(*p*-tolyl)-2,4-pentadienoic acid gave 2.18 g. of crystalline potassium salt. Acidification precipitated 1.85 g. (49%) of the acid, m.p. 132–135° and 170–172°. Two recrystallizations from benzene–cyclohexane gave a colorless analytical sample, m.p. 134–136° and 174–175°. Infrared absorption (in CCl_4): 1683 (α,β-unsaturated C=O), 1602 and 1512 (phenyl group), 1252 and 1175 (C–O–), 1035 (O–CH_3), and 864 cm.$^{-1}$ (trisubstituted ethylene). Ultraviolet absorption: $\lambda_{max}^{0.003\ NH^+CH_3OH}$ 309 (ϵ 21,700), 236–237 mμ (ϵ 9900). N.m.r. absorption (in $CDCl_3$): 3.03 (C-5 Ar-H), 3.14 (C-5 H), 7.96 (C-4 CH_3), 7.57 (C-3 methyl protons *cis* to carboxyl), 4.07 (C-2 H), and 6.24 τ (*p*-CH_3O).

Anal. Calcd. for $C_{14}H_{16}O_3$: C, 72.39; H, 6.94. Found: C, 72.45; H, 6.88.

Methyl 3,4-Dimethyl-5-(*p*-methoxyphenyl)-2-*trans*-4-*trans*-pentadienoate (IVD, R′ = CH_3).—The methyl ester was prepared by esterification of the 2-*trans*-4-*trans* acid with diazomethane and was recrystallized from petroleum ether at 0° to give colorless needles, m.p. 66–67°. No melting point depression was observed when the ester prepared in this manner was mixed with a sample of the ester, m.p. 66–67°, recovered from the *p*-toluenesulfonic acid dehydration. N.m.r. and infrared spectral data were identical.

Anal. Calcd. for $C_{15}H_{18}O_3$: C, 73.14; H, 7.37. Found: C, 73.00; H, 7.49.

3-Methylene-4-methyl-5-(*p*-methoxyphenyl)-4-*trans*-pentenoic Acid (VID).—Treatment of the filtrate from the potassium salt of the 2-*trans*-4-*trans* isomer according to the procedure described previously for 3,4-dimethyl-5-phenyl-2-*cis*-4-*trans*-pentadienoic acid gave 0.80 g. of crude, yellow acid, m.p. 93–98°. Fractional crystallization of this material from hexane (EK-P1135) gave fine, colorless needles, m.p. 103.5–106.5°. Infrared absorption (in CCl_4): 1706 (saturated C=O), 1251 (C–O–), 1175 and 1042 (O–CH_3), and 902 cm.$^{-1}$ (terminal methylene group). Ultraviolet absorption: $\lambda_{max}^{CH_3OH}$ 281 mμ (ϵ 23,000). N.m.r. absorption (in $CDCl_3$): 3.09 (C-5 Ar-H), 3.50 (C-5 H), 7.98 (C-4 CH_3), 4.68 and 4.89 (C-3 terminal methylene protons), 6.60 (C-2 internal methylene protons), and 6.25 τ (*p*-CH_3O).

Anal. Calcd. for $C_{14}H_{16}O_3$: C, 72.39; H, 6.94. Found: C, 72.45; H, 6.97.

Acknowledgment.—The authors acknowledge with appreciation support of this program under a National Science Foundation Cooperative Graduate Fellowship held by C. E. S. during 1960–1961 and 1961–1962 and, in part, under National Science Foundation Grant G-11108. Partial support under a grant from the Mead Johnson Company and funds from various sources for purchase of the n.m.r. and ultraviolet spectrometers used in the study are also gratefully acknowledged.

Steric Effects in Radical Coupling. Arylation of 1,3-Indandiones with Dimesityliodonium Chloride[1-4]

F. MARSHALL BERINGER AND SUZANNE A. GALTON[5]

The Department of Chemistry, Polytechnic Institute of Brooklyn, Brooklyn 1, New York

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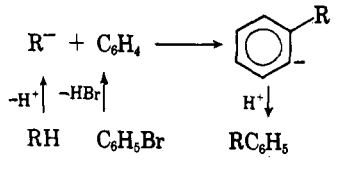
While the anion of 2-phenyl-1,3-indandione had given with diphenyliodonium chloride in *t*-butyl alcohol 85% of 2,2-diphenyl-1,3-indandione, it gave with dimesityliodonium chloride only 23% of the analogous 2-mesityl-2-phenyl-1,3-indandione and a small amount of 2-(*o*-mesitylphenyl)-1,3-indandione. 2-Mesityl-1,3-indandione, formed with related products from the anion of 1,3-indandione and dimesityliodonium chloride, was phenylated on oxygen to give the enol ether in good yield. These results are consistent with the previously proposed mechanism involving the formation and coupling of radical pairs, while the lowered yields of carbon-arylated products are believed to reflect steric hindrance to radical coupling.

