small volume gave 6.6 g. (70%) of the isomer mixture XXIV. A small portion upon fractional crystallization from glacial acetic acid gave analytical samples of the pure stereoisomers.

Anal. Calcd. for $C_{28}H_{25}Br_2O_2$: C, 61.33; H, 3.68. Found: Higher melting isomer, presumed to be *meso*, m.p. 275–277°: C, 61.61; H, 3.87. Lower melting isomer, presumably *racemic*, m.p. 238–240°; ϵ, 61.62; H, 3.95. Infrared carbonyl absorption bands: 5.99 and 6.04 μ, respectively.

3,4-Di-*p*-bromophenyl-2,5-diphenylfuran (**XX**). (**A**)—Furanization of the above stereoisomer mixture (XXIV) (10 g.) was effected in 200 ml. of boiling glacial acetic acid by 10 ml. of 47% hydriodic acid (5 min.). The furan (XX) was crystallized from ethanol (9.0 g., 93%) and identified by mixture m.p. with a sample prepared from dibenzoylacetylene (III) as described below.

(**B**) A solution of 0.40 g. of *trans*-dibenzoyl-*p,p'*-dibromostilbene (XIX) in 20 ml. of glacial acetic acid and 1 ml. of 47% hydriodic acid was refluxed for 1 hr. Cooling and crystallization of the resulting precipitate from ethanol gave the furan XX in near quantitative yield; m.p. 210.5–212°.

Anal. Calcd. for $C_{28}H_{18}Br_2O$: C, 63.42; H, 3.40. Found: C, 63.68; H, 3.55. Ultraviolet absorption maxima: 232.5, 259, 320 mμ, ϵ 25,800, 20,300, 18,400.

cis*-1,2-Dibenzoyl-*p,p'*-dibromostilbene** (cis*-2,3-Di-*p*-bromophenyl-1,4-diphenyl-2-butene-1,4-dione**) (**XXI**).—A suspension of 1.0 g. of the furan XX in a mixture of 1.5 g. of bromine, 100 ml. of ether and 50 ml. of water, was shaken for 30 min., separated, and the excess of bromine destroyed by sodium bisulfite solution. Evaporation of the ether solution and crystallization of the product from ethanol gave a 97% yield of the *cis*-diketone XXI, m.p. 228–230° (not raised by recrystallizations from absolute ethanol–benzene mixture).

Anal. Calcd. for $C_{28}H_{18}Br_2O_2$: C, 61.56; H, 3.32. Found: C, 61.85; H, 3.36. Absorption maxima: 258 mμ, ϵ 22,700; 5.99 μ.

***trans*-1,2-Dibenzoyl-*p,p'*-dibromostilbene** (**2,3-Di-*p*-bromophenyl-1,4-diphenyl-2-butene-1,4-dione**) (**XIX**).—In oven-baked apparatus *p*-bromophenyl Grignard reagent was prepared under nitrogen from 20 g. (0.85 g.-atom) of magnesium and 195 g. (0.825 mole) of 1,4-dibromobenzene in 500 ml. of ether. At 0°, 50 g. (0.21 mole) of dibenzoylacetylene (III) was added portionwise over 5 min. and allowed to react. After standing for 40 min. the reaction mixture was treated portionwise with 200 g. of iodine (30 min. at 0°). Hydrolysis with aqueous sodium bisulfite solution, isolation of the crude product and crystallization from glacial acetic acid gave 1.5 g. (3%) of this *trans* diketone XIX, m.p. 220–222°.

Anal. Calcd. for $C_{28}H_{18}Br_2O_2$: C, 61.56; H, 3.32. Found: C, 61.32; H, 3.14. Absorption maxima: 256 mμ, ϵ 26,700; 6.06 μ.

***cis*-Di-*p*-bromobenzoylstilbene (XVb) and 2,5-Di-*p*-bromotetraphenylfuran (XVIIIb).**—For data see ref. 5b.

Acknowledgment.—The authors are indebted to John I. Dale for carrying out one important experiment.

