

TABLE I
ULTRAVIOLET SPECTRA IN ISOCTANE SOLUTIONS AT 25°

Compound	Maxima Å	ϵ_m	Minima Å	ϵ_m
Ethylene sulfide	2610 (2450) ^a	34.3 ^b 24.6	2370	20.4
Propylene sulfide	2624 (2450) ^a	35.0 25.0	2373	19.7
Cyclohexenesulfide	2625	39.3	2370	19.7

ULTRAVIOLET SPECTRA IN THE GAS PHASE

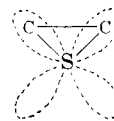
Compound	Maxima Å	$e \times 10^3$	Minima Å	$e \times 10^3$
Ethylene sulfide	2592 2430	1.13 ^c 1.16	2521 2364	1.06 1.09
Propylene sulfide	2611 2450	1.72 1.47	2500 2360	1.41 1.07

^a Inflection. ^b Units: A liter mole⁻¹ cm.⁻¹ ^c Units: A mm.⁻¹ cm.⁻¹

of perturbation effects. Thus the benzene bands in the region of 2600 Å are forbidden by selection rules based on the C₂ symmetry of benzene but vibrations of the atoms cause the absorption bands to appear with ϵ_m in the range of 100. These bands are called "partially forbidden".

Another explanation for the origin of the spectra can be built using the C_{2v} symmetry of the three membered ring compounds and some of the geometric requirements of some *d* orbitals. In this case the spectra would be considered as excitation

from an unbonded pair on the sulfur (*p* orbital) to a *d* orbital. The excited state would then appear as



Unfortunately it is difficult to describe the complete electronic states of these polyatomic sulfur compounds. Even hydrogen sulfide has not been analyzed with respect to the electronic spectrum. At least there are suggestive reasons why the ethylene sulfide system should exhibit some type of ultraviolet absorption above 2000 Å though the spectra might not be predicted before hand.

There is evidence in the literature of ultraviolet spectra of sulfur compounds that the degree of electronic charge on the sulfur atom in divalent sulfur compounds is related to the position of the absorption band. This will be considered in the following paper in this series on the effect of ring size upon the spectra of cyclic sulfides.

The author wishes to express his appreciation to Prof. W. E. Lyons for helpful discussions during the course of this investigation and to Prof. P. D. Bartlett for permission to publish this report.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF LOYOLA UNIVERSITY]

Skeletal Rearrangement of β,β,β -Triphenylpropionic Acid in the Hunsdiecker Reaction^{1,2}

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The reaction of silver β,β,β -triphenylpropionate with bromine under conditions normally employed for the Hunsdiecker degradation proceeds anomalously to give the phenyl esters of β,β -diphenylacrylic and α -bromo- β,β -diphenylacrylic acids in moderate yield, with little bromodecarboxylation. Evidence is presented that this skeletal transformation proceeds by an ionic process probably involving 1,4-phenyl migration *via* a five-membered ring intermediate.

Introduction. Curtin and Hurwitz³ in their preparation of a number of related radicals by decarbonylation of the appropriate aldehyde found evidence that the β,β,β -triphenylethyl radical (C₆H₅)₃CCH₂· gives 100% rearrangement under these conditions to the α,α,β -triphenylethyl radical (C₆H₅)₂CCH₂C₆H₅ by migration of a phenyl group. This rearrangement is appreciably faster than the

identically engendered transformation of the neophyl radical C₆H₅C(CH₃)₂CH₂· to the β -phenyl-*t*-butyl radical ·C(CH₃)₂CH₂C₆H₅,⁴ and presumably might occur even in the presence of an active substrate such as bromine.⁵

(4) W. H. Urry and M. S. Kharasch, *J. Am. Chem. Soc.*, **66**, 1438 (1944); S. Winstein and F. Seubold, *J. Am. Chem. Soc.*, **69**, 2916 (1947); F. Seubold, *J. Am. Chem. Soc.*, **75**, 2532 (1953). In the last reference, the neophyl rearrangement is deduced to possess an activation energy of about 8 kcal./mole.

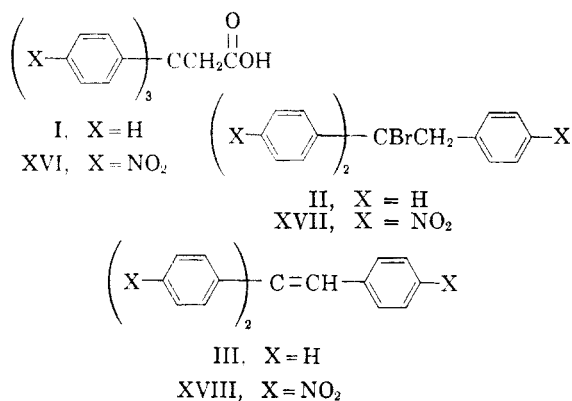
(5) The neophyl rearrangement is apparently absent or at best present to the extent of 5–10% in such a reactive medium. Cf. (a) C. E. Berr, Ph.D. thesis, University of California at Los Angeles (1952); (b) J. W. Wilt, *J. Am. Chem. Soc.*, **77**, 6397 (1955); (c) W. T. Smith, Jr., and J. T. Sellas, *Trans. Kentucky Acad. Sci.*, **16**, 72 (1955).

(1) Abstracted in part from the thesis of Donald D. Oathoudt presented to the faculty of the Graduate School of Loyola University in partial fulfillment of the requirements for the degree of Master of Science, February, 1957.

