[Contribution from the Cobb Chemical Laboratory of the University of Virginia]

α-Substituted β-Diketones. Stereoisomeric Enols of α-Phenacyldibenzoylmethane. Addition-Enolization of Unsaturated Triketones[1]

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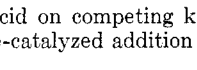
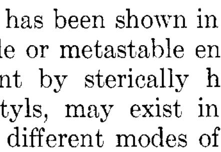
The persistence and instability of metastable α-substituted β-diketones are attributed to steric effects. The existence of two stereoisomeric α-phenacyldibenzoylmethane enols has been demonstrated. One (*cis*, crystalline) was obtained by enolization of the triketone and gave a normal chelated copper derivative. The other (*trans*, oil) was obtained by conjugate reduction of tribenzoylethylene which followed a predicted stereochemical course, and gave a non-chelated complex copper salt involving four molecules of enol. Steric factors affecting the ease of furanization of the *trans* enol and its 3-bromo derivative are discussed. Reversible addition-enolization of tribenzoylethylene by alkoxide ion was demonstrated, and the effect of acid on competing ketonization and elimination is discussed. *Trans*-dibenzoylethylene is shown to undergo reversible base-catalyzed addition of alcohol under similar conditions.

It has been shown in a number of cases that unstable or metastable enols which are rendered persistent by sterically hindering groups, especially mesityls, may exist in stereoisomeric forms, and that different modes of formation such as enolization of ketones, reductive-enolization of α-bromoketones, reductions of and additions to α,β-unsaturated ketone systems, may determine the configuration of the product.[2] Recent studies on enols of β-diketones unsubstituted on the α-methylene carbon such as Ia, which are the stable forms, have been directed toward the problem of structure, configuration and conformation.[3] In the α-substituted β-diketone series where both keto and enol forms are known, it is the keto form which is stable; and the enol forms where known are metastable or "persistent" (*cf.* II or III).[4] 1,1,2-Tribenzoylethane (Ie)[4e,f] is an α-phenacyldibenzoylmethane, and like the α-methyl- and α-phenyldibenzoyl-methanes (Ib,c) it is in the more stable keto form.

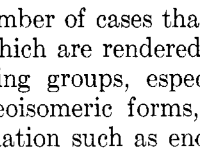


$R{-}CH(COC_6H_5)_2$

I R = (a) H; (b) CH_3; (c) C_6H_5; (d) Br; (e) $C_6H_5COCH_2$



II



III

Metastable enols of α-substituted β-diketones. The stable ketonic forms of α-methyl and α-phenyldibenzoylmethanes (Ib,c) show strong ultraviolet absorption maxima at 246 and 247 mμ respectively. Their persistent enol forms show much weaker absorptivities in this region and strong longer wave length bands at 330–355 mμ. The phenyl derivative is relatively stable in both isoöctane and absolute ethanol, and perhaps stilbene resonance is important here. The methyl compound is stable in isoöctane but it changes to the keto form in alcohol; this change was conveniently followed by the gradual drop in the long wave length absorptivity.

Dilute absolute-alcoholic solutions of the two keto forms, when treated with a slight excess of sodium hydroxide, developed similar long wave length bands which were a little less intense and at slightly different positions than those shown by the pure enols, and these bands evidently represent the enolates. Prompt acidification of these alkaline solutions with a slight excess of hydrochloric acid caused reversion of the enols to the more stable keto forms; this was shown by complete loss of the long wave length bands and restoration of the original absorptivities, with some rapidity in the case of the α-methyl compound and very slowly in the case of the α-phenyl compound. When acidifications of the alkaline solutions were delayed the intensities of the long wave length bands gradually dropped. This is explained in terms of slow hydrolytic cleavage of the enolates (specific analogy for which will be shown below) and consequent destruction of the chalcone system responsible for the long wave length bands.

The enol form of α-bromodibenzoylmethane (Id) has not been isolated[5] but its formation and ready reversion to the stable keto form is shown, by the development of a similar characteristic though weak

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[1] This work was supported by a contract with the Office of Ordnance Research and a grant-in-aid from the National Science Foundation.

[2] (a) E. P. Kohler, M. Tischler, and H. Potter, *J. Am. Chem. Soc.*, **57**, 2517 (1935); (b) R. E. Lutz and C. J. Kibler, *J. Am. Chem. Soc.*, **62**, 360 (1940); (c) R. E. Lutz and W. G. Reveley, *J. Am. Chem. Soc.*, **63**, 3180 (1941).

[3] (a) B. Eistert, F. Weygand, and E. Csendes, *Ber.*, **84**, 745 (1951); (b) B. Eistert and E. Merkel, *Ber.*, **86**, 895 (1953).

[4] (a) C. L. Bickel and R. Morris, *J. Am. Chem. Soc.*, **73**, 1786 (1951); (b) A. S. Dreiding and J. A. Hartman, *J. Am. Chem. Soc.*, **75**, 3723 (1953); (c) J. Meisenheimer and K. Weibezahn, *Ber.*, **54**, 3195 (1921); (d) S. Goldschmidt and F. Nagel, *Ber.*, **63**, 1212 (1930); (e) H. Kleinfeller and H. Trommsdorff, *Ber.*, **71**, 2448 (1938); (f) C.-K. Dien and R. E. Lutz, *J. Am. Chem. Soc.*, **78**, 1987 (1956).

[5] H. Heller and H. von Halban, *Helv. Chim. Acta*, **27**, 1253 (1944).

360 mμ absorption band when the dilute absolute-alcoholic solution was made slightly alkaline, and by the loss of this band on subsequent acidification. As above with Ib and c, upon longer standing of the alkaline solution there was a gradual lowering of the long wave length peak, caused presumably by slow hydrolytic cleavage.

As in the cases of Ib, c and d, α-phenacyldibenzoylmethane (1,1,2-tribenzoylethane; Ie) in dilute absolute-ethanol solution showed typical benzoyl group absorptivity (*cf.* Fig. 1A). Addition of potassium hydroxide caused appearance of a longer wave length band corresponding to that of an enolate system (Fig. 1B). This long wave length band diminished in intensity when the solution was allowed to stand (Fig. 1C), a phenomenon which was shown experimentally to be due to hydrolytic cleavage by isolation and identification of the cleavage product, dibenzoylethane, $C_6H_5COCH_2CH_2COC_6H_5$. Prompt acidification of the dilute basified absolute-ethanol solution by hydrochloric acid quickly eliminated the longer wave length band and restored the characteristic benzoyl-type absorptivity.