In recent years two methods have been under investigation for the direct phenylation of carbanions. One is that of Leake and Levine in which the carbanion reacts with benzyne formed *in situ* by the dehydrohalogenation of bromobenzene by sodamide in liquid



ammonia. This method has been used successfully with a series of dialkyl and aralkyl ketones,[6] esters,[7] and methylpyrazine.[8] The other method for the phenylation of carbanions is the reaction with diphenyliodonium salts. Phenyl derivatives of dimedone,[9] di- and tribenzoylmethane,[9] 1,3-indandiones,[3] esters,[10] and nitroparaffins[11] have been prepared by this method. The mechanism proposed[3] for these phenylations, discussed in more detail later, starts with electron transfer from carbanion (R^-) to an iodonium ion (ArI^+Ar) to give a radical pair, members of which largely combine to give ArR. Some radicals diffuse from the solvent cage and later combine to form ArR, RR, and ArAr, while some abstract hydrogen from solvent to form reduced product ArH.

Although experimental evidence[3] to date (influence of radical scavengers, dehydrogenation of solvent, formation of dimers) favors this proposed electron-transfer mechanism, the presence of a benzyne intermediate has not been definitely excluded. It was therefore of interest to use as the arylating agent dimesityliodonium chloride, from which a benzyne cannot be formed. The carbanions chosen for this study were those of 2-phenyl-1,3-indandione and 1,3-indandione, the phenylations of which previously have been reported.[3]

Reaction of 2-phenyl-1,3-indandione.—2-Phenyl-1,3 indandione (I)[3,12] reacted with sodium *t*-butoxide and

(1) This article is taken from the dissertation of S. A. G. submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy (chemistry).

(2) Diaryliodonium Salts. XX.

(3) Phenylation of 1,3-indandiones: F. M. Beringer, S. A. Galton, and S. J. Huang, *J. Am. Chem. Soc.*, **84**, 2819 (1962).

(4) For brevity the 2,4,6-trimethylphenyl radical will be called the mesityl radical and represented as mes.

(5) Eastman Kodak Co. Fellow 1961–1962; Texaco Co. Fellow 1963.

(6) W. W. Leake and R. Levine, *J. Am. Chem. Soc.*, **81**, 1169 (1959).

(7) W. W. Leake and R. Levine, *ibid.*, **81**, 1627 (1959).

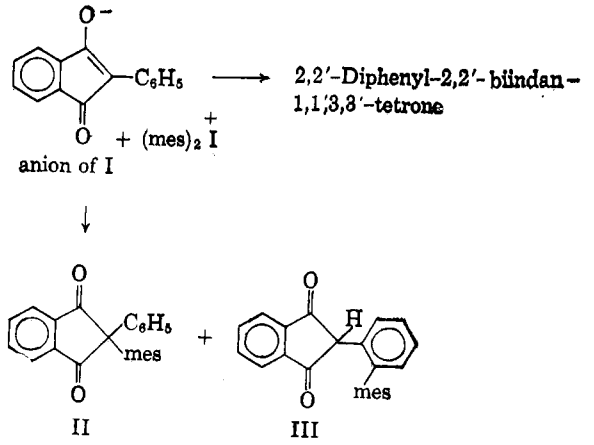
(8) J. D. Behun and R. Levine, *J. Org. Chem.*, **26**, 3379 (1961).

(9) F. M. Beringer, P. S. Forgione, and M. D. Yudis, *Tetrahedron*, **8**, 49 (1960). Phenylation on both carbon and oxygen was observed.

(10) (a) F. M. Beringer and P. S. Forgione, *J. Org. Chem.*, **28**, 714 (1963); (b) F. M. Beringer and P. S. Forgione, *Tetrahedron*, **19**, 739 (1963).

(11) N. Kornblum and H. J. Taylor, *J. Org. Chem.*, **28**, 1424 (1963).

(12) W. Dieckmann, *Ber.*, **47**, 1439 (1914).



dimesityliodonium chloride[13,14] in *t*-butyl alcohol to give two new compounds: 2-mesityl-2-phenyl-1,3-indandione (II, 23%) and, in very small yields, a weakly acidic compound to which structure III, 2-(*o*-mesitylphenyl)-1,3-indandione, is assigned. A dehydro dimer of I, 2,2′-diphenyl-2,2′-biindan-1,1′,3,3′-tetrone, was isolated also (40%); its structure and reactions have been elucidated in recent papers.[15] Other products were iodomesitylene (62%) and mesitylene (17%); see Table I.

TABLE I

ARYLATION OF 1,3-INDANDIONES[a]

Carbanion from	Iodonium ion ArI⁺Ar	Arylated product ArR	Yields, % ArR	ArI	ArH[b]	RR[c]	Time
I	$(C_6H_5)_2I^+$	2,2-diphenyl[d]	85–93	28	20	+	6 hr.
	$(mes)_2I^+$	II	23	62	17	40	20 min.
		III	1.7				
IV	$(C_6H_5)_2I^+$	2,2-diphenyl[d]	28	51	12	+	10 min.
	$(mes)_2I^+$	V	0.4	80	26	+	10 min.
		VI	6.8				
		VII	11				
V	$(C_6H_5)_2I^+$	IX	73	+			30 min.