(2) A preliminary report of this work appeared in *J. Org. Chem.*, **21**, 1550 (1956).

(3) D. Y. Curtin and M. J. Hurwitz, *J. Am. Chem. Soc.*, **74**, 5381 (1952).

Because of this work it was thought that an investigation of β,β,β -triphenylpropionic acid (I) in the Hunsdiecker reaction⁶ would be of interest.



Were this reaction homolytic in nature, as is commonly believed,^{6b} it would be likely to yield a halide or olefin, *viz.*, II or III, rearranged in accordance with the above observation, inasmuch as the same radicals would be involved. The detection of such rearranged substances would furnish needed support for the free radical interpretation of the Hunsdiecker reaction.

Results. The reaction of silver β,β,β -triphenylpropionate with dry bromine in anhydrous carbon tetrachloride was found not to proceed as expected from the above considerations. Rather, an anomalous reaction superceded the usual one of bromodecarboxylation. Indeed, carbon dioxide, normally evolved readily in such reactions, was not even detected in several of the reactions performed. When, however, a nitrogen gas sweep was used, the presence of carbon dioxide (about 3%) was determined in the effluent by precipitation in saturated barium hydroxide solution.

Treatment of the reaction mixture in the customary manner⁷ gave, in addition to much *original acid* (44%), a refractory semisolid material which resisted all conventional methods of purification. This crude product contained *halogen* (Beilstein test) and was shown to contain a phenyl ester function by the hydroxamic acid test and by the isolation of phenol (as tribromophenol) upon hydrolysis.

Eventually the crude material was separated by chromatography on alumina and vacuum fractional sublimation into two colorless solids, a halogen-free substance *A* in 17% yield (m.p. 123.5–124.5°) with an analysis corresponding to $\text{C}_{21}\text{H}_{16}\text{O}_2$, and a material *B* in 36% yield containing bromine (m.p. 90.5–91.5°) with an analysis corresponding to $\text{C}_{21}\text{H}_{15}\text{BrO}_2$. Evidence for the presence in the crude material of a *halide* in less than 4% yield was obtained *via* dehydrobromination with

(6) (a) H. Hunsdiecker and C. Hunsdiecker, *Ber.*, **75**, 295 (1942); (b) R. G. Johnson and R. K. Ingham, *Chem. Revs.*, **56**, 219 (1956).

(7) Cf. the references given in footnote 5.

alcoholic alkali and argentometric determination of bromide ion in the precipitated salt.⁸ Since a mass balance was achieved with the detection of these products and recovered acid, it seems no other significant products are formed.

Both *A* and *B* were phenyl esters and both possessed ultraviolet maxima of 285 $\text{m}\mu$ (in 95% ethanol), indicating similarly activated carbonyl excitation (see Figures 1 and 2). The infrared

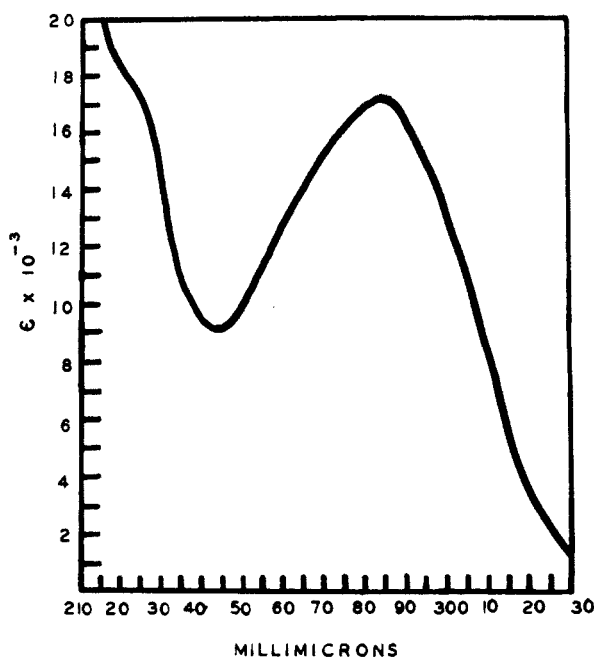


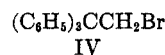
FIG. 1. THE ULTRAVIOLET SPECTRUM (in 95% ethanol) of phenyl β,β -diphenylacrylate, VI (*A*).

spectrum of *A* (bands at 1736, 1618, 1594, and 1579 cm^{-1}) was clearly that of an α,β -unsaturated aromatic ester, while that of *B* (bands at 1740, 1594, and 1494 cm^{-1}) failed to show unsaturation beyond that expected for aromatic nuclei.

In accord with these findings, *A* was quickly oxidized by dilute potassium permanganate while *B* was much more resistant. In addition, *A* when treated with bromine under reaction conditions was converted to *B* in an amount dependent on time of reflux. The halogenated substance *B* remained unaffected upon prolonged reflux with alcoholic silver nitrate.

Consideration of all the preceding information as well as possible subversions of the usual path of the Hunsdiecker reaction led us to speculate that β,β -diphenylacrylate esters had been produced in this reaction. This speculation was proved to be correct

(8) Unfortunately this halide could not be isolated. Because of the ready dehydrobromination under non-sololytic conditions, however, we believe this substance to be the partly expected II, since the non-rearranged halide (IV) would not be expected to lose hydrogen bromide under these conditions.



