroform gave a pure sample of *cyclo*-bis-dibenzoylethane-B. From the alcohol filtrate from the first digestion, a small crop of *cyclo*-bis-dibenzoylethanes-B and -C was obtained, and then a mixture of *cyclo*-bis-dibenzoylethane-A and dibenzoylethane. The latter mixture was separated by fractional crystallization from ethanol; or when small samples were involved, by the following procedure: the mixture was dissolved in boiling ethanol and allowed to crystallize quietly, long needles of dibenzoylethane forming first; when these appeared to be fully developed, the mixture was filtered suddenly, and immediately a granular crystalline precipitate formed in the filtrate (with a little luck and care, this separation may be semi-quantitative, and was so used in several instances).

Cyclo-bis-dibenzoylethane-A (1-phenyl-2,3,4-tribenzoylcyclopentanol-1) III, is best obtained by the action of zinc dust on *trans*-dibenzoylethylene in 6–1 benzene–glacial acetic acid solution at 30–40°. It is best purified by repeated recrystallization from benzene, and is obtained as short prisms of m. p. 161° (corr.).

Anal. Calcd. for $C_{32}H_{26}O_4$: C, 80.95; H, 5.53; mol. wt., 474. Found: C, 80.60, 81.08, 80.95, 80.92; H, 5.76, 5.77, 5.59, 5.53; mol. wt., 483, 499, 460.

Both dibenzoylethane and the above dimolecular product III have been found to be stable under the various reducing conditions. The very considerable amounts of resinous by-products found in various of the reductions are therefore not due to secondary reactions.

Cyclo-bis-dibenzoylethane-B (1-phenyl-2,3,4-tribenzoylcyclopentanol-1) III, was obtained from the sodium hydrosulfite reductions described above. It crystallized as tufts of needles from benzene, chlorobenzene, or ethanol; m. p. 202–203° (corr.).

Anal. Calcd. for $C_{32}H_{26}O_4$: C, 81.01; H, 5.48. Found: (dried *in vacuo* at 120°) C, 80.36, 80.44; H, 5.51, 5.76.

A solution of 0.05 g. in 2.5 cc. of methanol containing 0.03 g. of dissolved sodium was allowed to stand for three hours and deposited 0.05 g. of bis-dibenzoylethane-A which was identified by mixed melting point.

A solution of 1 g. in 30 cc. of warm acetic anhydride containing one drop of concd. sulfuric acid was decomposed in water and gave considerable brown resin from which 0.4 g. of the dehydro compound (1-phenyl-2,3,4-tribenzoylcyclopentene-1) was isolated and identified by mixed melting point.

Cyclo-bis-dibenzoylethane-C (1-phenyl-2,3,4-tribenzoylcyclopentanol-1) III, was obtained in only small amounts from the fractional crystallization of the products of reduction of dibenzoylethylene with sodium hydrosulfite or with the Zn–$ZnBr_2$–acetone combination. It crystallized from benzene, chlorobenzene, or large volumes of ethanol as square plates; m. p. 204–205° (corr.).

Anal. Calcd. for $C_{32}H_{26}O_4$: C, 81.01; H, 5.48. Found: C, 80.68; H, 5.64.

A solution of 0.1 g. in 5 cc. of ethanol containing 0.06 g. of dissolved sodium was allowed to stand for three hours and 0.06 g. of nearly pure bis-dibenzoylethane-A crystallized and was identified by mixed melting point.

Dehydration of 1 g. with 30 cc. of acetic anhydride and one drop of concd. sulfuric acid (warmed to solution) gave 0.92 g. of nearly pure dehydro compound of m. p. 179° (identified by mixed m. p.).

Sodium hydrosulfite reduction of dibenzoylethylene, carried out in 60–65% ethanol, produces almost exclusively monomolecular reduction. However, it was found that certain sam-

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[6] The elimination of bromine might perhaps be pictured as taking place stepwise, involving 1,4-reaction of the effective reducing agent with the α-bromo ketone system (*cf.* Ref. 4) rather than with the system Br–C–C–Br, since this would account for the failure of configuration to influence the reduction. The actual dimolecular coupling may take place according to the mechanisms described above or possibly through condensation of the intermediate dibenzoylethylene with unchanged dibromide or an enolate such as $C_6H_5COCHBrCH{=}C(OZnBr)C_6H_5$ (a 1,4-Reformatsky reaction).

