Hydrogen Transfer. Part IV. The Use of Quinones of High Potential as Dehydrogenation Reagents.*

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[Reprint Order No. 5155.]

The use of quinones of high potential for the dehydrogenation of hydroaromatic and hydroethylenic systems † has been investigated, tetralin, acenaphthene, and dibenzyl being used as standard donors. Amongst eleven quinones tested, the most effective was 2 : 3-dichloro-5 : 6-dicyano-1 : 4-benzoquinone, followed by tetrachloro-1 : 2-benzoquinone, tetrachloro-1 : 8-diphenoquinone, and tetrachloro-1 : 4-benzoquinone. Dichlorodicyanobenzoquinone converts tetralin into naphthalene in practically quantitative yield at room temperature (5 days) or in boiling benzene solution (2 hr.). Acenaphthene is similarly converted into acenaphthylene (20 hr.), while dibenzyl is partly dehydrogenated to stilbene.

The work described in the two preceding papers has established a definite relation between the oxidation–reduction potentials of quinones and their reactivities in hydrogen-transfer reactions with hydroaromatic compounds. In general, quinones of high potential exhibit high reactivity of this type, although, as would be expected, the precise sequence also shows some dependence on the donor which has not yet been fully elucidated. Chloranil (tetrachloro-1 : 4-benzoquinone), the quinone most frequently employed in the past as a dehydrogenation reagent for preparative purposes (for references, see Part I, *J.*, 1954, 3544), has a fairly high potential and is the most reactive yet studied kinetically (Part II), but has generally been used under comparatively drastic conditions, usually above 200°. In many cases, such conditions are probably excessive, but nevertheless it appeared that a systematic investigation of other suitable quinones might afford superior acceptors,

Transfer-dehydrogenation of hydrocarbons by quinones.
(In benzene at 80°, unless otherwise indicated.[1])

	Tetralin			Acenaphthene			Dibenzyl		
Acceptor	Time (hr.)	Recovety (%)[a]	Dehydrogn. (%)	Time (hr.)	Recovery (%)[a]	Dehydrogn. (%)	Time (hr.)	Recovery (%)[a]	Dehydrogn. (%)
1 : 4-*Benzoquinones*									
Tetrachloro-	2	80	<10	—	—	—	—	—	—
	20	65	100[4]	20	55	59[4]	20	80	<10[4]
2 : 5-Difluoro-[2]	2	60	13	20	95	17	—	—	—
2 : 5-Dibenzoyl-	2	70	11	20	90	13	—	—	—
2 : 5-Bismethylamino-[3]	2	75	11	20	95	12	—	—	—
2 : 3-Dicyano-	2	50	12	20	40	50	20	85	<10
	2	65	100[5]	—	—	—	—	—	—
2 : 3-Dichloro-5 : 6-dicyano-	2	70	100	20	65	79	20	50	43
	120	65	76[6]	120	65	53[6]	120	80	<10[6]
1 : 2-*Benzoquinones*									
Tetrachloro-	2	80	100	20	45	60	20	90	12[4]
Tetrabromo-	2	85	<10	20	30	35	20	85	13[4]
1 : 8-*Diphenoquinones*									
Unsubstituted	2	60	<10	20	85	<10	20	90	<10
Tetrachloro-	10	80	30	20	35	16	20	80	<10
Tetrabromo-	10	60	18	20	40	26	20	50	<10

[a] Of hydrocarbon. [1] For details of conditions, see Experimental section. [2] This quinone was kindly provided by Dr. G. C. Finger (cf. *J. Amer. Chem. Soc.*, 1951, **73**, 145). [3] As the bistrichloroacetate. [4] In boiling xylene solution (*ca.* 135°). [5] In boiling toluene solution (*ca.* 110°). [6] At room temperature.

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* Part III, preceding paper.

† The term "hydroethylenic" is used with reference to an aliphatic system which is particularly prone to conversion into an ethylenic system; *e.g.*, dehydrogenation of dibenzyl to stilbene.

provided that they combined high potential with reasonable thermal stability and did not undergo alternative reactions with ethylenic and benzenoid compounds.

