ated with ultraviolet light for 16 hr. The mixture then was washed with a solution of sodium sulfite and dried. Evaporation left 0.56 g. (13%) of dark oil, the infrared spectrum of which showed it to be largely 2-acetamido 2-ethylhexanethiolsulfonate (**5**), n^{25}_{D} 1.5103.

Reaction of *p*-toluenesulfonyl iodide (16 mmoles) and 2-acetamidoethyl disulfide (7.2 mmoles) in similar fashion gave a dark oil, which had an infrared spectrum indicating it to be largely **3**, but the yield was only 2%.

Irradiation of *p*-toluenesulfonyl iodide and *p*-tolyl disulfide, much as before, resulted in *p*-tolyl *p*-toluenethiolsulfonate in 7% yield; characterization was effected by melting point and the infrared spectrum. However, a control experiment in which the disulfide was omitted also resulted in about the same yield of the thiolsulfonate.

N,N,S-Tri-*p*-tolylisothiourea (7).—A solution of 8.37 g. of *p*-thiocresol in 50 ml. of benzene was added rapidly to a stirred refluxing solution of 15.00 g. of di-*p*-tolylcarbodiimide in 100 ml. of benzene; heating was continued for 4 hr. After 5 days at *ca.* 25°, the solution was evaporated and the solid was rubbed with boiling ethanol (175 ml.). Chilling of the entire mixture at 4° and filtration resulted in 19.85 g. (85%) of white solid, m.p. 85–90°. Recrystallization from hexane gave the adduct (**7**) as needles with constant m.p. 89.5–90.5°.

Anal. Calcd. for $C_{22}H_{22}N_2S$: C, 76.26; H, 6.40; S, 9.25. Found: C, 76.00; H, 6.45; S, 9.31.

Further Studies on the Anomalous Hunsdiecker Reaction of Triaryl-Substituted Aliphatic Acids

James W. Wilt and John A. Lundquist[1]

Department of Chemistry, Loyola University, Chicago 26, Illinois

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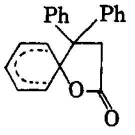
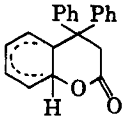
The phenyl shift previously observed in the Hunsdiecker reaction with β,β,β-triarylpropionic acids (such as I) failed to occur significantly with γ,γ,γ-triphenylbutyric acid (IV). Two sets of conditions were employed with IV. The normal Hunsdiecker reaction on the silver salt yielded primarily brominated parent acid, together with a small yield of the normal Hunsdiecker product, γ,γ,γ-triphenylpropyl bromide (VI). The recently described Cristol–Firth modification of the Hunsdiecker reaction using the free acid gave essentially the same results, though the yield of VI was increased. In addition, γ,γ,γ-triphenylbutyryl peroxide (X) was prepared and decomposed in refluxing carbon tetrachloride. No significant rearrangement of the γ,γ,γ-triphenylbutyryloxy radical (XII) was found. As a conclusion from these data, arguments are presented that the anomalous Hunsdiecker reaction of such triarylaliphatic acids proceeds in a radical fashion from the acyloxy radical and that it involves phenyl migration in this radical. The migration is, however, sensitive to the ring size created during the migration, proceeding *via* a five-, but not a six-membered ring.

Previous work[2,3] has shown that β,β,β-triarylpropionic acids such as the parent acid I undergo rearrangement to aryl β,β-diarylacrylates upon attempted degradation by the Hunsdiecker reaction,[4] with little bromodecarboxylation being observed. An Ar_1-5 type intermediate (II),[5] rather than an Ar_2-6 type intermediate (III), appeared to explain the course of the rearrangement, but the radical or ionic nature of the process has remained a difficult point to settle.[6]

As a natural extension of this work, the question arose as to whether rearrangement *via* an Ar_1-6 intermediate (V) might occur. A study of γ,γ,γ-triphenylbutyric acid (IV) in the Hunsdiecker reaction was made, therefore, and the results of this study are reported here. In addition, the recent report of Cristol and Firth[7] on the bromodecarboxylation of acids using the free acid, bromine, and excess mercuric oxide in the dark led us to examine both the above triphenylbutyric acid (IV) and the previously studied acid I in their process as well.