Diaryliodonium Salts. XVIII. The Phenylation of Esters in *t*-Butyl Alcohol[1-3]

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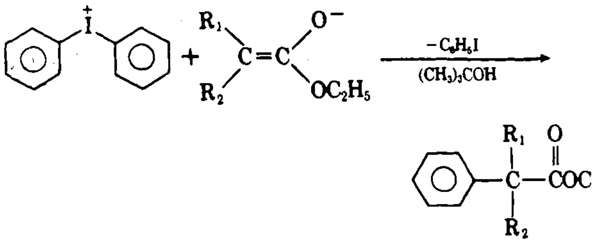
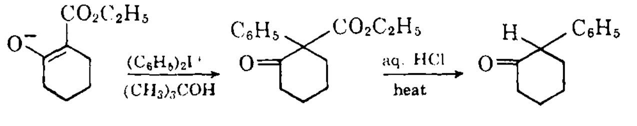
In *t*-butyl alcohol containing potassium *t*-butoxide substituted malonic and oxalacetic esters, ethyl cyclohexanone-2-carboxylate and ethyl diphenylacetate were converted by diphenyliodonium chloride to their phenyl derivatives, while in liquid ammonia containing sodamide ethyl phenylacetate gave a mixture of ethyl diphenylacetate and triphenylacetamide.

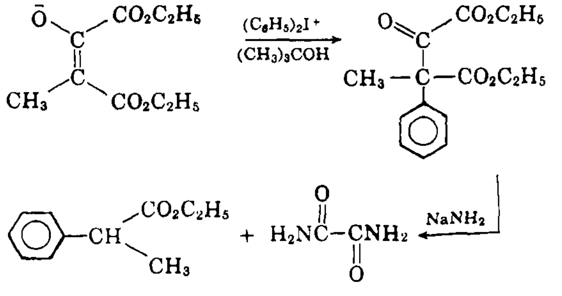
Before the completion of this research in 1959, there appeared a report on the phenylation of dimedone using a diphenyliodonium salt.[5] Since then there have been articles[2,6] on the phenylation of di- and triketones, the more recent[2] proposing a mechanism for the phenylation of carbanions by diphenyliodonium salts. The present work is concerned with the phenylation of esters in *t*-butyl alcohol containing potassium *t*-butoxide and was an exploration of the reaction's scope[3] and potential value in synthesis.



Ethyl Cyclohexanone-2-carboxylate.—A good yield (60%) of ethyl 2-phenylcyclohexanone-2-carboxylate was obtained when ethyl cyclohexanone-2-carboxylate was treated with diphenyliodonium chloride in *t*-butyl alcohol containing potassium *t*-butoxide. No O-phenylated product was found. Attempted saponification of this product with alcoholic potassium hydroxide failed, but after prolonged heating with concentrated hydrochloric acid 2-phenylcyclohexanone was isolated as the oxime.



Diethyl Methyloxalacetate.—While oxalacetic ester gave a mixture of products, including lactones, the



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(1) This article is taken from the dissertation of P. S. F., submitted in 1959 in partial fulfillment of the degree of Doctor of Philosophy (chemistry).

(2) Preceding article: F. M. Beringer, S. A. Galton, and S. J. Huang, *J. Am. Chem. Soc.*, **84**, 2819 (1962).

(3) The reactions of dimethyl and diethyl malonate with diphenyl- and 4,4-dichlorodiphenyliodonium chloride in various alcohols containing sodium or potassium alkoxide will be reported separately: F. M. Beringer and P. S. Forgione, *Tetrahedron*, in press.

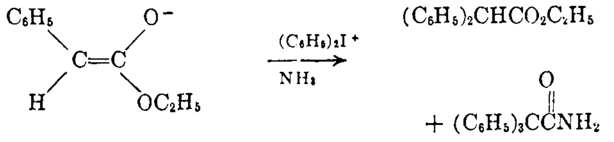
(4) Alfred P. Sloan Foundation Fellow, 1956–1959.

(5) O. Neiland, G. Ia. Vanag, and E. Iu. Gudrinietse, *J. Gen. Chem. USSR*, **28**, 1256 (1958) (in English).