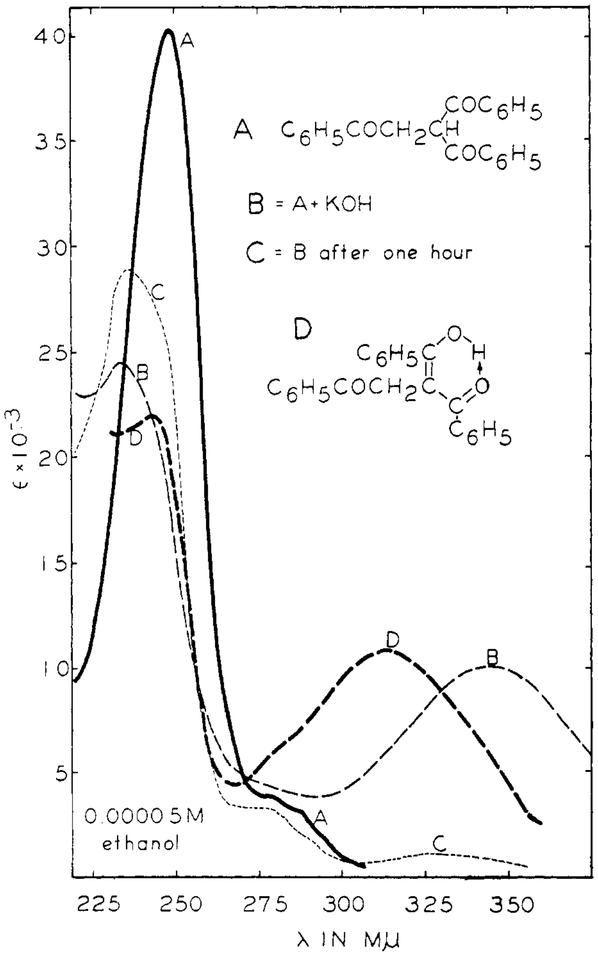
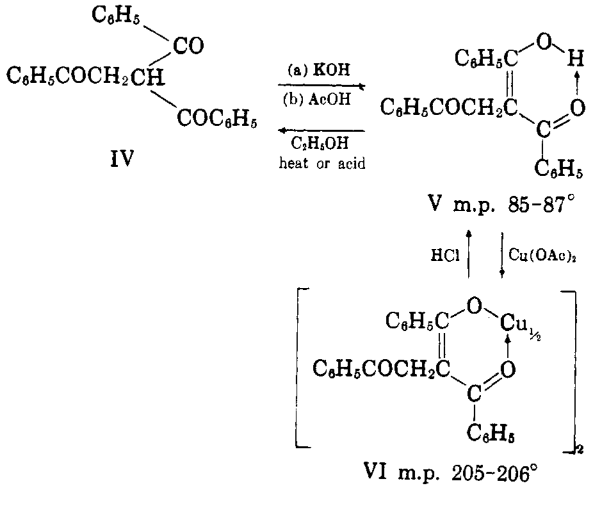


FIG. 1.—ULTRAVIOLET ABSORPTIVITIES OF KETO AND ENOL FORMS OF 1,1,2-TRIBENZOYLETHANE.

The striking and consistent effect of α-substitution in rendering dibenzoylmethane type enols unstable must be due chiefly to steric rather than electronic factors; this is shown by the fact that the α-substituents methyl, phenyl, bromine, and phenacyl, are of widely divergent polar character but of comparable bulk at the point of attachment. In the enol forms the severe steric interferences by the α-substituents with the planarity of the chalcone system must markedly decrease the effectiveness of the chalcone conjugation of that system in both *cis*-chelated and *trans*-non-chelated forms (II, III)[6] as it does in the phenylated chalcones.[7] The persistence of the enols may be attributed largely to steric interference with the facility of protonation of the α-carbon.[8]

Cis and trans phenacyldibenzoylmethane enols. A crystalline enol believed to be the *cis*-chelated enol (V) was obtained by enolization of tribenzoylethane (IV) with methanolic potassium hydroxide, conversion into its copper salt, and liberation again as the enol by acidification. Its ultraviolet absorption curve is shown in Fig. 1D. This enol in alcohol solution reverted to the keto form on heating or on treatment with acid. The *cis* configuration was assigned on the basis of the probable conformation of the molecule prior to loss of the proton and the apparently lesser steric strain in the *cis* form (judging from scalar models), and because this enol gives a normal type of chelated copper complex (VI), from which the enol can be liberated, and which is



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[6] The *cis* configuration here is defined as the one involving the *cis* relationship between the enolic hydroxyl group and the remaining β-benzoyl group of the parent β-diketone system.

[7] (a) W. B. Black and R. E. Lutz, *J. Am. Chem. Soc.*, **75**, 5990 (1953); (b) W. B. Black and R. E. Lutz, *J. Am. Chem. Soc.*, **77**, 5134 (1955); (c) R. E. Lutz and E. H. Rinker, *J. Am. Chem. Soc.*, **77**, 366 (1955).

[8] (a) *Cf.* recent work on steric effects on the course of ketonizations of enols to α-stereoisomeric ketones; (b) T. L. Jacobs and W. H. Florsheim, *J. Am. Chem. Soc.*, **72**, 256 (1950); (c) H. E. Zimmerman, *J. Org. Chem.*, **20**, 549 (1955); H. E. Zimmerman, *J. Am. Chem. Soc.*, **78**, 1168 (1956).

different from the abnormal complex copper salt of the presumably isomeric *trans* and non-chelated enol (X) prepared as described below. The ultraviolet absorptivities of the two copper derivatives VI and X are compared with that of the *cis* enol V in Fig. 2.

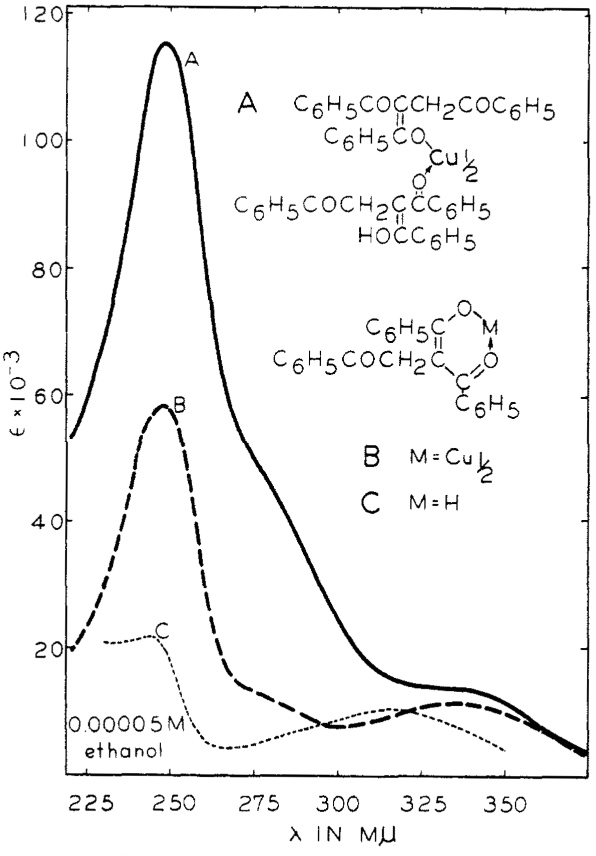
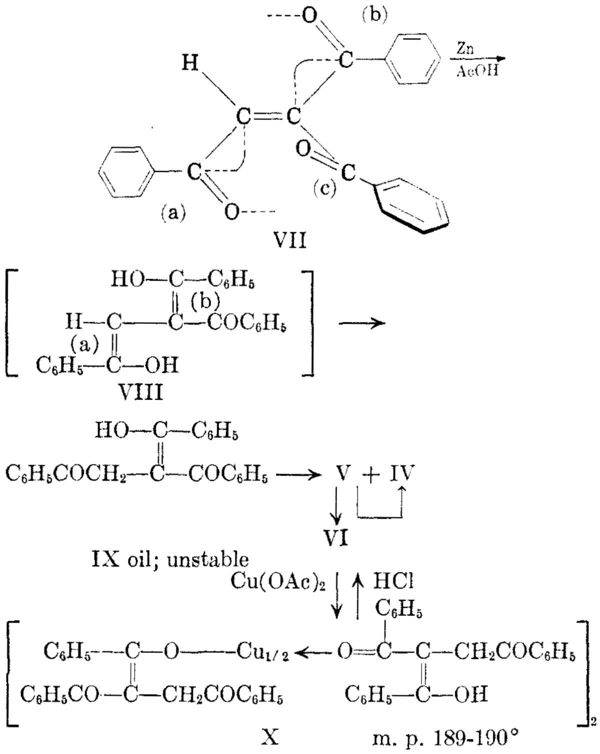


FIG. 2.—ULTRAVIOLET ABSORPTIVITIES OF THE ENOL OF 1,1,2-TRIBENZOYLETHANE AND OF THE *cis* AND *trans* COPPER SALTS.