[a] Reactions were run in *t*-butyl alcohol in the presence of sodium *t*-butoxide. [b] Determined by ultraviolet spectroscopy. [c] The notation "+" indicates that the compound was present but not determined. [d] Results taken from ref. 3 and included here for comparison.

The structure of II is supported by its infrared and n.m.r. spectra (Table II) and by its alkaline cleavage to a keto acid, formulated as α-mesityl-α-phenylacetophenone-*o*-carboxylic acid.

In the n.m.r. spectrum of compound III the single peak at 6.07 τ confirms the presence of a single hydrogen at the 2-position. It is probable from mechanistic and spectral considerations that the mesityl group is on the *ortho* or *para* positions of the 2-phenyl ring. Attachment of the mesityl group at the *ortho* position would give an *ortho* disubstituted benzene with four nonequivalent protons (ABCD or ABCX), which would produce comparatively complicated n.m.r. absorption in the phenyl region, as is observed. Thus, the structure 2-(*o*-mesitylphenyl)-1,3-indandione is favored.

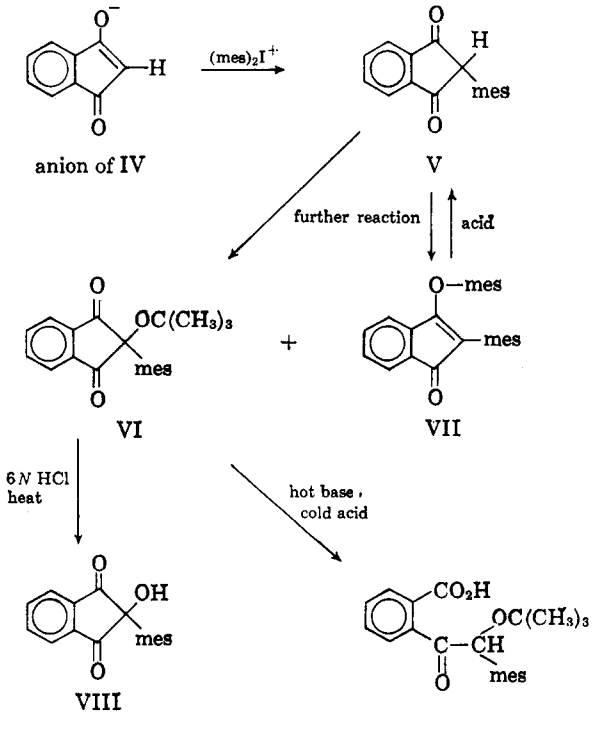
Reaction of 1,3-Indandione.—The anion of 1,3-indandione[3] (IV) reacted with dimesityliodonium chloride in *t*-butyl alcohol to give a complex mixture containing three new compounds: 2-mesityl-1,3-indandione (V) and two compounds probably derived from its further reaction, 2-mesityl-3-mesityloxy-1-indenone (VII) and 2-*t*-butoxy-2-mesityl-1,3-indandione (VI).

TABLE II

τ-VALUES OF NUCLEAR MAGNETIC RESONANCE ABSORPTION PEAKS FOR REPRESENTATIVE COMPOUNDS[a]

Compound	Ar–H: Indandione[b]	Phenyl[b]	Mesityl[b]	–CH₂ or CH	–CH₃
I	2.13[d]	2.80		5.80	
	2.19				
II	2.07[d]	2.83	3.24		7.79 (1)
	2.16				8.14 (2)
III	2.32[d]	2.83[g]	3.37	6.07 (1)	7.85 (3)
	2.37				8.00 (6)
IV	2.18[d] (1)			6.81 (1)	
	2.22 (1)				
V	2.12[d]		3.15	5.41 (1)	7.61 (3)
	2.27		3.31		7.74 (3)
					8.28 (3)
VI	2.15[e] (2)		3.40 (2)		7.72 (6)
	2.20 (2)				7.86 (3)
					8.81 (9)
VII			3.30[e]		7.76 (1)
					7.84 (2)
VIII			3.22[d]	5.83[e]	7.73 (1)
					7.78 (2)
IX		3.07[e]	3.47		7.85 (1)
					7.95 (2)
$(mes)_2I^+Cl^-$			3.04[f]		7.69 (2)
					7.86 (1)

[a] The numbers represent τ-values, as defined in S. L. M. Jackman, "Application of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press, New York, N. Y., 1959. Spectra were run on a Varian High Resolution n.m.r. spectrometer at a frequency of 60 Mc./sec., using tetramethylsilane as internal standard. Values in parentheses indicate the ratio of the peak heights. [b] Indandione = protons on the 4,5,6,7-positions of the 1,3-indandione structure. Phenyl = protons of the phenyl group in the 2-position. Mesityl = two *meta* protons of the mesityl group. [c] Spectrum was run in carbon tetrachloride. [d] Spectrum was run in deuteriochloroform. [e] This peak is due to the OH proton on the 2-position. [f] Spectrum was run in deuterium oxide (95%) using the water OH peak as internal standard (τ 5.47 from tetramethylsilane). [g] A complex fine structure centered around τ 2.83.