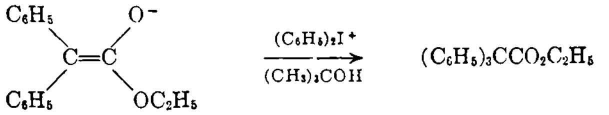
(6) F. M. Beringer, P. S. Forgione, and M. D. Yudis, *Tetrahedron*, **8**, 49 (1960).

monosubstituted ester diethyl methyloxalacetate gave a 70% yield of diethyl methylphenyloxalacetate, cleaved by sodamide to oxamide and ethyl α-phenylpropionate.

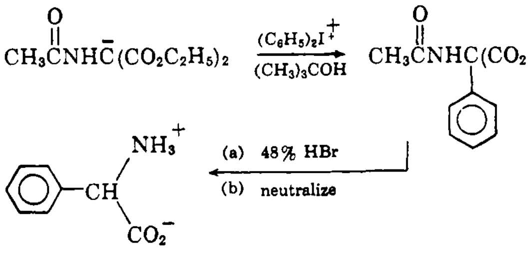
Ethyl Phenylacetate and Diphenylacetate.—Ethyl phenylacetate in liquid ammonia treated with sodamide and then with diphenyliodonium chloride gave ethyl diphenylacetate (57%) and triphenylacetamide (31%).



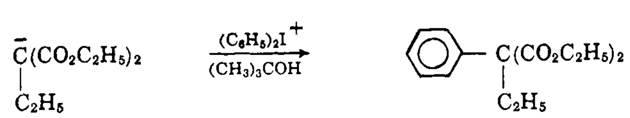
Ethyl diphenylacetate with potassium *t*-butoxide and diphenyliodonium chloride in *t*-butyl alcohol gave, in addition to the expected ethyl triphenylacetate (28%), small amounts of acetone (9%) and benzene[7] (18%).



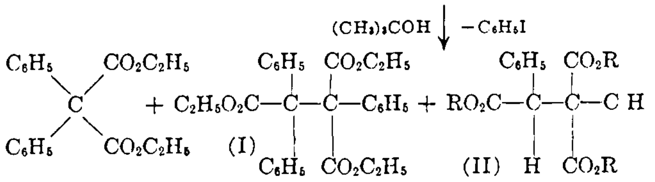
Diethyl Acetamidomalonate.—Phenylation of acetamidomalonic ester in *t*-butyl alcohol gave diethyl acetamidophenylmalonate (34%), hydrolyzed and decarboxylated almost quantitatively to phenylglycine (α-aminophenylacetic acid).



Diethyl Ethylmalonate and Phenylmalonate.—Diethyl ethylmalonate in *t*-butyl alcohol was phenylated to give 67% of crude and 55% of pure diethyl ethylphenylmalonate.



Similarly, the reaction of diethyl phenylmalonate with diphenyliodonium chloride in *t*-butyl alcohol produced the expected diethyl diphenylmalonate in 37% yield as well as a dimerlike product, probably ethyl 1,1,2-triphenylethanetricarboxylate (I), in about 25% yield and a small amount of a mixed ester, such as *t*-butyl diethyl 1,2-diphenylethanetricarboxylate (II). Low yields of this mixed ester were also obtained in the phenylation of diethyl malonate in *t*-butyl alcohol.[3]



(II. One R *t*-butyl, the others ethyl)

Discussion

In this early exploratory work no attempt was made to find optimum conditions, and the yields of phenylated products (28–70%) must therefore be considered susceptible to improvement.[8] Thus, phenylation of esters with diphenyliodonium salts seems of potential synthetic value and may supplement phenylation by benzyne produced *in situ*.[9]

Consideration of the present results in the light of the proposed mechanism[2] for phenylation by diphenyliodonium salts will be deferred to the article[3] concerned with reactions of dimethyl and diethyl malonate in various alcohols.

Experimental[10–13]

Starting Materials.—Diethyl methyloxalacetate, ethyl phenylacetate, diethyl ethylmalonate, and diethyl phenylmalonate were received from Distillation Products, Inc., and redistilled before use, while ethyl cyclohexanone-2-carboxylate,[14] dimethyl phenylmalonate,[15] and diphenyliodonium chloride[16] were prepared according to published procedures. *t*-Butyl alcohol was distilled from potassium metal and used immediately.