The formation and existence of the *trans*-non-chelated enol (IX) was predicted on the following basis: Tribenzoylethylene (VII) bears close analogy to *trans*-phenyldibenzoylethylene which has been shown to undergo 1,6-reduction by zinc and acetic acid through intermediate enols or enolates of configurations specifically determined by the mechanism of the reduction.[9] The unsaturated triketone may be regarded as a benzoyl-*trans*-dibenzoylethylene (VII) in which the one benzoyl group (c) is non-coplanar with the comparatively planar *trans*-dibenzoylethylene system [including (a) and (b)], as is pictured in the formulation VII. Conjugate reduction[c/,9] would be expected to proceed readily along the lines indicated in Thiele symbolism, with primary formation of the diene-diol of necessarily specific configuration VIII, and prompt ketonization at the unhindered end [(a) of VIII] to the metastable β-diketone *trans*-monoenol (IX); the latter was expected to have at least a moderate degree of persistence and to be in the *trans* configuration as pre-determined [at (b) of VIII].



In actual experiment tribenzoylethylene (VII) was reduced by a zinc and acetic acid-ether-water mixture, and the resulting ether solution was shown to contain a different enol, presumably IX and stereoisomeric with V, by conversion with copper acetate into a second and abnormal type of copper derivative which appears to be a complex non-chelated copper salt of formula X. From this copper salt an ether solution of the enol (IX) could be regenerated by careful hydrolysis under ether with dilute hydrochloric acid. Attempts to isolate the enol (IX) in crystalline form were unsuccessful. The ether solution, which was shown still to contain the enol by ability to regenerate the copper salt (X), underwent slow change on standing and gave the more stable chelated enol (V, isolated as the copper chelate, VI) and the saturated triketone (IV).

This second copper derivative (X) is distinguished not only by its properties [it is much less soluble in ether than is the chelate (VI)], but in composition; a copper-enolate ratio of 1:4 is shown by analysis. It is formulated as a true and non-chelated salt of two *trans* enolate molecules, coordinated through the copper atom with two extra molecules of enol, presumably through the free non-chelated and therefore strongly electron-donative β-carbonyl oxygens.

Although unfortunately we have not been able to isolate the unstable enol (IX) in pure form, crystalline derivatives of both the *cis* and *trans* enols

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[9] R. E. Lutz and C. R. Bauer, *J. Am. Chem. Soc.*, **73**, 3456 (1951).

TABLE I

ULTRAVIOLET ABSORPTION SPECTRA[a]

Compound	Time[c]	λ_{max}; mμ			$\epsilon \times 10^{-3}$			λ_{min}; mμ		$\epsilon \times 10^{-3}$	
$C_6H_5COCH{=}C(OH)C_6H_5$ (ref. 3a, 5)[d,e]	—	226	252.5	344	7.45	8.61	23.5	236	278	6.65	4.75
with added HCl[f,g]	5m	225	253	343	7.11	8.5	23.5	236	278	6.55	4.65
excess KOH added[i]	1m	240	349		13.88	20.85		226	290	10.4	1.82
then acidified with HCl[j,g]	5m	227	252.5	344	9.0	9.57	23.4	238	279	7.80	5.35
excess KOH added[i]	24h	240	352		13.90	20.05		226	290	10.9	1.74
then acidified with HCl[j,g]	5m	229	251	343	11.05	10.8	22.5	239	279	9.72	5.80
$C_6H_5COCH(CH_3)COC_6H_5$ (ref. 4b)[d]	—	246	280^s		23.65	2.3		—		—	
excess KOH added[i]	1m	232^s	355		16.2	9.29		292		2.3	
then acidified with HCl[j]	5m	246	280^s		24.6	3.8		—		—	
excess KOH added[i]	4h	233^s	273^s		21.8	1.9		—		—	
then acidified with HCl[j]	5m	233	278^s		23.9	3.3		—		—	
$C_6H_5COC(CH_3){=}C(OH)C_6H_5$[k]	—	246	280^s	330^b	19.2	2.3	2.18	300		1.62	
in isoöctane	—	243	330		10.7	13.7		272		2.4	
in isoöctane with added HCl[f]	5m	243	282^b	330^b	19.6	2.2	3.2	270	298	1.9	1.9
$C_6H_5COCH(C_6H_5)COC_6H_5$	—	247			26.1			—		—	
excess KOH added[i,l]	1m	325^b	370^b		5.9	6.8		340		5.7	
then acidified with HCl[j]	5m	247	330^b	350^b	18.0	6.6	7.05	290	340	3.6	6.5
then acidified with HCl[j]	30h	247	330^b	350^b	23.8	1.85	1.9	305	340	1.4	1.8
excess KOH added[i]	20m	340^s			3.2			—		—	
$C_6H_5COC(C_6H_5){=}C(OH)C_6H_5$[n]	—	249	331	355	12.4	10.5	11.2	280	342	3.99	10.3
$C_6H_5COC(C_6H_5){=}C(OH)C_6H_5$	62h	247	330^b	350^b	23.7	1.23	1.17	310	340	1.0	1.0
with added HCl[f]	5m	250	330	355	14.0	9.46	10.06	282	341	3.78	9.22
in isoöctane	—	250	335	355	12.1	12.6	13.22	280	342	3.6	12.4
$C_6H_5COCHBrCOC_6H_5$ (ref. 5)[d]	—	253			18.8			—		—	
excess KOH added[i,l]	1m	360			6.38			—		—	
then acidified with HCl[j]	5m	253			18.5			—		—	
excess KOH added[i]	20m	225	255^s	360	14.8	6.1	4.1	300		1.41	
$C_6H_5COCH(CH_2COC_6H_5)COC_6H_5$	—	247.5	282^s		40.2	3.5		—		—	
excess KOH added[i]	1m	234	277^s	345	24.4	4.3	10.0	290		3.7	
then acidified with HCl[j]	5m	247.5	280^s		39.6	5.0		—		—	
excess KOH added[i]	1h	235	275^s	330^b	28.8	3.3	1.2	305		0.88	
then acidified with HCl[j]	5m	243	280^s		34.6	5.3		—		—	
$C_6H_5COC(CH_2COC_6H_5){=}C(OH)C_6H_5$[k]	—	246	280^s	315^b	35.4	3.2	1.02	300		0.73	
in isoöctane	1m	244	312.5		21.8	10.8		267		4.4	
in isoöctane	1h	244	312.5		27.6	7.5		268		3.8	
in isoöctane with added HCl[f]	5m	244	280		36.7	3.6		272		3.05	
$C_6H_5COCH(CHClCOC_6H_5)COC_6H_5$	—	253.5			37.85			—		—	
excess KOH added[i,g]	1m	242^s	335		18.6	4.8		305		3.4	
then acidified with HCl[j]	5m	237.5	252.5		18.6	21.0		241		18.2	
$C_6H_5COCH(CHBrCOC_6H_5)COC_6H_5$	—	255			35.8			—		—	
excess KOH added[i,g]	1m	232^s	335		20.3	5.15		302		3.4	
then acidified with HCl[j]	5m	233^s	254	285^s	21.5	25.4	11.6	—		—	
$C_6H_5COCH[CH(NC_4H_8O)COC_6H_5]COC_6H_5$	—	249			35.2			—		—	
excess KOH added[i,g]	1m	235	355		23.4	3.0		225	310	22.2	2.55
then acidified with HCl[j]	5m	249	282^s		29.6	11.6		—		—	
excess morpholine added[p]	16h	249			35.1			—		—	