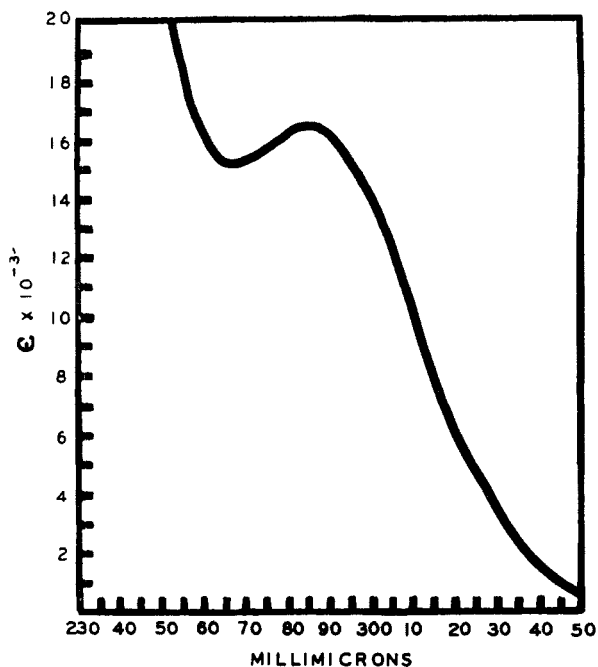
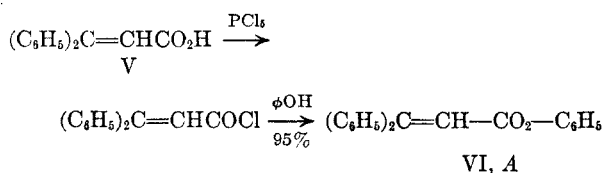


FIG. 2. THE ULTRAVIOLET SPECTRUM (in 95% ethanol) of phenyl α -bromo- β,β -diphenylacrylate, VIII (*B*).

by independent syntheses of both *A* and *B* by unequivocal routes.

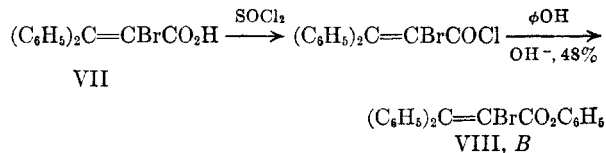
β,β -Diphenylacrylic acid⁹ (*V*) was converted to its acid chloride and thence directly to the pre-



viously unreported *phenyl* β,β -diphenylacrylate¹⁰ (*VI*) using standard techniques. Compound *VI* thus prepared was identical in every detail with *A* isolated from the reaction mixture. The finding of Newman and Owen^{9c} that β,β -diphenylacrylic acid derivatives are converted on treatment with bromine to dibromo addition products which readily lose hydrogen bromide to form α -bromo substituted compounds seemed to verify our suspicion, reached prior to knowledge of their work, that *B* was in fact *phenyl* α -bromo- β,β -diphenylacrylate (*VIII*), produced from *A* by bromine at the reflux temperature of carbon tetrachloride. This substance was therefore synthesized from α -bromo- β,β -diphenylacrylic acid^{9c} (*VII*) *via* the acid chloride and phenol.

(9) (a) H. Rupe and A. Busolt, *Ber.*, **40**, 4537 (1907); (b) M. S. Kharasch, S. S. Kane, and H. C. Brown, *J. Am. Chem. Soc.*, **64**, 333 (1942); (c) D. Newman and L. Owen, *J. Chem. Soc.*, 4726 (1952).

(10) Independently, this ester has been recently synthesized by S. Patai and R. Ikan, *J. Org. Chem.*, **21**, 1379 (1956).



The independently synthesized ester *VIII* and *B* were found to be identical.

In the light of its proven structure, the infrared spectrum and chemical behavior of *B* upon attempted characterization (*vide supra*) warrant some discussion. The absence of non-aromatic unsaturation in the infrared spectrum is not unexpected for *B* since tetrasubstituted ethylenes often exhibit such behavior.¹¹ Also, permanganate oxidation of such a compound might reasonably be expected to be slow.¹² The vinylic bromine, as is well known, resists displacement or solvolytic reactions.

Discussion. An interesting feature of this reaction is the overall *1,4-phenyl migration* observed, presumably by an intramolecular process. Such rearrangements have been observed previously in ionic reactions such as the solvolysis of certain bromobenzenesulfonates,^{13a} and in homolytic processes such as the peroxide-induced decarbonylation of 5-phenylpentanal,^{13a} the Kolbe electrolysis of β,β,β -triphenylpropionic acid,^{13b} and the thermal conversion of 2-phenoxybenzoyl peroxide to phenyl salicylate.^{13c} While ester formation is common in Hunsdiecker reactions,¹⁴ *intramolecular* ester formation apparently has been previously observed but once¹⁵ and *intramolecular ester formation accompanied by rearrangement* of the carbon skeletal system seems to be unreported previously.

Since *B* can be produced from *A* under reaction conditions, it is simpler to discuss the conversion of the silver salt of *I* to *A* alone. In this fashion, the formation of *B* may be viewed as a simple addition of bromine to the double bond of *A* followed by thermal dehydrobromination (perhaps assisted by the silver bromide and/or the unreacted silver salt of *I* present in the mixture). The rather large

(11) L. J. Bellamy, *The Infra-red Spectra of Complex Molecules*, John Wiley and Sons, Inc., New York, N. Y., 1954, p. 32.