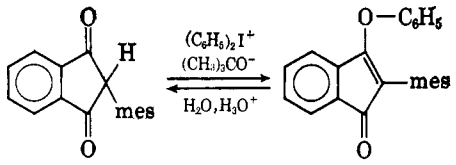
(13) C. Willgerodt and H. Roggatz, *J. prakt. Chem.*, **61**, 423 (1911).

(14) F. M. Beringer, R. A. Falk, M. Karniol, I. Lillien, G. Masullo, M. Mausner, and E. Sommer, *J. Am. Chem. Soc.*, **81**, 342 (1959).

(15)(a) F. M. Beringer, S. A. Galton, and S. J. Huang, *Tetrahedron*, **19**, 809 (1963); (b) F. M. Beringer and S. A. Galton, *J. Org. Chem.*, **28**, 3250 (1963).

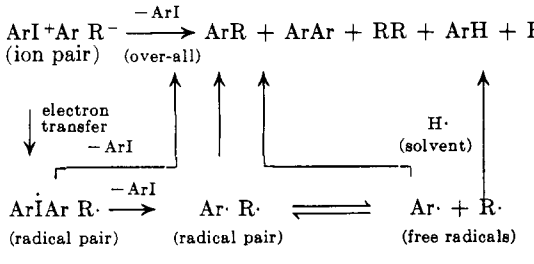
N.m.r. spectra (Table II) of V and VI show the presence of a 2-hydrogen in the former and its absence in the latter. The spectrum of VI also shows the protons of the *o*-methyl groups (τ 7.72), the *p*-methyl group (τ 7.86), and the *t*-butyl group (τ 8.81) in the ratio 2:1:3. In contrast, the mesityl methyl protons in 2-mesityl-1,3-indandione (V) give three equivalent distinct peaks at τ 7.61, 7.74, and 8.28. This strongly suggests that the plane of the mesityl ring is roughly perpendicular to that of the indandione ring and that rotation of the mesityl group is slow. This geometry also accounts for the two peaks for the mesityl ring protons at τ 3.15 and 3.31.

Reaction of 2-Mesityl-1,3-indandione with Diphenyliodonium Chloride.—Reaction of 2-mesityl-1,3-indandione (V) with diphenyliodonium chloride in *t*-butyl alcohol in the presence of potassium *t*-butoxide gave as the only arylated product 73% of 2-mesityl-3-phenoxy-1-indenone (IX), a compound not previously reported. This yellow neutral compound was easily hydrolyzed to 2-mesityl-1,3-indandione (V), as was compound VII, in the presence of 3 *N* hydrochloric acid in dioxane.



Mechanism.—The preceding results further confirm the proposed[3] mechanism of arylations of carbanions with diaryliodonium salts. Also, they show that in the present case a pathway not involving a benzyne must exist as the methyl groups in mesitylene preclude formation of a benzyne.

Let us consider the mechanism of the reaction of carbanions from 1,3-indandiones with iodonium salts, starting with electron transfer within an iodonium ion–carbanion pair to form a radical pair.

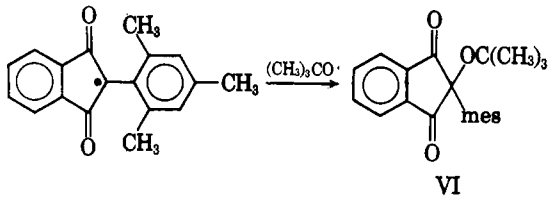


Most of the radical pairs enclosed in a solvent cage react by coupling faster than they separate by diffusion. The 2-phenyl-1,3-indandion-2-yl free radical couples with the phenyl free radical essentially exclusively and in good yield through the 2-position, presumably because C,C-coupling has a lower energy of activation than O,C-coupling. If, however, either of these phenyl groups is enlarged to a mesityl group, then coupling through the 2-position is slowed, as evidenced by decreased yield of 2-arylated product II and increased yields of other products. Thus mesitylation of 2-phenyl-1,3-indandione gives a decreased yield (23%) of arylated product, a small amount of product (III) resulting from coupling through the phenyl group, and increased amounts of ArH (mesitylene) and RR (dehydro dimer). The larger amounts of the last two suggest that while the rate of coupling was slowed by the extra methyl groups, the rate of diffusion out of the solvent cage was substantially unchanged.

The phenylation of 2-mesityl-1,3-indandione is interesting in that still another mode of coupling is seen. The phenyl radical is diverted from both the 2-position and the aryl substituent by the methyl groups and finds a less hindered position on the oxygen,[9] forming compound IX.