TABLE I *Continued*

Compound	Time[c]	$\lambda_{max.}$ mμ			$\epsilon \times 10^{-3}$			$\lambda_{min.}$ mμ	$\epsilon \times 10^{-3}$
$C_6H_5COCBr(CH_2COC_6H_5)COC_6H_5$	—	251.5			27.8			—	—
excess KOH added[i,g]	1m	231	335		23.15	8.56		290	4.45
then acidified with HCl[j]	5m	253.5	280		23.4	12.2		—	—
$C_6H_5COCH{=}C(COC_6H_5)COC_6H_5$	—	252.5			25.2			—	—
excess KOH added[i,g]	1m	229	335		24.1	8.9		290	4.45
then acidified with HCl[j]	5m	252.5	284[s]		27.58	8.8		—	—
excess HCl added[f]	1m	252.5			23.6			—	—
	12h	251	285[s]		24.1	10.4		—	—
KOH added[q,g]	1m	230	335		23.1	8.8		290	4.55
neutralized with HCl[r]	5m	233	327		22.25	7.2		295	5.40
	16h	250			25.10			—	—
morpholine added[p,t]	16h	250	285[s]		29.8	7.8		—	—
$C_6H_5COC(OCH_3){=}C(COC_6H_5)COC_6H_5$	—	261			33.5			—	—
excess KOH added[i,u]	1h	260			33.4			—	—
cis copper enolate (VI)[v]	—	247	280[s]	337.5	58.5	12.0	11.3	229	7.73
trans copper enolate (X)[w]	—	248	280[s]	335[s]	116.5	46.0	14.0	—	—
trans-$C_6H_5COCH{=}CHCOC_6H_5$	—	269			18.80			—	—
HCl added[q,g]	1m	269			18.8			—	—
KOH added[q,g]	1m	246	280[s]		23.4	5.0		—	—
neutralized with HCl[r,g]	5m	246	280[s]		23.4	4.6		—	—
$C_6H_5COCH(OCH_3)CH_2COC_6H_5$	—	246.5	280[s]		25.0	2.76		—	—
HCl added[q,g]	1m	246.5	280[s]		24.9	2.59		—	—
KOH added[q,g]	1m	246.5	280[s]		23.1	5.40		—	—
trans-$C_6H_5COCH{=}CHCOC_6H_5$[x]	—	268.5			19.1			—	—
KOH added[q,y]	1m	246	280[s]		23.8[y]	4.00[y]		—	—
$C_6H_5COCH(OCH_3)CH_2COC_6H_5$[x]	—	246	280[s]		24.8	2.75		—	—
KOH added[q,y]	1m	246	280[s]		23.5[y]	4.35[y]		—	—

[a] These data were obtained using a Beckman DU quartz spectrophotometer, and about 0.00005 *M* absolute ethanol solutions except where isoöctane (2,2,3-trimethylpentane) is specified. [b] The bands carrying this superscript are unusually broad. [c] The time given in this column (m = minutes; h = hours) represent the beginning of measurements. The time taken to complete a measurement averaged 30 min. Where no time is indicated, it means that the determinations were made in a normal and leisurely manner. [d] References here given are to earlier determinations of ultraviolet absorptivities. [e] The form of dibenzoylmethane of m.p. 78° was used, and the values for this compound in neutral and in basified solutions agree with those reported (ref. 3a). It should be noted that upon acidification of the basified solution the higher ϵ values of the lower wave length bands (229 and 251 mμ) were retained. This seems to indicate that partial isomerization of *cis* to *trans* enols occurred under basic conditions and that the isomer content was retained, even on long standing, in the subsequently acidified solution. Acidification of the original solution of the enol (m.p. 78°) did not affect the ϵ value even on long standing. These results indicate that both *cis* and *trans* forms are moderately stable under acidic conditions. An earlier attempt to isolate a pure solid isomer (ref. 3a) however was not successful. [f] Three drops of conc'd hydrochloric acid were added to *ca.* 90 ml. of 0.00005 *M* solution and the mixture was shaken for 5 min. [g] No significant change after 12–16 hrs. [i] Three drops of 10% aqueous potassium hydroxide solution were added to *ca.* 90 ml. of the 0.00005 *M* solution. [j] Three drops of conc'd hydrochloric acid then were added to the above solution; this made the solution acidic. Filtration removed the precipitated potassium chloride. [k] Determined in absolute ethanol. It is unstable in this solvent. [l] Only the long wave length peak was measured. [n] The compound shows also λ_{max} 234, ϵ 10,500, and λ_{min} 240, ϵ 11,780. [p] A quantitative amount of morpholine was added to make a 0.0009 *M* morpholine solution. [q] A quantitative amount of KOH (or HCl) was added to make a 0.0007 *M* KOH (or HCl) solution. [r] The above solution was exactly neutralized by calculated amount of HCl solution. [s] These values represent shoulders rather than distinct bands. [t] The addition of morpholine evidently caused slow addition-enolization but because of the weak basicity there was no building-up of addition-enolates. It would appear that the morpholinyltribenzoylethane is not the only reaction product, however, because the rise in absorptivity reached a fairly constant point considerably below the expected level (the absorptivity of this addition compound was shown in separate experiment to be essentially unchanged upon standing for 16 hours). [u] The constancy of the characteristic ultraviolet absorptivities of methoxytribenzoylethylene in absolute ethanol upon addition of potassium hydroxide shows that this compound does not add hydroxide or ethoxide ion to any significant degree as does tribenzoylethylene itself. [v] A 0.00002 *M* solution was used. [w] A 0.00001 *M* solution was used. [x] Methanol solution was used. [y] These solutions on standing for 44 hrs. showed almost identical ϵ values of 23.9 and 3.88.

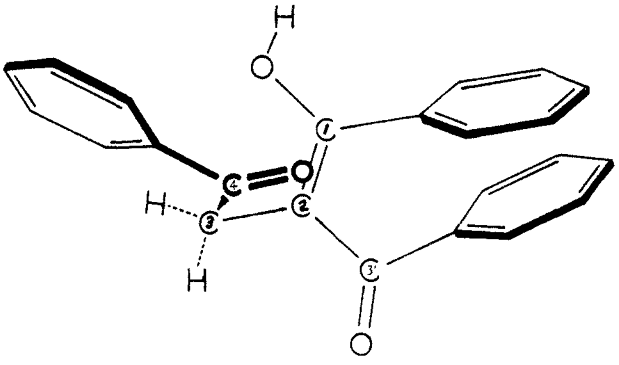
have been made and characterized, and the facts are consistent with and thereby support the postulations made. We hope that further studies of metal complexes now in progress will offer a practical approach to the problem of stereoisomeric enols in these and other systems.