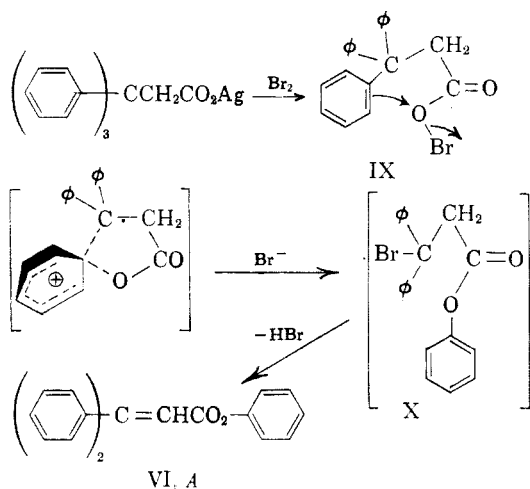
(12) (a) E. E. Royals, *Advanced Organic Chemistry*, Prentice-Hall, Inc., Englewood Cliffs, N. J., 1954, p. 330; (b) *Cf.*, however, R. L. Shriner, R. C. Fuson, and D. Y. Curtin, *The Systematic Identification of Organic Compounds*, John Wiley and Sons, Inc., New York, N. Y., 1956, p. 134.

(13) (a) S. Winstein, *et al.*, *Experientia*, **12**, 138 (1956); (b) E. C. Kooyman and H. Breederveld, *Rec. trav. chim.*, **76**, 297 (1957). This reaction yields phenyl β,β -diphenyl- β -methoxypropionate and is closely allied to that described herein since the carbon skeletal changes are identical. (c) D. F. DeTar and A. Hlynsky, *J. Am. Chem. Soc.*, **77**, 4411 (1955).

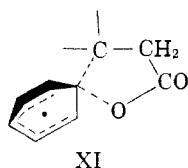
(14) Ester formation under these conditions is known as the Simonini reaction (*cf.* reference 6b, p. 259). Generally *intermolecular* ester formation is observed.

(15) C. E. Berr (reference 5a) obtained a lactone from silver β -phenylisovalerate in a Hunsdiecker reaction, probably by an "internal" Simonini reaction.

amount of recovered acid may be attributed in part¹⁶ to the reaction *in situ* of the silver salt with the two moles of hydrogen bromide stoichiometrically liberated in this reaction. There are three mechanisms for the conversion of the silver salt of I to A that find analogy or precedent in the literature. The first of these, Mechanism 1, involves a five-membered ring intermediate with phenonium-ion characteristics,¹⁷ an *ionic mechanism* similar to that proved useful in the interpretation of certain solvolyses.^{13a} As applied to the present case, this mechanism would be the following:



The formation of an acyl hypobromite, such as IX, is generally accepted as the first stage in Hunsdiecker reactions.¹⁸ Mechanism 2 utilizes the free radical analog of the above and resembles the mechanism proposed for the Kolbe electrolysis of β,β,β -triphenylpropionic acid.^{13b} Applied to the present reaction, this mechanism would be the same as Mechanism 1, except that the entity XI

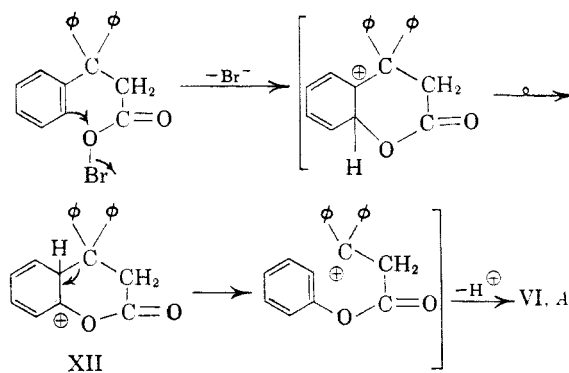


would be the cyclic intermediate, attacking bromine to give the unstable bromoester X. A final mechanism, Mechanism 3, has direct precedent in Hunsdiecker reactions. It employs a six-membered ring intermediate produced by the attack of an adjacent phenyl group at its *ortho* position upon the hypobromite function:

(16) Original acid is often recovered from Hunsdiecker reactions, anhydrous though the system may be. How this occurs is as yet not fully known.

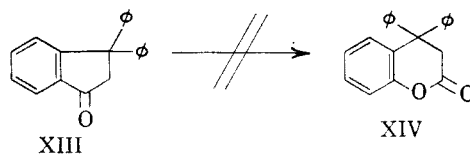
(17) D. J. Cram, *J. Am. Chem. Soc.*, **71**, 3863 (1949).

(18) Reference 6b, pp. 260 ff.

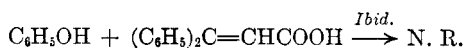
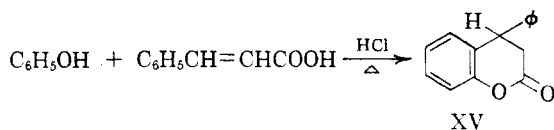


A similar mechanism (here shown as ionic, though a free radical analog is also possible) served to explain the formation of a 4,4-dimethyl-3,4-dihydrocoumarin derivative in the reaction of silver β -phenylisovalerate and bromine.^{5a,15} Presumably proton loss from an intermediate akin to XII, rather than carbon-carbon cleavage, accounts for the formation of this lactone.

Certain considerations lead us to reject Mechanism 3. For example, repeated and varied attempts to oxidize 3,3-diphenylindanone-1 (XIII) to 4,4-diphenyl-3,4-dihydrocoumarin (XIV) by the Baeyer-Villiger ring expansion¹⁹ gave only trace amounts of lactone material, indicating serious resistance to the formation of the as yet unknown ring system of 4,4-diphenyl-3,4-dihydrocoumarin.



