of the ion R^+. The great increase in the ease of ionization of $R-X$ along this series is found to be due to the very marked decrease in the ionization potential of the radical R from methyl to *tert.*-butyl. The values of the ionization potentials of methyl and ethyl have been determined as 232 and 200 kcal. respectively[4]. The ionization potentials of the *sec.*-propyl and *tert.*-butyl radicals can be estimated from the results of electron impact experiments on *n*-propane, *n*-butane, *iso*-butane, *n*-propyl chloride and *tert.*-butyl chloride[7] as about 179 and 165 kcal. respectively. This decrease of about 70 kcal. in the ionization potential of the radical R from methyl to *tert.*-butyl is the main cause of the increase in the unimolecular reaction-rate of $R-X$ along this series.

The decrease in the bimolecular S_N2 reaction-rate as $R-X$ changes from a primary to a tertiary halide has been attributed by Polanyi and co-workers to the increase in steric hindrance along this series[8,4]. Calculations of this steric hindrance have been made for the methyl to the *tert.*-butyl series[9], and it has been found possible to account for the decrease in the bimolecular rate from MeX to *tert.*-BuX in terms of carbon-halogen bond-strengths and steric hindrance.

Strong evidence for the view that the decrease in the bimolecular rate from primary to tertiary halides is due to an increase in steric hindrance and not due to an increase in electron accession to the reactive carbon atom may be obtained by considering the reactions of allyl chloride and its α- and γ-methyl derivatives. It is found that the unimolecular rate sequence of these chlorides is γ-methylallyl $\simeq$ α-methylallyl > allyl[10]. The equivalence of the unimolecular reaction-rates of the γ-methylallyl chloride and α-methylallyl chloride would indicate that the electron-releasing capacity of the methyl group is transmitted with undiminished power to the seat of substitution[10]. The methyl group, therefore, should cause the same increase in electron accession to the reaction centre, whether it is in the α- or the γ-position, and thus on the Hughes and Ingold theory one would expect the bimolecular S_N2 reactions of these two halides to show the same rate. The observed bimolecular rate sequence, however, is γ-methylallyl > allyl > α-methylallyl[10]. (Rate sequences similar to those given by Hughes have been obtained for the unimolecular and bimolecular reactions of α-methylallyl and γ-methylallyl chlorides by Young and Andrews[11].) This bimolecular rate-sequence is in contradiction to that which would be expected on the Hughes and Ingold theory, and the only factor that can account for this marked difference between the unimolecular and the bimolecular rate sequences of these three halides is the steric hindrance caused by the substituent methyl group. This steric hindrance is present in the bimolecular S_N2 reaction of α-methylallyl chloride but is absent both in the bimolecular S_N2 reaction of γ-methylallyl chloride and in the unimolecular S_N1 reactions of α- and γ-methylalyl chlorides. This is strong evidence for the conclusion that the decrease in the bimolecular reaction-rate as the reactive carbon atom changes from primary to secondary is due to an increase in steric hindrance, as suggested by Polanyi and co-workers, and not due to an increase in electron accession to the reactive carbon atom as postulated by Hughes and Ingold.

The bimolecular S_N2 reaction-rate of $R-X$ decreases as R changes along the series ethyl, *n*-propyl, iso-butyl, neopentyl[10]. Hughes has estimated the steric effect for this series of R and concludes that it may in principle enter in at all stages of β-substitution, but that it assumes real importance only in the case of the neopentyl halides[10]. We have estimated the steric hindrance for this series, and we attribute the decrease in rate of the bimolecular reaction along the whole of this series to the increase in steric hindrance as in the case of the methyl to *tert.*-butyl series.

ALWYN G. EVANS.

Chemistry Department,
University of Manchester.
Dec. 10.

[1] Ingold and Rothstein, *J. Chem. Soc.*, 1217 (1928). Hughes, Ingold and Patel, *J. Chem. Soc.*, 526 (1933). For further references see "General Discussion on Mechanism of Organic Reactions in Liquid Systems", *Trans. Farad. Soc.*, 37, 601 (1941).
[2] Bateman and Hughes, *J. Chem. Soc.*, 945 (1940).
[3] Bateman, Cooper, Hughes and Ingold, *J. Chem. Soc.*, 925 (1940).
[4] Ogg and Polanyi, *Trans. Farad. Soc.*, 31, 604 (1935).
[5] Baughan, Evans, M. G., and Polanyi, *Trans. Farad. Soc.*, 37, 377 (1941).
[6] Hipple and Stevenson, *Phys. Rev.*, 63, 121 (1943).
[7] Hipple and Stevenson, *J. Amer. Chem. Soc.*, 64, 1590, 2766, 2769 (1942).
[8] Meer and Polanyi, *Z. phys. Chem.*, B, 19, 164 (1932).
[9] Evans, A. G., and Polanyi, *Nature*, 149, 608 (1942).
[10] Hughes, *Trans. Farad. Soc.*, 37, 603 (1941).
[11] Young and Andrews, *J. Amer. Chem. Soc.*, 66, 421 (1944).

