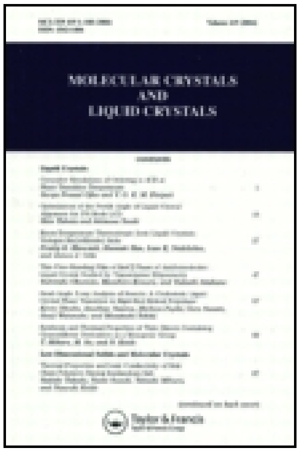


Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl17

Cationic Photoinitiators: Solid State Photochemistry of Triphenylsulfonium Salts

Nigel P. Hacker [a] , Daniel V. Leff [a] & John L. Dektar [a]

[a] IBM Research Division, Almaden Research Center, San Jose, California, 95120-6099, U.S.A.

Version of record first published: 04 Oct 2006.

To cite this article: Nigel P. Hacker , Daniel V. Leff & John L. Dektar (1990): Cationic Photoinitiators: Solid State Photochemistry of Triphenylsulfonium Salts, Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics, 183:1, 505-511

To link to this article: http://dx.doi.org/10.1080/15421409008047490

Mol. Cryst. Liq. Cryst., 1990, vol. 183, pp. 505–511
Reprints available directly from the publisher
Photocopying permitted by license only

Printed in the United States of America

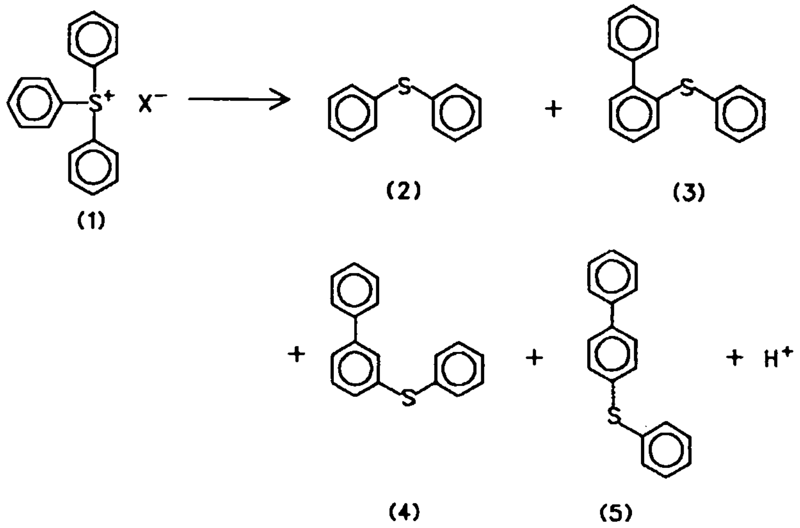
CATIONIC PHOTOINITIATORS: SOLID STATE PHOTOCHEMISTRY OF TRIPHENYLSULFONIUM SALTS

NIGEL P. HACKER, DANIEL V. LEFF and JOHN L. DEKTAR
IBM Research Division, Almaden Research Center, San Jose, California 95120-6099, U.S.A.

Abstract: Triphenylsulfonium bromide, triflate, tetrafluoroborate, hexafluoroarsenate, hexafluorophosphate and hexafluoroantimonate were irradiated in solution and in the solid state. The photoproducts, 2-, 3- and 4-phenylthiobiphenyl are formed by an in-cage fragmentation-recombination mechanism, whereas diphenylsulfide is formed by a cage-escape reaction. In dilute solution, the ratio of cage to escape products is approximately one for each salt. Also in concentrated solutions, an identical cage : escape ratio is observed for all salts except for the bromide, which favors the escape reaction. Photolysis of the salts in the solid state shows remarkable counter ion dependence and cage : escape ratios as high as 5 : 1 are observed. The mechanism for both in-cage and escape reactions is described.

