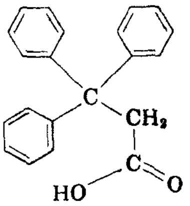
Communications TO THE EDITOR

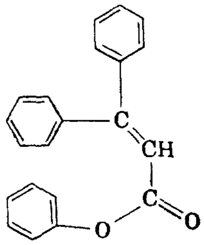
An Anomalous Hunsdiecker Reaction Involving Rearrangement

Sir:

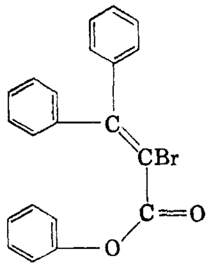
We have recently observed the conversion of β,β,β-triphenylpropionic acid (I) to phenyl β,β-diphenylacrylate (II) and phenyl α-bromo-β,β-diphenylacrylate (III) during an attempted Hunsdiecker[1] degradation. This appears to be the first reported instance in silver salt-bromine reactions of *internal ester formation accompanied by rearrangement.*[2] Bromodecarboxylation, the expected reaction, only amounted to *ca.* 3–5%.



I



II



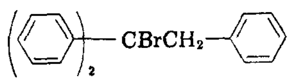
III

β,β,β-Triphenylpropionic acid[3] (m.p. 179–180°, Calc'd for $C_{21}H_{18}O_2$: C, 83.40; H, 6.00. Found:[4] C, 83.24; H, 6.11; Neut. equiv., 302.8) was converted to its silver salt (0.078 mole) and treated while being stirred in dry carbon tetrachloride (30 ml.) under a slow nitrogen gas sweep with bromine (0.078 mole) at 25° over a period of $^3/_4$ hour, followed by reflux (76°) for 1 hour. Only *ca.* 3% of the theoretical carbon dioxide was evolved. The standard workup followed by chromatography (alumina, petroleum ether-benzene eluant) and vacuum sublimation gave II [8.6%, m.p. 123.5–124.5°, λ_{EtOH}^{max} 285 mμ (log ϵ 4.23), λ_{EtOH}^{min} 245 mμ (log ϵ 3.96), I. R. (KBr pellet) 1736s cm.$^{-1}$ (ester C=O), 1618s—1594s—1579s cm.$^{-1}$ (aromatic with conj. double bond). Decolorized $^1/_2$% $KMnO_4$. Calc'd for $C_{21}H_{16}O_2$: C, 83.98; H, 5.37. Found: C, 84.15; H, 5.38] and III [20.5%, m.p. 90.5–91.5°, λ_{EtOH}^{max} (shoulder) 285 mμ (log ϵ 4.22), λ_{EtOH}^{min} 267 mμ (log ϵ 4.18), I.R. (KBr pellet) 1740s cm.$^{-1}$ (ester C=O), 1594w—1494m cm.$^{-1}$ (aromatic), stable to $^1/_2$% $KMnO_4$ and to hot, ethanolic $AgNO_3$. Calc'd for $C_{21}H_{15}BrO_2$: C, 66.60; H, 3.99; Br, 21.05. Found: C, 66.42; H, 4.07; Br, 20.80]. I (67%, m.p. 179–180°) was recovered from the reaction.

The structure of II was confirmed by mixture melting points and identity of spectra with authentic material prepared from $\beta\beta$-diphenylacrylic acid[5] and phenol *via* the acid chloride.

The structure of III was similarly confirmed by mixture melting points and identity of spectra with authentic material prepared from α-bromo-β,β-diphenylacrylic acid[6] and phenol *via* the acid chloride.

The identity of the bromodecarboxylated product is uncertain, but preliminary results indicate it to be an easily dehydrobrominated substance, possibly the expected compound IV.



IV

Work on this reaction and its mechanism is continuing.

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[1] Hunsdiecker and Hunsdiecker, *Ber.*, **75**, 291 (1942).

[2] Roberts and Simmons, *J. Am. Chem. Soc.*, **73**, 5487 (1951) showed the presence of cyclopropylcarbinyl cyclobutanecarboxylate in the Hunsdiecker reaction of cyclobutanecarboxylic acid. This is, however, not internal ester formation and is distinctly different from the situation described herein.

[3] Hellerman, *J. Am. Chem. Soc.*, **49**, 1738 (1927).

[4] Analyses by Galbraith Laboratories, Knoxville, Tenn.

[5] Kharasch, Kane, and Brown, *J. Am. Chem. Soc.*, **64**, 333 (1942).

[6] Newman and Owen, *J. Chem. Soc.*, 4726 (1952).

Synthesis of Histidyl Peptides

Sir:

Since histidine occurs widely in proteins and polypeptides, the development of methods for the synthesis of histidyl peptides is desirable. Holley and Sondheimer[1] employed the azide procedure for preparation of a number of histidyl peptides but alternate methods are needed.

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[1] R. Holley and E. Sondheimer, *J. Am. Chem. Soc.*, **76**, 1326 (1954).