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DIARYLIODONIUM SALTS—XII

THE PHENYLATION OF DIMEDONE, DIBENZOYLMETHANE AND TRIBENZOYLMETHANE[1–4]

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Abstract—Diphenyliodonium salts in t-butyl alcohol have converted the anions of dimedone, dibenzoylmethane and tribenzoylmethane to C-phenyl, C, C-diphenyl, O-phenyl and O, C-diphenyl derivatives, the structures of which have been proved by degradation and synthesis. Reactions of dimedone in methanol or ethanol gave mainly products arising from dehydrogenation of the solvent.

INTRODUCTION

PAPERS of this past year have dealt with the synthesis[6,7] of diphenyliodonium salts, their reactions with nucleophilic reagents[3,8–10] (including their copper-catalyzed reactions[7,9–11]) their electroreduction,[11,12] their use in the synthesis of diphenylenes,[7a] terphenyls[7b] and organometallic compounds[13] and the synthesis and properties of iodonium salts from thiophene.[12b]

In the present paper there are reported the reactions of the carbanions from

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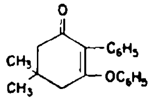
[1] This paper is taken from the dissertations of P. S. Forgione and of M. D. Yudis, submitted in partial fulfillment of the requirements of the degree of Doctor of Philosophy at the Polytechnic Institute of Brooklyn.

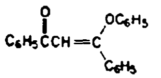
[2] The phenylation of dimedone by the present authors was reported at the New York Meeting of the Amer. Chem. Soc. Sept. (1957) (Abstracts of Papers, p. 36P).

[3] While this manuscript was in preparation there appeared an independent report of the phenylation of dimedone by Russian workers: O. Neilands, G. Vanags and E. Gudriniece, *J. Gen. Chem. U.S.S.R.* **28**, 1201 (1958); *Chem. Abstr.* **52**, 19988 (1958).

[4] For brevity, the trivial name dimedone is used here in place of the systematic names 5, 5-dimethyl-1-cyclohexen-1-ol-3-one and 5, 5-dimethylcyclohexane-1, 3-dione but with their numbering systems. Phenyl ethers of the enolic forms of the ketones are named as O-phenyl derivatives; eg.,



O, 2-diphenyldimedone



O-phenyldibenzoylmethane

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[b] Alfred P. Sloan Foundation Fellow, 1956–1959.

[c] Alfred P. Sloan Foundation Fellow, 1959.

[6a] F. M. Beringer, R. A. Falk, I. Lillien, M. Karniol, G. Masullo, M. Mausner and E. Sommer, *J. Amer. Chem. Soc.* **81**, 342 (1959); [b] F. M. Beringer and R. A. Falk, *Ibid.* **81**, 2997 (1959).

[7a] W. Baker, J. W. Boston and J. F. W. McOmie, *J. Chem. Soc.* 2658 (1958); [b] R. C. Fuson and R. L. Albright, *J. Amer. Chem. Soc.* **81**, 487 (1959).

[8] F. M. Beringer, E. M. Gindler, M. Rapoport and R. J. Taylor, *J. Amer. Chem. Soc.* **81**, 351 (1959).

[9] M. C. Caserio, D. L. Glusker and J. D. Roberts, *J. Amer. Chem. Soc.* **81**, 336 (1959).

[10] F. M. Beringer and M. Mausner, *J. Amer. Chem. Soc.* **80**, 4535 (1958).

[11] H. E. Bachofner, F. M. Beringer and L. Meites, *J. Amer. Chem. Soc.* **80**, 4269 (1958).

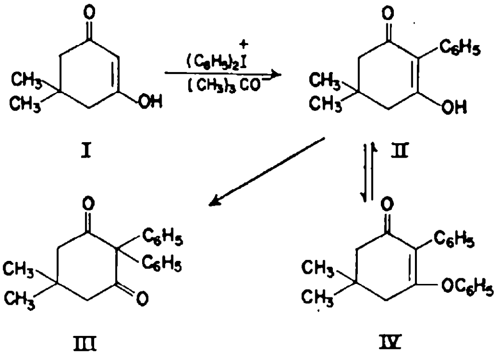
[12a] H. E. Bachofner, F. M. Beringer and L. Meites, *J. Amer. Chem. Soc.* **80**, 4274 (1958); [b] F. M. Beringer H. E. Bachofner, R. A. Falk and M. Leff, *J. Amer. Chem. Soc.* **80**, 4279 (1958).

[13] O. A. Reutov, O. A. Ptitsyna and H. Hung-Weng, *Dokl. Akad. Nauk SSSR* **122**, 825 (1958); O. A. Reutov, O. A. Ptitsyna and N. B. Stiazhkina, *Ibid.* **122**, 1032 (1958).

dimedone, dibenzoylmethane and tribenzoylmethane with the diphenyliodonium cation in t-butyl alcohol. The reactions of the carbanion from dimedone with both the diphenyliodonium and the 2-nitrodiphenyliodonium ions were also studied in methanol and ethanol (in which solvents quite different results were obtained).

The phenylation products from dimedone[2–4]

In t-butyl alcohol at reflux dimedone (I) was converted by sodium t-butoxide and diphenyliodonium chloride or tosylate into 2-phenyldimedone (II) and 2,2-diphenyldimedone (III), while at room temperature 0,2-diphenyldimedone (IV) was also obtained. In water 2,2-diphenyldimedone was obtained, but no monophenylated product could be isolated. It was shown that 2-phenyldimedone could be converted under the first conditions to 2,2-diphenyldimedone, while mild acid hydrolysis of 0,2-diphenyldimedone gave 2-phenyldimedone and phenol.



In Table 1 the results obtained in the present work in t-butyl alcohol or water are summarized and compared with those of Neilands *et al.*[3]

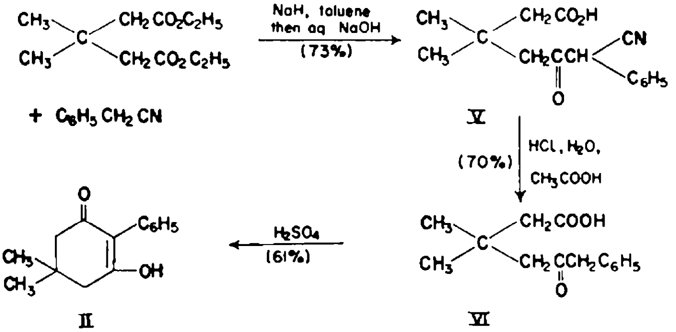
The structure of 2-phenyldimedone (II) was unequivocally established by its

TABLE 1. PHENYLATION PRODUCTS OF DIMEDONE AND 2-PHENYLDIMEDONE

Reaction conditions			Reagents		% Yield of products (based on diketone)		
Solvent	T (°C)	hr	Ketone	Anion	II	III	IV
1 : 1 w–d[a]	100°	2	I	Br	8·5	4	9
$(CH_3)_3COH$	83°	4	I	Cl	22	23	
$(CH_3)_3COH$[b]	83°	5	I	Cl	16	25	
$(CH_3)_3COH$	83°	4	I	TsO[c]	18	19	9
$(CH_3)_3COH$	25°	72	I	Cl	13	5	9
$(CH_3)_3COH$	83°	2	II	Cl		71	
H_2O	100°	4	I	Cl		14	

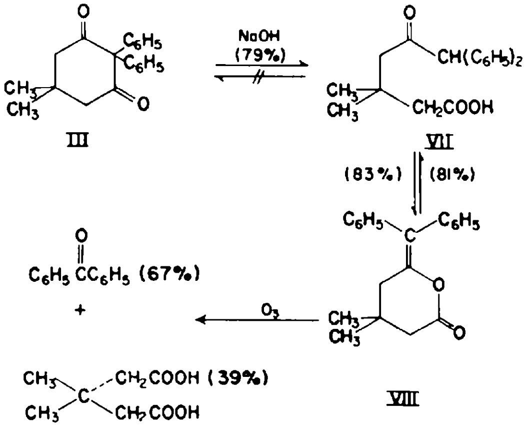
[a] The reaction in 1:1 water–dioxane was reported[3]; a very small amount of O-phenyldimedone was also obtained. The other reactions are those of the present work. [b] Reverse addition: anion of dimedone added slowly to diphenyliodonium chloride. [c] *p*-Toluenesulfonate (tosylate).

synthesis from ethyl β, β-dimethylglutarate.[14] The first step of the condensation gave in good yield the acid nitrile V, from which the nitrile group could be removed, also in good yield, by acid hydrolysis to VI. Ring closure to 2-phenyldimedone was best effected by the brief heating to 120° of keto acid VI in 72 per cent sulphuric acid.[15] The 2-phenyldimedone prepared by ring closure of VI was identical to that



obtained by the phenylation of dimedone. This established also the structure of 0,2-diphenyldimedone (IV). The direct reaction of V and its ethyl ester under these conditions gave high yields of crude product which unfortunately proved difficult to purify.