Esters with Diphenyliodonium Chloride. Ethyl Cyclohexanone-2-carboxylate.—Diphenyliodonium chloride (48.7 g., 154 mmoles) was added to a solution of 154 mmoles each of ethyl cyclohexanone-2-carboxylate and potassium *t*-butoxide in 1 l. of *t*-butyl alcohol. Reaction under reflux with stirring for 36 hr. was followed by removal of 800 ml. of solvent, dilution of the residue with 2.5 l. of saturated aqueous sodium chloride, and acidification. Distillation of the dried ethereal extract gave 24.2 g. (119 mmoles, 77%) of iodobenzene and 22.8 g. (92 mmoles, 60%) of **ethyl 2-phenylcyclohexanone-2-carboxylate**, b.p. 144–147°/0.6 mm.; on redistillation b.p. 141°/0.4 mm.

Anal. Calcd. for $C_{15}H_{18}O_3$: C, 73.14; H, 7.37. Found: C, 73.31; H, 7.50.

Treatment of this ester with hydroxylamine hydrochloride and excess 10% aqueous sodium hydroxide formed the ketoxime, colorless needles, m.p. 151.0–151.5°, from aqueous ethanol.

Anal. Calcd. for $C_{15}H_{19}NO_3$: C, 68.94; H, 7.33; N, 5.36. Found: C, 69.00; H, 7.42; N, 5.02.

Hydrolysis of the keto ester with concentrated hydrochloric acid (90°, 1 hr.; reflux, 2 hr.) was followed by removal of solvent, treatment of the residue with alkaline hydroxylamine, and crystallization from aqueous ethanol to give a 95% yield of **the oxime of 2-phenylcyclohexanone**, m.p. 168–169°, reported[17] m.p. 169°, no depression on admixture with the oxime from authentic 2-phenylcyclohexanone.[18]

Diethyl Methyloxalacetate.—Diphenyliodonium chloride (158 g., 0.5 mole) was added at 20° to a solution of 0.5 mole each of

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[7] A mechanism for the formation of benzene and for dehydrogenation of the solvent has been proposed (ref. 2) and will be separately considered in connection with the present results (ref. 3).

[8] Investigation of reaction conditions has allowed the phenylation of 2-phenyl-1,3-indandione in 93% yield (ref. 2).

[9] W. W. Leake and R. Levine, *J. Am. Chem. Soc.*, **81**, 1169, 1627 (1959).

[10] Analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside 77, N. Y., and by Dr. K. Ritter, Basel, Switzerland.

[11] Capillary melting points, taken in a Hershberg apparatus, are corrected.

[12] Infrared spectra were taken with a Perkin-Elmer 21 double-beam spectrophotometer, while ultraviolet spectra were taken with a Process and Instruments Co. Model RS-3 recording spectrophotometer using Fisher spectral grade methanol.

[13] Vapor phase chromatographic analyses were made with a Perkin–Elmer 154-B instrument and an "A" universal-type partition column.

[14] H. R. Snyder, L. A. Brooks, and S. H. Shapiro, "Organic Synthesis," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 531.

[15] M. Rising and J. Stieglitz, *J. Am. Chem. Soc.*, **40**, 728 (1918).

[16] F. M. Beringer, I. Kuntz, and M. Mausner, *J. Phys. Chem.*, **60**, 141 (1956).

[17] J. Levy and J. Sfiras, *Bull. soc. chim. France*, [4] **49**, 1834 (1931).

[18] M. S. Newman and M. D. Farbman, *J. Am. Chem. Soc.*, **66**, 1550 (1944).

diethyl methyloxalacetate and potassium *t*-butoxide in 1.2 l. of *t*-butyl alcohol. After reaction with stirring (10 hr. at 20°, 24 hr. under reflux), removal of 800 ml. of solvent, dilution with 2.5 l. of saturated aqueous sodium chloride, and acidification, the reaction mixture was extracted portionwise with 2 l. of ether. The extract was concentrated, boiled under reflux at 70 mm., and distilled, giving three fractions.