We chose tetralin, acenaphthene, and dibenzyl as standard donors to represent three types of hydroaromatic and hydroethylenic systems. These were tested against chloranil and ten other quinones under comparable conditions, generally in boiling benzene, toluene, or xylene. The extent of dehydrogenation was determined by isolating the mixture of unchanged and dehydrogenated hydrocarbon chromatographically, and estimating the percentage composition spectrometrically; the ultra-violet absorption bands of naphthalene at 2750 Å, of acenaphthylene at 3230 Å, and of stilbene at 2950 Å proved convenient for this purpose since the hydro-derivatives exhibit only weak absorption at these wavelengths. In most cases, the dehydrogenation product was also identified separately and the extent of transfer was confirmed by isolating the quinol. Details are given in the Experimental section; the main results are collected in the Table.

It may be noted, first, that the relative ease of dehydrogenation of the three donors in the Table is qualitatively independent of the quinone; and comparison with rate measurements on dihydronaphthalenes (Parts II and III, and unpublished work by J. S. Shannon) allows the following sequence to be written :

	1 : 4-Dihydronaphthalene	1 : 2-Dihydronaphthalene	Tetralin	Acenaphthene	Dibenzyl
r (approx.)	1	10^{-2}	10^{-3}	10^{-4}	10^{-5}
ΔE_R (kcal.)	30	25	4	<15	7

This sequence is understandable on the basis of the principles previously discussed. One of the more important factors determining the relative rates (r) will be the stabilisation of the transition state arising from the gain in resonance energy (ΔE_R) accompanying dehydrogenation of the donor. The relevant values, based on the experimental resonance energies (enthalpies) tabulated by Klages (*Ber.*, 1949, **82**, 367; cf. Part III), are shown above; it is assumed that the dehydrogenation of tetralin proceeds in two steps, the formation of 1 : 2-dihydronaphthalene followed by that of naphthalene, and that the first of these is rate-determining. In the three compounds containing a partially hydrogenated six-membered ring, r and ΔE_R decrease in the same order, though by no means proportionally. No thermochemical data are available for the conversion of acenaphthene into acenaphthylene which, in our experiments, takes place distinctly less readily than that of tetralin to naphthalene. [The reverse has been reported by Dost (*Rec. Trav. chim.*, 1952, **71**, 857) for dehydrogenation by chloranil in chlorobenzene. Dost's results are based, however, on determinations of the rate of disappearance of quinone without isolation of products, and this may conceivably be the reason for the discrepancy.] Theory predicts a considerable gain in resonance energy in acenaphthylene (*ca.* 15 kcal.) (cf. Syrkin and Diatkina, *Acta Physicochim. U.R.S.S.*, 1947, **21**, 529; Klement, *Helv. Chim. Acta*, 1949, **32**, 1777; Pullman and Pullman, "Les Théories Electroniques de la Chimie Organique," Masson, Paris, 1952), but this will be partly off-set by an increase in ring-strain in the unsaturated fused five-membered ring. The magnitude of the steric factor is unknown and not readily estimated, but may well be comparable with the quantum-mechanical resonance energy and thus account for the relatively slow dehydrogenation of acenaphthene. Dibenzyl is still less reactive than tetralin or acenaphthene in spite of a larger value of ΔE_R, and an additional factor evidently comes into play when an acyclic ethane unit is undergoing dehydrogenation. Whereas the cyclic systems already possess an approximately uniplanar arrangement in their partly hydrogenated state, the conversion of dibenzyl into stilbene entails a severe loss in freedom of rotation which will result in a decrease in the entropy of activation. A rate factor of 10^2, corresponding to 10 entropy units, arising from this cause is not unreasonable, but the correctness of this interpretation remains to be checked kinetically. Somewhat analogous observations have recently been made by Kooyman (*Discuss. Faraday Soc.*, 1951, **10**, 163; *Rec. Trav. chim.*, 1953, **72**, 330, 342) in regard to homolytic dehydrogenation by trichloromethyl radicals, and discussed in similar terms.