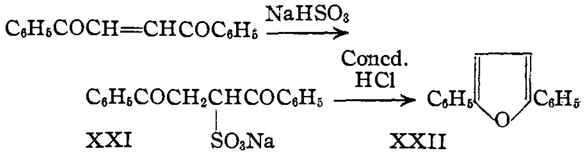
SOME TYPICAL REDUCTIONS OF UNSATURATED 1,4-DIKETONES

Subst., g.	Red. agent, g.	Conditions of the experiment	Yield of products, % Mono-mol.[a]	Cyclo-[b] dimol.-A	Other[c] products
		Trans-Dibenzoylethylene—Reductions with Sodium Hydrosulfite			
1	1	60 cc. 90% EtOH, refluxed 1 hr.	N. q.[d]	...	......
..	..[e]	90% $EtOH_3$ (several runs)	L[f]	S	S (II-B, II-C) 30–60% (XXI)
10	8	200 cc. 73% EtOH; 2 hrs. shaking at 25–30°	S	L	L (II-B, II-C); 45% (XXI)
1	1	60 cc. 90% EtOH; 4 hrs. shaking at 25–30°	L	...	S (II-B, II-C)
10	4	70 cc. 90% EtOH; $Na_2S_2O_4$ added slowly; 25–30°	vs.	vl	vs (II-B, II-C); S (XXI)
75	140[g]	300 cc. H_2O soln. of $Na_2S_2O_4$ added to boiling soln. of I in 800 cc. 95% EtOH	S[h]	...	L (XXI); 40% (IV-B)
		Trans-Dibenzoylethylene—Reductions with Zinc Dust			
10	40	200 cc. acetone; 4 g. $ZnBr_2$; 2 g. ZnO; reflux 8 hrs.	10–20	55–60[i]	
10	40	Subst. in acetone added over 2.5 hrs. to boiling acetone–Zn dust mixture +4 g. $ZnBr_2$ + 2 g. ZnO	L	...[j]	
2	10–20	Add Zn to boiling 25 cc. AcOH (duplicated)	N. q.	...	
5	10	Add Zn to boiling 100 cc. AcOH	68	26	
2	4	50 cc. AcOH; 2.5 hrs.; 25–30°	15	45	
2	4	10 cc. AcOH; 2.5 hrs.; 25–30°	30	50	
10	20	150 cc. C_6H_6, 25 cc. AcOH; 5–15°; Zn added slowly	..	41[k]	
20	20	150 cc. C_6H_5; 5–15°; 50 cc. AcOH added slowly	..	50[k]	
20	20	150 cc. C_6H_6 + 25 cc. AcOH; 5–30° (4 runs)	S	50–55[k]	
20	20	150 cc. C_6H_6 + 25 cc. AcOH; 30–40°	..	70–88[k]	
20	20	150 cc. C_6H_6 + 25 cc. AcOH; 44–47°	S	60	
1	4	Add Zn slowly to boiling 12 cc. AcOH + 3 cc. Ac_2O	85	7	
		Cis-Dibenzoylethylene (V)			
2	4	10 cc. AcOH; 3 hrs. at 25–30°	95	tr	
2	2	10 cc. AcOH + 2 cc. C_6H_6; 10 hrs. at 25–30°	100	..	
2	2	5 cc. AcOH + 15 cc. C_6H_6; 24 hrs. at 25–30°	18	80	
25	100	400 cc. acetone + 8 g. $ZnBr_2$ + 4 g. ZnO; reflux 7 hrs.	36	20	
		dl- and *meso*-dibenzoyldibromoethanes (XIX)			
..	..	AcOH (ordinary conditions)	N. q.	..	
15	40	Acetone; refluxing 8 hrs. (both give identical yields)	45	50[l]	
..	..	Acetone cont. 10% EtOH; refluxing 8 hrs.	vl	..	
		Dibenzoylchloroethane (XII)			
3	4	Acetone + 6 g. KI; reflux 1.5 hrs.	97		

[a] The corresponding saturated 1,4-diketone. [b] *Cyclo*-bis-dibenzoylethane-A. [c] The various products are indicated by symbol. The open chain bis-dibenzoylethanes = IV-A and -B and the cyclic isomers III-A, -B and -C; dibenzoylethane sulfonate = XXI. [d] N. q. = nearly quantitative. This was the case, however, only when good sodium hydrosulfite was used. [e] Using samples of sodium hydrosulfite which had been standing in the laboratory for several years and which had very evidently deteriorated and contained considerable amounts of $NaHSO_3$. [f] Due to the difficulty of separating the mixtures many of the yields were determined only roughly, and indicated by the symbols: L = large amounts, vl = very large, S and vs = small and very small, tr = trace. [g] Technical $Na_2S_2O_4$ used. [h] A considerable amount of unchanged material was recovered. [i] There was isolated also a 5% yield of II-C. [j] A considerable yield of a new compound of m. p. 248.5° (long thin rectangular scales from butanone) was isolated but has not yet been identified. It is probably not a simple dimolecular isomer since it is unaffected by boiling Ac_2O and H_2SO_4. [k] The product was nearly pure and the rest of the material resinous. [l] Traces of by-products were isolated from larger scale runs but not enough material was obtained for study.