Factors affecting furanization of 4-keto[10] *enols.* Furanization is presumed to proceed only through enol forms of favorable configuration (*trans* in the present case), ring-chain tautomeric equilibrium between the 4-keto and 2,3-dihydro-2-hydroxyfuran forms, and aromatization by loss of water.[2c,11] The *cis* isomer (V) would be expected not to cyclize but rather to ketonize readily, as it does. The *trans* isomer (IX) has the requisite configuration for furanization yet does not do so spontaneously in competition with isomerization and ketonization, as do some other 4-keto enols.[2c,9] This is in contrast with the ready furanization of the corresponding 3-bromo-4-keto enol (XII) which was postulated on the basis of good evidence as the key intermediate in the conversion of tribenzoylethylene (VII) by bromination into the 3-benzoyl-4-bromofuran[4f] [the steps postulated in this reaction are formation of the dibromide, reductive-enolization of the α-bromo-β-diketone system to the 4-keto-3-bromo-*trans*-1-ènol (XII), and furanization of this in successful competition with ketonization and dehydrohalogenation[4f]].

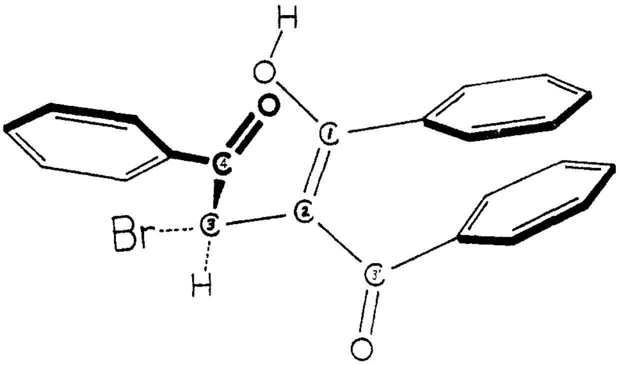
The seeming anomaly between the behavior of the two *trans* enols can be rationalized on steric grounds by comparison and manipulation of scalar models as follows: [Although they do not adequately show the steric effects, the projection formulas (XI and XII) represent the main conformational features and illustrate some of the conclusions drawn.]

Comparison of scalar models of the parent *cis* and *trans* enols (V and IX) shows that the *cis* (chelated) isomer involves very considerably less steric interferences with over-all planarity of the conjugated systems than does the *trans* isomer, and that the *cis* isomer should be, as it is, the more stable of the two forms. In the case of the bromo derivatives the differences in steric interferences are not nearly as marked but nevertheless indicate that the *trans* form (XII) should be the more stable of the *cis*-*trans* pair (this was not subject to experimental confirmation[12]).

In comparing scalar models of the *trans* bromo enol (XII) with the parent *trans* enol (XI) it is seen that steric shielding of the enol β-carbon is much the greater in the bromo derivative. From the point of view of ketonization therefore the bromo compound should be the more persistent.



XI



XII

The planar *trans*-β-hydroxyvinyl ketone system of XI and XII is the principal part of the chromophore responsible for the long wave length ultraviolet absorptivities, and the *cis*-chalcone phenyls involve considerable overlap and consequent deviation from coplanarity. The planar phenacyl group in the parent enol (XI) must lie well out of the β-hydroxyvinyl ketone plane, with the 4-carbonyl oxygen pointing inward, and it must have a considerable degree of freedom with respect to the location of the 4-keto carbon relative to the enol oxygen. Consequently, relatively, the 4-carbonyl possesses a maximum of conjugation and chemical stability, and a minimum probability of approach to the enolic oxygen with which it must react in furanization. In the bromo compound (XII) the steric freedom and planarity of the 4-carbonyl group is much more restricted because of the added hindrance by the bulky bromine atom, and the probability of approach of the 4-carbonyl carbon to both the enol and to the 3′-carbonyl oxygens is relatively much greater; or one could say that the probability of the midway position of the 4-carbonyl carbon between the 3′-carbonyl and enol oxygens is minimized. Again, furanization should be favored.

There must be an appreciable inductive activation of the 4-carbonyl group by the α (or 3)-bromine; and this would favor furanization.

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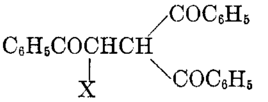
[10] The two keto groups of the forked system are numbered 4 and 3′ relative to the 1-enol group in formulas XI-XII.

[11] R. E. Lutz and W. G. Reveley, *J. Am. Chem. Soc.*, 61, 1854 (1939).

[12] Neither of the two enols have been isolated and study of them would be complicated by the great facility of dehydrohalogenation.

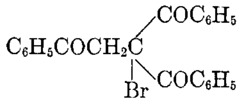
All of the effects enumerated above are in one and the same direction, favoring furanization over competing alternatives. The above interpretations by virtue of unequivocal prediction of the observed results offer strong support for the several postulations involved. It is hoped that this type of analysis can successfully be applied in other cases to explain or predict the effects of substituents on the furanizations of the many 1,4-diketones and 4-keto enols.

Addition-enolization of tribenzoylethylene. This study stemmed from the following anomalous spectrophotometric results which are illustrated in Fig. 3. Four derivatives of 1,1,2-tribenzoylethane, namely the 2-chloro, 2-bromo (Fig. 3A), 2-morpholinyl, and 1-bromo (XIIIa,b,c, and XIV), in absolute ethanol, showed absorptivities at the wave length and (except for XIV[13]) of the intensity range expected of compounds containing three benzoyl groups. Addition of a small excess of potassium hydroxide in each case caused a sharp drop in the benzoyl type absorptivity and the development of a chalcone-type band at *ca.* 335 mμ (*cf.* Fig. 3B) which seemed at first to be due to the formation of the corresponding enolates. However, acidification of the solutions with excess hydrogen chloride destroyed the long wave length absorptivity but failed to restore fully the original individual absorption characteristics; and there developed a broader and lower unsymmetrical absorption peak resembling but not coincident with that of acidified tribenzoylethylene (VII), (Fig. 3C and 4D).



$C_6H_5COCHXCH(COC_6H_5)_2$

XIII X = (a) Cl; (b) Br; (c) morpholinyl; (d) OC_2H_5; (e) OCH_3



$C_6H_5COCH_2CBr(COC_6H_5)_2$

XIV

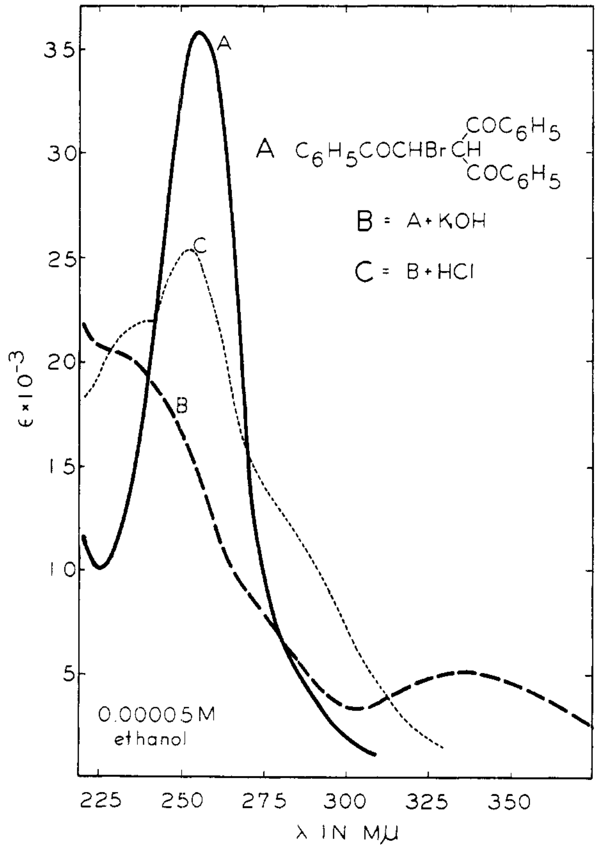


FIG. 3.—THE ULTRAVIOLET ABSORPTION OF 2-BROMO-1,1,2-TRIBENZOYLETHANE AND THE EFFECT OF ALKALI.