We now turn to the comparison of acceptors. Chloranil (E^0 0·70 v) does not react at a useful rate with any of the three standard donors at 80°, but causes slow dehydrogenation of tetralin and acenaphthene at 130°. Tetrachloro-1 : 2-benzoquinone (E^0 0·87 v; Conant and Fieser, *J. Amer. Chem. Soc.*, 1924, **46**, 1873) is more effective and dehydrogenates tetralin to naphthalene almost quantitatively within 2 hr. at 80°, but diphenoquinone (E^0 0·95 v; Fieser, *ibid.*, 1930, **52**, 4915) and tetrachloro-1 : 8-diphenoquinone, though they have still higher potentials, are considerably less reactive than tetrachloro-1 : 2-benzoquinone, as are the corresponding bromo-quinones. The reactions of tetralin and dibenzyl with chloranil and with tetrachloro-*o*-benzoquinone have also been investigated in other laboratories (Horner and Merz, *Annalen*, 1950, **570**, 89; Buchta and Kallert, *ibid.*, 1951, **573**, 220; Dost and van Nes, *Rec. Trav. chim.*, 1951, **70**, 403). The results for tetralin are in good agreement with those obtained here, but the results for dibenzyl are not. Dost and van Nes initially reported a 64% conversion of dibenzyl into stilbene with chloranil at 130° (16 hr.), and Dost later revised this figure to 14% (*ibid.*, 1952, **71**, 858); but they gave no details of their analytical procedure. Buchta and Kallert obtained a 23% conversion into stilbene, which was isolated and identified by mixed m. p., under similar conditions (20 hr.). In our hands, repeated experiments yielded no detectable amount (<2%) of stilbene although the total recovery of hydrocarbon was similar (70%) to that (80%) obtained by the German workers. Variations in experimental conditions, such as the exclusion or admission of air or oxygen, had no effect on the result. Moreover, spectroscopic measurements on the reaction mixture showed no measurable decrease in the quinone concentration. It appears that the discrepancy is to be explained either by the initial presence of stilbene in the dibenzyl employed by Buchta and Kallert, or by the existence of some unidentified catalytic influences. Evidence of a reaction consuming quinone was obtained at very high ratios (100 : 1) of hydrocarbon to quinone; this suggests that an impurity in the dibenzyl might be responsible.

Thus, although tetrachloro-1 : 2-benzoquinone exhibits a higher order of reactivity than chloranil, its range of practical application is still rather limited. Since it has been claimed that cholesteryl acetate can be partly converted into the 7-dehydro-derivative by benzoquinone (Milas and Heggie, *J. Amer. Chem. Soc.*, 1938, **60**, 984; Sah, *Rec. Trav. chim.*, 1940, **59**, 454) and that dehydrogenation is promoted by ultra-violet light (Mazza and Migliardi, *Chem. Abs.*, 1943, **37**, 3762), we have examined the use of tetrachloro-1 : 2-benzoquinone for this purpose. The results were entirely negative, however; no spectroscopic evidence for the formation of 7-dehydrocholesteryl acetate was obtained and 85% of the starting material was recovered. The possible effect of illumination was also tested on the reaction between the quinone and 9 : 10-dihydroanthracene which is dehydrogenated at a convenient rate at room temperature, but neither visible nor ultra-violet light had any marked effect under the conditions employed.

Since the completion of the present work, Moore and Waters (*J.*, 1953, 3405) have reported the dehydrogenation of tetralin by chloranil under mercury-arc illumination. Using a large excess of tetralin, they obtained a 50% yield (based on quinone) of 1 : 2-dihydronaphthalene after 39 days and interpreted the reaction as a photochemical one. No control experiments were recorded and as the reaction temperature was not determined comparison with our results is rendered somewhat uncertain. However, the fact that thermal dehydrogenation is complete within less than one day at 130° indicates that illumination had no very large accelerating effect, and quite possibly had none.