INTRODUCTION

Triphenylsulfonium salts have found wide application in polymer films as photoinitiators for acid catalyzed processes. [1] Photolysis of triarylsulfonium salts results in efficient cross-linking of epoxides, deprotection of functionalized polystyrenes and depolymerization of polyphthalaldehydes. [2-4] Early studies reported formation of diphenylsulfide, biphenyl, substituted benzene derivatives and acid from photolysis of triphenylsulfonium salts and both heterolytic and homolytic cleavage processes were proposed to account for the observed photoproducts. [5-9] However, more recent studies on arylonium salts have detected new photoproducts. [10-20] We have recently reported a new decomposition pathway from direct photolysis of triphenylsulfonium salts in solution which yields phenylthiobiphenyls (3, 4 and 5) as the major products, in addition to diphenylsulfide (Figure 1). [10] The phenylthiobiphenyls are formed by an in-cage fragmentation-recombination mechanism, and diphenylsulfide is a cage-escape product. The in-cage reactions are favored by viscous media, resulting in an increase in the ratio of phenylthiobiphenyls : diphenylsulfide, and a decrease in quantum yield, due to recombination without rearrangement. While photoproduct distribution and quantum yield are somewhat sensitive to polarity and extremely sensitive to viscosity



$X^- = Br^-, CF_3SO_3^-, BF_4^-, AsF_6^-, PF_6^-, SbF_6^-$

FIGURE 1. **Products from Photolysis of Triphenylsulfonium Salts.**

of the environment, [10, 12, 19] to date all studies on sulfonium salts have found that photoproduct formation and efficiency is unaffected by the counter ion associated with the salt. [5 - 9] We have recently found that bromide ion, can intercept one of the in-cage fragments from photolysis of sulfonium salts in solution and increase the relative yield of escape products. [19] We report here a study of the photochemistry of triphenylsulfonium salts in the solid state and a new counter ion effect which favors the formation of in-cage photoproducts.

RESULTS AND DISCUSSION

Photolysis ($\lambda = 254$ nm, 5 min.) of triphenylsulfonium bromide, triflate, hexafluoroantimonate, hexafluorophosphate and tetrafluoroborate in dilute acetonitrile solution (0.01 M) gave the three phenylthiobiphenyls and diphenylsulfide. Table I shows that the product ratio was similar for each salt. A 1 : 1 ratio of 2-phenylthiobiphenyl : diphenylsulfide is obtained from irradiation of all salts, except the bromide which gives a 0.82 : 1 ratio. Bromide anion can act as a nucleophile and trap phenyl cation, the initial cleavage product, and thus prevent subsequent reactions which would normally give in-cage recombination products. The conversions were high (25 - 30 %) but similar results can be obtained at low conversion of sulfonium salt. [10] However in each case, regardless of the cage : escape ratio, the relative yield of the phenylthiobiphenyl isomers is 5 : 1 : 2 for the 2-, 3- and 4-phenylthiobiphenyls respectively.

TABLE I. Product Distribution from Photolysis of Triphenylsulfonium Salts in Acetonitrile (0.01 M) at λ = 254 nm (Relative to Diphenylsulfide = 1).

X	Br	CF_3SO_3	BF_4	AsF_6	PF_6	SbF_6
3	0.82	1.03	1.00	1.01	1.00	1.00
4	0.091	0.103	0.101	0.103	0.103	0.102
5	0.181	0.223	0.223	0.219	0.224	0.217

The crystalline salts were irradiated under identical conditions to those described above. The conversions were lower in the solid state (1 - 5%), due to a combination of scattering of the incident light and rigidity of the environment favoring recombination of the initially formed intermediates to starting material. However, there are significant changes in product distribution from solution to crystalline solid, and there also appears to be an anion effect. Table II shows that the ratio of diphenylsulfide : 2-phenylthiobiphenyl (PTB) varies from 0.89 : 1 for the bromide to 5.15 :1 for the hexafluorophosphate counter ion. The large non-nucleophilic counter ions MF_n seem to favor the formation of the cage product, 2-phenylthiobiphenyl, whereas the more nucleophilic counter ion, bromide, gives relatively more escape product, diphenylsulfide. Also, the ratio of 2-PTB : 3-PTB : 4-PTB is no longer 5 : 1 : 2, but varies from 2-5 : 1 : 45 - 120. The higher ratios of 2-PTB to the other two isomers may be attributed to the rigidity of the environment in the solid state. While the conversions varied for equal irradiation time in each photolysis experiment, the ratios of isomers gave good reproducibility (10 %) from run to run.

TABLE II Product Distribution from Photolysis of Triphenylsulfonium Salts in the Solid State at λ = 254 nm (Relative to Diphenylsulfide = 1).