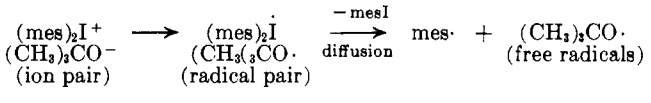
While the separate mesitylation of 2-mesityl-1,3-indandione was not attempted (because of the difficult preparation of this compound), there seems to be no appreciable chance of substitution at the 2-position. This follows not only from the results of the preceding phenylation but also from the fact that mesitylation of 1,3-indandione gave 2-mesityl-1,3-indandione (V) and the mesityl ether of its enol form VII but no 2,2-dimesityl-1,3-indandione.

It remains now to consider the formation of 2-*t*-butoxy-2-mesityl-1,3-indandione (VI) in the reaction of 1,3-indandione with dimesityliodonium chloride. While several possible routes can be written for the formation of this compound, the most reasonable seems to be the coupling of *t*-butoxyl free radicals with 2-mesityl-1,3-indandion-2-yl radicals. The latter free radicals are both stabilized by resonance and sterically inhibited from coupling with similar radicals or mesityl free



radicals. It is assumed that the *t*-butoxyl free radical would be able to approach the reactive 2-position along a line approximately perpendicular to the five-membered ring.

The *t*-butoxyl free radical might be formed by electron transfer.



Experimental[16]

Starting Materials.—Diphenyliodonium chloride was prepared according to a previously described procedure.[17] 2-Phenyl-1,3-indandione and 1,3-indandione were purchased from Aldrich Chemical Co. or prepared as described.[3] *t*-Butyl alcohol from Matheson Coleman and Bell was distilled from calcium hydride before use.

Dimesityliodonium Chloride.—This compound was prepared by the condensation in acetic acid of mesitylene with iodyl sulfate, prepared from iodine and iodine pentoxide[18] in sulfuric acid. A mixture of 40.8 g. (0.16 mole) of iodine and 120 g. (0.36 mole) of iodine pentoxide in 500 ml. of concentrated sulfuric acid was

(16) Analyses were performed by Schwarzkopf Microanalytical Laboratories, Woodside, N. Y. Infrared spectra were taken on a Perkin-Elmer double beam recording spectrophotometer, Model 21, and a Perkin-Elmer Infracord spectrophotometer. Ultraviolet spectra were taken on a Cary Model 11 recording spectrophotometer. Melting points were taken in capillary tubes and were corrected. For n.m.r. methods and results see Table II.

(17) F. M. Beringer, E. J. Geering, I. Kuntz, and M. Mausner, *J. Phys. Chem.*, **60**, 141 (1956).

(18) J. T. Plati, U. S. Patent 2,839,583 (June 17, 1958).

stirred for 20 hr. at room temperature, giving bright yellow crystals of iodyl sulfate suspended in a colorless solution. The precipitate was separated by decantation, stirred with 400 ml. of glacial acetic acid at 15°, and again separated by decantation. To a stirred suspension of the precipitate in 400 ml. of glacial acetic acid at 10–15° was added over 1 hr. 200 ml. of mesitylene (1.43 moles) in 200 ml. of glacial acetic acid. The temperature was allowed to rise gradually to 25°, and the stirring was continued for 2 hr. At the end of this time all the yellow crystals of iodyl sulfate had reacted, and an amber solution was obtained. After filtration to remove some unchanged iodine pentoxide the solution was diluted with 3 l. of water and a solution of 400 g. of ammonium chloride in a liter of water. The oily yellow precipitate was collected and washed with acetone, water, and again with acetone. White crystals, 131 g. (0.33 mole, 41%) of **dimesityliodonium chloride**, were obtained, m.p. 128–129° dec. Two recrystallizations from methanol–water raised the melting point to 138.5–139.5° dec. (capillary), 162–163° dec. (block), lit. m.p. 122°[13] and 146°.[14] The ultraviolet absorption maximum was λ_{max}^{EtOH} 245 mμ (ϵ_{max} 17,200), shoulder at 285 mμ.

Anal. Calcd. for $C_{18}H_{22}ClI$: C, 53.94; H, 5.54. Found: C, 53.80; H, 5.57.

2-Phenyl-1,3-indandione with Dimesityliodonium Chloride.—To a solution of 2.3 g. (100 mg.-atoms) of sodium in 800 ml. of *t*-butyl alcohol and 22.2 g. (0.1 mole) of 2-phenyl-1,3-indandione there was added with stirring 40.0 g. (0.1 mole) of dimesityliodonium chloride. After 20 min. of heating under reflux, during which time the solution turned from red to orange, no unchanged iodonium salt was detectable. The solvent removed by distillation at 80–100 mm. was collected in a Dry Ice–acetone trap. This distillate contained 16.7% of **mesitylene** as determined from the optical density of the solution at 264 mμ. The residue was dissolved in 400 ml. of methylene chloride and extracted with 1 *N* sodium hydroxide until the aqueous phase was colorless (about five times). The neutral organic phase after evaporation of the solvent was chromatographed on a 500-g. Florisil column.

The hexane eluate yielded 15.1 g. (61.5 mmoles, 61.5%) of **iodomesitylene**, whose infrared spectrum was identical with that of an authentic sample.