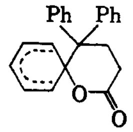
Ph_3CCH_2COOH





I II III

$Ph_3CCH_2CH_2COOH$



IV V

II, III, and V apply either as ionic or radical species

The preparation of acid I was as before,[2] while the synthesis of acid IV was straightforward and followed the sequence shown (eq. 1). The displacement reaction

$$\mathrm{I} \xrightarrow[(2)\ LiAlH_4]{(1)\ SOCl_2} \underset{(92\%)}{Ph_3CCH_2CH_2OH} \xrightarrow{P + I_2} \underset{(77\%)}{Ph_3CCH_2CH_2I} \xrightarrow[DMSO]{NaCN}$$

$$\underset{(71\%)}{Ph_3CCH_2CH_2CN} \xrightarrow[\Delta]{H_2SO_4} \underset{(IV,\ 94\%)}{Ph_3CCH_2CH_2COOH} \quad (1)$$

using sodium cyanide failed under the other conditions tried, *viz.*, refluxing the reactants in aqueous alcohols or ethylene glycol. The beneficial use of dimethyl sulfoxide solvent in such reactions previously has been

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[1] Taken in part from the M. S. thesis of J. A. L., Loyola University, May, 1963.

[2] J. W. Wilt and D. D. Oathoudt, *J. Org. Chem.*, **21**, 1550 (1956); **23**, 218 (1958).

[3] J. W. Wilt and J. L. Finnerty, *ibid.*, **26**, 2173 (1961).

[4] R. G. Johnson and R. K. Ingham, *Chem. Rev.*, **56**, 219 (1956).

[5] Throughout this paper, our designation of these as Ar_m-n type rearrangements carries no implication that anchimeric assistance is involved. Our use of the term is meant simply to convey the site of the eventual substitution on the aromatic ring and the size of the ring in the intermediate.

[6] The absence of rearrangement with β,β,β-tris(*p*-nitrophenyl)propionic acid led us to suggest an *ionic* pathway earlier,[2] but the small substituent effects observed later[3] confused the issue and no compelling evidence either way had been found prior to the present study. It is interesting to note that the Ar_2-6 pathway is equally effective as the Ar_1-5 in certain solvolyses [R. Heck and S. Winstein, *J. Am. Chem. Soc.*, **79**, 3114 (1957)] and, therefore, it might be expected to be an equally likely route for the present rearrangement. Though the Ar_2-6 route (see III) does not occur in the anomalous Hunsdiecker reactions of β,β,β-triarylpropionic acids,[3] it seemingly has been observed with β-phenylisovaleric acid (dissertation, C. E. Berr, University of California at Los Angeles, 1952) and quite recently with β,β-diphenylpropionic acid [U. K. Pandit and I. P. Dirk, *Tetrahedron Letters*, **14**, 891 (1963)]. In both cases dihydrocoumarin derivatives were the products. Steric effects probably occasion the switch from Ar_2-6 to Ar_1-5 as the acid studied changes from the two mentioned above to I and its derivatives.

[7] S. J. Cristol and W. C. Firth, Jr., *J. Org. Chem.*, **26**, 280 (1961).

TABLE I

SUMMARY OF RESULTS

Acid	Method	Reaction, %[a]	Decarboxylation, %[b]	Rearrangement, %[c]	RBr, %[d]
I[e]	Hunsdiecker	24	1	23	None
IV[e]	Hunsdiecker	10	10	None	3
I	Cristol–Firth	47	21	26	4
IV	Cristol–Firth	36	34	2	28

[a] The sum of the per cents of decarboxylation and rearrangement. [b] Measured as carbon dioxide evolved, through precipitation as barium carbonate. [c] Measured as phenol, collected as tribromophenol, produced by the saponification of the reaction product. [d] The yield of isolated and characterized halide. [e] As silver salt.

noted for bromides and chlorides[8] and the present instance would indicate its utility for iodides also.

The acids I and IV[9] proved to be decidedly different under the usual Hunsdiecker conditions. No rearrangement of IV[9] was detected and the normal halide product, γ,γ,γ-triphenylpropyl bromide (VI), was isolated, albeit in low yield, together with a slight amount of carbon dioxide. The major product was an

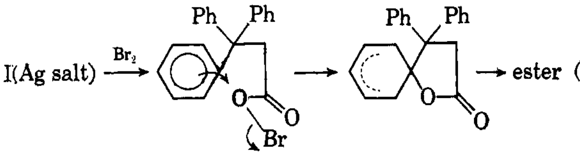
$$\text{IV} \longrightarrow \text{Ag salt} \xrightarrow[\text{CCl}_4]{\text{Br}_2} \underset{\text{VI}}{\text{Ph}_3\text{CCH}_2\text{CH}_2\text{Br}} + \text{CO}_2 + \text{acid mixture}$$

inseparable mixture of a brominated acid derived from starting material together with IV. In order to confirm its unrearranged structure, the bromide VI was converted into γ,γ,γ-triphenylbutyronitrile through reaction with sodium cyanide in dimethyl sulfoxide. This nitrile was identical with that produced from the iodide (eq. 1). In addition, the n.m.r. spectrum was in accord with the structure proposed for VI. The acid I[9] afforded no halide, very little carbon dioxide, and a significant amount of rearrangement under these same conditions, as reported.[2,3]

When both I and IV were subjected to the Cristol–Firth modification[7] of the Hunsdiecker reaction, significant differences were again noticed. The acid I again gave rearranged phenyl ester (determined as phenol) in essentially the same yield as under normal conditions. There was, however, a considerable increase in the carbon dioxide evolved and it proved possible for the first time in any of the studies on I to identify a halide product, triphenylbromoethylene (VII), isolated in low yield.[10] The acid IV, on the other hand, again failed to rearrange significantly. The major product was the halide VI, isolated in fair yield. These results are tabulated in Table I.