An attempt to prepare 2, 2-diphenyldimedone by a similar cyclization of keto acid (VII) with polyphosphoric acid[16] gave a six-membered cyclic enol lactone (VIII), whose structure was proved by ozonolysis to benzophenone and β,β-dimethylglutaric acid.



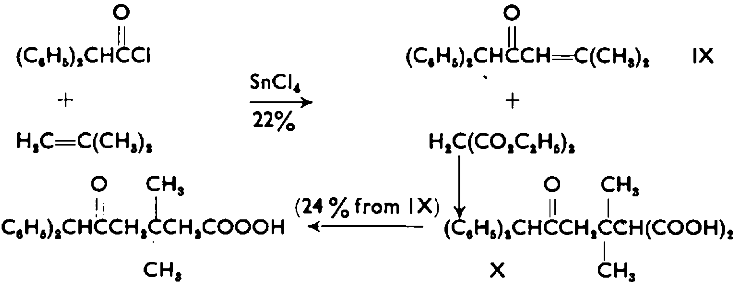
The structure of 2,2-diphenyldimedone was finally established by showing the

[14] The synthesis was patterned after the work of T. Henshall, W. E. Silbermann and J. G. Webster, *J. Amer. Chem. Soc.* 77, 6656 (1955); W. E. Silbermann and T. Henshall, *Ibid.* 79, 4107 (1957).

[15] 2-Phenyl-4,4-dimethylcyclohexane-1,3-dione has been prepared from ethyl 2,2-dimethyl-5-oxo-6-phenylhexanoate by condensation with sodium hydride in toluene: H. Born, R. Pappo and J. Szmaskocicz, *J. Chem. Soc.* 1779 (1953).

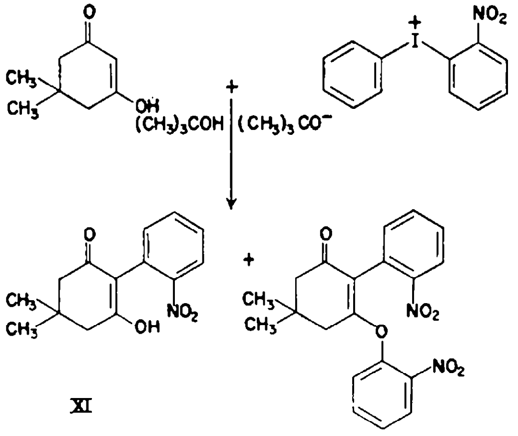
[16] P. D. Gardner and W. J. Horton, *J. Amer. Chem. Soc.* 75, 4976 (1953) prepared the enol lactone of 2,3,4-trimethoxybenzosuber-5-one-6-acetic acid from β,β-dicarboxy-3,4,5-trimethoxyphenylcaproic acid with polyphosphoric acid. J. H. Helberger, S. Ulubay and H. Civelekoglu, *Liebigs Ann.* 561, 215 (1949) prepared α-angelica lactone from levulinic acid in nearly quantitative yield using catalytic amounts of syrupy phosphoric acid.

identity of keto acid VII obtained from III to that synthesized independently. The first step utilized the method of Colonge and Chambion.[17]



$$(C_6H_5)_2CH\overset{O}{\overset{\|}{C}}Cl + H_2C{=}C(CH_3)_2 \xrightarrow[22\%]{SnCl_4} (C_6H_5)_2CH\overset{O}{\overset{\|}{C}}CH{=}C(CH_3)_2 \ \text{IX} + H_2C(CO_2C_2H_5)_2 \longrightarrow (C_6H_5)_2CH\overset{O}{\overset{\|}{C}}CH_2\underset{CH_3}{\overset{CH_3}{C}}CH(COOH)_2 \ \text{X} \xrightarrow{(24\%\text{ from IX})} (C_6H_5)_2CH\overset{O}{\overset{\|}{C}}CH_2\underset{CH_3}{\overset{CH_3}{C}}CH_2COOOH$$

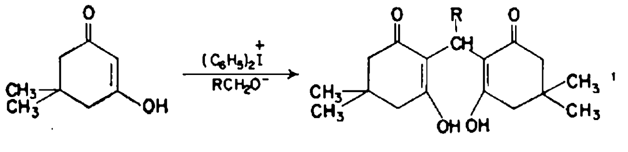
When 2-nitrodiphenyliodonium bromide replaced diphenyliodonium chloride in the reaction with dimedone in t-butyl alcohol, 2-(*o*-nitrophenyl)-dimedoue (XI) and 0,2-bis-(*o*-nitrophenyl)-dimedone (XII) were isolated but 2,2′-di-(*o*-nitrophenyl)-dimedone was not found. The structure of XI was confirmed by its periodate oxidation[18] to *o*-nitrobenzoic and β,β-dimethylglutaric acids, while the structure of XII was demonstrated by its hydrolysis with hydrobromic acid to XI.



XI

XII

The replacement of t-butyl alcohol by methanol or ethanol brought about a complete change in the nature of the main products. The reaction of 2-nitrodiphenyliodonium bromide in methanol produced 2,2-methylene-bis-dimedone (XIIIa) as the only isolable product in 66 per cent yield. With diphenyliodonium chloride in



XIIIa, R=H; XIIIb, R=CH3

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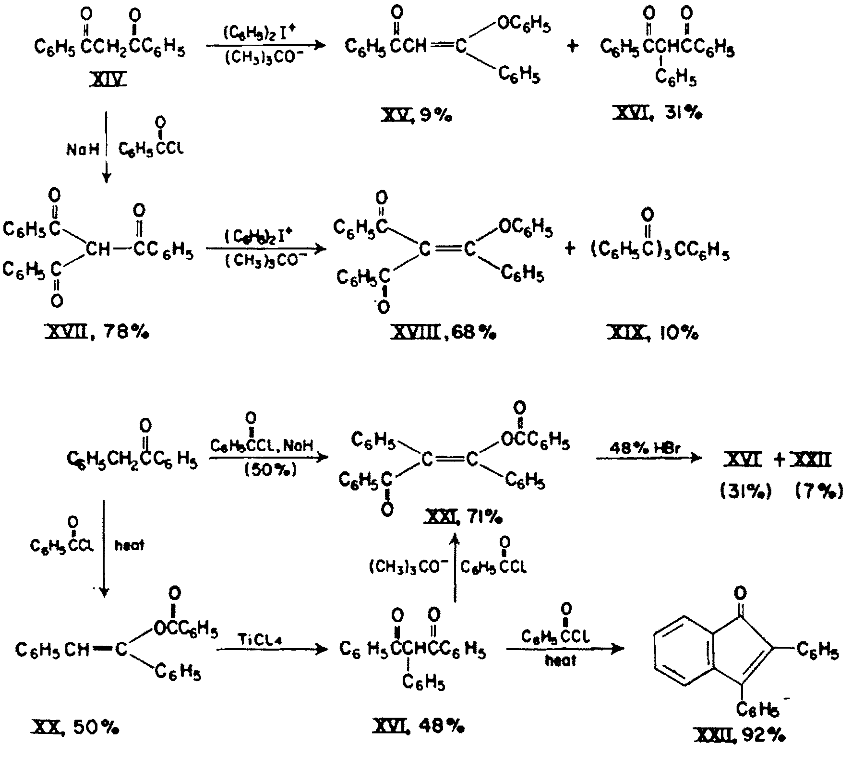
[17] J. Colonge and J. Chambion, *C.R. Acad. Sci., Paris* **224**, 128 (1947).