X	Br	CF_3SO_3	BF_4	AsF_6	PF_6	SbF_6
3	0.89	1.81	2.63	5.15	4.88	3.87
4	0.019	0.020	0.019	0.049	0.043	0.052
5	0.045	0.11	0.082	0.11	0.11	0.18

In a second series of experiments the crystals were finely ground. For each anion photolysis under the same conditions gave the similar product distributions found for the whole crystal. However the conversion was usually higher in the finely ground samples due to the increase in surface area exposed to the irradiation source. To determine the effect of prolonged photolysis, the solid crystalline samples were irradiated for 20 min. The same products were obtained, however the relative yield of 2-PTB decreased by about 10%. A similar observation has been made from solution experiments, where prolonged photolysis causes a corresponding decrease in the yield of 2-, 3- and 4-PTB relative to diphenylsulfide.[12, 19] The extinction coefficients for the sulfonium salt (9,600 cm^{-1} M^{-1}), 2-PTB (13,900 cm^{-1} M^{-1}) and diphenylsulfide (10,600 cm^{-1} M^{-1}), are comparable, but 2-PTB and diphenylsulfide are formed at the crystal surface and therefore absorb more of the incident light. 2-PTB is formed in excess of diphenylsulfide, and also has a 25% higher absorbance, and therefore is more likely to be subject to photodecomposition. Solution photolysis of 2-PTB is known to give diphenyldisulfide and biphenyl. [19] GLC/FID traces of the products from prolonged photolysis of sulfonium salts in the solid state does show peaks with the same retention times as biphenyl and diphenyldisulfide.

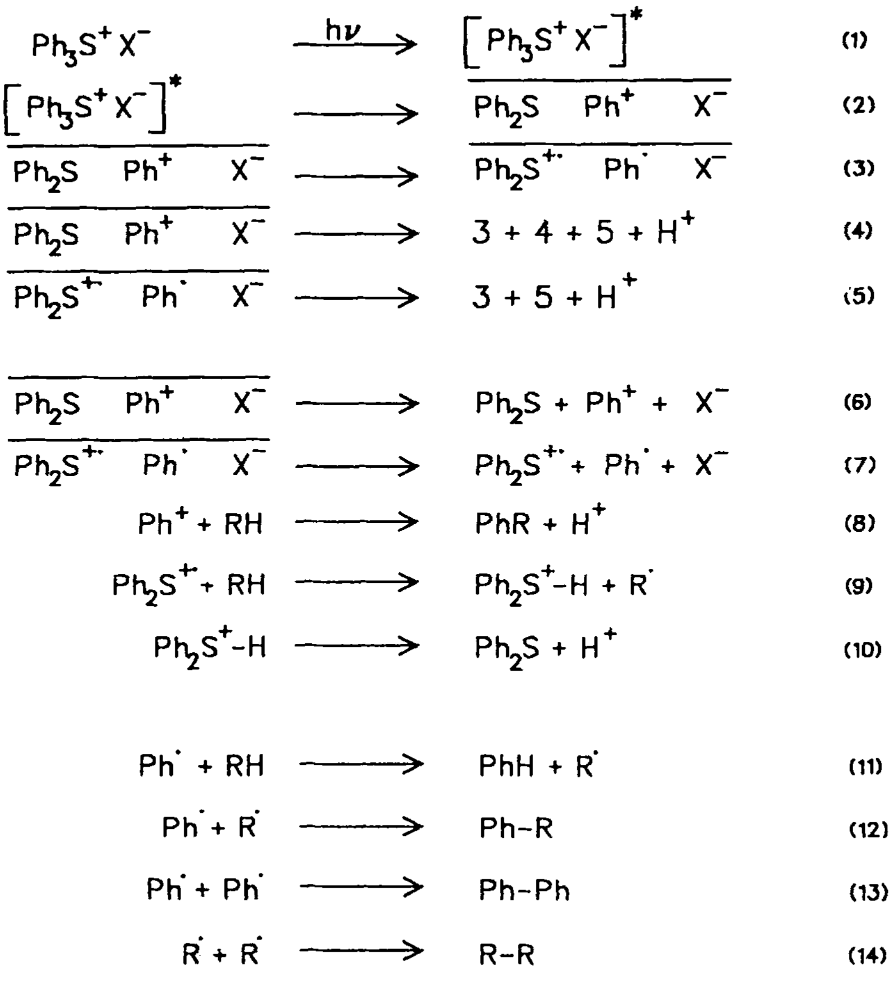
TABLE III. Product Distribution from Photolysis of Triphenylsulfonium Salts in Acetonitrile (0.10 M) at λ = 254 nm (Relative to Diphenylsulfide = 1).