In all the reactions here studied, as before,[2,3] considerable amounts of the parent acids were recovered from the residues so that yields of products are higher than conversions in Table I would indicate. Certain other apparent reaction products were partially characterized, though their exact structures remain uncertain.

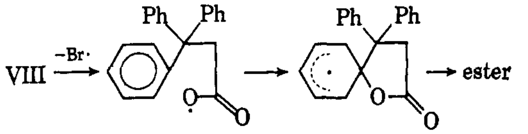
It is felt that the pronounced difference in the behavior of I and IV under the two sets of conditions employed in this study has a bearing on the mechanism of the 1,4-phenyl shift observed with I. *A priori*, the shift could occur in the hypobromite VIII[11] as shown (eq. 2). Such a path could proceed *via* either radical or ionic transition states. The possible *radical* displacement of bromine by phenyl in the hypobromite VIII can be dismissed, however, since neighboring group assistance in radical reactions is rare[12] and, specifically, such assistance by phenyl is absent in a number of radical rearrangements involving a phenyl shift.[13]



VIII

(2)

Alternatively, the hypobromite could first dissociate to the acyloxy radical IX followed by rearrangement of this radical as shown (eq. 3). Other possible paths *via* Ar₂-6 intermediates are believed from earlier studies[2,3] not to be followed by I. We feel the bulk of the evidence favors a radical pathway for rearrangement from the acyloxy radical IX (eq. 3), at least for the reactions above room temperature.



IX

(3)

Thus, generation of the (presumably nearly "free") acyloxy radical IX in three other studies, the Kolbe electrolysis of I (at 60°),[14] the decomposition of β,β,β-triphenylpropionyl peroxide (refluxing chlorobenzene),[15a] and the decomposition of *t*-butyl β,β,β-triphenylperpropionate (chlorobenzene, 100°),[15b] has produced in each case the very same skeletal transformation observed in the Hunsdiecker reaction of I.[2] Since none of the other studies mentioned had done so, we thought the corresponding γ,γ,γ-triphenylbutyryl peroxide (X) should be similarly decomposed to test the rearrangement ability of the acyloxy radical XII. Decomposition of this peroxide in refluxing carbon tetrachloride was rather slow, but the carbon dioxide yield was essentially quantitative (for the incomplete conversion of about 39%) and, significantly, only a trace of phenyl ester was found—in good agreement with the result of the Cristol–Firth treatment of IV (see Table I).

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[8] L. Friedman and H. Shechter, *J. Org. Chem.*, **25**, 877 (1960).

[9] As the silver salts.

[10] Earlier,[2] a halide was detected (<4%), but we were unable to isolate it. The low yield in the present instance may well reflect the difficulty of isolation.

[11] The formation of an acyl hypobromite is generally accepted as the first stage in Hunsdiecker reactions; *cf.* ref. 4.

[12] D. L. Tuleen, W. G. Bentrude, and J. C. Martin, *J. Am. Chem. Soc.*, **85**, 1938 (1963), and earlier papers; J. W. Wilt and A. A. Levin, *J. Org. Chem.*, **27**, 2319 (1962).

[13] E. S. Gould, "Mechanism and Structure in Organic Chemistry," H. Holt and Co., New York, N. Y., 1959, pp. 755 ff.

[14] H. Breederveld and E. C. Kooyman, *Rec. trav. chim.*, **76**, 297 (1957).

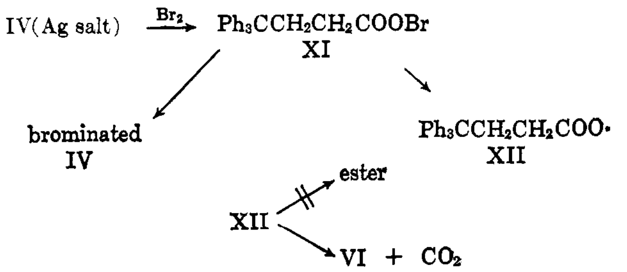
[15] (a) W. Rickatson and T. S. Stevens, *J. Chem. Soc.*, 3960 (1963); (b) W. H. Starnes, Jr., *J. Am. Chem. Soc.*, **85**, 3708 (1963).

$$\mathrm{IV} \xrightarrow{SOCl_2} Ph_3CCH_2CH_2COCl \xrightarrow[\text{ether}]{Na_2O_2} \underset{\mathrm{X}}{(Ph_3CCH_2CH_2COO)_2}$$

$$\mathrm{X} \xrightarrow[\Delta]{CCl_4} CO_2 + \text{unchanged X} + \text{other products (trace phenyl ester)}$$

Therefore, it appears that the acyloxy radicals IX and XII *can* account for the experimental results, *viz.*, rearrangement in one case but not the other.