[18] M. L. Wolfrom and J. M. Bobbitt, *J. Amer. Chem. Soc.* **78**, 2489 (1956).

ethanol a complex mixture was formed from which 2-phenyl- and 2,2-diphenyldimedone and 2,2'-ethylidene-bis-dimedone (XIIIb), as the corresponding octahydroxanthene,[19] were all isolated in low yields. In some manner, to be discussed in a later paper, the iodonium cation had apparently dehydrogenated alcohol to aldehyde, which then condensed with the dimedone.[19]

Phenylation products from di- and tribenzoylmethane[4]

The products of the reactions of the carbanions of di- and tribenzoylmethane with diphenyliodonium chloride in t-butyl alcohol are now shown with their alternative syntheses.[20]



On vigorous alkaline hydrolysis products XV and XVIII gave phenol, acetophenone and benzoic acid and are thus phenyl ethers. The isomeric products XVI and XIX under similar conditions gave desoxybenzoin and benzoic acid and are thus C-phenyl derivatives.[21]

The preceding reaction scheme includes two routes to phenyldibenzoylmethane (XVI) from desoxybenzoin: (a) the formation and rearrangement of enol benzoate XX in overall yield of about 25 per cent, and (b) the formation and hydrolysis of enol

[19] E. C. Horning and M. G. Horning, *J. Org. Chem.* **11**, 95 (1946).

[20] Di- and tribenzoylmethane and phenyldibenzoylmethane are conventionally represented in their nonenolic forms. The geometry of compounds XV, XX and XXI is not known.

[21] It has been reported that C-phenyltribenzoylmethane (XIX) was formed by the reaction of excess ethereal benzoyl chloride with the sodium salt of desoxybenzoin: J. Meisenheimer and K. Weibezahn, *Ber.* **54** 3195 (1921). That the product so prepared is, rather, the vinyl benzoate XXI is shown by a depression of m.p. with authentic XIX and by the presence in the infrared spectrum of ester carbonyl absorption (5·74 μ) and conjugated ketone absorption (6·0 μ).

benzoate XXI in overall yield of about 15 per cent. Neither is as attractive as the direct phenylation of dibenzoylmethane.

An attempt at direct C-benzoylation of phenyldibenzoylmethane by heating with benzoyl chloride gave instead the red dehydration product 2,3-diphenylindenone (XXII).

t-Butyl phenyl ether. When reactions were first run in t-butyl alcohol, it was thought that one product might be that of the t-butoxide ion with the diphenyliodonium cation, namely t-butyl phenyl ether.

$$(CH_3)_3CO^- + C_6H_5\overset{+}{I}C_6H_5 \rightarrow (CH_3)_3COC_6H_5 + C_6H_5I$$

It was found that the two ions reacted smoothly, but that direct separation of the products was difficult. However, catalytic hydrogenation of the mixture converted the iodobenzene to benzene and biphenyl and allowed isolation of t-butyl phenyl ether in 40 per cent overall yield.

This result is especially interesting in view of the recent failure of Scardiglia and Roberts[22] to produce this ether by addition of the t-butoxide ion to benzyne produced from bromobenzene with amide ion in liquid ammonia.

No t-butyl phenyl ether was found in runs with di- or triketones, however, presumably because the concentration of t-butoxide ion was so low.

DISCUSSION

The synthesis of compounds of the type C_6H_5CHYZ (where Y and Z are aryl or electron-attracting groups) might be accomplished in the following general sequences; each arrow may represent one or more preparative steps.

$$\text{(I)}\quad C_6H_5CH_3 \rightarrow C_6H_5CH_2Y \rightarrow C_6H_5CHYZ$$

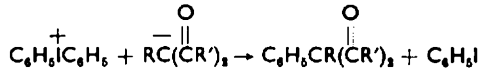
$$\text{(II)}\quad C_6H_4\ \text{(benzyne)} + H_2CYZ \rightarrow C_6H_5CHYZ$$

$$\text{(III)}\quad C_6H_5X + HCYZ \rightarrow C_6H_5CHYZ + X$$

Sequence I involves the conversion of toluene through mono-substituted and disubstituted compounds by a series of substitutions, condensations and alterations. A synthesis of phenylmalonic ester is an example.[23]

Sequence II is exemplified by the work of Levine and Leake[24] in which a carbanion is added to benzyne, and the ring of the adduct is protonated. An example is the phenylation of malonic ester (51 per cent yield).[24]

Sequence III involves the replacement of an aromatic substituent by a group HCYZ, which could be anionic, radical or cationic. In the present work, C_6H_5X is the diphenyliodonium cation and HCYZ is a carbanion derived from a diketone. In the following equation R may be hydrogen or an alkyl, aryl or acyl group.



$$C_6H_5\overset{+}{I}C_6H_5 + R\overset{-}{C}(\overset{\overset{\displaystyle O}{\|}}{C}R')_2 \rightarrow C_6H_5CR(\overset{\overset{\displaystyle O}{\|}}{C}R')_2 + C_6H_5I$$

The few cases studied so far show that phenylation of carbanions with iodonium salts has two problems well-known in alkylation: substitution on oxygen and disubstitution. Regarding the alkylation of ambident ions it has been stated: "the

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[22] F. Scardiglia and J. D. Roberts, *Tetrahedron* **3**, 200 (1958).

[23] P. A. Levene and G. M. Meyer, *Organic Syntheses* Coll. Vol. II, p. 288. John Wiley, New York (1943).

[24] R. Levine, San Francisco meeting of the Amer. Chem. Soc., April (1958) (Abstracts of Papers, p. 9M); W. W. Leake and R. Levine, *Chem. & Ind.* 1160 (1955); *J. Amer. Chem. Soc.* **81**, 1169 (1959).

greater the S_N1 character of the transition state the greater is the preference for covalency formation with the atom of higher electronegativity and, conversely, the greater the S_N2 contribution to the transition state the greater the preference for covalency formation with the atom of lower electronegativity."[25] Of ambident ions previously studied with the iodonium salts,[26] most (nitrite, sulfite, sulfinate, cyanide and the anions from sulfonamides and from ethyl oxalacetate) have given products with the new covalency to the less electronegative atom; only phenoxide ions have formed products (ethers) through the more electronegative atoms.

With respect to disubstitution, in one case it was not observed (dibenzoylmethane), while in another (dimedone) both O,C- and C,C-disubstituted products were formed. With the latter diketone the relative amounts of monophenyl and diphenyl derivatives seemed to be relatively insensitive to the order of addition.

It is planned to discuss the mechanisms of these reactions in forthcoming papers on reactions of iodonium salts with organometallic compounds and with carbanions from esters.

EXPERIMENTAL[27]

Starting materials. Dimedone was used as received from Eastman Organic Chemicals, while dibenzoylmethane[28] and the various iodonium salts were prepared according to published procedures. Phenylacetonitrile was redistilled before use. Ethyl β,β-dimethylglutarate was obtained by the esterification of β,β-dimethylglutaric acid prepared by the Guareschi synthesis from acetone and cyanoacetamide.[29] Diphenylacetyl chloride was prepared from diphenylacetic acid (obtained from Eastman Organic Chemicals) by the action of thionyl chloride. Absolute methanol and ethanol were used as received, while t-butyl alcohol was redistilled from sodium.

Tribenzoylmethane was made by a modification of the procedure of Abell[30] as follows. To a suspension of 12·0 g (0·5 mole) of sodium hydride in 2 l. of anhydrous ether, dibenzoylmethane (112 g, 0·5 mole) was added over 1 hr. After 3 hr at room temp. the stirred mixture containing a gel-like suspension was treated with 70 g (0·5 mole) of benzoyl chloride in 50 ml anhydrous ether. As the addition progressed, the suspension could be stirred more easily. Twelve hours later there were added 10 ml ethanol, 300 ml water and, finally, 100 ml 6 N HCl. The solid precipitate was collected, washed with water and dried to give 156 g (0·39 mole 78%) of tribenzoylmethane, m.p. 225–226°; reported[30] m.p. 224–226°. No other product was obtained from the ether layer. Several crystallizations from acetonitrile raised the m.p. to 237–238°; λ_{max} 250 and 330 mμ, ϵ 26,700 and 6500.

(Found: C, 80·62; H, 4·95. Calc. for $C_{22}H_{16}O_3$: C, 80·47; H, 4·91%).

t-Butyl Phenyl Ether

Diphenyliodonium chloride with potassium t-butoxide in t-butyl alcohol

Diphenyliodonium chloride (270 g, 0·854 mole) was added over 30 min to a solution of 35·1 g (0·9 g atom) of potassium in 1500 ml t-butyl alcohol. The temperature was allowed to reach but not exceed 60°. After 6 hr at room temp. the reaction mixture was filtered to give 56 g (0·76 mole) potassium chloride.