Attention was then directed to benzoquinones containing more strongly electron-attracting substituents than chlorine or bromine. Difluoro-, dibenzoyl- and dicyano-1 : 4-benzoquinone (E^0 0·97 v; Rideal, *Trans. Faraday Soc.*, 1925, **21**, 143) all cause slow dehydrogenation of tetralin at 80°, but the improvements in acceptor properties in comparison with chloroanil are not spectacular and the relatively low recoveries of hydrocarbon indicate the occurrence of side reactions, such as the formation of quinol ethers which has been observed by Criegee (*Ber.*, 1936, **69**, 2578). A similar result was obtained with the 2 : 5-bismethylamino-1 : 4-benzoquinone bistrichloroacetate; presumably the concentration of the bisammonium ion, which should have a very high potential, is too small in non-polar solvents to be effective. A striking enhancement in reactivity was observed, however, with 2 : 3-dichloro-5 : 6-dicyano-1 : 4-benzoquinone which was first described by Thiele and Günther (*Annalen*, 1906, **349**, 59) but has not since been studied. This quinone, the preparation of which has been improved, reacts with tetralin rapidly at 80°, or more slowly at room temperature, to give naphthalene and the quinol in almost quantitative yield. 1 : 4-Dihydronaphthalene is rapidly dehydrogenated at room temperature, and acenaphthene and dibenzyl are dehydrogenated slowly at 80°. Dichlorodicyanoquinone is thus by far the most powerful dehydrogenating agent yet investigated but, although it has proved of great value for thermochemical studies of hydrogen transfer reactions, its wider practical application is unfortunately limited by the incidence of side reactions, particularly at elevated temperatures. Thus, the reaction of the quinone with *cyclo*hexene or ethylbenzene afforded 30—50% yields of the quinol, but no simple dehydrogenation products could be isolated.

Even more powerful dehydrogenator properties might be expected for the unknown tetracyanobenzoquinones and for nitrobenzoquinones. However, attempts to induce reaction between tetrachlorocatechol, tetrachloroquinol, the corresponding diacetates, or chloranil with cuprous cyanide in pyridine gave only intractable products, and attempts to oxidise dinitrocatechol (Kehlmann, *Helv. Chim. Acta*, 1923, **6**, 952) and dinitroquinol (Nietzki and Noll, *Ber.*, 1893, **26**, 2183) to the corresponding quinones were also unsuccessful.

EXPERIMENTAL

Materials.—Chloranil was a recrystallised commercial sample, m. p. 290°. 2 : 5-Difluorobenzo-1 : 4-quinone was kindly provided by Dr. G. C. Finger (cf. *J. Amer. Chem. Soc.*, 1951, **73**, 145). 2 : 5-Dibenzoylbenzoquinone, prepared according to Bogart and Howells (*ibid.*, 1930, **52**, 837), formed orange needles, m. p. 163—164°. 2 : 5-Bismethylaminobenzoquinone, prepared according to Mylius (*Ber.*, 1885, **18**, 467), formed red needles, m. p. 173—174°; its bistrichloroacetate, m. p. 111—113°, was precipitated when a warm solution of the quinone (1 mol.) and trichloroacetic acid (2 mols.) in benzene was cooled. 2 : 3-Dicyano-, m. p. 176°, and 2 : 3-dicyano-5 : 6-dichloro-benzoquinone, m. p. 202°, were prepared according to Thiele (*Ber.*, 1900, **33**, 675; *Annalen*, 1906, **349**, 45; Helferich, *Ber.*, 1921, **54**, 155; 1923, **56**, 1112) but oxidation of the quinols was carried out by a modified procedure (Brook *J.*, 1952, 5040) which greatly accelerated the reaction and improved the yield. The finely ground dicyano-quinol (20 g.) was suspended in carbon tetrachloride (300 ml.), and nitrogen oxides (6 g., prepared by adding 100 g. of arsenious oxide to a cooled mixture of 83 ml. of fuming nitric acid and 33 ml. of concentrated sulphuric acid, warming gently if necessary to initiate reaction, and condensing the red-brown fumes by means of a water-condenser and ice-cooled receiver) were added during 10 min. with vigorous stirring. The carbon tetrachloride layer became initially blue and finally yellow. Stirring was continued for a few minutes, and the suspension was then filtered. The solid product was washed with carbon tetrachloride and crystallised from chloroform–benzene, giving the quinone (18 g., 90%). By this method, the 5-step preparation of dichlorodicyanoquinone from quinol can be carried out in 2 days with an overall yield of 70%. Tetrachlorobenzo-1 : 2-quinone, m. p. 131—132°, and tetrabromobenzo-1 : 2-quinone, m. p. 148—150°, were prepared according to Jackson and Koch (*Amer. Chem. J.*, 1908, **39**, 83, 497). 1 : 8-Diphenoquinone was obtained from 4 : 4′-dihydroxydiphenyl (Willstätter and Kalb, *Ber.*, 1905, **38**, 1232) by oxidation with active lead dioxide in boiling benzene–dioxan (5 : 1) (Kuhn and Hammer, *Chem. Ber.*, 1950, **83**, 413) or, more conveniently, by shaking an ethereal solution with a solution of ceric ammonium sulphate in dilute sulphuric acid. The quinone was precipitated and, after one crystallisation from boiling benzene in the presence of charcoal, had m. p. 165° (decomp.). Tetrachloro- and tetrabromo-diphenoquinone were prepared according to Magatti (*Ber.*, 1880, **13**, 224).