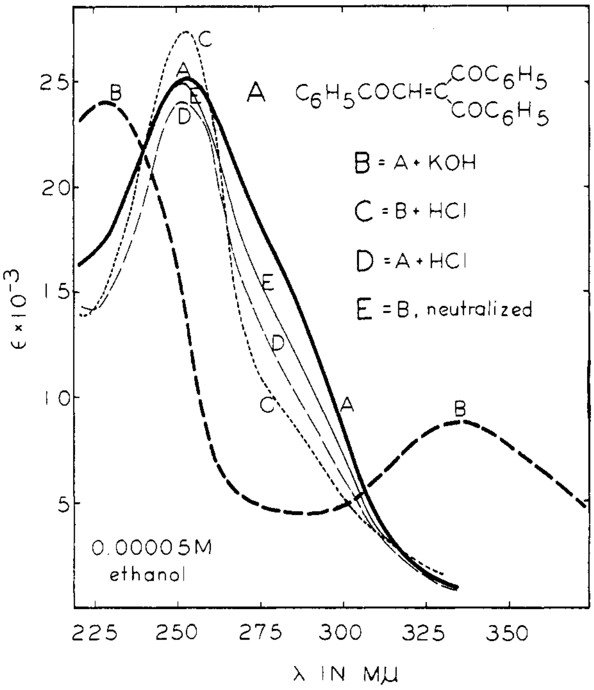


FIG. 4.—ULTRAVIOLET ABSORPTIVITIES OF 1,1,2-TRIBENZOYLETHYLENE AND ITS ADDITION-ENOLATE.

Direct basification of a dilute absolute ethanolic solution of tribenzoylethylene itself (VII) (Fig. 4A) caused development of a similar chalcone-like absorptivity (Fig. 4B). Acidification caused loss of the longer wave length band and immediate development of a 252.5 mμ band (Fig. 4C) somewhat similar to that of tribenzoylethylene; however the narrowness and distinctly higher ϵ value of the band indicated the presence of a considerable amount of a new substance containing isolated benzoyl groups, which is shown by the very slow subsequent change in absorptivity to be moderately stable under these acid conditions. It is evident from the nature of the deviation in absorptivity from that of tribenzoylethylene, and from analogy to the parent dibenzoylethylene (see next section) where methoxydibenzoylethane is known to be formed under similar conditions, that this new substance is the completed-

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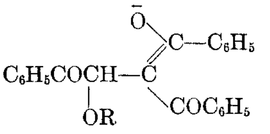
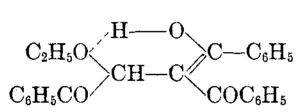
[13] The 1-bromo triketone has a somewhat lower absorptivity; *cf.* ref. 4f.

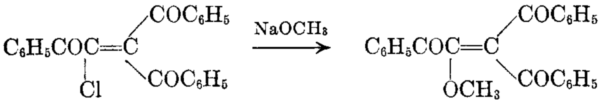
addition product (XIIId).[14] Only tribenzoylethylene was recovered however when more concentrated solutions were studied with a view toward isolation of the enol involved (free or as the copper salt) and the new (and relatively stable) end product (XIIId).

From these experiments it is concluded that the effect of strong base on the four substituted triketones (XIIIa,b,c, and XIV) is enolization and loss of halide or morpholine to produce tribenzoylethylene (VII), that the latter compound undergoes ready and reversible addition of ethoxide ion (incompleted "1,4-addition") to give the *trans* enolate ion (XV), and that the free enol (XVI) produced upon subsequent acidification is unstable and undergoes slow loss of ethanol and competing ketonization to give VII and XIIId respectively.

XV R = (a) C_2H_5; (b) CH_3 XVI

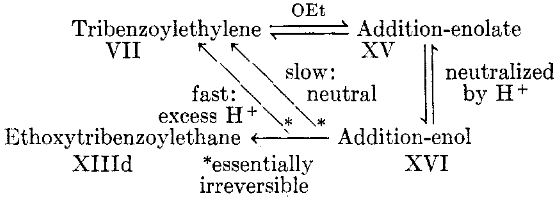
Unsuccessful attempts were made to obtain methoxytribenzoylethane (XIIIe) and the corresponding furan through chlorotribenzoylethylene (XVII) by conversion into methoxytribenzoylethylene (XVIII) and reductions.



XVII XVIII

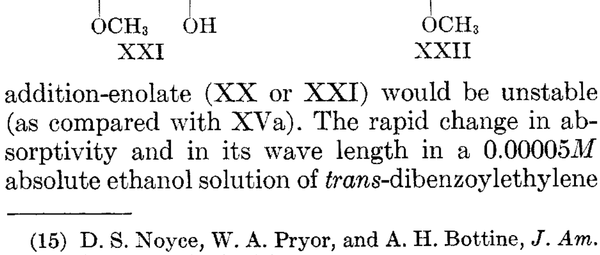
In a check quantitative experiment on the effect of potassium hydroxide on tribenzoylethylene in which the development of the long wave length absorptivity was duplicated, exact neutralization of the added base by hydrogen chloride (rather than addition of excess acid) produced the enol (XVI) as shown by the retention of the long wave length absorptivity. When the neutral solution was allowed to stand the long wave length band gradually diminished and after 16 hours disappeared with simultaneous development of a band very nearly coincidental with that of tribenzoylethylene (Fig. 4E). This result indicated that relatively little of the completed addition product (XIIId) was formed and that reversion to tribenzoylethylene was the chief result.

From the foregoing results it would appear that acidification of the addition-enolate (XV) and action of excess acid on the enol (XVI) causes a significantly greater proportion of ketonization to XIIId (which is relatively stable under these conditions), in competition with loss of alcohol to give VII, than did exact neutralization where the ketonization reaction is minimized. These results may be summarized as follows:



These results seem in the main to be consistent with an enolization mechanism of formation of chalcone from the ketol or its acetate,[15] but they involve the following points of difference which are due essentially to steric factors; in the present case the enol (XVI) is persistent, and the enolization steps (XIIId → XVI and VII → XVI under neutral conditions) are not rapid enough to be important. Since acid-catalysis appears to be far less effective in promoting elimination of alcohol from the enol than it is in causing ketonization, it is suggested that the loss of alcohol from the enol (XVI) takes place in neutral solution by steps such as: loss of the enol hydrogen to the solvent (suppressed by excess acid), loss of alkoxyl ion from XV (suppressed by excess base), and combination of the released ions to form alcohol; or possibly *via* chelation between the relatively acidic enol hydrogen and the alkoxyl oxygen (*cf.* the favorable set-up for this in formulation XVI).

The action of potassium hydroxide on trans-dibenzoylethylene (XIX) in absolute ethanol solution was of interest in view of the foregoing and because methanolic triethylammonium chloride containing a trace of hydrogen chloride apparently causes rapid equilibration with methoxydibenzoylethane.[14] It was believed that *trans*-dibenzoylethylene (XIX), like tribenzoylethylene (VII) would undergo ready addition of alkoxide ion, but that in this case the



addition-enolate (XX or XXI) would be unstable (as compared with XVa). The rapid change in absorptivity and in its wave length in a $0.00005M$ absolute ethanol solution of *trans*-dibenzoylethylene

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[14] (a) It should be noted in this connection by way of contrast that triethylammonium chloride and a trace of hydrogen chloride in methanol appear to cause equilibration between *trans*-dibenzoylethylene and methoxydibenzoylethane and that here the intermediate addition-enol corresponding to XVb is not (and should not be) stable and could (and does) furanize to 3-methoxy-2,5-diphenylfuran. [(b) P. S. Bailey and R. E. Lutz, *J. Am. Chem. Soc.*, **69**, 498 (1947); (c) P. S. Bailey and J. T. Kelley, *J. Am. Chem. Soc.*, **70**, 3442 (1948).] *cf.* Also the addition of methanol by means of sodium methoxide to *p*-bromobenzoylacrylic ester. [(d) R. E. Lutz and G. W. Scott, *J. Org. Chem.*, **13**, 284 (1948)].