The filtrate was concentrated to 300 ml by distillation of t-butyl alcohol. To the residue a solution

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[25] N. Kornblum, R. A. Smiley, R. K. Blackwood and D. C. Iffland, *J. Amer. Chem. Soc.* **77**, 6269 (1955).

[26] F. M. Beringer, A. Brierley, M. Drexler, E. M. Gindler and C. C. Lumpkin, *J. Amer. Chem. Soc.* **75**, 2708 (1953); F. M. Beringer and E. M. Gindler, *J. Amer. Chem. Soc.* **77**, 3203 (1955).

[27] Analyses were performed by the Schwarzkopf Micro-analytical Laboratories, Woodside, New York, by Dr. K. Ritter, Basel, Switzerland, and by the analytical laboratories of the Schering Corp. Melting points were corrected. Ultraviolet spectra were obtained in methanol and alkaline methanol where noted. Neutralization equivalents and dissociation constants were determined potentiometrically in 50% (v/v) aqueous ethanol.

[28] C. F. H. Allen, R. D. Abell and J. B. Normington, *Organic Syntheses* (2nd Ed.) Coll. Vol. I, p. 205. John Wiley, New York (1941).

[29] F B. Thole and J. F. Thorpe, *J. Chem. Soc.* **99**, 422 (1911).

[30] R. D. Abell, *J. Chem. Soc.* **101**, 998 (1912).

of 60 g KOH in 20 ml water and 100 ml methanol was added. This solution was treated with hydrogen at 2–3 atmospheres press. in the presence of 10 g 5% palladium on calcium carbonate until uptake ceased. After removal of the catalyst, the reaction mixture was diluted with 1 l. water and extracted with ether. Distillation gave 51 g (0·34 mole, 40%) of *t-butyl phenyl ether*, b.p. 84–85° at 19 mm η_D^{37} 1·4905.

(Found: C, 79·74; H, 9·31; Calc. for $C_{10}H_{14}O$: C, 79·94; H, 9·38%).

Constants previously reported for t-butyl phenyl ether are the boiling point[31] (80°/20 mm) and the refractive index[32] (n_D^{20} 1·4880).

Isomerization of t-butyl phenyl ether to 4-t-butylphenol

Addition with cooling of 1·0 g anhydrous titanium tetrachloride to 2·0 g (13·3 mmoles) t-butyl phenyl ether gave a solution which soon turned red and solidified. After 5 min 115 ml water containing 1·5 g NaOH was added, giving a white precipitate of hydrated titanium dioxide. This was collected and washed with 10 ml 0·1 N NaOH. The aqueous solutions were combined and made weakly acid with HCl. The precipitate was collected and recrystallized from water to give 1·4 g (9·2 m moles, 60%) of 4-t-butylphenol, m.p. 98–99°, undepressed by admixture with an authentic sample.

Reference Compounds Related to Dimedone

(a) 2-*Phenyldimedone by ring closure*

3,3-*Dimethyl-5-oxo-6-cyano-6-phenylhexanoic acid* (V). To 95 g of a 25% suspension of sodium hydride (0·99 mole) in mineral oil was added 55·2 g (0·47 mole) phenylacetonitrile in 300 ml dry toluene and the mixture was stirred for 12 hr at room temp. After 102 g ethyl β,β-dimethylglutarate in 100 ml toluene was slowly added (exothermic reaction), the suspension was heated at 60° for 6 hr with vigorous stirring. Material which separated from the toluene solution was repeatedly extracted with benzene and then discarded. The condensation product (acidic due to the α-cyano-ketone group) was extracted from the combined organic phase with 1 N NaOH and saponified by heating for 3 hr on the steam bath. The aqueous solution was acidified, and the ethereal extract of the acid was washed with water, decolorized with charcoal and dried. Evaporation of the ether gave 90·2 g (0·347 mole, 73%) crude 3,3-*dimethyl-5-oxo-6-cyano-6-phenylhexanoic acid* (V), m.p. 100–104°. Recrystallization from acetic acid–hexane and from benzene gave material of m.p. 108–110°; λ_{max} 270 mμ, : 14,300; $\lambda_{max}^{0\cdot1N\ NaOH}$ 254 and 305 mμ, ε 8900 and 17,300.

(Found: C, 70·35; H, 6·76; N, 5·29; neut. equiv. 262 ± 2. Calc. for $C_{15}H_{17}O_3N$: C, 69·47; H, 6·61; N, 5·40%; neut. equiv., 259·3.)

The ethyl ester of V was prepared by refluxing the acid with ethanol in benzene containing 1% conc. H_2SO_4. Distillation gave as the main product the ethyl ester of V, b.p. 153–155°/0·3 mm, d_4^{24} 1·084, n_D^{37} 1·5304; λ_{max} 266 mμ, ε12,200; $\lambda_{max}^{0\cdot1N\ NaOH}$ 254 and 305 mμ, ε 9070 and 17,400.

(Found: C, 70·87; H, 7·27; Calc. for $C_{17}H_{21}O_3N$: C, 71·05; H, 7·37%).

3,3-*Dimethyl-5-oxo-6-phenylhexanoic acid* (VI). A 3 : 1 : 1 solution (260 ml) acetic acid, conc. HCl and water containing 21·3 g (82 mmoles) of cyanoacid V was boiled for 25 hr. After removal of solvent the residue was shaken with water and ether, giving 2·4 g of crude insoluble material, which was removed and crystallized from ethanol–water to give 1·48 g (6·84 mmoles, 8·3%) of 2-*phenyldimedone* (II), m.p. 195–197°; mixed m.p. with material from dimedone and diphenyliodonium chloride 196–197°; infrared spectra were superposable.

The ethereal extract from which the solid had been removed was concentrated to give 18·2 g of a yellow oil, whose infrared spectrum showed no nitrile absorption. (A run of 18 hr indicated about 10% nitrile absorption in the crude product.) Vacuum distillation gave 13·4 g (57·2 mmoles, 70%) of *ketoacid* VI, of b.p. 139–141°/0·1 mm, as a light yellow oil, n_D^{24} 1·527.

(Found: C, 71·59; H, 7·58; neut. equiv. 232 ± 2. Calc. for $C_{14}H_{18}O_3$: C, 71·76; H, 7·74%; neut. equiv. 234·3).

The ethyl ester of VI, prepared as described for the ester of V, was distilled at 153–157°/4 mm, d_4^{25} 1·028, n_D^{25} 1·492.

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[31] D. R. Stevenson, *J. Org. Chem.* **20**, 1232 (1955).

[32] W. T. Olson, H. F. Hipshen, C. M. Buess, I. A. Goodman, I. Hart, J. H. Lamneck and L. C. Gibbons, *J. Amer. Chem. Soc.* **69**, 2451 (1947).

(Found: C, 72·86; H, 8·42; Calc. for $C_{16}H_{22}O_3$: C, 73·24; H, 8·46%).

Cyclization of 3,3-*dimethyl*-5-*oxo*-6-*phenylhexanoic acid* (VI) *to* 2-*phenyldimedone* (II). A preliminary cyclization[14] of 5·41 g ketoacid VI in 55 ml 72% by weight H_2SO_4 was run at 120°. Aliquots (10 ml) were poured into ice water, and the products were filtered and dried.

Minutes	% Yield	M.p.
25	86	187–191°
75	77	182–187°
110	71	179–186°

On a preparative scale, 5·87 g (25 mmoles) ketoacid VI in 60 ml 72% H_2SO_4 was heated at 120° for 20 min, cooled and poured into ice water. The solids were recrystallized from aqueous ethanol and from ethyl acetate to give 3·3 g (15·2 mmoles, 61%) of 2-*phenyldimedone* (II), m.p. 197–198°; mixed m.p. with material from the reaction of dimedone with diphenyliodonium chloride, 197–198°; the infrared spectra were superposable.

The cyclization was attempted with cyanoacid V and its ester under similar conditions. Maximum yield of crude product (81%) was obtained after 2·7 hr, but the m.p. was broad and low, 156–174°, and only a small quantity of pure 2-phenyldimedone could be isolated after a number of crystallizations.