The 1:1 benzene–cyclohexane eluate gave a pale yellow oil, which was triturated with ether to yield 7.8 g. (23 mmoles, 23%) of pale yellow crystals of **2-mesityl-2-phenyl-1,3-indandione (II)**, m.p. 202–205°. Two recrystallizations from ethanol raised the melting point to 213–214°. The ultraviolet absorption maximum was λ_{max}^{EtOH} 225 mμ (ϵ_{max} 58,200), shoulder at 250 mμ.

Anal. Calcd. for $C_{24}H_{20}O_2$: C, 84.68; H, 5.92. Found: C, 84.56; H, 5.93.

The combined benzene and methylene chloride eluates yielded 8.8 g. (20 mmoles, 40%) of a pale orange glass which on trituration with ether gave white crystals of a dehydro dimer of 2-phenyl-1,3-indandione (**2,2′-diphenyl-2,2′-biindan-1,1′,3,3′-tetrone**),[15] m.p. 206–208°, lit. m.p. 213–214°. The infrared spectrum of this compound was identical with that of an authentic sample.

The red aqueous layer, containing the acidic components of the reaction, was acidified and extracted with methylene chloride. After evaporation of the solvent the residue was chromatographed on a 500-g. Florisil column. The 1:1 methylene chloride–ether eluate on evaporation of the solvent and trituration of the residue with ether gave 565 mg. (1.7 mmoles, 1.7%) of white crystals of **2-(*o*-mesitylphenyl)-1,3-indandione (III)**, m.p. 210–219°. Two recrystallizations from ethanol raised the melting point to 224.5–225°. Two sublimations at 175–200° (0.5 mm.) further raised the melting point to 227–227.5°.

Anal. Calcd. for $C_{24}H_{20}O_2$: C, 84.68; H, 5.92; mol. wt., 340.4. Found: C, 84.73, 84.39; H, 5.79, 5.85; mol. wt., 322.

The infrared spectrum showed a doublet in the carbonyl region, 1710–1740 cm.$^{-1}$, characteristic for the 1,3-indandione system along with methyl and mesityl groups. The ultraviolet absorption spectrum showed the following bands, given as λ_{max}^{EtOH} 225 (ϵ_{max} 49,000) and 248 mμ (15,400).

From the ether eluate 525 mg. (2.36 mmoles, 2.4%) of unchanged **2-phenyl-1,3-indandione** was recovered.

Ring Cleavage of 2-Mesityl-2-phenyl-1,3-indandione.—A solution of 1 g. (2.94 mmoles) of II in 30 ml. of dioxane and 15 ml. of 1 *N* sodium hydroxide was refluxed overnight, becoming deep red. After removal of the solvent the residue was partitioned between methylene chloride and water. The red aqueous phase was acidified and extracted with methylene chloride. The extract on evaporation yielded an oil which on trituration with benzene–hexane gave 147 mg. (0.41 mmole, 14%) of **α-mesityl-α-phenylacetophenone-*o*-carboxylic acid**. After two recrystallizations from benzene–hexane white needles were obtained, m.p. 153–154°.

Anal. Calcd. for $C_{24}H_{22}O_3$: C, 80.42; H, 6.19. Found: C, 80.54; H, 6.24.

The infrared spectrum of this compound showed the characteristic broad band for a carboxylic acid in the 3500–3000-cm.$^{-1}$ region and two carbonyl bands, one at 1740 cm.$^{-1}$ assigned to the acid carbonyl, the other at 1710 cm.$^{-1}$ attributed to the aromatic carbonyl absorption. The presence of the mesityl group was shown by CH_3 stretching at 1420 cm.$^{-1}$ and 1390 cm.$^{-1}$ and by a band at 850 cm.$^{-1}$ characteristic of the mesityl group.

Dimesityliodonium Chloride with 1,3-Indandione.—To a solution of 2.30 g. (100 mg.-atoms) of sodium in 1 l. of *t*-butyl alcohol there was added 14.61 g. (0.1 mole) of 1,3-indandione. After a few minutes of stirring orange-red crystals formed, believed to be the sodium salt of 1,3-indandione. The mixture was heated to reflux, and 40.0 g. (0.1 mole) of dimesityliodonium chloride was added. After 10 min. of stirring at reflux the mixture became a clear red-brown, and no unchanged iodonium salt was detected. The solvent distilled at atmospheric pressure contained **mesitylene** (26.3%) as determined by ultraviolet spectroscopy.

The residue was separated into neutral and acidic fractions as before. The neutral fraction was then chromatographed on Florisil to yield in the hexane fraction 19.7 g. (80 mmoles, 80%) of **iodomesitylene**, identified by its infrared spectrum.

