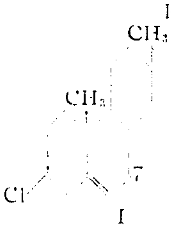
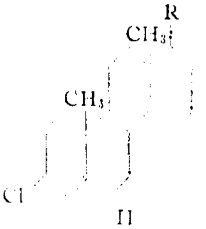
now generally accepted to occur with Walden inversion,[2,6] with one exception, if the halogenide belongs to the allyl derivatives. In this case the possibility of allylic rearrangement prevents any prediction of the steric course taken by a substitution reaction. Therefore, the above difficulty would be overcome if cholesteryl chloride were able to react in the form (II),[7] deriving from *allo*-cholesterol.[8] The reaction of form (II) with sodium acetate would be accompanied by a shift of the double bond.[9] In the case of 7-oxocholesteryl chloride the conjugation with the carbonyl group would stabilize the $C=C$ double bond in the "classical" 5,6-position.

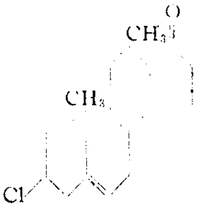
It is interesting to note that similar conditions have been observed by Linstead and Rydon[10] in the case of buten-(1)-ol-(4), which is converted by a mixture of sulfuric and hydrobromic acids partly into 4-bromobutene-(1), and partly into 4-bromobutene-(2). On the basis of Juvala's[11] results, the high substitution velocity, too, of cholesteryl chloride would be understood more easily.



I



II



III

Analogous considerations apply to the case of chloroandrostenone (III), which in contrast with the corresponding saturated chloroandrosterone is able to react with sodium benzoate without configurational inversion. This behavior may again be due to the possibility of III reacting in an allylic form.

Finally, it may be mentioned that this possibility is not necessarily limited to (I) and (III), but may apply to corresponding derivatives of other strong acids as, *e. g.*, toluenesulfonic acid.[12]

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(6) *Cf.* also Cowdrey, Hughes, Ingold, Masterman and Scott, *J. Chem. Soc.*, 1252 (1937). Fieser, in "The Chemistry of Natural Products Related to Phenanthrene," Reinhold Publishing Corp., New York, 1937, p. 392, has not yet taken these facts into account.

(7) The allylic nature of certain reactions of cholesteryl chloride has been discussed by Wagner-Jauregg and Werner [*Z. physiol. Chem.*, **213**, 119 (1932)] on the basis of the old allylic formula for cholesterol.

(8) The preparation of the chloride corresponding with *allo*-cholesterol is prevented by the easy dehydration of this substance: Schoenheimer and Evans, THIS JOURNAL, **58**, 182 (1936); *J. Biol. Chem.*, **114**, 567 (1936).

(9) The ability of cholesteryl chloride to react as (I) will account for the hydrogenative formation of a cholestane and not a coprostane derivative.

(10) Linstead and Rydon, *J. Chem. Soc.*, 1995 (1934).

(11) Juvala, *Ber.*, **63**, 1989 (1930).

(12) Compare Stoll, *Z. physiol. Chem.*, **246**, 6 (1937).

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Racemization During Esterification by Diazomethane

BY ERNST BERGMANN AND YAÏR SPRINZAK

In the course of experiments on Walden inversion, we had to prepare optically active methyl bromosuccinate. While esterification with methyl alcohol in the presence of concentrated sulfuric acid[1] gave satisfactory results, a series of experiments carried out with diazomethane gave invariably a racemic ester.

(−)-Bromosuccinic acid (1.5 g., rotation in acetone: c 3.000; l 9.9 cm.; α_D $-2.18°$, hence $[\alpha]_D$ $-72.7°$), finely pulverized, was added at zero temperature to a solution of diazomethane, prepared from ethyl nitrosomethylcarbamate (5 g.) and 25% methyl-alcoholic potash solution (7 cc.) in ether (30 cc.). The acid disappeared quickly; after thirty minutes of standing, the yellow solution was evaporated and the remaining racemic methyl bromosuccinate distilled *in vacuo;* b. p. 87° (2.5 mm.); yield 1.4 g. (Calcd. for $C_6H_9O_4Br$: Br, 35.5. Found: Br, 35.4).

As check experiments, a sample of the same (−)-bromosuccinic acid was kept for thirty minutes with a mixture of ether and methyl alcohol (6:1) and the optically active methyl ester in contact with diazomethane solution, prepared as above, for two hours. In both cases, no changes in optical rotation were observed.

Therefore we are inclined to assume that the racemization is connected in some way with the esterification mechanism. An analogous observation has been made incidentally by Stoermer and Starck[2] in the case of the optically active acid

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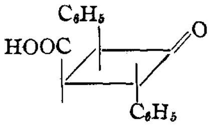
(1) Holmberg, *Ber.*, **59**, 125 (1926).

(2) Stoermer and Starck, *ibid.*, **70**, 479 (1937).



which is racemized too in the course of esterification by diazomethane.

Furthermore, the observation reported by Schlenk and Bergmann[3] may be recalled, that fluorene-9-carboxylic acid behaves—at least to a certain extent—abnormally toward diazomethane, giving dimethyl dibiphenylenesuccinate.

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(3) Schlenk and Bergmann, *Ann.*, **463**, 194 (1928).