ples of the reagent which had deteriorated gave considerable quantities of dimolecular products and of sodium bisulfite addition compound XXI. These results could be partially duplicated with the best grades of sodium hydrosulfite only under special conditions, namely, adding the solid reagent slowly to a 90% ethanol solution of dibenzoylethylene. Under these conditions there were produced large amounts of *cyclo*-bis-dibenzoylethane-A and smaller amounts of the cyclic isomers-B and -C, dibenzoylethane, and the sodium bisulfite addition compound. In one experiment when a concentrated aqueous solution of technical sodium hydrosulfite was added to a hot alcohol solution of dibenzoylethylene, the *open chain* bis-dibenzoylethane-B (IV) was obtained as the chief product; this is the only case aside from catalytic reduction where an open chain dimolecular product was formed in considerable amounts and isolated.

The sodium bisulfite addition compound XIX is a typical product of a 1,4-addition, and is formed nearly quantitatively when dibenzoylethylene is treated in 90% ethanol with sodium bisulfite. It is not easily hydrolyzed and is converted into diphenylfuran XXII by the action of boiling concd. hydrochloric acid.



The sulfonate was best prepared by allowing a mixture of 5 g. of *trans*-dibenzoylethylene, 4 g. of sodium bisulfite, and 110 cc. of 85% ethanol to stand for two hours. The solution was evaporated and the residue crystallized from ethanol: yield 84%; m. p. 255–262° (corr.). The analyses for S, C and H were unsatisfactory but approximated the values calculated for the formula XXI.

When refluxed for one hour with concd. hydrochloric acid, the sulfonate was converted into 2,5-diphenylfuran which was identified by mixed melting point with an authentic sample prepared by the action of acetic anhydride and a trace of concd. sulfuric acid on dibenzoylethane.[7]

Summary

The reduction of *trans*-dibenzoylethylene with zinc and acetic acid under varying conditions leads to the formation of dibenzoylethane and the cyclic dimolecular reduction product, *cyclo*-bis-dibenzoylethane-A, but *cis*-dibenzoylethylene gives largely, and other unsaturated 1,4-diketones exclusively, monomolecular products.

The formation of the cyclic dimolecular product is regarded as evidence for the conjugate mechanism.

The catalytic effect of zinc bromide in the reductions of dibenzoylphenylethylene and dibenzoylphenylbromoethylene is discussed, together with the probable mechanism.

The zinc–acetone reductions of the halogeno derivatives of dibenzoylethane are considered and a mechanism for the dimolecular reduction of the dibenzoyldibromoethanes is proposed.

Circumstances are described under which sodium hydrosulfite reduction of dibenzoylethylene gives large amounts of dimolecular products and sodium bisulfite addition compound.

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[7] *Cf.* Kapf and Paal, *Ber.*, **21**, 3057 (1888).

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The Catalytic Hydrogenation of Unsaturated 1,4-Diketones

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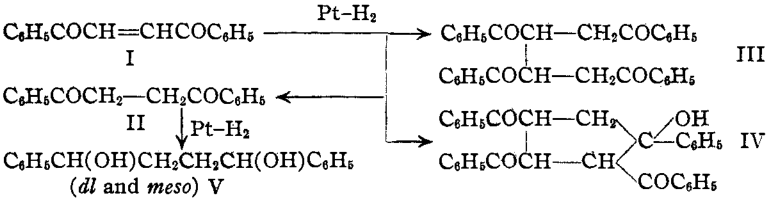
These studies were made in order to compare the catalytic hydrogenation of the unsaturated 1,4-diketones with reductions utilizing ordinary homogeneous and heterogeneous combinations. In the case of *trans*-dibenzoylethylene (Table I) chiefly the platinum catalyst was used with the following as solvents: methanol, 95% ethanol, dilute ethanol, acidified ethanol, glacial acetic acid, dioxane, ethyl acetate and decalin. With few exceptions there resulted mixtures of dibenzoylethane II and open chain and cyclic bis-dibenzoylethanes-A, III and IV, the relative yields varying considerably. Small yields of bis-dibenzoylethane-B also were obtained in many cases, but neither *cyclo*-bis-dibenzoylethane-B nor -C was isolated.



The yields of the difficultly soluble bis-dibenzoylethane-A, which crystallizes out during reaction, are probably fairly accurate as listed in the tables. However, the yields of the other products could be determined only approximately in many cases because of the difficulty of separating the mixtures and because there was undoubtedly some loss through further reduction. The primary stage of the reaction goes very rapidly, but the products are all reducible further slowly, as was