The first was iodobenzene (84 g., 411 mmoles, 82%). The second fraction, b.p. 150–161°/4 mm., was redistilled to give 97.8 g. (352 mmoles, 70%) of **diethyl methylphenyloxalacetate**, b.p. 121.5°/0.2 mm., n^{25}D 1.4958.

Anal. Calcd. for $C_{15}H_{18}O_5$: C, 64.73; H, 6.52. Found: C, 65.05; H, 6.58.

The third fraction was 5.3 g. of a viscous yellow oil, b.p. 167–190° (0.2 mm.). Redistillation at 167–178°/0.2 mm. gave 4.2 g. of material. An infrared spectrum for this compound showed bands characteristic for phenyl, ester, and lactone adsorption, but the material was not identified further.

Anal. Found: C, 64.46; H, 6.52; mol. wt. 427.

The structure of the second fraction as diethyl methylphenyloxalacetate was confirmed by reaction with sodamide in benzene to give 26% of oxamide, m.p. above 310°, infrared spectrum identical to that of an authentic sample, and 57% of ethyl α-phenylpropionate, b.p. 99–100°/8 mm., n^{25}D 1.4912; reported[19] b.p. 100.5°/8 mm., n^{18}D 1.4943.

Ethyl Phenylacetate.—To a 3-l. flask equipped with a cold-finger condenser and containing 1.5 moles of sodamide in 1.5 l. of liquid ammonia there was added 82 g. (0.5 mole) of ethyl phenylacetate and, after 15 min., 158 g. (0.5 mole) of diphenyliodonium chloride. Thirty minutes later the unchanged sodamide was destroyed with excess ammonium chloride, and the ammonia was allowed to evaporate. The residual slurry was added to 3 l. of cold water, acidified, and extracted with ether (extract 1). Filtration of the aqueous phase gave 44.1 g. (0.14 mole) of recovered diphenyliodonium chloride; the filtrate after basification was extracted with ether (extract 2).

Extract 1 was distilled to give as a first fraction 47 g. of a dark red oil, b.p. 80–95°/6 mm. During the distillation dark red needles were deposited on the cold finger of the distilling head. Washing of this red oil with aqueous sodium bisulfite solution, extraction with ether, and treatment of the aqueous phase with chlorine gas produced 4.2 g. (18 mmoles) of iodine; the ether extract was dried and distilled to give 40.1 g. (0.244 mole) of recovered ethyl phenylacetate, b.p. 92–94°/6 mm.

The second fraction gave 35.1 g. (0.146 mole, 57% based on recovered ester) of **ethyl diphenylacetate** which solidified on standing. Crystallization from ethanol gave ethyl diphenylacetate as white needles, m.p. 58°, reported[20] m.p. 58°.

Anal. Calcd. for $C_{16}H_{16}O_2$: C, 79.97; H, 6.71. Found: C, 80.20; H, 6.70.

The ester on hydrolysis gave diphenylacetic acid, m.p. 148°, no depression on admixture with an authentic sample.

A third fraction of 15.2 g., b.p. 170–220°/1 mm., on crystallization from benzene gave 11.6 g. (40 mmoles, 31% based on unrecovered ester) of **triphenylacetamide**, m.p. 236–237° alone and when mixed with an authentic sample.[21]

Distillation of extract 2 gave 3.2 g. (34 mmoles, 9%, based on unrecovered iodonium salt) of aniline, b.p. 70°/9 mm., from which acetanilide was prepared, m.p. 113°; no depression on admixture with an authentic sample.

Ethyl Diphenylacetate.—A solution of 0.3 mole each of ethyl diphenylacetate, diphenyliodonium chloride, and potassium *t*-butoxide in 1.2 l. of *t*-butyl alcohol was stirred for 12 hr. at 20° and for 60 hr. under reflux. Solvent (800 ml.) removed by distillation contained 1.6 g. (28 mmoles, 9%) of acetone and 4.2 g. (54 mmoles, 18%) of benzene. The residue was diluted with 3 l. of water, acidified, and extracted with ether.