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Remark on the Mechanism of the Fittig Reaction

BY O. BLUM-BERGMANN

(1) Bachmann and Clarke[1] have shown, some years ago, that the by-products formed in the biphenyl synthesis from boiling chlorobenzene and sodium metal indicate the intermediary formation of free phenyl radicals. Analogous results are obtained at room temperature, working in benzene solution.

To bromobenzene (50 g.), dissolved in benzene (50 g.) in a Schlenk tube,[2] sodium slices (10 g.) were added in nitrogen atmosphere, reaction starting quickly and causing a marked rise in temperature. When this first reaction ceased, the mass was shaken for two days, diluted with benzene (100 cc.) and separated by decantation from the excess sodium metal. Water was added, the benzene solution washed several times with water, dried and evaporated *in vacuo* and the residue fractionated at 13–15 mm. (a) B. p. 123–129°. This fraction crystallized completely; it consisted of pure biphenyl; m. p. 69–71°; yield 6.8 g. (b) B. p. 165–200°. The yellowish oil solidified almost quantitatively, on trituration with methyl alcohol; yield 2.1 g. From methyl alcohol, stout prisms, m. p. 56–57°, which according to their physical properties and the analysis proved to be *o*-phenyl-biphenyl, described before by Bachmann and Clarke.[1] (Calcd. for $C_{18}H_{14}$: C, 93.9; H, 6.1; mol. wt., 230. Found: C, 93.5; H, 6.0; mol. wt. (camphor), 241, 236.) (c) B. p. 200–250°, yellowish oil, which crystallized on trituration with light petroleum (b. p. 80–100°) (yield 0.26 g.) and was purified from the same solvent. Long needles of triphenylene; m. p. and mixed m. p. with an authentic sample, 195° (Calcd. for $C_{18}H_{12}$: C, 94.7; H, 5.3; mol. wt., 228. Found: C, 94.6; H, 5.3; mol. wt. (camphor), 257, 255).

(2) Theoretically free phenyl radicals may occur either in the formation from sodium and bromobenzene of phenylsodium[3] or in the interaction between the latter compound and a second bromobenzene molecule or in both processes. Horn and Polanyi[4] showed that, on interaction with dilute sodium vapor, bromobenzene forms biphenyl, undoubtedly via phenyl radicals. On the surface of metallic sodium, on the other hand, it will be expected that a second sodium atom will always be near enough for phenylsodium formation when the first metal atom has removed the halogen from the C-Hal bond,[5] although, obviously, temporary radical formation cannot be excluded. Therefore it is more likely that the reaction of the alkylsodium compound with bromobenzene involves the intermediary production of the radicals. In favor of this, the observation may be reported that phenylsodium, on interaction with bromobenzene, gives triphenylene $(C_6H_4)_3$ too, indicating formation of phenyl radicals and their disproportionation into benzene and phenylene radicals C_6H_4.[6]

Diphenylmercury (6 g.) was shaken in benzene solution with sodium slices (10 g.) for two days;[7] the phenylsodium containing mass was then separated by decantation from the excess metal, and bromobenzene (7 cc.) (twice the theoretical amount) added. The mixture was kept at 70° for forty-eight hours and poured out into water. Treatment as above gave (besides some bromobenzene) (a) biphenyl, b. p. 120–160° (22 mm.), m. p. 65°, yield 1.45 g.; (b) triphenylene, b. p. 200–220° (13 mm.) after trituration of the crude product (1 g.) with light petroleum and recystallization from the same solvent, m. p. 194–195.5°.

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(1) Bachmann and Clarke, THIS JOURNAL, **49**, 2089 (1927). *Cf.* J. v. Braun and Kurtz, *Ber.*, **70**, 1224 (1937); Oldham and Ubbelohde, *J. Chem. Soc.*, 201 (1938).

(2) Compare Houben-Weyl, "Die Methoden der organischen Chemie," Vol. IV, Georg Thieme Leipzig, 1924, p. 959.

(3) Schlubach and Goes, *Ber.*, **55**, 2889 (1922).

(4) Horn and Polanyi, *Z. physik. Chem.*, **25B**, 151 (1934).

(5) Ziegler and Schaefer, *Ann.*, **479**, 150 (1930).

(6) In the famous experiments of Wieland, Popper and Seefried [*Ber.*, **55**, 1816 (1922)] on the dissociation of benzene-azotriphenylmethane, the occurrence of benzene instead of free phenyl may also be due to incidental formation of triphenylene which so far has not been isolated from the reaction mixture.

(7) Compare Schlenk and Holtz, *ibid.*, **50**, 268 (1917).

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Hydrogenation of Ethylene and Partially Deuterized Ethylene on Catalytic Metal Surfaces

BY G. G. JORIS AND J. C. JUNGERS

The hydrogenation on catalytic copper of ethylene, ethylene-d_4 and partially deuterized ethylene (50%D) has been measured and found to be faster for the heavy compound.[1] To gain further information on this reaction and establish that this was not due to accidental circumstances, the hydrogenation of ethylene and partially deuterized ethylene was carried out on nickel, cobalt and platinum surfaces. The rates measured for mixtures of 5 cm. of ethylene and 7.5 cm. of hydrogen are given in the table and show

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(1) G. G. Joris, H. S. Taylor and J. C. Jungers, THIS JOURNAL 1982 (1938).