X	Br	CF_3SO_3	BF_4	AsF_6	PF_6	SbF_6
3	0.396	1.025	0.990	0.936	0.968	0.930
4	0.0383	0.0892	0.0903	0.0893	0.0890	0.0891
5	0.0757	0.185	0.181	0.171	0.201	0.170

A final series of experiments were run in concentrated acetonitrile solution. The object of these experiments was to determine if a higher concentration of anion would lead to the counter ion dependence of photoproducts found in the solid state. Table III shows the product distributions for all anions except bromide are similar. Typically a 1 : 1 ratio of diphenylsulfide to 2-PTB is obtained and the ratio of 2-PTB : 3- PTB : 4-PTB is 5 : 1 : 2. This is very similar to the dilute solution experiments. The bromide anion, however gives a 2.53 : 1 ratio for diphenylsulfide : 2-PTB. Bromide is a good trap for phenyl cation, the initial photoproduct, and thus diverts further in-cage reactions of phenyl cation, which would normally give 2-, 3- and 4-PTB, to give diphenylsulfide and bromobenzene. Indeed, bromobenzene accounts for 30 % of the diphenylsulfide formed in 0.1M acetonitrile solutions. The other counter ions are less efficient traps for phenyl cation. Phenyl triflate accounts for only 1.3 % of the diphenylsulfide formed, whereas fluorobenzene, the expected product from reaction of phenyl cation with BF_4 and MF_6 is not observed above its detection limit. Interestingly in the solid state experiments bromobenzene accounts for 9-11 % of the diphenylsulfide formed from the sulfonium bromide, whereas the other salts do not give phenyl triflate or fluorobenzene, the possible products from reaction of phenyl cation with the respective counter ion.

MECHANISM

The mechanism for product formation for direct photolysis in solution can be described by three types of processes; in-cage reactions, cage-escape reactions and termination reactions. [19] The in-cage processes (Figure 2, steps 1-5) show that the singlet excited state cleaves initially to the phenyl cation - diphenylsulfide pair, which can recombine to give sulfonium salt or 2-, 3- and 4-PTB's, or undergo electron transfer to give the diphenylsulfinyl radical cation-phenyl radical pair followed by similar in-cage recombination reactions. The escape processes (steps 6-10), consist of reaction of these fragments with solvent to give acid and diphenylsulfide. The termination processes



$$\mathrm{Ph_3S^+X^-} \xrightarrow{h\nu} \left[\mathrm{Ph_3S^+X^-}\right]^* \tag{1}$$

$$\left[\mathrm{Ph_3S^+X^-}\right]^* \longrightarrow \overline{\mathrm{Ph_2S\quad Ph^+\quad X^-}} \tag{2}$$

$$\overline{\mathrm{Ph_2S\quad Ph^+\quad X^-}} \longrightarrow \overline{\mathrm{Ph_2S^{+\cdot}\quad Ph^\cdot\quad X^-}} \tag{3}$$

$$\overline{\mathrm{Ph_2S\quad Ph^+\quad X^-}} \longrightarrow 3 + 4 + 5 + \mathrm{H^+} \tag{4}$$

$$\overline{\mathrm{Ph_2S^{+\cdot}\quad Ph^\cdot\quad X^-}} \longrightarrow 3 + 5 + \mathrm{H^+} \tag{5}$$

$$\overline{\mathrm{Ph_2S\quad Ph^+\quad X^-}} \longrightarrow \mathrm{Ph_2S + Ph^+ + X^-} \tag{6}$$

$$\overline{\mathrm{Ph_2S^{+\cdot}\quad Ph^\cdot\quad X^-}} \longrightarrow \mathrm{Ph_2S^{+\cdot} + Ph^\cdot + X^-} \tag{7}$$