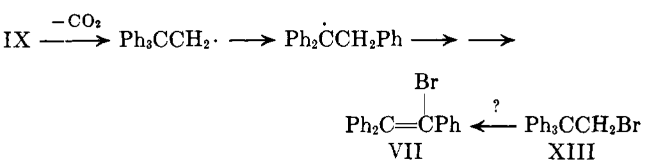
The situation in the usual (*i.e.*, silver salt) Hunsdiecker reaction of I and IV is, however, not quite so apparent. Thus, the rearrangement of I[9] occurs readily at 25° (and lower[16]), while the major process with IV[9] under these conditions is (ring) bromination, as shown.



Because the dissociation of the hypobromites to the acyloxy radicals would be slower under these conditions, it could be that some rearrangement is occurring directly from the hypobromite VIII under these conditions; but it is simpler to explain the lower temperature results in the same way as the higher temperature ones. Thus, though the equilibrium (see below) might be less favorable, both hypobromites VII and XI are somewhat dissociated to their acyloxy radicals, IX then undergoing facile Ar$_1$-5 rearrangement and little competitive decarboxylation (which is more strongly temperature dependent)[17] while XII suffers decarboxylation instead, since rearrangement *via* an Ar$_1$-6 state is difficult. If one assumes a reversible hypobromite formation as shown, $R\text{-}COOBr \rightleftarrows R\text{-}COO\cdot + Br\cdot$, the (ring) bromination of IV is likewise understandable. The equilibrium above for VIII would be continuously shifted to the right since the acyloxy radical IX is removed *via* rearrangement. For XI the concentration of the hypobromite would be higher, since the acyloxy radical XII is removed primarily through decarboxylation, and this is slight (see Table I) at this temperature. The higher concentration of XI then affords more bromination of IV.[18]

The contrast in decarboxylation per cents obtained from I under the normal and modified (Cristol–Firth) Hunsdiecker conditions may be explained by the different temperatures involved. Earlier work[3] had indeed shown that the hypobromite intermediate involved underwent more decarboxylation with increasing temperature at the expense of rearrangement, presumably because the dissociation rate to acyloxy radical IX increased. It is of interest, however, that under Cristol–Firth conditions (77°) the rearrangement of I remained an effectively competitive process. This probably is a result of the excess mercuric oxide present. The hydrogen bromide produced in the rearrangement step is removed through reaction with the oxide and, therefore, does not convert the hypobromite reactant (which is believed to be formed under these conditions as well[7]) to the inert free acid. The primary change with the acid IV under the Cristol–Firth conditions was the expected one of more decarboxylation and bromide (VI) formation, in keeping with the proposed increase in the dissociation rate of the hypobromite XI.

The isolation of triphenylbromoethylene (VII) represents the first decarboxylated product ever characterized in the Hunsdiecker reaction with I.[10] While its rearranged structure is in keeping with the rearrangement of the β,β,β-triphenylethyl radical[19] formed by decarboxylation of the acyloxy radical IX, as shown,

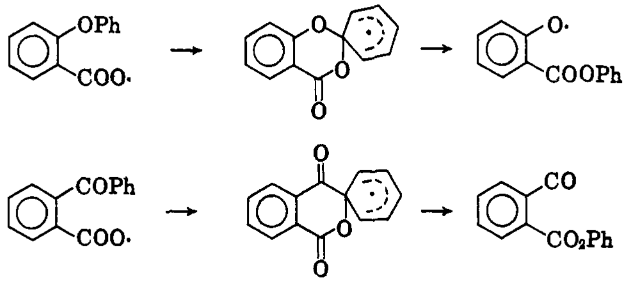


$$\mathrm{IX} \xrightarrow{-CO_2} Ph_3CCH_2\cdot \longrightarrow Ph_2\dot{C}CH_2Ph \longrightarrow \longrightarrow$$

$$\underset{\mathrm{VII}}{Ph_2C{=}\overset{\overset{Br}{|}}{C}Ph} \xleftarrow{?} \underset{\mathrm{XIII}}{Ph_3CCH_2Br}$$

such seeming support for the now accepted radical nature of the normal Hunsdiecker reaction may be misplaced. Even if the unrearranged β,β,β-triphenylethyl bromide (XIII) had been formed, it would most surely have been rearranged to VII by the mercuric bromide present.[20]