(b) *Synthesis of* 3,3-*dimethyl*-5-*oxo*-6,6-*diphenylhexanoic acid* (VII), *a cleavage product of* 2,2-*diphenyldimedone and its attempted ring closure*

Benzhydryl isobutenyl ketone (IX). To a solution of 138 g (0·61 mole) of diphenylacetyl chloride and 50·5 g (0·9 mole) of isobutylene in 700 ml carbon disulfide protected from moisture and cooled to −5°, there was added over 15 min 22 g (85 mmoles) of stannic chloride from a freshly opened bottle. The mixture was stirred for 4 hr at −5°, brought slowly to room temp. and stirred overnight.

The reaction mixture was treated with 600 ml 1 : 1 HCl, the phases were separated, and the aqueous phase was extracted three times with carbon disulfide. The carbon disulfide phase and extracts were combined, washed with aqueous potassium carbonate and with water, dried and concentrated to a dark brown oil. This residue was heated with 300 ml N,N-dimethylaniline for 2 hr at 180°. The cooled mixture was poured into 600 ml 1 : 1 HCl and extracted with three 300 ml portions ether. The ether extract was washed, dried and distilled to give 58 g crude product, b.p. 160–177°/3 mm. This was crystallized twice from ethanol to give 32·5 g (13·0 mmoles, 22%) *benzhydryl isobutenyl ketone* (IX), m.p. 75–76°, λ_{max} 245 mμ, ε 16,050.

(Found: C, 86·67; H, 7·30; Calc. for $C_{18}H_{18}O$: C, 86·36; H, 7·25%).

The 2,4-*dinitrophenylhydrazone of* IX, formed in the usual way and recrystallized from ethanol, melted at 148–149°.

(Found: N, 12·97. Calc. for $C_{24}H_{22}O_4N_4$: N, 13·02%).

A duplicate run yielded 19% of the desired unsaturated ketone IX. However, when the above procedure was varied in that 130 g (0·5 mole) stannic chloride was added to 115 g (0·5 mole) diphenylacetyl chloride and 56 g (1·0 mole) isobutylene in carbon disulfide at −5°, vacuum distillation of the crude product after treatment with dimethylaniline gave 41 g of a light yellow oil, b.p. 177–197°/4 mm, which gave no solid material after repeated attempts at crystallization. The infrared spectrum indicated phenyl, methyl and ketonic (saturated and unsaturated) absorption, suggesting a mixture of the desired unsaturated ketone IX with 1-phenyl-2-oxo-4,4-dimethyl-1,2,3,4-tetrahydronaphthalene. This material was not further investigated.

1,1-*Dimethyl*-3-*oxo*-4,4-*diphenylbutylmalonic acid* (X). Equimolar quantities (53 mmoles) of benzhydryl isobutenyl ketone and diethyl sodiomalonate were boiled in ethanol for 5 hr. After saponification with KOH and an attempted decarboxylation with a small excess (20 mmoles) HCl, the usual treatment afforded 11·8 g (44 mmoles) crude recovered ketone and 2·54 g (7·2 mmoles) 1,1-*dimethyl*-3-*oxo*-4,4-*diphenylbutylmalonic acid* (X) m.p. 147–148° (with gas evolution) after crystallization from aqueous ethanol and from benzene.

(Found: C, 71·03; H, 6·12; neut. equiv. 352 ± 3; two breaks in titration curve typical of malonic acids. Calc. for $C_{21}H_{22}O_5$: C, 71·17; H, 6·26%; neut. equiv., 354·4).

3,3-*Dimethyl-5-oxo-6,6-diphenylhexanoic acid* (VII). A solution of 1·56 g (68 mg atom) of sodium, 10·9 g (68 mmoles) of diethyl malonate and 14·75 g (59 mmoles) of benzhydryl isobutenyl ketone in 125 ml ethanol was boiled under reflux for 25 hr. After a solution of 4·6 g KOH in 125 ml water had been added and 125 g ethanol–water had been removed by distillation, the solution was refluxed for 6 hr. The cooled solution was extracted with ether both before and after acidification; the latter extract on evaporation gave 11·0 g of a light yellow oil which did not crystallize. A part of this (8·85 g) in 100 ml acetic acid, 50 ml conc. HCl and 50 ml water was refluxed for 12 hr under nitrogen. Concentration of this solution, followed by extraction with ether and evaporation gave 4·47 g (14·4 mmoles, 30%) of *3,3-dimethyl-5-oxo-6,6-diphenylhexanoic acid* (VII), m.p. 96–99°. One crystallization from ligroin and one from aqueous methanol gave material of m.p. 103–103·5°; mixed m.p. 102–103° with material obtained from the cleavage of 2,2-diphenyldimedone. The infrared spectra of the acid obtained from these two sources were identical.

Attempted ring closure of VII *to 2,2-diphenyldimedone* (III)

Formation of β,β-dimethyl-δ-benzyhdrylidene-δ-valerolactone (VIII). To a solution of 3·10 g (10 mmoles) acid VII in 10 ml acetic acid was added 60 g polyphosphoric acid, and the mixture was shaken by hand with intermittent cooling to give a uniform, viscous solution, which was then heated at 55–60° for 1 hr. The reaction mixture was poured onto ice and gave a yellow oil which solidified after prolonged stirring. The solids were collected after the mixture had stood overnight, washed with water, dried and crystallized from ethanol to give 2·41 g (8·3 mmoles, 83%) of *β, β-dimethyl-δ-benzhydrylidene-δ-valerolactone* (VIII), m.p. 128–130°. Recrystallization from ethanol raised the m.p. to 131–132°; λ_{max} 254 mμ, ε 16, 030.

(Found: C, 78·36; H, 7·53. Calc. for $C_{20}H_{20}O_2 . C_2H_5OH$: C, 78·07; H, 7·74%).

The infrared spectrum had prominent bonds at 5·67 μ (lactone carbonyl), 6·00 μ (C═C—O) and 6·23, 6·33 μ (phenyl). The lactone rapidly took up bromine in carbon tetrachloride but only slowly decolorized potassium permanganate. A solution of 1·79 g (6·1 mmoles) of the lactone in 300 ml 2 : 1 water-dioxane, 0·05 molar with potassium carbonate, was heated at 100° for 1 hr. Acidification and the usual workup, including crystallization from aqueous ethanol, gave 1·53 g (4·9 mmoles, 81%) of starting material acid VII, m.p. 100–102°, no depression on admixture with acid from the cleavage of 2,2-diphenyldimedone.

Ozonolysis of 585 mg (2·0 mmoles) of lactone VIII in 20 ml chloroform and 15 ml methanol at —10° gave 244 mg (1·34 mmoles, 67%) of benzophenone, m.p. 37–43°, and 125 mg (0·78 mmoles, 39%) of 3,3-dimethylglutaric acid, m.p. 101–102°; no depression on admixture with an authentic sample. The benzophenone gave a 2,4-dinitrophenylhydrazone of m.p. 236–238°; no depression on admixture with an authentic sample.

Reactions of Dimedone and 2-Phenyldimedone with Iodonium Salts

Dimedone with diphenyliodonium chloride and tosylate in t-butyl alcohol at reflux temperature. Dimedone (28·4 g, 202 mmoles) and after a few minutes diphenyliodonium chloride (64 g, 202 mmoles) were added to 1 l. t-butyl alcohol in which 4·6 g (200 mg atoms) sodium had been dissolved. The stirred suspension was boiled under nitrogen for 4 hr. The reaction mixture rapidly turned a deep yellow color at reflux temp., then slowly became lighter; at the end of the reaction the color was only slightly yellow. After steam distillation to remove iodobenzene (whose infrared spectrum showed the absence of benzene), the mixture was treated with a solution of 27·6 g potassium carbonate in 200 ml water and extracted thoroughly with ethyl acetate. The extract was washed with water, dried and concentrated to give 14·9 g crude product, which was crystallized from ethanol to give 13·3 g (45·5 mmoles, 23%) *2,2-diphenyldimedone* (III). Two additional crystallizations raised the m.p. to 181–182°.

(Found: C, 81·81; H, 7·17. Calc. for $C_{20}H_{20}O_2$: C, 82·15; H, 6·86%).

The extracted alkaline solution was acidified and chilled overnight. Solids (11·7 g) were collected and recrystallized from methanol to give 8·74 g *2-phenyldimedone* (II), m.p. 184-186°. Another 0·92 g of this product was obtained from the aqueous filtrate by extraction with ethyl acetate and recrystallization of the crude product from this solvent. There was thus obtained in all 9·66 g (44·6 mmoles, 22%) of *2-phenyldimedone* (II). The analytical sample which was crystallized from aqueous methanol and from ethyl acetate melted at 197–198°; λ_{max} 268 mμ, ε 11,560.