$$\mathrm{Ph^+ + RH} \longrightarrow \mathrm{PhR + H^+} \tag{8}$$

$$\mathrm{Ph_2S^{+\cdot} + RH} \longrightarrow \mathrm{Ph_2S^+\text{-}H + R^\cdot} \tag{9}$$

$$\mathrm{Ph_2S^+\text{-}H} \longrightarrow \mathrm{Ph_2S + H^+} \tag{10}$$

$$\mathrm{Ph^\cdot + RH} \longrightarrow \mathrm{PhH + R^\cdot} \tag{11}$$

$$\mathrm{Ph^\cdot + R^\cdot} \longrightarrow \mathrm{Ph\text{-}R} \tag{12}$$

$$\mathrm{Ph^\cdot + Ph^\cdot} \longrightarrow \mathrm{Ph\text{-}Ph} \tag{13}$$

$$\mathrm{R^\cdot + R^\cdot} \longrightarrow \mathrm{R\text{-}R} \tag{14}$$

FIGURE 2. Mechanism for Photodecomposition Triphenylsulfonium Salts.

(11-14), are radical-solvent reactions and radical-radical reactions. One in-cage reaction, not shown in Figure 2, is reaction of phenyl cation with the counter-ion and is significant only in the case of the bromide anion. In the solid state, cage-escape reactions with solvent and termination processes involving solvent cannot occur. In-cage recombination reactions, reactions with anion, intermolecular reactions or reactions with impurities, e.g. oxygen or the reaction vessel, are the only processes which can occur. Furthermore the environment is rigid and therefore favors in-cage recombination processes. Thus for the non-nucleophilic MF_n and triflate anions, the in-cage recombination to give phenylthiobiphenyls predominates. The rigidity of the environment is such that the phenyl fragment reactions in the 2-position to give 2-PTB in over a 50 : 1 ratio to 3- or 4- PTB. The bromide anion is more nucleophilic and traps some of the phenyl cation to give bromobenzene, and therefore increases the relative amount of the other escape product, diphenylsulfide. However the bromide trapping of phenyl cation is not so efficient in the solid state, 11 % versus 30 % in solution, and so the ratio of diphenylsulfide to 2-PTB is 1.1 : 1 in the solid state and 2.5 : 1 in solution. Clearly, reactions of the cage-escape phenyl moiety, other than formation of bromobenzene, do occur, however phenol and biphenyl, two likely products from phenyl radical in the absence of solvent, were not detected.

CONCLUSIONS

Photolysis of triphenylsulfonium salts in the solid state shows strong dependence on the nature of the counter ion which does not occur in acetonitrile solutions. Non-nucleophilic anions favor formation of in-cage recombination products over escape reactions. Phenyl cation is implicated by trapping with bromide anion to give bromobenzene. The trapping of phenyl cation by bromide anion is more efficient in solution and leads to more escape products being formed.

EXPERIMENTAL

Triphenylsulfonium hexafluoroantimonate, hexafluorophosphate, trifluoromethanesulfonate (triflate) and phenylthiobiphenyl isomers were prepared as previously reported. [15, 19] Triphenylsulfonium bromide was prepared by a modification of the Grignard procedure reported by Wildi. [19, 21] Triphenylsulfonium tetrafluoroborate was prepared by the same method but using aqueous tetrafluoroboric acid in place of aqueous hydrobromic acid in the work-up. [21] Triphenylsulfonium hexafluoroarsenate was prepared using Crivello's procedure. [6]

Capillary GLC analysis was performed on a Hewlett-Packard 5890 chromatograph equipped with a Hewlett-Packard 7673A autosampler and a Hewlett-Packard 3396A integrator. The column used in all analyses was a J & W Scientific DB-1 (cross-linked methyl silicone) 0.4 μ by 0.18 mm by 20 m.

Aliquots (4ml) of the acetonitrile (0.01M and 0.1M) solutions were irradiated in a Rayonet reactor (λ = 254 nm) for 5 and 20 minutes. After irradiation, the samples were transferred to tubes containing 1.00 mL of hexanes containing a small amount of *n*-tetradecane as internal standard, and 10.00 mL of 0.5 M saturated NaCl. The tubes were stoppered and thoroughly mixed. After standing for 4 hr, the hexane layer was removed and analyzed by capillary GLC. The integrator was calibrated against similar concentrations of authentic samples of the photoproducts, which were treated to a similar work-up as the photolysis solutions.