One can only speculate as to *why* an Ar$_1$-5 migration of phenyl is so facile compared to an Ar$_1$-6 migration in the acyloxy radicals IX and XII. It is curious, as a matter of fact, since Ar$_1$-6 phenyl to oxygen migrations have indeed been reported. Thus, the acyloxy radicals shown readily undergo phenyl to oxygen shifts.[21] However, and this may be crucial, these radicals have less tendency to decarboxylate, being aroyloxy, than would the acyloxy radical XII and, therefore, more time to rearrange.[22] Since scale models (Fisher–Taylor–Hirschfelder or Dreiding) indicate that both the Ar$_1$-5 and Ar$_1$-6 intermediates, *once formed*, are reasonably comparable in strain (in fact, the model of V is easier to construct), it is clear that either the transition states



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[16] The tri-*p*-*t*-butyl derivative of I rearranged at −12°.[3]

[17] The rearrangement step must have a rather low activation energy since it can occur at low temperatures,[16] while decarboxylation is known to increase with temperature (C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957, p. 476) and, from the data of Table I, must possess a higher activation energy than the rearrangement step.

[18] Ring halogenation *via* the acyl hypobromite has been observed frequently; *cf.* ref. 4, pp. 253 and 254.

[19] As observed in the decarbonylation of β,β,β-triphenylpropionaldehyde by D. Y. Curtin and M. J. Hurwitz, *J. Am. Chem. Soc.*, **74**, 5381 (1952).

[20] The rearrangement of the corresponding chloride is "powerfully catalyzed" by metallic halides [J. C. Charlton, I. Dostrovsky, and E. D. Hughes, *Nature*, **167**, 986 (1951)].

[21] For the rearrangement of *o*-phenoxybenzoyloxy radical, *cf.* D. F. DeTar and A. Hlynsky, *J. Am. Chem. Soc.*, **77**, 4411 (1955). For the rearrangement of *o*-benzoylbenzoyloxy radical, *cf.* P. J. Bunyan and D. H. Hey, *J. Chem. Soc.*, **324**, 2771 (1962).

[22] The rearrangements cited[21] occurred in preference to decarboxylation by large ratios. Aroyloxy radical decarboxylation has been quoted to be endothermic by 4 kcal./mole, while acyloxy radical decarboxylation is exothermic by 12-14 kcal./mole [C. Walling, ref. 17, p. 493].

leading to the intermediates differ in some important regard, or that the cleavage rates of the intermediates are quite different. It is our feeling that the formation of the highly conjugated phenyl β,β-diphenylacrylate from II is of importance. The intermediate V cannot cleave to such a conjugated product. Further work is required to investigate this point and we are so engaged at present.

Experimental

All melting points were obtained on a calibrated Fisher-Johns block. Infrared spectra were obtained on a Perkin-Elmer Model 21 infrared spectrophotometer using a sodium chloride prism. Ultraviolet spectra were obtained with a Cary Model 11 recording spectrophotometer equipped with an IP-28 phototube using 1-cm. silica cells. The samples were prepared by incremental dilution as 95% alcoholic solutions. All carbon–hydrogen microanalyses were performed by Mr. R. L. Kilboy of Sinclair Research, Inc., Harvey, Ill. The n.m.r. spectrum was determined by Nuclear Magnetic Resonance Specialties, New Kensington, Pa.

β,β,β-Triphenylpropionic Acid (I).—Preparation from malonic acid and triphenylcarbinol by the literature route[23] gave white needles, m.p. 184° after one recrystallization from acetone, in 44% yield. The infrared spectrum has been reported.[2]

γ,γ,γ-Triphenylpropyl Alcohol.—The above acid was converted into its acid chloride (m.p. 142–143°, lit.[24] m.p. (crude) 132°) by means of thionyl chloride and reduced in the usual fashion with lithium aluminum hydride in ether. The alcohol was obtained as white crystals, 92%, m.p. 107.5–108°, lit.[25] m.p. 107–108°, after one recrystallization from petroleum naphtha (b.p. 118–144°).

γ,γ,γ-Triphenylpropyl Iodide.—This compound was prepared from the above alcohol *via* its interaction with a mixture of red phosphorus and iodine as given in the literature.[25] After one recrystallization from a benzene–ethanol mixture, the iodide was obtained as white crystals (77.5%, m.p. 178.5–179°, lit.[26] m.p. 174.5–175°). The infrared spectrum was in accord with the proposed structure, though some slight contamination by the starting alcohol was apparent (an absorption at 2.9 μ).

γ,γ,γ-Triphenylbutyronitrile.—By a literature method,[8] the above iodide was converted into the nitrile by the action of sodium cyanide in dimethyl sulfoxide. The nitrile was recrystallized from 95% ethanol and formed white crystals (71%, m.p. 139–140°, lit.[27] m.p. 137.5–138°, infrared 4.44 μ).