Tetralin, purified by refluxing with sodium in nitrogen and fractionation, had b. p. 207—208°, n_D^{20} 1·5463. Acenaphthene was recrystallised from ethanol and had m. p. 96°. Dibenzyl was recrystallised from ethanol and had m. p. 52°. Benzene, toluene, xylene, and tetrahydrofuran were purified by refluxing with sodium and distillation.

Dehydrogenations. General Procedure.—Solutions, approx. 1M with respect to donor and 1·05M with respect to the quinone, were heated under reflux, generally in nitrogen. All the solutions were initially homogeneous at the b. p. At the end of the appropriate period (see Table), the reaction mixture was diluted with about five volumes of light petroleum (b. p. 40—60°) and the precipitate of quinol and unchanged quinone was filtered off and extracted with boiling light petroleum. The combined petroleum solutions were passed through a short (8″ × ½″) alumina column, and the column was washed with additional petroleum until no more hydrocarbon could be eluted. The petroleum eluates were dried and evaporated, and the residue was weighed, giving the total hydrocarbon recovery (see Table). In a few cases, the hydrocarbon was isolated by steam-distillation instead of by extraction with petroleum. The extent of dehydrogenation in the recovered hydrocarbon was determined spectrometrically in ethanol solution, using the maxima at 2750 Å ($E^{1\%}_{1\,\text{cm.}}$ 440) for naphthalene, at 3230 Å ($E^{1\%}_{1\,\text{cm.}}$ 650) for acenaphthylene, and at 2950 Å ($E^{1\%}_{1\,\text{cm.}}$ 1500) for stilbene. Tetralin, acenaphthene, and dibenzyl have $E^{1\%}_{1\,\text{cm.}}$ <10, 90, and <10, respectively, at the corresponding wave-lengths. Some typical experiments are recorded in detail below.

Dibenzyl and Chloranil (with J. S. SHANNON).—(*a*) Dibenzyl (1·8 g.), chloranil (2·7 g.), and xylene (11 ml.) were refluxed for 20 hr. under nitrogen. The solution was diluted with light petroleum, filtered, passed through alumina, and evaporated, giving only unchanged dibenzyl (1·3 g., 70%), m. p. 52°, $E^{1\%}_{1\,\text{cm.}}$ at 2940 Å <10.

(*b*) The above experiment was repeated, but with access of air during the refluxing period, to simulate the conditions employed by Dost and van Nes (*Rec. Trav. chim.*, 1951, **70**, 403). The result was the same as in (*a*). In a further experiment, a slow stream of air was passed through the solution : only unchanged dibenzyl (70%) was again obtained.

(*c*) Dibenzyl (6 g.), chloranil (13 g.), and xylene (60 ml.) were heated under reflux for 24 hr. The solution was cooled, filtered, washed with alkaline sodium dithionite (hydrosulphite) and water, dried ($CaCl_2$), and distilled at atmospheric pressure through a 6″ column to remove most of the xylene. The remaining liquid was distilled under reduced pressure through a 6″ Steadman column. Four fractions (total 4·2 g., 70%) were collected all of which solidified on cooling and then had m. p. 53°. The first three fractions all had b. p. 148°/12 mm., $E^{1\%}_{1\,\text{cm.}}$ <10 at 2950 Å. The fourth fraction (0·9 g.) had b. p. 150—160°/12 mm., $E^{1\%}_{1\,\text{cm.}}$ 60 at 2950 Å. This corresponds to a maximum stilbene content of 4% in this fraction, and of 1% in the total product. For apparently identical conditions, Buchta and Kallert (*Annalen*, 1951, **573**, 220) reported a 23% yield of stilbene.