Distillation of the dried extract gave 55.4 g. (0.26 mole, 87%) of iodobenzene, 31.6 g. (0.132 mole) of recovered ethyl diphenylacetate, and 27.2 g. of viscous liquid, b.p. 180–240°/0.1–0.25 mm. Chromatographing on alumina, elution with petroleum ether, and crystallization from ethanol gave 11.3 g. (47 mmoles, 28% based on unrecovered ester) of **ethyl triphenylacetate**, m.p. 119–120°, reported[22] m.p. 120–121°. Hydrolysis gave triphenylacetic acid, m.p. 266–267°, reported[23] m.p. 265°, with no depression on admixture with an authentic sample.

Diethyl Acetamidomalonate.—A solution of 0.23 mole each of diethyl acetamidomalonate, diphenyliodonium chloride, and potassium *t*-butoxide in 1 l. of *t*-butyl alcohol was stirred for 1 hr. at 20° and for 4 hr. under reflux. The mixture was diluted with 4 l. of water, acidified, and extracted with ether. Distillation of the dried extract gave 39.2 g. (193 mmoles, 84%) of iodobenzene and 23.1 g. (79 mmoles, 34%) of **diethyl acetamidophenylmalonate** as a viscous yellow oil, b.p. 160–172°/0.5 mm. Redistillation at 0.1 mm. in a Hickman still gave a light yellow oil, n^{27}D 1.5025, which on treatment with benzene-petroleum ether gave **diethyl acetamidophenylmalonate**, m.p. 72°.

Anal. Calcd. for $C_{15}H_{10}O_5N$: C, 61.42; H, 6.53; N, 4.78. Found: C, 61.60; H, 6.70; N, 4.37.

A mixture of 2.0 g. (7 mmoles) of the above ester, b.p. 160–172°/0.5 mm., and 12 ml. of 48% hydrobromic acid was stirred under reflux for 7 hr., cooled, treated with activated carbon, and filtered. After addition of ammonium hydroxide to pH 6, the chilled solution deposited crystals. Recrystallization from water gave 0.73 g. (4.8 mmoles, 69%) of **phenylglycine**, m.p. 253–255°, reported[24] m.p. 255–256°, infrared spectrum identical to that of an authentic sample.

Diethyl Ethylmalonate.—A solution of 0.5 mole each of diethyl ethylmalonate, diphenyliodonium chloride, and potassium *t*-butoxide in 1.3 l. of *t*-butyl alcohol was stirred under reflux for 40 hr. Solvent (800 ml.) removed by distillation contained no detectable benzene or acetone. The residue was diluted with 3.5 l. of water, acidified, and extracted with ether.

Distillation of the dried extract gave 4.1 g. (39 mmoles, 8%) of ethyl butyrate, b.p. 120–121°, n^{25}D 1.3906, and 74.8 g. (368 mmoles, 74%) of iodobenzene. A main fraction b.p. 155–170°/15 mm. of **diethyl ethylphenylmalonate** weighing 89.6 g. (377 mmoles, 67%) was collected; redistillation gave 72.3 g. (274 mmoles, 55%) of ester, b.p. 160–163°/10 mm. An analytical sample had a b.p. 163°/10 mm., $n^{24.5}$D 1.4892. The infrared spectrum was found to be identical with an authentic sample of diethyl ethylphenylmalonate.

Anal. Calcd. for $C_{15}H_{20}O_4$: C, 68.16; H, 7.63. Found: C, 68.06; H, 7.76.

Diethyl Phenylmalonate.—To a solution containing 1 mole of potassium *t*-butoxide in 1.5 l. of dry *t*-butyl alcohol was added 236.3 g. (1.0 mole) of redistilled diethyl phenylmalonate giving a gel-like suspension. Addition of 316 g. (1.0 mole) of diphenyliodonium chloride over 0.5 hr. caused the white gel to break and produced a yellow suspension. The temperature of the reaction rose from room temperature to 65° and was held there. After 7 hr. about 800 ml. of solvent was removed, and the residue was diluted with 3 l. of water and acidified. Extraction with ether and distillation of the dried extract gave 73.2 g. (354 mmoles) of iodobenzene, b.p. 70–78°/10 mm., in addition to 80.1 g. (340 mmoles) of recovered diethyl phenylmalonate

Continued distillation gave 77.4 g. (250 mmoles, 37%) of **diethyl diphenylmalonate**, b.p. 147–153°/0.05 mm. Seeding with pure diethyl diphenylmalonate gave crystals, m.p. 56–57°, reported[25] m.p. 58°, infrared spectrum identical to that of an authentic sample.