(Found: C, 77·84; H, 7·53; neut. equiv. 216; pK_a 6·51 ± 0·05. Calc. for $C_{14}H_{16}O_2$: C, 77·74; H, 7·46%; neut. equiv., 216·3).

The 2-phenyldimedone prepared above proved in all ways identical to that prepared by the ring closure of 3,3-dimethyl-5-oxo-6-phenylhexanoic acid (VI). There was no depression of m.p., and infrared spectra were superposable.

2,2-Diphenyldimedone was cleaved to the ketoacid VII as follows. To a solution of 11·7 g (40 mmoles) of 2,2-diphenyldimedone in 400 ml warm ethanol there was added rapidly 300 ml 15% NaOH aq, and the mixture was boiled under nitrogen for 2 hr. After removal of most of the ethanol by distillation and extraction of the remaining aqueous solution with ether, the aqueous phase was acidified and extracted with ether. Evaporation left an oily residue, which was crystallized from 1 : 1 methanol–water to give 9·88 g (31·7 mmoles, 79%) of *3,3-dimethyl-5-oxo-6,6-diphenylhexanoic acid*, VII, m.p. 101–102°. Crystallization from ligroin raised the m.p. to 102–103°.

(Found: C, 77·22; H, 6·82; neut. equiv. 311 ± 2. Calc. for $C_{20}H_{22}O_3$: C, 77·39; H, 7·14%; neut. equiv. 310·4).

There was no depression of m.p. on mixing VII prepared from III and that from IX. Also, the infrared spectra of the two samples were superposable.

A similar reaction with diphenyliodonium *p*-toluenesulfonate and dimedone in refluxing t-butyl alcohol for 4 hr yielded 16% of 2-phenyldimedone (II) and 19% of 2,2-diphenyldimedone (III). From the neutral fraction was obtained 9% 0,2-diphenyldimedone (IV) after chromatographic separation on alumina and recrystallization from aqueous ethanol.

Dimedone with diphenyliodonium chloride in t-butyl alcohol at reflux temperature; *Reverse addition of reagents*. Dimedone (14·0 g, 100 mmoles) was added to a solution of sodium (2·30 g, 100 mg atom) in 500 ml t-butyl alcohol. This solution was added dropwise under nitrogen over 5 hr to a boiling suspension of 31·8 g (100 mmoles) diphenyliodonium chloride in 500 ml t-butyl alcohol. Addition was sufficiently slow to prevent a yellow coloration of the suspension. A work-up similar to that described above gave 7·26 g (24·7 mmoles, 25%) *2,2-diphenyldimedone*, m.p. 179–180°, and 3·48 g (16·1 mmoles, 16%) of *2-phenyldimedone*, m.p. 193–195°.

Dimedone with diphenyliodonium chloride in t-butyl alcohol at room temperature; *0,2-diphenyldimedone* (IV). A suspension of 63·4 g (200 mmoles) of diphenyliodonium chloride in 1 l. of t-butyl alcohol in which 4·60 g (200 mg atom) of sodium and 28·0 g (200 mmoles) of dimedone had previously been dissolved was stirred for 72 hr at room temp. under nitrogen. After iodobenzene had been removed by steam distillation and after 43 g (300 mmoles) of potassium carbonate had been added, the mixture was extracted twice with ethyl acetate (extract A). The alkaline phase was now acidified and extracted with ethyl acetate, which yielded 17·2 g of yellow oily solids. Crystallization from ethanol gave 5·76 g (26·6 mmoles, 13%) of crude *2-phenyldimedone* (II) m.p. 171–178°. Infrared spectroscopy indicated that the residue was largely recovered dimedone.

The ethyl acetate solution (extract A) was washed with water, dried and evaporated to give 23·2 g of a dark, gummy residue, which was chromatographed on 550 g alumina. Elution with 3 : 1 hexane-ether gave 3·11 g crystalline 2, *2-diphenyldimedone* (III). Recrystallization from ethanol gave 2·88 g (9·9 mmoles, 5%) III, m.p. 180–182°; mixed m.p. 181–182° with 2,2-diphenyldimedone from the reaction under reflux. Elution with 3 : 1 and 1 : 1 hexane–ether gave 6·05 g of a light yellow oil, having a strong ultraviolet absorption maximum, λ_{max} 270 mμ, E 1% 433. Crystallization from aqueous ethanol gave 5·24 g (17·9 mmoles, 9%), 0, *2-diphenyldimedone* (IV), m.p. 73–75°. Recrystallization from ethanol gave IV of m.p. 77–78°, λ_{max} 271 mμ, ϵ 13,900.

(Found: C, 81·98; H, 7·11. Calc. for $C_{20}H_{20}O_2$: C, 82·15; H, 6·89%).

Further elution with ether and with methanol gave 4·38 g of a dark brown oil which solidified on standing but from which it was not possible to isolate crystalline material.

The structure of 0,2-diphenyldimedone (IV) was proved by its hydrolysis as follows. A solution of 2·92 g (10 mmoles) IV in 100 ml 2 : 1 methanol–water 1 N in hydrochloric acid was boiled for 1 hr, The mixture was concentrated to 50 ml, 100 ml water was added, and 2·03 g (9·40 mmoles, 94%) of *2-phenyldimedone*, m.p. 193–195°, was collected from the chilled solution. Crystallization from aqueous ethanol raised the m.p. to 196–197°. Ultraviolet and infrared spectra on this material were identical to those of material obtained by ring closure.

The filtrate was adjusted to pH 8·5 with sodium carbonate and extracted five times with ether, which on evaporation gave a pink oil with a phenolic odor. Bromination with a potassium tribromide solution gave 1·22 g (3·70 mmoles, 37%) of 2,4,6-tribromophenol, m.p. 92–93°; authentic sample, m.p. 96°; mixed m.p. 93–94°.

Dimedone with diphenyliodonium chloride in water. Diphenyliodonium chloride (31·7 g 100 mmoles) was treated with dimedone (14·0 g, 100 mmoles) previously dissolved in 400 ml water containing 100 mmoles of NaOH at reflux under nitrogen for 6 hr. After steam distillation to remove iodobenzene the usual work-up gave 6·9 g of a yellow neutral solid. Crystallization from ethanol gave 4·2 g (14·3 mmoles, 14%) of 2, *2-diphenyldimedone*, m.p. 178–179°; mixed m.p. with material from a run in *t*-butyl alcohol, 178–180°. Some crude dimedone (8·35 g, 59·6 mmoles) was recovered. Infrared spectra showed the absence in the acidic fractions of any appreciable 2-phenyldimedone.

2-Phenyldimedone with diphenyliodonium chloride in t-butyl alcohol. A suspension of 19·5 g (61 mmoles) of diphenyliodonium chloride in 300 ml t-butyl alcohol in which 1·40 g (61 mg atoms) of sodium and 13·2 g (61 mmoles) of 2-phenyldimedone had been dissolved was boiled under nitrogen for 2 hr. The initial deep yellow-orange color lightened as the reaction proceeded. A work-up similar to that described above for dimedone under comparable conditions gave 14·5 g crude neutral product. Crystallization from ethanol gave in two crops 12·64 g (43·3 mmoles, 71%) of 2, *2-diphenyldimedone* (III), m.p. 180–181°; mixed m.p. with a sample from dimedone, 181–182°.

Dimedone with 2-nitrodiphenyliodonium bromide in t-butyl alcohol. 2-Nitrodiphenyliodonium bromide (40·6 g, 100 mmoles) was added to a solution of 2·3 g (100 mg atoms) of sodium and 14·5 g (104 mmoles) of dimedone in 400 ml t-butyl alcohol. The suspensation was stirred at 60° under nitrogen for 4 hr. A standard work-up gave 12·2 g crude acidic 2-(o-*nitrophenyl*)-*dimedone* (XI), m.p. 205–222°. Trituration with hot benzene yielded 7·61 g (29·1 mmoles, 29%) XI, which on crystallization from benzene–methanol gave light yellow platelets of m.p. 235–236°; λ_{max} 261, ϵ 16,100; $\lambda_{max}^{0.01\ N\ NaOH}$ 288 mμ, ϵ 22,100.