[15] D. S. Noyce, W. A. Pryor, and A. H. Bottine, *J. Am. Chem. Soc.*, **77**, 1402 (1955).

upon addition of 0.0007 mole of potassium hydroxide was distinctive and in the expected direction. The very broad *trans*-dibenzoylethylene peak at 269 mμ was depressed from ε 18,800 to a broad shoulder of ε 5,000 at *ca.* 280 mμ and indicated 10–20% retention of dibenzoylethylene in an equilibrium mixture. The development of a strong narrow peak at 246 mμ, ε 23,400, approaching that of methoxydibenzoylethane (XXII) which did not change when the solution was neutralized or acidified with hydrogen chloride, corresponded to 80–90% of ethoxydibenzoylethane (this however includes any small amounts of addition-enolate such as XX, and of dimolecular products, which would absorb similarly).

The above interpretation was substantiated by carrying out this reaction using a larger and practical concentration of dibenzoylethylene in methanol, and actual isolation in good yield of the difficultly - crystallizable methoxydibenzoylethane (XXII). It was then shown that the steps, XIX $\rightleftharpoons$ XX $\rightleftharpoons$ XXII, actually did involve rapid equilibrium in the presence of base, by treating separate methanol solutions of *trans*-dibenzoylethylene and pure methoxydibenzoylethane with base under identical conditions. The absorptivity curves for the equilibrium mixtures, determined promptly, (Fig. 5C and D), coincided within very close limits. A value for percent of dibenzoylethylene at equilibrium of 7.4 ± 1.0 was arrived at by proportions from the absorptivities at the wave lengths 246 and 280 mμ for the pure compounds, XIX and XXII (Fig. 5A, B), and the equilibrium from XXII (Fig. 5D, which is probably more nearly correct than curve 5C).

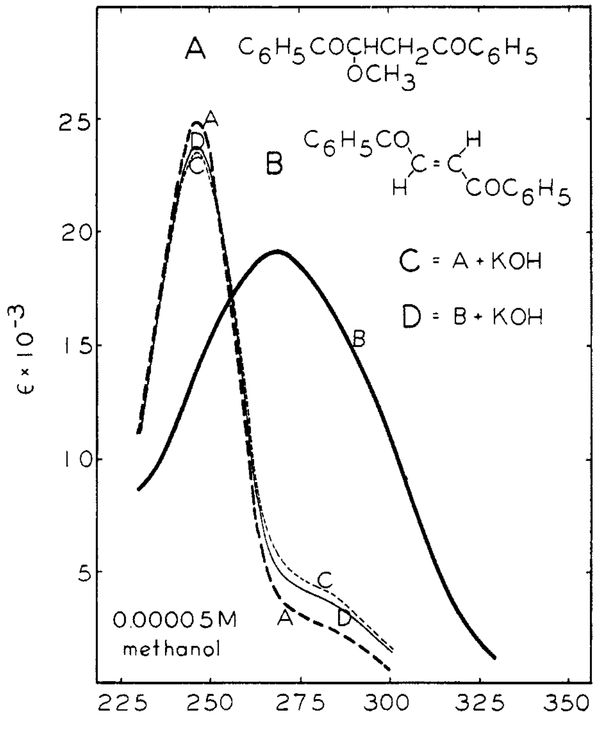

FIG. 5.—ULTRAVIOLET ABSORPTIVITIES OF *trans*-DIBENZOYLETHYLENE AND METHOXYDIBENZOYLETHANE AND BASE-CATALYZED EQUILIBRIUM MIXTURES.

The deviations between the two equilibrium curves (Fig. 5C and D), using both methanol and ethanol, were very small but were very similar and significant. The curves obtained by addition of base to *trans*-dibenzoylethylene indicated consistently 2–3% less of this constituent than did the curves obtained in starting from methoxydibenzoylethane. This indicated that a slow reversible secondary reaction was involved in which the concentration of dibenzoylethylene was important. On standing for two days the absorptivities came practically to coincidence at a slightly different point. This indicated a further but exceedingly slow change involving a drop in the dibenzoylethylene absorptivity. From these facts it is suggested that the slow secondary reactions involve a typically reversible Michael condensation between enolate (XX) and dibenzoylethylene and formation of a dimolecular product which would have an absorptivity unlike that of XIX and very like that of XXII.

Further investigations suggested by these results are in progress.

EXPERIMENTAL[16]

1,1,2-Tribenzoylethane (*α-phenacyldibenzoylmethane*) (IV) was prepared by reduction of VII with sodium hydrosulfite,[4f] and in 80% yield by a modification of the K. and T. method[4e] from sodio dibenzoylmethane and phenacyl bromide (in propanol-2, refluxing for 20 min.).

Hydrolysis in 0.00005 *M* absolute ethanol solution by a small excess of potassium hydroxide (room temperature for 3 hours) gave 1,2-dibenzoylethane, m.p. 143–145°, identified by mixture m.p. with an authentic sample.

cis-1,1,2-Tribenzoylethane enol (V). A mixture of 0.18 g. of the *cis* copper enolate (VI), 30 ml of ether, and 20 ml. of 5% aqueous hydrochloric acid, was shaken vigorously until all of the copper salt had disappeared (15 min.). The ether layer was washed with water until free from acid and the enol was separated as pale yellow crystals after partial evaporation of the ether by a stream of air. After recrystallization from ether-ligroin mixture, it melted at 85–87°; after solidification it remelted at 155°; yield 0.06 g. (37%).

Anal. Calc'd for $C_{23}H_{18}O_3$: C, 80.68; H, 5.30. Found: C, 80.67; H, 5.33.

The enol gave a deep red color test with alcoholic ferric chloride. In alcohol solution it ketonized to IV, upon heating or upon standing with a little added acid as catalyst. It was converted back to the copper salt (VI) when an ether solution was shaken with saturated aqueous copper acetate solution.

Bromination of a solution of 0.45 g. of enol (V) in 150 ml. of methanol by titration with standardized methanolic bromine used up nearly one equivalent amount of bromine. Dilution of the solution with water and recrystallization. from warm ethyl acetate-methanol gave 0.43 g. (80%) of 1-bromo-1,1,2-tribenzoylethane; identified by mixture m.p. with a sample prepared previously.[4f]

Reaction of 1,1,2-tribenzoylethane (IV) with bromine failed to go to completion under the same condition.

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(16) Microanalyses were by Misses Y. M. Lai and B. G. Williamson.

cis-Copper enolate of 1,1,2-tribenzoylethane (VI). Addition of 0.25 g. of potassium hydroxide in 10 ml. of methanol to a solution of 0.25 g. of IV in 30 ml. of methanol brought about rapid coloration to a bright yellow. The solution was allowed to stand for half a minute at room temperature and was poured into ice-water, acidified with 3 ml. of conc'd acetic acid, and immediately extracted with ether. The ether extract was shaken vigorously with 10 ml. of saturated aqueous copper acetate for several minutes and the deep-green copper salt gradually separated. After filtering, washing, and drying, the precipitate was crystallized from a 1:2 chloroform-ether mixture, 0.187 g. (70%); deep green. After recrystallization from the same solvent it melted at 205–206°.