From the benzene eluate 2.3 g. of a yellow glass (6.8 mmoles, 6.8%) of crude **2-*t*-butoxy-2-mesityl-1,3-indandione (VI)** was obtained. Trituration with ether gave 0.67 g. of a light yellow solid (2.0 mmoles, 2.0%), m.p. 154–158°, after recrystallization from ethanol, m.p. 158.8–159.8°. Sublimation at 150–160° (0.05 mm.) raised the melting point to 160–161°; ultraviolet absorption maximum, λ_{max}^{EtOH} 229 mμ (ϵ_{max} 52,200), shoulder at 249 mμ.

Anal. Calcd. for $C_{22}H_{24}O_3$: C, 78.54; H, 7.19; mol. wt., 336.4. Found: C, 78.37 and 78.55; H, 7.27 and 7.11; mol. wt., 350 and 324.

The infrared spectrum showed the carbonyl doublet at 1710–1730 cm.$^{-1}$ characteristic of the indandione system, a doublet for the *gem*-dimethyl group at 1370–1396 cm.$^{-1}$, and strong CH_3 absorption in the 3000-cm.$^{-1}$ region. The presence of a mesityl group is also indicated by a band at 850–860 cm.$^{-1}$.

The methylene chloride fraction yielded 4.4 g. of an orange glass (11.5 mmoles, 11%) of crude **2-mesityl-3-mesityloxy-1-indenone (VII)**. On trituration with ether 1.56 g. of an orange solid was obtained, (4.1 mmoles, 4.1%), m.p. 197–202.4°, two recrystallizations from ethanol gave orange needles, m.p. 204–205°; ultraviolet absorption maximum, λ_{max}^{EtOH} 248 mμ (ϵ_{max} 43,000).

Anal. Calcd. for $C_{27}H_{26}O_2$: C, 84.78; H, 6.85. Found: C, 84.74; H, 6.63.

The infrared spectrum showed bands at 1710 cm.$^{-1}$ and at 1640 cm.$^{-1}$, the latter probably due the α,β-unsaturated carbonyl group. Bands due to methyl and mesityl groups were also present.

The acidic fraction from the reaction was also chromatographed on Florisil. The ether eluate on evaporation gave 1.0 g. of a yellow glass which on trituration with ether yielded 0.1 g. (0.4 mmole, 0.4%) of pale yellow **2-mesityl-1,3-indandione (V)**, m.p. 205–206°. Two recrystallizations from ethanol gave yellow needles, m.p. 224–225°. Recrystallization from benzene gave a white solid with no change in melting point or infrared spectrum. The ultraviolet absorption spectrum showed the following bands, given as λ_{max}^{EtOH} 228 (ϵ_{max} 16,120) and 250 mμ (20,400):

Anal. Calcd. for $C_{18}H_{16}O_2$: C, 81.79; H, 6.10. Found: C, 81.80; H, 5.84.

The rest of the compounds isolated from this reaction were highly colored; their infrared spectra showed no methyl groups. From their analyses and molecular weights these appear to be higher condensation products of 1,3-indandione.

When the reaction was run with potassium *t*-butoxide as the base 9% of VII, 0.15% of VI, and 0.76% of V were obtained.

Ring Cleavage of 2-*t*-Butoxy-2-mesityl-1,3-indandione.—A solution of 200 mg. of VI in 20 ml. of dioxane and 15 ml. of 1 *N* sodium hydroxide was refluxed for about 20 hr. The solution was concentrated to a small volume by distillation of the solvent, and the residue was diluted with 50 ml. of water and extracted with methylene chloride. The organic layer yielded some unchanged starting material, while the aqueous phase gave after acidifica-

tion, extraction with methylene chloride, and removal of the solvent a small amount of white solid. This solid was recrystallized twice from hexane to yield white needles of **α-*t*-butoxy-α-mesitylacetophenone-*o*-carboxylic acid**, m.p. 115–116°.

Anal. Calcd. for $C_{22}H_{26}O_4$: C, 74.55; H, 7.39; mol. wt., 354.43. Found: C, 74.50; H, 7.36; mol. wt., 392 and 311.

Removal of the *t*-Butyl Group in Compound VI.—A solution of 250 mg. of VI in 15 ml. of dioxane and 5 ml. of 6 *N* hydrochloric acid was heated on a steam bath for 2 hr. During this time the solution was reduced to half the volume, with formation of light ivory colored needles. The mixture was diluted with 25 ml. of water, the solid was collected and chromatographed on silica gel. The ether eluate on removal of the solvent gave white crystals of **2-hydroxy-2-mesityl-1,3-indandione (VIII)**, which was purified by two sublimations at 150–175° (0.05 mm.) to yield white needles, m.p. 198–199°.

The infrared spectrum showed a hydroxyl band at 3500 cm.$^{-1}$, carbonyl bands at 1710 and 1640 cm.$^{-1}$, the latter arising from hydrogen bonding of one of the carbonyl groups with the hydroxyl group. Other bands in the spectrum included a C–O stretching at 1100 cm.$^{-1}$, characteristic of tertiary alcohols, along with CH_3 and mesityl absorption.

Anal. Calcd. for $C_{18}H_{16}O_3$: C, 77.12; H, 5.76. Found: C, 76.99; H, 5.86.