(Found: C, 64·35; H, 5·83; N, 5·27; neut. equiv. 263 ± 4; pK_a 5·83 ± 0·06. Calc. for $C_{14}H_{15}NO_4$: C, 64·35; H, 5·79; N, 5·36%; neut. equiv., 261).

The dark yellow oil obtained from the neutral fraction was chromatographed on alumina. Fractions eluted with benzene and crystallized from aqueous methanol afforded 2·97 g (7·8 mmoles, 8%) of 0,2-*bis*-(o-*nitrophenyl*)-*dimedone* (XII). m.p. 127–140°. Recrystallization from acetone–ether raised the m.p. to 140–141°; λ_{max} 254 mμ, ϵ 23,100, no change in λ_{max} in dilute base.

(Found: C, 63·06; H, 4·95; N, 7·54. Calc. for $C_{20}H_{18}O_6N_2$: C, 62·82; H, 4·74; N, 7·33%).

The structure of XII was demonstrated by hydrolysis as follows. A solution of 0·790 g (2·06 mmoles) XII in 25 ml acetic acid and 25 ml 48% HBr was heated 3 hr on the steam bath. The solution was concentrated to 10 ml and slowly diluted with water. From the chilled solution was collected 0·502 g (1·92 mmoles, 93%) of 2-(o-*nitrophenyl*)-*dimedone* (XI), m.p. 233–235°. The infrared spectrum was identical to that of XI obtained by arylation. An attempt at mild acid hydrolysis under the same conditions as was successful for 0,2-phenyldimedone (IV) yielded only unreacted starting material.

Dimedone with 2-nitrodiphenyliodonium bromide in methanol. 2-Nitrodiphenyliodonium bromide (41·1 g, 101 mmoles) was added to 450 ml methanol in which 2·3 g (100 mg atoms) of sodium and 14·6 g (104 mmoles) of dimedone had been dissolved. The stirred reaction mixture was boiled under gentle reflux for 13 hr. After removal of a small amount of insoluble material by filtration, the filtrate was cooled to −50° to give 4·38 g 2, 2-methylene-bis-dimedone (XIIIa). After concentration of the filtrate there was obtained additional crude XIIIa. This was crystallized from methanol-water to give 5·37 g material of m.p. 190–192°, for a total yield of 9·75 g (33·4 mmoles, 66%). Comparison of XIIIa with authentic material prepared from dimedone and formaldehyde showed that they had identical infrared spectra and no depression of melting point on mixing.

Reference Compounds Related to Di- and Tribenzoylmethane

1, 2-*Diphenylvinyl Benzoate* (XX). The procedure used was a modification of that recently described by Gogan *et al.*[23] A mixture of 14·0 g (0·714 mmoles) of desoxybenzoin and 35 ml benzoyl chloride was heated under a nitrogen atmosphere for 13 hr at 170°. The excess benzoyl chloride was evaporated at reduced pressure and the solution was cooled and taken up in ether, which was washed twice with potassium carbonate and then with water. Evaporation of the ether and addition of 200 ml ligroin gave on stirring a yellow-orange precipitate. Crystallization from

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[23] F. Gogan, A. E. O'Brianin, E. M. Philbin, N. S. O'Connor, R. F. Timoney and T. S. Wheeler, *Tetrahedron* 3, 143 (1958).

ethanol and treatment with charcoal gave white needles weighing 10·8 g (50%), m.p. 122–122·5° with softening at 120°; reported m.p. 119°.[33]

The infrared spectrum (KBr pellet) showed bands at 5·74 (ester C=O stretching vibration) and a band at 6·11 μ (C=C), while the ultraviolet spectrum exhibited maxima at 286 mμ, ε 34,600 and 226 mμ, ε 30,650.

(Found: C, 84·34; H, 5·37. Calc. for $C_{21}H_{16}O_2$: C, 84·00; H, 5·37%).

Phenyldibenzoylmethane (XVI). The rearrangement of enol benzoate XX using aluminum chloride[33] gave in our hands mostly tars and only a few percent of phenyldibenzoylmethane (XVI). A mixture of 1·0 g, (33 mmoles) 1,2-diphenylvinyl benzoate (XX) and 15 g titanium chloride were heated under reflux in a dry flask for 1·5 hr. At the end of this time the solution was poured into 44 ml conc. HCl and 40 g chopped ice. The solution was cooled to 5°, and the insoluble product was heated under reflux in 200 ml ethanol for 3 hr, treated with some charcoal and filtered. The solvent was evaporated on a steam bath, and the residue was treated with 5 ml methanol to give 0·55 g tan material, m.p. 135–138°. Crystallization from methanol gave 0·48 g (48%) phenyldibenzoylmethane (XVI) as tan needles, m.p. 146–147°. Repeated sublimation, taking the second half of each crop, gave white needles of product, m.p. 149–150°. A mixed melting point with the C-phenylated product of dibenzoylmethane, m.p. 149–150·5°, gave a m.p. 149–150°.

(Found: C, 84·16; H, 5·26. Calc. for $C_{21}H_{16}O_2$: C, 84·00; H, 5·37%).

2, 3-*Diphenylindenone* (XXII). A mixture of 0·51 g (17 mmoles) phenyldibenzoylmethane (XVI) and 10 ml benzoyl chloride was heated under an atmosphere of nitrogen for 15 hr at 160°. At the end of this time the excess of benzoyl chloride was evaporated at reduced pressure, and the oily residue was taken up in ligroin. This gave on standing 0·44 g (92%) dark red crystals, m.p. 151–152°. Further crystallization from ethanol gave red needles, m.p. 152–153°; reported m.p. 150–151°,[34] m.p. 153–155°[35].

(Found: C, 89·25; H, 5·16. Calc. for $C_{21}H_{14}O$: C, 89·33; H, 5·00%).

The phenylhydrazone derivative showed m.p. 175–176°; reported m.p. 175–176°.[36] The infrared spectrum (KBr pellet) of the ketone showed a strong band at 1710 cm^{-1}(C=O); reported[37] 1710 cm^{-1}. The ultraviolet spectrum showed a maximum at 258 mμ, ε 41,000.

2-*Benzoyl*-1, 2-*diphenylvinyl benzoate* (XXI). To 1500 ml anhydrous ether containing 16·8 g (0·7 mole) sodium hydride there was added with vigorous stirring over a period of 1 hr 137 g (0·7 mole) desoxybenzoin. The mixture was stirred for an additional hour, and then 98·4 g (0·7 mole) benzoyl chloride dissolved in 50 ml dry ether was added dropwise over a 2 hr period. The solution warmed up somewhat during the addition and turned from yellow to white when allowed to stir for 24 hr at room temp. At the end of this time 30 ml ethanol and 350 ml 1·2 N NaOH were added, giving a white solid, insoluble in both ether and water. Upon filtration 49·2 g material of m.p. 142–144° was isolated. Crystallization of this ester from ethanol gave 43·6 g of XXI, m.p. 152–153°, reported m.p. 152°.[31] The ethereal filtrate on evaporation gave 89 g (0·454 mole) of recovered desoxybenzoin. The yield of ester XXI based on unrecovered starting material was 50%. Admixture with phenyltribenzoylmethane (XIX) obtained from the phenylation of tribenzoylmethane gave a depression in melting point to 136–140°. The infrared spectrum (KBr pellet) showed bands at 5·74 μ (ester C=O), 6·0 μ (conjugated ketone); λ_{max} 233 mμ, ε 30,600.

(Found: C, 83·34; H, 5·19. Calc. for $C_{28}H_{20}O_3$: C, 83·15; H, 4·98%).

Phenyldibenzoylmethane (XVI, 1·0 g, 3·3 mmoles) was added with vigorous stirring to 70 ml dry t-butyl alcohol in which 76 mg (3·3 mg atoms) sodium had been dissolved. The mixture was stirred for 3 hr at 60°, forming a yellow sodium salt; 0·55 g (3·9 mmoles) benzoyl chloride was then added, and heating at 65° for 3 more hr gave a white suspension. After the alcohol was evaporated at reduced pressure, 400 ml water was added to the residue. The insoluble precipitate formed was collected, washed with cold water and crystallized from methanol-water to give 0·95 g (71%) enol benzoate XXI of m.p. 152–153°. A mixed melting point with authentic 2-benzoyl-1,2-diphenylvinyl benzoate (see above) gave no depression in m.p.; also the infrared spectra proved to be identical.