The solid samples (4 x 10^{-5} mole) irradiated in their crystalline form or as finely ground solids in the same tubes used above for 5 and 20 minutes. After photolysis, the samples were dissolved in 4 ml of acetonitrile and analyzed using the same workup procedure used for the solution samples above.

References

1. (a) J. V. Crivello, "UV Curing: Science and Technology", Ed. S. P. Pappas, Technology Marketing Corporation, Stamford, 1978, p. 23. (b) J. V. Crivello, *CHEMTECH*, **10**, 624 (1980). (c) S. P. Pappas, *Radiation Curing*, **8**, 28 (1981). (d) J. V. Crivello, *Polym. Eng. Sci.*, **23**, 953 (1983). (e) J. V. Crivello, *Adv. Polym. Sci.*, **62**, 1 (1984). (f) S. P. Pappas, *Prog. Org. Coat.*, **13**, 35 (1985). (g) S. P. Pappas, *J. Imag. Technol.*, **11**, 146 (1985). (h) J. V. Crivello, *Makromol. Chem., Macromol. Symp.*, **13/14**, 145 (1988). (i) Y. Yagci, W. R. Schnabel, *Makromol. Chem., Macromol. Symp.*, **13/14**, 161 (1988). (j) C. G. Willson, M. J. Bowden, *CHEMTECH*, **19**, 182 (1989).
2. J. V. Crivello, *J. Radiat. Curing*, **5**, 2 (1978).
3. H. Ito and C. G. Willson, *Polym. Eng. Sci.* **23**, 1012 (1983).
4. H. Ito and C. G. Willson, in *Polymers in Electronics* ACS Symposium series No. 242 T. Davidson, Ed., American Chemical Society, Washington, D. C., 1984, pg. 11.
5. (a) J. W. Knapzyck and W. E. McEwen, *J. Amer. Chem. Soc.* **91**, 145 (1969). (b) J W. Knapzyck and W. E. McEwen, *J. Org. Chem.* **35**, 2539 (1970).
6. J. V. Crivello and J. H. W. Lam, *J. Polym. Sci., Polym. Chem. Ed.*, **17**, 977 (1979).
7. S. P. Pappas and J. H. Jilek, *Photo. Sci. Engr.* **23**, 140 (1979).
8. S. P. Pappas, L. R. Gatechair and J. H. Jilek, *J. Poly. Sci. Poly. Chem. Ed.* **22**, 77 (1984).
9. S. P. Pappas, B. C. Pappas, L. R. Gatechair, J. H. Jilek and W. Schabel *Poly. Photochem.* *5*, 1 (1984).
10. J. L. Dektar and N. P. Hacker, *J. Chem. Soc., Chem. Commun.*, 1591 (1987).
11. J. L. Dektar and N. P. Hacker, *J. Org. Chem.*, **53**, 1833 (1988).
12. N. P. Hacker and J. L. Dektar, *Polym. Preprints*, **29**, 524 (1988).
13. J. L. Dektar and N. P. Hacker, *J. Photochem. Photobiol., A: Chem.*, **46**, 233 (1989).
14. N. P. Hacker and J. L. Dektar, *Polym. Mater. Sci. Eng.*, **60**, 22 (1989).
15. N. P. Hacker and J. L. Dektar, *Polym. Mater. Sci. Eng.*, **61**, 76 (1989).
16. K. M. Welsh, J. L. Dektar, N. P. Hacker and N. J. Turro, *Polym. Mater. Sci. Eng.*, **61**, 181 (1989).
17. N. P. Hacker and J. L. Dektar, in *Radiation Curing of Polymeric Materials*, ACS Symposium Series, C. E. Hoyle and J. F. Kinstle, Editors, in press.
18. J. L. Dektar and N. P. Hacker, *J. Org. Chem.*, in press.
19. J. L. Dektar and N. P. Hacker, *J. Amer. Chem. Soc.*, submitted.
20. R. J. Devoe, M. R. V. Sahyun, N. Serpone and D. K. Sharma, *Can. J. Chem.* **65**, 2342 (1987).
21. B. S. Wildi, S. W. Taylor and H. A. Potratz, *J. Amer. Chem. Soc.*, **73**, 1965 (1951).