Anal. Calcd. for $C_{19}H_{20}O_4$: C, 73.04; H, 6.45. Found: C, 72.78; H, 6.63.

The residue was distilled further to give 27.2 g. of a high-boiling fraction, b.p. 200–220°/0.05 mm., n^{27}D 1.5705. Molecular distillation of this oil gave 25.4 g. (55 mmoles, 25%) of **triethyl 1,1,2-triphenylethanetricarboxylate** (I), b.p. 170° at 0.003 mm., n^{27}D 1.5794. A middle cut of this oil was submitted for analysis.

Anal. Calcd. for $C_{19}H_{30}O_6$: C, 73.40; H, 6.37. Found: C, 73.23; H, 6.23.

The infrared spectrum (neat) of this compound showed bands at 1738, shoulder 1751 cm.$^{-1}$ (ester), 698 cm.$^{-1}$ (phenyl), and 1415, 1449 cm.$^{-1}$ (shoulder) (*o*-ethyl).

About 1 g. of this triester was heated under reflux for 4 hr. in an excess of aniline. Cooling of the reaction mixture gave a solid, which when filtered and recrystallized from ethanol–dimethylformamide gave white powdery crystals, m.p. 259–260°.

Anal. Calcd. for $C_{41}H_{33}O_3N_3$: C, 79.87, H, 5.40, N, 6.82. Found: C, 80.03; H, 5.28; N, 6.55.

Treatment of a portion of the crude oil, b.p. 200–220°/0.05

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(19) H. Olsson, *Z. physik. Chem.* **125**, 247 (1927).

(20) D. Vorlander and E. Rack, *Ber.*, **56**, 1126 (1923).

(21) A. Bistrzycki and I. Landtwing, *ibid.*, **41**, 691 (1908).

(22) J. Schmidlin and H. H. Hodgson, *ibid.*, **41**, 444 (1908).

(23) J. Schmidlin, *ibid.*, **39**, 636 (1906).

(24) N. Zelinsky and G. Stadnikoff, *ibid.*, **39**, 1726 (1906).

(25) A. W. Dox and A. Thomas, *J. Am. Chem. Soc.*, **45**, 1813 (1923).

mm., with a mixture of benzene and petroleum ether gave 0.7 g. (2 mmoles, 0.3%) of a white powder, m.p. 121–122°. Elemental analysis and the infrared spectrum of the solid showed it to be the same as the small amount of material isolated from the reaction of diethyl malonate and diphenyliodonium chloride in *t*-butyl alcohol.[3] The available information suggests the structure **t-butyl diethyl 1,2-diphenylethane-1,1,2-tricarboxylate** (II) for this compound.

The infrared spectrum (KBr) of this compound showed bands at 1738, and a shoulder at 1749 cm^{-1} (ester), 698 cm.$^{-1}$ (phenyl), 1389, 1415, 1449 cm.$^{-1}$ (*o*-ethyl), and 1415, 1365 cm.$^{-1}$ (*t*-butyl).

Acknowledgment.—The support of this research by the Alfred P. Sloan Foundation is gratefully acknowledged.

The Ultraviolet Absorption Spectra of Polyphenyl- and Polybenzylacetones

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Received July 24, 1962

Previously proposed statistical equations can be used successfully to predict the ketonic absorption maximum for most phenyl- and benzylacetones, connecting the two series in a useful manner. Other such ketones, not cleanly members of either of these classes, have spectral values which can not be accommodated similarly.

The previous publication in this series[1] suggested that two statistical equations (1 and 2) could be used to correlate the magnitude of the molecular extinction coefficients of the $n - \pi^*$ transitions of, respectively, phenylacetones and benzylacetones in hydrocarbon solvents.

$$\epsilon = 20\,(1 - 1/X^2)^n + k[1 - (1 - 1/X^2)^n] \quad (1)$$

$$\epsilon = 20\,(1 - 1/2X^3)^m + k[1 - (1 - 1/2X^3)^m] \quad (2)$$

In these equations, both X and k are constants and have the values of 3 and 810, respectively, n is the number of phenyl groups, and m is the number of benzyl groups.