Anal. Calcd. for $C_{22}H_{19}N$: C, 88.85; H, 6.44; N, 4.71. Found: C, 88.86; H, 6.47; N, 4.51.

All attempts to prepare the nitrile from the iodide by displacement using aqueous methanol, aqueous ethanol, or pure ethylene glycol were unsuccessful.

γ,γ,γ-Triphenylbutyric Acid (IV).—The above nitrile was hydrolyzed by a lengthy (*ca.* 12 hr.) reflux with a solution of sulfuric and acetic acids in water (1:1:1 by volume). The acid was recrystallized from aqueous alcohol and isolated as a white solid (94.4%, m.p. 159–160°, lit.[25] m.p. 154–156°, infrared 5.84 μ).

Hunsdiecker Reactions.—The preparation of the silver salts and the Hunsdiecker reactions were carried out as described elsewhere [2,3] In addition to the precautions mentioned there, all glassware for the present study was oven-dried for at least 45 min. at 110–115° just prior to use.

Reaction of I (Silver Salt).—A repetition of the reported reaction[2] gave 1% carbon dioxide, 23% rearrangement, and 57% recovered I, in excellent accord with earlier results.[3]

Reaction of IV (Silver Salt).—Silver γ,γ,γ-triphenylbutyrate (14 g., 0.033 mole) was treated as before[2] at 25 ± 2° with bromine (5.3 g., 0.033 mole) in carbon tetrachloride as solvent. The carbon dioxide evolved was collected as barium carbonate (0.685 g., 0.0033 mole, 10.1%). Processing the reaction mixture yielded an acidic reddish material (8.79 g., m.p. 52–60°) which possessed an infrared spectrum virtually identical with that of IV. There were, however, some differences and an absorption at 12.25 μ indicated some aromatic *para* substitution had occurred.

Anal. Calcd. for a mixture of $C_{22}H_{20}O_2$ (42%) and $C_{22}H_{19}BrO_2$ (58%): C, 73.86; H, 5.58; Br, 11.71. Found: C, 73.75; H, 5.69; Br, 12.20.

The spectrum and analysis indicated that this crude product was a mixture of parent acid IV and its mono-*p*-bromo derivative, although we have only the spectral evidence for the position of the bromine. A chromatographic separation of the mixture was tried on alumina (Alcoa F-20) on a 150-cm. column, using successive elution with pentane, ether, ethanol, and acetic acid. A less-colored product (97.6% recovery) was obtained, but little separation was achieved. The chromatographed product (m.p. 69–70°) failed to give any evidence of reaction with warm alcoholic silver nitrate or with sodium iodide in acetone, again pointing toward an aromatic bromo compound, although not certainly, because even bromide VI (nonaromatic halide) failed to react with these reagents under these conditions.

Anal. Calcd. for $C_{22}H_{20}O_2$ (45%) and $C_{22}H_{19}BrO_2$ (55%): C, 74.36; H, 5.53; neut. equiv., 360. Found: C, 74.33; H, 5.54, neut. equiv., 383.

From the carbon tetrachloride phase, after removal of the solvent and extraction of the residue with warm hexane, there was obtained γ,γ,γ-triphenylpropyl bromide (VI, 0.33 g., 3%, m.p. 137.5–138.5°) which had an infrared spectrum identical with the bromide isolated later. Their mixture melting point was not depressed. There also was isolated from the carbon tetrachloride phase, a small amount of an unidentified compound that showed carbonyl absorption in the infrared. "Saponification" and acidification, followed by steam distillation, yielded no phenol, however, and this side product was not considered to be a phenyl ester.

Reaction of the Acids I and IV with Mercuric Oxide and Bromine (Cristol–Firth Treatment).—These reactions were performed in a light-sealed hood in a darkened room using flasks wrapped in lightproof cloth.

Reaction of I.—Reaction of I (10 g., 0.033 mole) in dry refluxing carbon tetrachloride (150 ml.) with bromine (5.3 g., 0.033 mole) and red mercuric oxide (ACS reagent, 5.4 g., 0.025 mole) under the literature conditions[7] led to the isolation of carbon dioxide as barium carbonate (1.33 g., 20.8%). Work-up of the reaction material by alkaline extraction and subsequent acidification gave recovered I (1.65 g., 17%, m.p. 183°). Removal of the carbon tetrachloride solvent and hexane treatment as before led to the isolation of triphenylbromoethylene [VII, 0.43 g., 4%, m.p. 113.5–115.5°, lit.[28] m.p. 115.5°, infrared 6.25 and 6.35 μ, $\lambda_{\max}^{\text{alc}}$ 285 mμ (ε 11,300)], which was identical in all respects with authentic material (*vide infra*). Saponification of the reaction mixture from another run (same scale) with aqueous-alcoholic sodium hydroxide under reflux, followed by acidification and steam distillation into bromine water, yielded tribromophenol (2.17 g., 26%, m.p. 92°, mixture melting point with authentic material undepressed). This established the presence of at least 26% phenyl ester (undoubtedly phenyl β,β-diphenylacrylate and its α-bromo derivative[2]) in the reaction product.