In this regard the recent synthesis of 4-phenyl-3,4-dihydrocoumarin²⁰ (XV) by treatment of phenol and cinnamic acid with hot concentrated hydrochloric acid is of interest. Work performed in this present study indicates that this technique *fails* with β,β -diphenylacrylic acid (V).



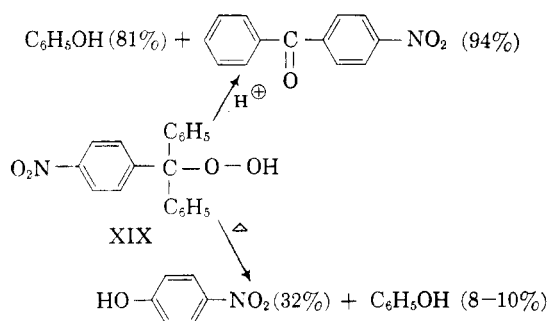
These reactions undoubtedly proceed through intermediates just like or closely related to those in Mechanism 3, involving electrophilic attack upon a phenolic ring. Furthermore, examination of molecular models of the intermediates (such as XII) in Mechanism 3 reveals serious steric crowding at the 4-position. The possibility, therefore, of

(19) (a) A. Baeyer and V. Villiger, *Ber.*, **32**, 3625 (1899); (b) W. D. Emmons and G. B. Lucas, *J. Am. Chem. Soc.*, **77**, 2287 (1955).

(20) J. Simpson and H. Stephen, *J. Chem. Soc.*, 1382 (1956).

the acyl hypobromite IX proceeding to VI (A) via such a ring system is considered unlikely if other, less crowded, paths are possible.²¹

In order to investigate the polar or radical nature of this reaction, use was made of a proposal first advanced by Bartlett and Cotman.²² From a variety of earlier data, and particularly from their own study of mono-*p*-nitrotriphenylmethyl hydroperoxide (XIX), they proposed that a criterion of ionic *vs.* free radical mechanisms may be found in the relative rearrangement ability of the *p*-nitrophenyl group and the unsubstituted phenyl group. Thus, in their study,



the ionic (acid catalyzed) rearrangement gave migration of the phenyl group to the exclusion of the *p*-nitrophenyl group, while the free radical (thermally induced) rearrangement gave a migration ratio of *p*-nitrophenyl/phenyl ~ 4 . Such a reversal of the "normal" migration ability ratios may be taken as evidence for a homolytic process. To this end, β,β,β -tris(*p*-nitrophenyl)propionic acid (XVI) was prepared from I and its silver salt treated with bromine under the same conditions used previously. Carbon dioxide evolution increased nearly tenfold (3 \rightarrow 27%) over that from I. No ester product was detected and the halide and olefin (probably XVII and XVIII, respectively) isolated indicate that the reaction here is the usual one of bromodecarboxylation. Apparently the two processes of ester formation by rearrangement and bromodecarboxylation are in competition, the former occurring with the unsubstituted system, the latter occurring with the nitrated system. Since, as has been noted above, radical rearrangement processes in so far as they have been studied

(21) The useful technique of testing for *ortho* attack by phenyl by placing substituents on the benzene rings and noting whether isomerization occurs during the phenyl migration is at present under study and will be reported at a later date. NOTE ADDED IN PROOF: Recent work by Mr. J. Finnerty and one of the authors (J.W.W.) indicates that the rearrangement of β,β,β -tris(*p*-*t*-butylphenyl)propionic acid (I, X = *t*-butyl) in this reaction yields the *p*-*t*-butylphenyl ester of α -bromo- β,β -di(*p*-*t*-butylphenyl)acrylic acid exclusively. Such a result renders Mechanism 3 an unlikely path for these rearrangements, and supports either Mechanism 1 or 2. Details of this and of other related experiments will be reported at a later date.

(22) P. D. Bartlett and J. D. Cotman, Jr., *J. Am. Chem. Soc.*, **72**, 3095 (1950).

are somewhat faster with the *p*-nitrophenyl group than with the unsubstituted phenyl group, while the analogous ionic rearrangements are just the reverse, the evidence points to a polar path for the ester formation observed in this work. From these considerations, Mechanism 1 seems favored.

EXPERIMENTAL

All melting points and boiling points are uncorrected. Ultraviolet spectra were determined in previously scanned 95% ethanol with a manually operated Beckman DU spectrophotometer equipped with an 1P28 photo tube using 1-cm. silica cells. The infrared spectra were determined in potassium bromide pellets on a Perkin-Elmer Model 21 spectrophotometer. Analyses were performed by the Galbraith Laboratories, Knoxville, Tenn.

Preparation of β,β,β -triphenylpropionic acid (I). The procedure of Hellerman²³ gave an average 50% yield of the acid, m.p. 180–181° (reported²³ 180°), as white needles from ethanol.

Anal. Calcd. for $C_{21}H_{18}O_2$: C, 83.4; H, 6.00. Found: C, 83.24; H, 6.11.

The infrared spectrum of I (chloroform) showed peaks at 3049s cm^{-1} (aromatic C—H), 1718m cm^{-1} (saturated acid C=O), 1215s cm^{-1} (broad) (C_3 —C), 929m cm^{-1} (confirmatory —COOH).

The silver salt of I was prepared in 80% yield in the usual fashion and dried in an oven at 70° for two days.

Reaction of the silver salt of I with bromine. This reaction was carried out seven times and the following is a representative description of the procedure.