These equations may be derived utilizing the original proposal of Cookson[2] which suggested that the maximum exaltation of the $n-\pi^*$ transition occurred when the orbitals at C_1 and C_1' (Fig. 1) were directed toward each other as shown. The fact that Cookson has recently modified[3] this early view does not affect the argument; there need only be a position of maximum exaltation. The position shown (in Fig. 1) is maintained here for simplicity and consistency with the earlier writing.[1] It is further assumed, with full recognition of obvious limitations, that the acetyl group and the unsaturated group are both freely rotating about, respectively, the axes C_1-C_2 and C_2-C_1'. Certain events therefore have the following probabilities: atom C-3′ is a minimum distance from C-1, $1/2X$; a π-orbital at C-1′ is directed maximally toward C-1, $1/X$; a π-orbital at C-1 is directed maximally toward C-1′, $1/X$; orbitals at C-1 and C-1′ are directed maximally towards each other, $1/X^2$; and an orbital at C-3 of a γ,δ-unsaturated ketone and an orbital at C-1 are directed maximally toward each other, $1/2X^3$. With a large number of molecules present, these probabilities can be directly equated to fractions of the total molecules. A ketone with one β,γ-unsaturated group thus has a fraction $(1/X^2)$ of molecules with maximum exaltation (k) and a fraction $(1 - 1/X^2)$ with substantially normal (20) $n - \pi^*$ transitions. The total extinction coefficient is then equal to $20\,(1 - 1/X^2) + k\,(1/X^2)$. This relationship can be adapted to the case of a molecule with n unsaturated groups in analogy with the classic combinatorial treatment of coin tossing. If the probability of "no heads" in one toss is 1/2, the probability of "no heads" in n tosses is $(1/2)^n$. Since the probability of no maximum exaltation with one unsaturated group is $(1 - 1/X^2)$, the probability with n equivalent groups is $(1 - 1/X^2)^n$. The final expressions (1 and 2) follow directly from this observation.

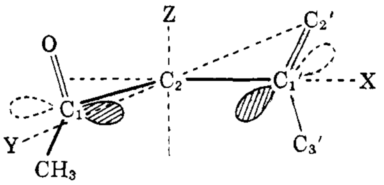

Fig. 1.—A possible position of π-orbitals on carbon atoms in a β,γ-unsaturated ketone.

While these equations in simplified form appeared to serve well[1] in a number of series [Ar—$(CH_2)_{1-2}$—CO—R, Ar = phenyl or 2-furyl, R = CH_3; and Ar = phenyl, R = phenyl], the number of compounds in any one series was small and it seemed desirable to evaluate the results which would be obtained with a much larger group of ketones.

Discussion

In Table I or Fig. 2 it can be seen that the values for the molecular extinction coefficients of all of the seven benzylacetones[4] (m = 1–4) and of the less symmetrical isomers of each pair in the polyphenylacetone series agree quite well with the predicted values. The observed values for the more symmetrical isomers are generally higher than the calculated, but that for the highly substituted pentaphenylacetone is profoundly lower. In certain cases, therefore, equations 1 and 2 may be helpful in predicting exalted $n-\pi^*$ transitions in other series of unsaturated ketones.

Well known at the time of the previous writing was the fact that certain ketones containing phenyl groups, by virtue of the geometric factors involved, exhibited no exaltation of the $n - \pi^*$ transition. This was cited[1] as one item of proof that the spectral values of benzylacetones, while small, are definite exaltations and are not due, for example, to aryl spectrum tailings. The

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[1] S. F. Marsocci and S. MacKenzie, *J. Am. Chem. Soc.*, **81**, 4513 (1959).

[2] R. C. Cookson and N. S. Wariyar, *J. Chem. Soc.*, 2302 (1956).

[3] R. C. Cookson and J. Hudec, *ibid.*, 429 (1962).

[4] The values for many of these differ considerably from those reported by J. M. Conia and P. Gosselin, *Bull. soc. chim. France*, 836 (1961), although excellent correlation of melting point and infrared spectral values was obtained.