Hydrolysis of 2-*benzoyl*-1,2-*diphenylvinyl benzoate* (XXI). To a 50 ml flask containing 0·9 g (21 mmoles) XXI there was added 15 ml 48% HBr and, after 20 min of refluxing, 10 ml ethanol.

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[34] H. Loewenbein and G. Ulich, *Ber.* **58**, 2662 (1925).

[35] R. Weiss and R. Sauerman, *Ber.* **58**, 2736 (1925).

[36] A. Orekjoff, *Bull. Soc. Chim. Fr.* (4) **25**, 598 (1919).

[37] E. D. Bergmann, G. Berthier, D. Ginsburg, Y. Hirschberg, D. Lavie, S. Pinchas, B. Pullman and A. Pullman, *Bull. Soc. Chim. Fr.* **18**, 661 (1951).

The solution was heated further for a total of 1·5 hr, concentrated by evaporative distillation, cooled and poured into 100 ml water. The red oil was extracted with ether, washed with dil. NaOH aq and with water and finally concentrated on a steam bath. The viscous red oil in ethanol gave as a first crop material of m.p. 145°. Recrystallization gave 0·2 g (31 %) of *phenyldibenzoylmethane* (XVI) of m.p. 149–150°, no depression in melting point with authentic material.

As a second crop 50 mg (7 %) red needles, m.p. 151–152°, were collected. This material did not depress the m.p. of an authentic sample of 2, 3-diphenylindenone.

Di- and Tribenzoylmethane with Diphenyliodonium Chloride

Dibenzoylmethane with diphenyliodonium chloride in t-butyl alcohol. After dibenzoylmethane (74 g, 330 mmoles) had been added to a solution of 330 mmoles of potassium t-butoxide in 1200 ml t-butyl alcohol, the mixture was stirred until solution was complete. Diphenyliodonium chloride (104·3 g, 330 mmoles) was added with no appreciable temperature rise, and there was unreacted iodonium salt after 2 hr at room temp. After 5 hr at reflux, the iodonium salt had completely reacted, and t-butyl alcohol (800 ml) was removed by distillation. The residue was diluted with 2 l. water, acidified to pH 6 and repeatedly extracted with ether. Distillation of the dried extract gave three fractions: *A*, 64·2 g crude iodobenzene, b.p. 60–90°/10 mm; *B*, 45·0 g of an oily yellow solid, b.p. 190–220°/0·6 mm; *C*, 22·1 g of a red-brown solid, b.p. 225–235°/0·6 mm.

Crystallization of fraction *B* from ethanol gave 16·2 g unreacted dibenzoylmethane and 15·3 g (51 mmoles, 20 %) colorless needles of phenyldibenzoylmethane (XVI) m.p. 147–148°. Recrystallization from methanol–ligroin raised the m.p. to 149–150·5°, reported m.p.'s 119–120°[38] and 149°[31,39]; λ_{max} 246 mμ, ϵ 34,000.

(Found: C, 84·29; H, 5·37. Calc. for $C_{21}H_{16}O_2$: C, 84·00; H, 5·37 %).

Treatment of XVI with aqueous methanolic KOH at 100° for 2 hr gave desoxybenzoin (85 %), m.p. 55–56°, and benzoic acid (78 %), m.p. 121–122°; neither m.p. was depressed by admixture with an authentic sample.

Treatment of XVI with hydroxylamine hydrochloride in ethanolic pyridine at 100° for 1 hr gave 97 % of crude 3, 4, 5-*triphenylisoxazole*, m.p. 201–206°. Recrystallization from acetonitrile raised the m.p. to 209–210°.

(Found: C, 84·77; H, 5·09; N, 4·99. Calc. for $C_{21}H_{15}NO$: C, 84·83; H, 5·08; N, 4·71 %).

It has been reported[39] that dehydration of the monoxime of phenyldibenzoylmethane with phosphorus pentachloride gave 3, 4, 5-triphenylisoxazole, m.p. 212°.

Fraction *C* (*vide supra*) was triturated with ligroin and with benzene to give 10·9 g of a light yellow solid, m.p. 128–132°. Recrystallization from methanol gave 8·9 g (29·6 mmoles, 11 %) of *phenyldibenzoylmethane* (XVI) m.p. 149–150·5°; the total yield of this compound based on unrecovered dibenzoylmethane was 31 %.

The residue (9·4 g) from evaporation of the benzene–ligroin filtrate was distilled to give 7 g of an oil, b.p. 145–150°/0·25 mm, n_D^{25} 1·6169, o-*phenyldibenzoylmethane*, (1, 3-diphenyl-3-phenoxy-2-propene-1-one, XV); λ_{max} 342 and 243 mμ, ϵ 10,325 and 10,625. The yield of XV based on unrecovered dibenzoylmethane was about 9 %. This material on standing slowly decomposes to dibenzoylmethane.

(Found: C, 83·92; H, 5·50. Calc. for $C_{21}H_{16}O_2$: C, 84·00; H, 5·37 %).

Treatment of crude XV with aqueous methanolic potassium hydroxide at 100° for 4 hr gave acetophenone (isolated in 23 % yield as the 2, 4-dinitrophenylhydrazone, m.p. 248–249°), benzoic acid (63 %), m.p. 121–122° and phenol (isolated in 14 % yield as 2,4,6-tribromophenol, m.p. 95–96°).

Tribenzoylmethane with diphenyliodonium chloride in t-butyl alcohol. Tribenzoylmethane (65·6 g, 200 mmoles) in 1300 ml t-butyl alcohol in which 7·8 g (200 mg atoms) potassium metal had been dissolved was stirred at room temp. for an hour and gave a deep yellow suspension. Diphenyliodonium chloride (63·2 g 200 mmoles) was added with no appreciable temperature rise. After 48 hr at reflux, the mixture had no unreacted iodonium salt. t-Butyl alcohol (500 ml) was removed by distillation. The mixture was then treated with a solution of 28 g potassium carbonate in 800 ml water and extracted thoroughly with ethyl acetate. The extract was washed with water, dried and concentrated on a steam bath to give a dark brown oil. This oil was boiled with 800 ml ligroin, giving 57·6 g crude product of m.p. 117–121°. This was crystallized from ethanol to give 49·2 g

[38] F. R. Japp and G. D. Lander, *J. Chem. Soc.* **69**, 742 (1896).

[39] J. Marshall, *J. Chem. Soc.* **107**, 521 (1915).

(121 mmoles, 68%) of *O-phenyltribenzoylmethane* (1, 1-dibenzoyl-2-phenoxy-2-phenylethene, XVIII), m.p. 129–130°; infrared spectrum (KBr) showed bands at 6·04 μ (conjugated ketone) and 8·30 μ (C—O-phenolic stretching); λ_{max} 258 mμ, ε 27,500.

(Found: C, 83·14; H, 5·10. Calc. for $C_{28}H_{20}O_3$: C, 83·15; H, 4·98%).

Treatment of XVIII with aqueous methanolic potassium hydroxide at reflux for 6 hr gave tribenzoylmethane (9%) m.p. 236–237°, acetophenone (isolated in 14% yield as the 2, 4-dinitrophenylhydrazone, m.p. 248–249°), benzoic acid (70%) m.p. 121–122°, and phenol (isolated in 58% yield as 2, 4, 6-tribromophenol, m.p. 94–95°).

The ligroin filtrate after the removal of XVII (*vide supra*) was then concentrated to about 200 ml and cooled in an acetone dry-ice bath to give an insoluble brown oil which was isolated by decantation. This oil was dried (*in vacuo* for 24 hr over H_2SO_4) to a hard viscous wax, which was dissolved in methanol and gave 7·1 g (17 mmoles), 10% of *C-phenyltribenzoylmethane* (α,α,α-tribenzoyltoluene, XIX), white crystals m.p. 185–187°. Two additional crystallizations from ethanol raised the m.p. to 190–192°, λ_{max} 256 and 321 mμ, ε 36,000 and 3005 respectively.

(Found: C, 82·90; H, 5·10. Calc. for $C_{28}H_{20}O_3$: C, 83·15; H, 4·98%).

Treatment of XIX with aqueous methanolic potassium hydroxide at reflux for 5 hr gave 87% of desoxybenzoin m.p. 52–53° (m.p. 55·6° after recrystallization) and 74% of benzoic acid, m.p. 120–121°.

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