To silver β,β,β -triphenylpropionate (66.0 g., 0.161 mole), dispersed in dry carbon tetrachloride (100 ml., stored over phosphorus pentoxide for one week and azeotropically freed from water by distillation), was added dropwise with stirring a solution of bromine (27.7 g., 0.173 mole, dried over phosphorus pentoxide for three days) in further dry carbon tetrachloride (15 ml.) at a temperature of 25–50° over a period of 20 min. A gentle nitrogen gas sweep was employed to carry any evolved gas through a condenser into a trap containing saturated barium hydroxide solution. When all the bromine had been added, the mixture was refluxed (77°) with continued stirring for a further 0.5 hr. The evolved carbon dioxide (collected as barium carbonate) amounted to 0.0042 mole (2.6% yield).

Filtration of the rust colored mixture gave silver bromide (30.3 g., 0.161 mole, 100% yield, washed thoroughly with hot ethanol). The filtrate was washed once with successive portions (100 ml.) of 5%, 2.5%, and 1.25% sodium hydroxide solutions. Acidification of the aqueous alkaline extracts with dilute hydrochloric acid yielded original β,β,β -triphenylpropionic acid (18.5 g., m.p. 165–170°, raised to 180° with one recrystallization from ethanol). Further acid (2.9 g.) was obtained from the alcohol washings of the crude silver bromide. Total I recovered was 21.4 g. (44%). The carbon tetrachloride layer from the alkaline wash was dried over sodium sulfate and freed from solvent by distillation under reduced pressure. The golden, semisolid residue (about 30 g.) was then treated as described below.

Chromatographic separation of A and B. When the residue from the Hunsdiecker reaction was dissolved in various solvents, in attempted fractional crystallizations, or sublimed in a vacuum, oils, semisolids, or wide-range melting substances were obtained. Separation into sharp-melting materials was achieved by chromatography on alumina (Fisher Chromatographic Alumina, 80–200 mesh) in a 65 cm. tube (a converted Jones reductor). Elution of the crude residue (about 30 g.) with petroleum ether (b.p. 30–60°)—benzene fractions (twenty fractions, 30 ml. each), followed by vac-

(23) L. Hellerman, *J. Am. Chem. Soc.*, **49**, 1738 (1927).

uum sublimation (100°, <1 mm.) of the crystalline material so obtained, gave a colorless solid (*B*) which contained halogen (Beilstein test) (m.p. 90.5–91.5°, 22.2 g., 36.4%).

Anal. Calcd. for $C_{21}H_{15}BrO_2$: C, 66.6; H, 3.99; Br, 21.05. Found: C, 66.42; H, 4.07; Br, 20.8.

Further elution of the column with benzene (eight fractions, 30 ml. each), followed by vacuum sublimation as before (125°, <1 mm.) gave a colorless solid (*A*) which was halogen-free (Beilstein test) (m.p. 123.5–124.5°, 7.4 g., 16.7%).

Anal. Calcd. for $C_{21}H_{16}O_2$: C, 83.98; H, 5.37. Found: C, 84.15; H, 5.38.

Characterization of A and B. The ultraviolet spectrum of *A* (see Fig. 1) possessed $\lambda_{\text{alc}}^{\text{max}}$ 285 μ (ϵ 17,180), $\lambda_{\text{alc}}^{\text{min}}$ 245 μ (ϵ 9130). Its infrared spectrum (KBr pellet) had peaks at 1736s cm^{-1} (ester C=O), 1618s–1594s–1579s cm^{-1} (aromatic with conjugated —C=CH—). *A* quickly (5 min.) decolorized potassium permanganate solution (0.5%) and gave a positive ester test in the hydroxamic acid reaction.²⁴ The ultraviolet spectrum of *B* (see Fig. 2) possessed $\lambda_{\text{alc}}^{\text{max}}$ 285 μ (shoulder) (ϵ 16,500), $\lambda_{\text{alc}}^{\text{min}}$ 267 μ (ϵ 15,160). Its infrared spectrum (KBr pellet) had peaks at 1740s cm^{-1} (ester C=O), 1594w–1494m cm^{-1} (aromatic). *B* slowly (overnight) decolorized potassium permanganate solution (0.5%) and was positive in the hydroxamic acid test for esters.²⁴ Extended reflux (3 hr.) of *B* with alcoholic silver nitrate (5%) gave no reaction. The phenyl ester nature of the crude reaction material was established by a procedure similar to that described here for the examination of *B*. *B* (0.05 g.) was saponified by refluxing with an excess of alcoholic potassium hydroxide and then treated with solid carbon dioxide chunks. Microsteam distillation of the mixture and collection of the distillate in bromine water gave tribromophenol (0.04 g., m.p. 93–94°, 92% yield).

Conversion of A to B under reaction conditions. *A* (1.0 g., 3.3 millimoles, m.p. 123.5–124.5°) dissolved in dry carbon tetrachloride was treated at reflux with excess bromine in the presence of silver bromide for one hour. Conventional work-up and recrystallization from alcohol gave a white solid, m.p. 72–80°. The ultraviolet spectrum of this material exhibited $\lambda_{\text{alc}}^{\text{max}}$ 285 μ and $\lambda_{\text{alc}}^{\text{min}}$ 262 μ and matched that of crude *B* isolable from the chromatographic column (m.p. 75–78°). The shift in λ^{min} here is 17 μ . Longer reaction times (2 hr.) produced further λ^{min} shifts, but some bromophenol also was detectable (odor) under these conditions.