Hydrolysis of 2-Mesityl-3-mesityloxy-1-indenone.—A solution of 885 mg. (2.32 mmoles) of VII in 25 ml. of dioxane and 25 ml. of 6 *N* hydrochloric acid was refluxed for 3 days with stirring. The mixture was then concentrated to about 20 ml., diluted with 50 ml. of methylene chloride, and extracted five times with 1 *N* sodium hydroxide. The organic layer contained unchanged starting material. The red aqueous phase on acidification, extraction with methylene chloride, and removal of solvent yielded after trituration of the residue with ether 245 mg. (0.93 mmole, 40%) of pale yellow needles of **2-mesityl-1,3-indandione (V)**, m.p. 223–224°. The reaction mixture had a strong odor of mesitol, but no attempt was made to isolate it.

2-Mesityl-1,3-indandione with Diphenyliodonium Chloride.—To a solution of 84.8 mg. (0.76 mmole) of potassium *t*-butoxide in 20 ml. of *t*-butyl alcohol there was added with stirring 200 mg. (0.76 mmole) of V and 243 mg. (0.76 mmole) of diphenyliodonium chloride. The orange solution was refluxed overnight, during which time it turned a light yellow, and all the iodonium cation was consumed. The solvent was removed, and the residue was chromatographed on a 100-g. Florisil column. The ether eluate yielded a yellow oil which after two distillations at 180–200° (0.05 mm.) gave 188 mg. (0.55 mmole, 73%) of a yellow glass of **2-mesityl-3-phenoxy-1-indenone (IX)**. A small sample of this glass was crystallized from isopropyl alcohol to give a pale yellow solid, m.p. 70.2–71°; ultraviolet absorption maximum, λ_{max}^{EtOH} 246 mμ (ϵ_{max} 42,200).

Anal. Calcd. for $C_{24}H_{20}O_2$: C, 84.68; H, 5.92. Found: C, 84.94; H, 6.06.

The infrared spectrum of this compound was similar to that of compound VII.

The acetone eluate from the chromatography column yielded 30 mg. of unchanged starting material.

When the reaction was run with sodium *t*-butoxide as the base, the reaction time was shortened to 0.5 hr., with otherwise identical results.

Hydrolysis of 2-Mesityl-3-phenoxy-1-indenone.—A solution of 50 mg. of IX in 3 ml. of isopropyl alcohol and 3 ml. of 3 *N* hydrochloric acid was heated on a steam bath for 3 hr. The mixture was concentrated to *ca.* 3 ml. by solvent removal; an odor of phenol was detected. The mixture was diluted with 5 ml. of water, and the gummy solid formed was collected. Trituration with ether gave an ivory solid, m.p. 219–222°, whose infrared spectrum was identical with that of **2-mesityl-1,3-indandione (V)**.

An Improved Synthesis of Carbamates

BERNARD LOEV AND MINERVA F. KORMENDY

Research and Development Division, Smith Kline and French Laboratories, Philadelphia, Pennsylvania

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A simple synthesis of the hitherto difficultly prepared carbamates of tertiary alcohols has been developed. The method also has been found applicable to the synthesis of the carbamates of other alcohols (including steroids, as well as primary and secondary alcohols), polyols, phenols, mono- and polythiols, and oximes. Stereoisomeric (*syn* and *anti*) ketoximes were converted to the corresponding stereoisomeric oxime carbamates. The preparation of any of these involves simply stirring the substrate, sodium cyanate, and trifluoroacetic acid in an inert solvent for several hours at room temperature.

Although the carbamates of primary and secondary alcohols, and the N-substituted carbamates of tertiary alcohols are relatively easily prepared,[1] the synthesis of unsubstituted carbamates of tertiary alcohols is generally quite difficult, owing to the ease of dehydration and rearrangement of the alcohols.[2,3] The method usually employed involves conversion of the alcohol to a mixed carbonate using phenyl chloroformate, then treatment with liquid ammonia.[2,3]

During the course of a study which necessitated the preparation of a number of carbamates of tertiary alcohols, we developed a simple method for their synthesis which has been found to be broadly applicable not only to the synthesis of the carbamates of alcohols (primary, secondary, and tertiary alcohols, steroids, polyols, and phenols), but also to the synthesis of the carbamates of mono- and polythiols and oximes.

This method involves stirring the alcohol (mercaptan, oxime, etc.) with sodium cyanate and trifluoroacetic acid in certain solvents at room temperature.

Although the reaction of alcohols with cyanic acid had been presumed always to give allophonates,[2,4,5] Werner[6] reported a 56% yield of urethan from the reaction of ethanol in an aqueous solution of sodium cyanate and hydrochloric acid. McLamore[2] reported, however, that reaction of a tertiary alcohol with potassium cyanate in acetic acid led to dehydration or rearrangement and gave *no* carbamate. Moderate (approximately 50%) yields of the carbamates of tertiary alcohols were described by Marshall,[7] employing *in situ* generation of cyanic acid from an anhydrous mixture of sodium cyanate in trichloroacetic acid.

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