(*d*) In an attempt to throw some light on the discrepant results with this system, a number of experiments were carried out in which any disappearance of choranil rather than appearance of stilbene was sought by spectrometric measurements in the visible range. Solutions of chloranil in xylene or phenetole exhibit $E^{1\%}_{1\,\text{cm.}}$ 35·5 at 4400 Å and 0·285 at 5700 Å, and are stable for 24 hr. at 135°. With 0·1M-choranil, no significant change was detectable during 6 hr. in the presence of 0·1M- or 1M-dibenzyl. However, a phenetole solution 0·02M with respect to chloranil and 1M with respect to dibenzyl shows a rapid decrease in chloranil, $E^{1\%}_{1\,\text{cm.}}$ at 4400 Å falling from 35·5 to 2·6 in 3 hr. These results indicate that disappearance of chloranil under such conditions is due to reaction with an unidentified impurity in the dibenzyl.

Tetralin and Tetrachloro-1 : 2-*benzoquinone*.—Tetralin (1·3 g.), the quinone (5·0 g.), and benzene (15 ml.) were refluxed for 2 hr. in nitrogen. The solution was steam-distilled and the distillate extracted with ether. The ether solution was dried and evaporated, giving naphthalene (1·0 g., 78%), m. p. and mixed m. p. 80°. The non-volatile residue from the distillation was recrystallised from acetic acid, and then from aqueous ethanol, giving tetrachlorocatechol (3·0 g., 60%), m. p. and mixed m. p. 193°.

Dibenzyl and Tetrachloro-1 : 2-*benzoquinone*.—Dibenzyl (1·8 g.), the quinone (2·2 g.), and xylene (10 ml.) were refluxed for 20 hr., during which some hydrogen chloride was evolved. The solution was diluted with light petroleum (50 ml.), chromatographed, and evaporated, giving a colourless solid product (1·6 g.), m. p. 44—62°. A solution in ethanol showed $\lambda_{\text{max.}}$ 2950 Å, $E^{1\%}_{1\,\text{cm.}}$ 175, corresponding to a stilbene content of 12%.

Tetralin and Dichlorodicyanoquinone.—Tetralin (0·65 g.), the quinone (1·14 g.), and benzene (5 ml.) were refluxed for 45 min., during which the initially red solution became colourless. More quinone (1·14 g.) in benzene (2 ml.) was added and the solution was refluxed for a further 75 min. After dilution with light petroleum, the solution was filtered, passed through alumina, and evaporated, giving naphthalene (0·42 g., 70%), m. p. and mixed m. p. 79—80°. The petroleum-insoluble residue was crystallised from aqueous ethanol, giving colourless dichlorodicyanoquinol (0·7 g., 61%), decomp. 263°.

Acenaphthene and Dichlorodicyanoquinone.—Acenaphthene (0·38 g.), the quinone (0·57 g.), and benzene (5 ml.) were refluxed for 20 hr., a white precipitate being formed. The mixture was diluted with light petroleum, filtered, passed through alumina, and evaporated, giving a bright yellow solid (0·25 g., 66%), m. p. 91—94°. A solution in ethanol showed $\lambda_{\text{max.}}$ 3240 Å, $E^{1\%}_{1\,\text{cm.}}$ 535, corresponding to an acenaphthylene content of 79%. Two crystallisations from ethanol raised the m. p. to 94—95°, undepressed on admixture with pure acenaphthylene.

Dibenzyl and Dichlorodicyanoquinone.—Dibenzyl (1·27 g.), the quinone (1·68 g.) and benzene

(7 ml.) were refluxed for 20 hr. in nitrogen. The solution was diluted with light petroleum (40 ml.) passed through alumina which was washed with additional solvent (150 ml.), and evaporated, giving a colourless, solid product (0·61 g., 50%), m. p. 62—104°. A solution in ethanol exhibited $\lambda_{\text{max.}}$ 2950 Å, $E^{1\%}_{1\,\text{cm.}}$ 650, corresponding to a stilbene content of 43%. After several crystallisations from ethanol, the m. p. was raised to 123°, undepressed on admixture with pure *trans*-stilbene.

Grateful acknowledgment is made to the Nuffield Foundation for a Fellowship (A. G. B.). We thank Dr. L. M. Jackman and Mr. J. S. Shannon for assistance.

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[*Received, February 24th,* 1954.]