Detection of halide in crude residue. Crude semisolid residue (5.4 g.) was refluxed (1 hr.) with absolute ethanolic potassium hydroxide (1.86 g. in 100 ml.). The precipitated salts were collected, dissolved in distilled water, and treated with aqueous silver nitrate. Gravimetric determination of silver bromide (characteristic pale yellow solid) showed 0.55 millimole of bromide ion present. With the assumption that the crude material contains about 33% *A* and 67% *B* (the values found by chromatography), the bromide ion found is 3.5 mole %. The close agreement (within the error of the measurements) of the carbon dioxide and bromide percentages indicates that dehydrobromination and not some spurious reaction occurred here.

Preparation of phenyl β,β -diphenylacrylate (VI). β,β -Diphenylacrylic acid (*V*, 2.24 g., 0.01 mole, m.p. 161–162°, reported^{9b} 161°), prepared according to the method of Rupe and Busolt,^{9a} or by that of Kharasch, *et al.*,^{9b} and benzene (60 ml.) were refluxed for 10 min. to effect solution. Phosphorus pentachloride (2.61 g., 0.0125 mole) was added and the mixture refluxed for 1 hr. To the slightly cooled solution phenol (1.18 g., 0.0125 mole) was then added and reflux again initiated and continued until no further hydrogen chloride evolution was noticed (another hour). A wash of the cooled material with aqueous sodium carbonate (40 ml., 10%), and separation, drying, and evaporation of the benzene phase left a crystalline residue which crystallized

from ethanol as a colorless solid (m.p. 123.5–124.5°, 2.8 g., 95% yield, $\lambda_{\text{alc}}^{\text{max}}$ 285 μ (ϵ 17,150), $\lambda_{\text{alc}}^{\text{min}}$ 245 μ (ϵ 9100)). A mixture melting point determination of this substance with *A* showed no depression and their spectra were identical.

Preparation of phenyl α -bromo- β,β -diphenylacrylate (VIII). α -Bromo- β,β -diphenylacrylic acid (*VII*, 1.0 g., 3.3 millimoles, m.p. 150–152°, reported^{9c} 150°), prepared by the method of Newman and Owen^{9c} in 56% yield, and thionyl chloride (1.8 g., 15 millimoles) were refluxed for 15 min. Excess thionyl chloride was codistilled from the solution with benzene and the residual benzene removed by aspiration. To the oil remaining was added water (10 ml.), phenol (0.94 g., 100 millimoles), and sodium hydroxide solution (20%, 10 ml.), the last in portions. The mixture was vigorously shaken for an extended time and allowed to stand overnight. The crystalline precipitate (0.6 g., 48% yield) was washed with water, chromatographed on alumina to remove a small amount of colored impurity (petroleum ether–benzene eluant), and finally vacuum sublimed to a colorless solid (m.p. 91–92°, $\lambda_{\text{alc}}^{\text{max}}$ 285 μ (ϵ 16,450), $\lambda_{\text{alc}}^{\text{min}}$ 267 μ (ϵ 15,000)). This substance was identical with *B* from mixture melting point determinations and identity of spectra.

Attempted oxidation of 3,3-diphenylindanone-1 (XIII). XIII, prepared by the cyclization of the acid chloride of I²⁵ as a colorless solid (m.p. 130–131°, reported²⁵ 130–131°, 88% yield), was treated under several different sets of conditions with peroxyacetic, perbenzoic, and trifluoroperoxyacetic acids with little evidence of reaction. Since the latter acid has proven to be the most efficient reagent for the Baeyer-Villiger reaction,^{19b,20} an illustrative experiment with this acid is described here. Trifluoroperoxyacetic acid [prepared from trifluoroacetic anhydride (0.018 mole) and hydrogen peroxide (90%, 0.015 mole) in cold methylene chloride (10 ml.)] was added in small portions to a solution of XIII (0.01 mole) in further methylene chloride (10 ml.) under reflux. A self-sustaining reaction commenced with the mixture deepening in color, after which the solution was refluxed further for fifteen minutes. After neutralization with sodium carbonate solution (10%), separation, drying, and evaporation of the organic phase, a small amount of a tan solid remained, m.p. 92–102°, which was primarily still ketonic since the material was positive to 2,4-dinitrophenylhydrazine reagent. Workup of the alkaline washings gave only intractable gums. Lactone material was present in traces in the tan solid as evidenced by very weak hydroxamic acid results.

Attempted synthesis of 4,4-diphenyl-3,4-dihydrocoumarin (XIV) from β,β -diphenylacrylic acid (V). *V* (1.8 g., about 8 millimoles, m.p. 160°, reported^{9b} 161°), phenol (0.78 g., about 8 millimoles), and concentrated hydrochloric acid (42 ml.) were treated as described by Simpson and Stephen.²⁰ The isolated material was completely bicarbonate soluble and gave a negative hydroxamic acid test for lactones. The acidic nature of the product implies that no reaction of consequence occurred here.

*Preparation of β,β,β -tris(*p*-nitrophenyl)propionic acid (XVI).* *I* (1.9 g., 6.3 millimoles, m.p. 180°) was added in portions to a stirred mixture of nitric acid (concentrated, 12 g.) and sulfuric acid (concentrated, 18.5 g.) held at 0–2°. Slow solution of the solid occurred and a brown color developed. The mixture was allowed to warm to room temperature by stirring in a melting ice bath. When completely homogeneous, the solution was poured into a large volume of cold water. The white solid was collected and dried (2.6 g., 95% yield, m.p. 220–223°). This material gave a positive test for the nitro group with ferrous hydroxide²⁷ and dissolved

(25) C. F. Koelsch and C. D. LeClaire, *J. Org. Chem.*, **6**, 516 (1941).