Anal. Calc'd for $C_{46}H_{34}CuO_6$: C, 74.03; H, 4.59; Cu, 8.51. Found: C, 73.78; H, 4.50; Cu, 8.71.

trans-Copper enolate of 1,1,2-tribenzoylethane (X). Zinc dust (2 g.) was added slowly with stirring to an ice-cooled solution of 0.8 g. of VII in 30 ml. of conc'd acetic acid, 30 ml. of ether, and 3 ml. of water at a maintained temperature of 0°. After 10 min. the deep greenish-yellow mixture was filtered and diluted with water. The product was extracted with ether and washed with ice-water until free from acid. The ether extract then was shaken with a saturated aqueous copper acetate solution. The pale greenish-gray copper salt precipitated; yield 0.33 g. (39%), m.p. 184–188°. Repeated recrystallizations from chloroform-ether mixture raised the m.p. to 189–190°. A mixture melting point with the *cis* copper enolate (VI) was 189–195°.

Anal. Calc'd for $C_{92}H_{70}CuO_{12}$: C, 77.21; H, 4.93; Cu, 4.44. Found: C, 77.36; H, 4.70; Cu, 4.81.

Treatment of the copper enolate (X) *with acid.* (*a*). A suspension of X in ether was treated with dilute hydrochloric acid (30 min.) by the procedure above (for VI). A 17% yield of the enol (V), m.p. 85–87°, was obtained as the first crop; the rest of the material upon recrystallization several times from ethanol gave the saturated triketone IV, m.p. 153–155° (identified by mixture m.p.).

(*b*). A solution of 0.2 g. of X in 20 ml. of chloroform was shaken with dilute hydrochloric acid. The deep-green chloroform solution, which was almost immediately decolorized, was separated and washed. A few milliliters of this solution when shaken with copper acetate solution reproduced the copper salt X, m.p. 188–190°. The residue after evaporation of the rest of the chloroform solution was crystallized from ether-ligroin, m.p. 81–96°; after repeated recrystallization it melted at 150–154° and was identified as IV by mixture m.p.

(*c*). The following experiment was designed to release the *trans* enol (IX) in chloroform solution containing a small amount of hydrogen bromide, in order to show in a separate experiment that the *trans* enol ketonizes under conditions identical with those involved in the conversion of tribenzoylethylene by bromination into 3-benzoyl-4-bromo-2,5-diphenylfuran where the analogous bromo *trans* enol is postulated as intermediate.

To a solution of 0.2 g. of X in 20 ml. of chloroform was added 0.34 g. of 20% hydrogen bromide-acetic acid. After standing at room temperature for 6 hrs., washing with water, and evaporation, the residue was crystallized from methanol; yield of IV 0.16 g. (82%), m.p. 151–154° (identified by mixture m.p.).

Attempted preparations of 2-methoxy-1,1,2-tribenzoylethane (XIIIe) from VII with equivalent amounts of potassium hydroxide in methanol (at room temperature for 14 hrs.), or with triethylamine hydrochloride according to the method of Bailey and Lutz,[14b] gave only unchanged material and oils which could not be converted into a solid derivative by acetic anhydride and sulfuric acid.

2-Methoxy-1,1,2-tribenzoylethylene (XVIII) was prepared from 1.1 g. of XVII by treatment with an equivalent amount of sodium methoxide in absolute methanol at room temperature for 2 hrs., addition of water, and work-up in the usual way; crystallized from methanol, 0.73 g. (67%); recrystallized from methanol, m.p. 106–107°.

Anal. Calc'd for $C_{24}H_{18}O_4$: C, 77.82; H, 4.90. Found: C,77.55; H, 5.35.

Attempted reduction with sodium hydrosulfite in 60% methanol (refluxing for 5 min.) gave only oil. Reduction with stannous chloride in conc'd acetic and hydrochloric acids gave an oil and a small amount of 2,2′-bis(4-benzoyl-2,5-diphenylfuranone-3)[4f], m.p. 255–260°, identified by mixture m.p.

Phenyldibenzoylmethane enol (*cf.* Ic) was prepared by the general method employed for other β-diketones by Hauser, *et al.*[17] using phenol benzoate, desoxybenzoin, and sodium amide (molar ratio, 1:1:2) in anhydrous ether (refluxing 2 hrs.). After washing the mixture with dilute hydrochloric acid, extracting with 10% potassium hydroxide, and acidifying the aqueous extract, phenyldibenzoylmethane enol separated as yellow needles, m.p. 152–158°; yield 9%. It melted at 156–158° (rapid heating) after several recrystallizations from ether, and after solidification it re-melted at 148–149° (M. and W.[4c] m.p. 148–151°).

Anal. Calc'd for $C_{21}H_{16}O_2$: C, 83.98; H, 5.37. Found: C, 83.68; H, 5.49.

Infrared absorptivity:[18] no normal hydroxyl or keto bands; strong serrated absorptivities over the range 6.3–7.6 mμ.[19]

It gave a deep red-brown color with alcoholic ferric chloride.

A *copper enolate* (m.p. 282–284°) was obtained by the method described for VI.

Anal. Calc'd for $C_{42}H_{30}CuO_4$: Cu, 9.60. Found: 9.05.

The colorless *keto form* (Ic) was obtained from the enol by refluxing an acidic ethanol solution for 3 hours, m.p. 148.5–149°.[20] It did not react with alcoholic ferric chloride or aqueous copper acetate.

Anal. Calc'd for $C_{21}H_{16}O_2$: C, 83.98; H, 5.37. Found: C, 83.77; H, 5.37.

Infrared absorptivities:[18] it showed strong sharp peaks at 5.96 and 6.04 μ.

A new preparation of methoxy-1,2-dibenzoylethane (XXII). A solution of 1.5 g. of XIX in 500 ml. of methanol and 20 ml. of 0.2% methanolic potassium hydroxide, after standing at room temperature for 16 hrs., was diluted with water and extracted with benzene. Evaporation of the benzene and crystallization from ethyl bromide-petroleum ether mixture gave 0.03 g. (m.p. 119–131°, colorless) and 1.39 g. (82%) of XXII (m.p. 41–44°); recrystallized from a small amount of methanol (m.p. 48–49°); identified by analysis and mixture m.p. with an authentic sample.[21]

Acknowledgments. We are indebted to Dr. W. Bruce Black who in the earlier stages of this work prepared some of the simple dibenzoylmethane derivatives and entered into discussions of the problems, and also to Dr. T. I. Crowell for helpful discussions and criticisms.

CHARLOTTESVILLE, VIRGINIA

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(17) C. R. Hauser, B. I. Ringler, F. W. Swamer, and D. F. Thompson, *J. Am. Chem. Soc.*, 69, 2649 (1947).

(18) A Baird spectrophotometer was used. The solvent was chloroform. Further more detailed studies on infrared absorptivities in this field are in progress.

(19) R. S. Rasmussen, D. D. Tunnicliff, and R. R. Brattain, *J. Am. Chem. Soc.*, **71**, 1068 (1949).

(20) Both Marshall [*J. Chem. Soc.*, **107**, 820 (1915)] and Goldschmidt (ref. 4d) reported m.p. 149° but Bartlett and Cohen [*J. Org. Chem.*, **4**, 88 (1939)] reported m.p. 144.5–145.6°.

(21) R. E. Lutz, *J. Am. Chem. Soc.*, **51**, 3008 (1929).