Reaction of IV.—Similar reaction of IV (10.43 g., 0.033 mole), red mercuric oxide (5.4 g., 0.025 mole), and bromine (5.3 g., 0.033 mole) in refluxing carbon tetrachloride (150 ml.) yielded carbon dioxide (33.5%, weighed as barium carbonate, 2.18 g.). The carbon tetrachloride phase was washed with two 100-ml. portions of 2% sodium hydroxide solution and then with water to neutrality. Removal of the solvent and extraction with hexane gave γ,γ,γ-triphenylpropyl bromide (VI, 3.26 g., 28%), m.p. (after two recrystallizations from a hexane–ethanol mixture) 144–145°; infrared in accord with structure proposed; n.m.r., singlet at 431 c.p.s. (downfield from TMS standard, A-60 instrument), 15 protons, and a triplet at 186 c.p.s., 4 protons. This triplet was in the ratio 1:5:1 with a very small separation of peaks and indicated nearly magnetic equivalence (A_4) for the methylene protons instead of the possible A_2B_2 system.

Anal. Calcd. for $C_{21}H_{19}Br$: C, 71.80; H, 5.45. Found: C, 71.90; H, 5.19.

From acidification of the alkaline wash of the solvent phase and from the hexane-insoluble portion of the residue left upon removal of the solvent there was obtained a crude mixture (6.32 g.) which was probably a mixture of acids, as isolated from the Hunsdiecker reaction on IV. There was, however, a slight amount of a phenyl ester present because the ferric hydroxamate test for esters was

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

(24) A. Simonini, *Monatsh.*, **14**, 81 (1893).

(25) W. D. McPhee and E. G. Lindstrom, *J. Am. Chem. Soc.*, **65**, 2177 (1943).

(26) C. B. Wooster and R. A. Morse, *ibid.*, **56**, 1735 (1934).

(27) G. Wittig and D. Wittenberg, *Ann.*, **606**, 1 (1957).

(28) S. Apelgot, *et al.*, *Bull. soc. chim. France*, 533 (1952).

faintly positive and saponification, acidification, and steam distillation into bromine water did yield tribromophenol (0.16 g., 2%, m.p. 92°, mixture melting point undepressed). The reaction material after this treatment no longer gave a positive ester test. This reaction mixture was considered to be essentially entirely an acid mixture, however, by its behavior and infrared. The fact that not all of it was removed from the solvent by the alkaline wash is explained by the reluctance of acids like IV to be so extracted. They form soaps and emulsions, complicating such extraction techniques.

Triphenylbromoethylene (VII).—For comparison purposes (see above) this halide was prepared by the reaction of bromine in acetic acid with triphenylethylene (K & K Laboratories), as reported.[28] From the hydrocarbon (6.0 g., 0.0234 moles) the bromide was obtained as white needles (7.5 g., 97%), m.p. 117–118°, lit.[28] m.p. 115.5°, $\lambda_{\max}^{\text{alc}}$ 285 mμ (ε 9720). The infrared spectrum was in accord with the proposed structure and was identical with that of the halide isolated from the Cristol-Firth treatment of I (see above).

γ,γ,γ-Triphenylbutyryl Peroxide (X).—The acid IV was converted to its acid chloride in the usual fashion with thionyl chloride. The acid chloride (4.18 g., crude material *ca.* 12.5 mmoles) was added to dry ether (50 ml.) in which was suspended sodium peroxide (0.55 g., 7 mmoles). Three drops of water were added and the mixture was stirred at 0°. Another drop of water was added after each hour. After 2.5 hr., further sodium peroxide (*ca.* 0.1 g.) was added. After 3 hr., the initial yellow color (due to the sodium peroxide) had faded, whereupon the material was placed in the refrigerator overnight. Water (10 ml.) was added and the mixture was filtered at the pump. Acetone washes of the glassware were added to the collected precipitate, and the solution was allowed to evaporate in the air (4.05 g., quantitative yield). The peroxide was difficult to purify, but the following method afforded pure material, though with great loss. The crude peroxide above was treated with hot acetone (300 ml.), filtered from insoluble matter, and, while warm, diluted with water to cloudiness. The peroxide settled out on cooling as a white, microcrystalline solid (1.1 g., 28%), m.p. 116° dec. (on a block preheated to 100°), infrared 5.48 and 5.58 μ (peroxide C=O), iodometric titration gave a purity of >90%).