(26) W. F. Sager and A. Duckworth, *J. Am. Chem. Soc.*, **77**, 188 (1955).

(27) Reference 12b, p. 113.

(24) Reference 12b, pp. 122–23.

in alkali to give a yellow solution. Two recrystallizations of this solid from ethanol gave XVI as pale yellow, short needles, m.p. 248–250° decomposing to a red liquid.

Anal. Calcd. for $C_{21}H_{15}N_3O_3$: N, 9.61. Found: N, 9.55.

The infrared spectrum of XVI (chloroform) showed peaks at 3049s cm^{-1} (aromatic C—H), 1730w cm^{-1} (saturated acid C=O), 1527s–1351s cm^{-1} (C—NO₂), 1215s cm^{-1} (broad) (C_s—C), 929m cm^{-1} (confirmatory —COOH).

The silver salt was prepared in the usual way and dried at 80° for two days.

Reaction of the silver salt of XVI with bromine. The silver salt of XVI (3.0 g., 5.5 millimoles) was suspended in dry carbon tetrachloride (30 ml.) and treated with dry bromine (1.0 g., 6 millimoles) in further solvent (10 ml.) under a nitrogen gas sweep as described previously for the silver salt of I. Carbon dioxide evolution commenced in about five minutes at room temperature and was completed at the reflux temperature (77°) in thirty minutes. The carbon dioxide evolved (measured as barium carbonate) was 1.47 millimole (26.8% yield). Treatment of the reaction mixture as described before gave recovered XVI (70%) and a yellow solid (about 25–30%), m.p. 70–85°. This solid gave a precipitate of silver bromide readily in alcoholic silver nitrate (5%) and developed acidity when refluxed in aqueous alcohol. Potassium permanganate in acetone (0.5%) was

quickly decolorized by the solid. While the alkaline conditions required for the hydroxamic acid test for esters appeared to affect the substance, a negative ester test was obtained.

The ready solvolytic loss of hydrogen bromide from the substance suggests that it contains XVII, while the unsaturation evident implies the presence of at least some olefin, probably XVIII.²⁸

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(28) While the purpose of using XVI in this study was strictly the comparison of the carbon dioxide percentage (bromodecarboxylation percentage) with I, the reaction of XVI is of great interest in itself, perhaps being the first reported instance of appreciable rearrangement, not caused by side reactions, in the Hunsdiecker reaction series. A more detailed investigation of this point is under way in this laboratory and will be reported separately.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, FORDHAM UNIVERSITY]

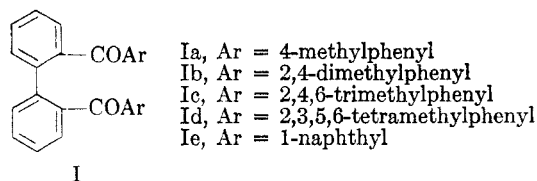
Steric Interactions in the Absorption Spectra of 2,2'-Diaroylbiphenyls

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The electronic absorption spectra of 2,2'-biphenylaldehyde, (+) 6,6'-dinitro-2,2'-di(2,4-dimethylbenzoyl)biphenyl, and a series of 2,2'-diaroylbiphenyls in which the 2,2'-diaroyl substituents increase in bulk (Aroyl = 4-methylbenzoyl, 2,4-dimethylbenzoyl, 1-naphthoyl, 2,4,6-trimethylbenzoyl, and 2,3,5,6-tetramethylbenzoyl) are discussed in terms of current theories.

As part of a configurational study of *cis*- and *trans*- 9,10-diaryl-9,10-dihydro-9,10-phenanthrene-diols in which the 9,10-diaryl substituents increase in bulk, five 2,2'-diaroylbiphenyls (I) have been prepared as intermediates.² The structures of these diketones, synthesized by a Friedel-Crafts reaction



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(3) W. E. Bachmann, *J. Am. Chem. Soc.*, **54**, 1969 (1932); W. E. Bachmann and E. J. Chu, *J. Am. Chem. Soc.*, **57**, 1095 (1935); D. Nightingale, H. E. Heiner, and H. E. French, *J. Am. Chem. Soc.*, **72**, 1875 (1950); R. C. Fuson and C. Hornberger, *J. Org. Chem.*, **16**, 637 (1951); R. C. Fuson and R. O. Kerr, *J. Org. Chem.*, **19**, 373 (1954).

between diphenoyl chloride and the appropriate arene, have been previously established by unequivocal methods.³

Compounds of this type should also be of special interest since they provide examples in which steric effects are known to cause changes in the light absorption properties. In particular, steric effects in electronic spectra of organic compounds have been classified into two types: Type I steric effects, which give rise to intensity changes only, and Type II steric effects, which normally also cause appreciable wavelength displacements.⁴ Acetophenones show steric effects of the former type, whereas biphenyls show steric effects of the latter type. Consequently, it would be a matter of interest to determine which type of steric effect occurs in the compounds under investigation. With this in mind, a spectral analysis of the compounds Ia to Ie and of a suitable reference compound, 2,2'-biphenylaldehyde (II), has been carried out.

(4) E. A. Braude, F. Sondheimer, and W. F. Forbes, *Nature*, **173**, 117 (1954); E. A. Braude and F. Sondheimer, *J. Chem. Soc.*, 3754 (1955).