Anal.[29] Calcd. for $C_{44}H_{38}O_4$: C, 83.78; H, 6.07; O, 10.15. Found: C, 84.01; H, 6.06; O, 10.04.

Decomposition of the Peroxide X.—Several decompositions were carried out in the following way. A weighed amount of peroxide X (*ca.* 130 mg.) was refluxed in pure dry carbon tetrachloride (10 ml.) in a slow stream of nitrogen for 15 min., followed by 2-min. standing, with a previously tared Ascarite tube attached to the condenser. After the reaction, the Ascarite tube was reweighed to determine the carbon dioxide evolution. Evaporation (air) of the solvent left crystalline material which was then titrated for peroxide iodometrically. The results (averaged) indicated 39% carbon dioxide evolution (on the basis of 2 moles of carbon dioxide/mole of peroxide) and 67% peroxide recovered, implying (within error) essentially complete carbon dioxide evolution for the amount of peroxide reacted. From a decomposition carried out in the higher boiling solvent chlorobenzene, the entire reaction product was saponified and acidified. Steam distillation into bromine water indicated a trace (at most) of tribromophenol.

Conversion of γ,γ,γ-Triphenylpropyl Bromide (VI) to γ,γ,γ-Triphenylbutyronitrile.—The reaction product VI (1.8 g.), sodium cyanide (0.3 g.), and dimethyl sulfoxide (25 ml.) were heated with stirring at 130–140° for 50 min., at which time another 0.3 g. of sodium cyanide was added and the mixture heated 10 min. further. Addition of water and treatment of the ether phase in the usual way[8] gave the nitrile, which was recrystallized from ethanol (0.6 g., 40%), m.p. 135.5–137°, undepressed when admixed with the nitrile prepared from the iodide, infrared identical with that of the known.

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(29) Galbraith Laboratories, Inc., Knoxville, Tenn.

Substituted γ-Lactones. XIII.[1] Nitration of Substituted α-Benzylidene-γ-butyrolactones

Hans Zimmer, Roderich Walter[2] and Dilip K. Genge[3]

The Department of Chemistry, University of Cincinnati, Cincinnati 21, Ohio

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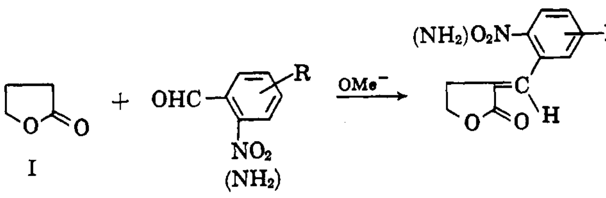
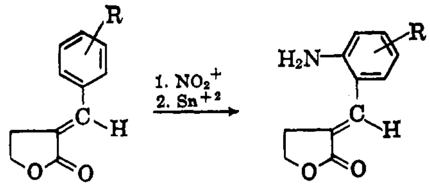
The nitration of various substituted α-benzylidene-γ-butyrolactones and -γ-valerolactones is reported. The substitution occurred generally at the same position where the corresponding benzoic acids and benzaldehydes were reported to undergo nitration. The factors influencing these electrophilic substitutions are discussed. The structures of the obtained nitro compounds were proved by oxidative degradation to the corresponding benzoic acids. Derivatives of the nitro compounds were prepared and some of their properties are reported.

Further exploration of a new rearrangement which α-(2-aminobenzylidene)-γ-butyrolactone (III) undergoes was attempted. This rearrangement was principally investigated as a convenient route toward a synthesis of dictamnine alkaloids.[1,4] Consequently, type III compounds with substituents like methoxy, ethoxy, and methylenedioxy were prepared. Two general methods for the synthesis of this type of compound are available: (1) condensation of the appropriate substituted benzaldehyde with γ-butyrolactone (I), or (2) nitration and reduction of an appropriate substituted α-benzylidene-γ-butyrolactone (II).



I

(1)



II III

(2)

It was shown in a previous paper of this series[5] that the condensation of I with electron-withdrawing groups, *e.g.*, nitro or cyano groups, proceeded poorly or not at all. Attempts to use aminobenzaldehydes in this type of reaction led to excessive tar formation. Conse-

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(1) Part XII: H. Zimmer and R. Walter, *Z. Naturforsch.*, **18b**, 669 (1963).

(2) National Institute of Health Fellow, 1961-1963.

(3) Postdoctoral Research Fellow, 1961-1963.

(4) (a) H. Zimmer, *Angew. Chem.* **73**, 144 (1961); 140th National Meeting of the American Chemical Society, Chicago, Ill., Sept., 1961; (b) H. Zimmer, F. Haupter, J. Rothe, W. E. Schrof, and R. Walter, *Z. Naturforsch.*, **18b**, 165 (1963).

(5) H. Zimmer and J. Rothe, *J. Org. Chem.*, **24**, 28 (1959).