An Isomeride of Abietic Acid

DURING the course of a series of oil investigations, an oil loaded with resin was distilled *in vacuo* (28 in. mercury); subsequent to distillation the residue was found to contain a substance having the chemical properties of abietic acid but which differed physically in spite of the fact that the nature of the resin present suggested abietic acid. The different physical properties were discovered after purification.

The compound in question is moderately soluble in alcohol and crystallized from such solution in the form of plates having a hexagonal periphery. The molecular weight was found to be 412 and it was easy to prepare retine from it by the normal reduction method.

The physical characteristics contrasted with normal abietic acid are:

	Normal abietic acid	New compound
Melting point	159/161° C.	193/195° C.
$(a)_D$	−77	−72

As in the case of normal abietic acid, it was easy to prepare a sodium salt from the new compound; circumstances prevented a check being made to ascertain whether the salts of the normal and new acids possessed similar properties, but further work on this point is in hand.

It should be noticed that the fixed constants of this isomeride differed from those of the isomerides produced by heating abietic acid with acetic acid and hydrochloric acid.

A more detailed account is to be published shortly; in the meantime, I should be very pleased if anyone interested in terpene chemistry who has found similar reactions would take up the matter with me.

J. H. CHRISTIE.

Chemical Laboratory,
Humber, Ltd.,
Coventry.

[1] Steele, *J. Amer. Chem. Soc.*, 1333 (1922); 1935 (1934).

Quinoxaline and its Monohydrate

ALTHOUGH quinoxaline, $C_8H_6N_2$, was synthesized in 1884[1,2], and has been mentioned in the literature[1–12] several times since that date, it is rather surprising that the existence of quinoxaline monohydrate has not been noticed, the more so since several physico-chemical determinations have been carried out with quinoxaline; namely, vapour density in diphenylamine vapour[3]; density and refractive indices measured at 48°[4]; depression of the freezing point in diphenyl[6] and use of quinoxaline as the cryoscopic solvent for the molecular weight estimation of naphthalene[5].

Recorded values for the melting point of quinoxaline have varied from 27°[1] to 32·0° (corr.)[5]. It has now been found that quinoxaline as obtained by crystallization from light petroleum (b.p. 40–60°) or by distillation (b.p. 227–229°) is the anhydrous form with m.p. 28° (found: C, 74·1; H, 4·6; N, 21·4; calc. for $C_8H_6N_2$: C, 73·8; H, 4·6; N, 21·5 per cent). On exposure to air the anhydrous quinoxaline is converted within a short time, depending on the humidity, into quinoxaline monohydrate with m.p. 37° (found: C, 65·4; H, 5·4; N, 18·8; $C_8H_6N_2.H_2O$ requires C, 64·9; H, 5·4; N, 18·9 per cent).

Occasionally the anhydrous quinoxaline is precipitated from light petroleum as an oil, but this readily solidifies on the addition of a few drops of water to give quinoxaline monohydrate, m.p. 37°. The existence of the monohydrate is further proved by its behaviour on distillation, when water (identified by its b.p. 100°, and ability to turn anhydrous copper sulphate blue) distils over first, followed by the anhydrous quinoxaline, b.p. 227–229° and m.p. 28°.

A further property of quinoxaline which has escaped mention in the literature is that of its volatility both in air at room temperature and in the vapours of organic solvents at their boiling point; for example, 0·4 gm. quinoxaline distils over per litre of benzene. The quinoxaline can be removed from the distillate and identified as the hydrochloride, and can be detected by the yellow colour given with a drop of concentrated sulphuric acid or by the yellow precipitate given with a benzene or petroleum solution of 2 : 4-dinitro phenol.

In contrast to the interaction of quinoxaline and potassamide in liquid ammonia to give the dipotassium salt of fluorubin[8], quinoxaline reacts with sodamide in dimethyl aniline at 210–225° to give two products: 2 : 2′-diquinoxalyl, m.p. 274–276° (found C, 74·4; H, 3·9; N, 21·6; calc. for $C_{16}H_{10}N_4$; C, 74·4; H, 3·9; N, 21·7 per cent. Maurer and Boettger[16] obtained 2 : 2′-diquinoxalyl from *o*-phenylene diamine and dihydro quinoxalyl glycolaldehyde and give m.p. 274°), and 2 : 3-dihydroxyquinoxaline, m.p. 386–390° decomp. (found: C, 60·6; H, 3·7; N, 17·8; calc. for $C_8H_6N_2O_2$: C, 59·3; H, 3·7; N, 17·3 per cent. Motylewski[15] gives m.p. 410° for 2 : 3-dihydroxyquinoxaline obtained by oxidation of 1 : 2-dihydro-3-hydroxyquinoxaline). The identity of the 2 : 3-dihydroxyquinoxaline was also confirmed by its conversion to 2 : 3-dichloro quinoxaline, m.p. 147° (Hinsberg and Pollak[14] give m.p. 150°).

B. C. PLATT.

Wellcome Laboratories of Tropical Medicine,
London, N.W.1. Dec. 20.

[1] Hinsberg, O., *Ber. deut. chem. Ges.*, 17, 320 (1884); *Ann.*, 237, 334 (1887).
[2] Koerner, W., *Acc. dei Lincei, Trans.*, 8, 219 (1884).
[3] Merz, V., and Ris, C., *Ber. deut. chem. Ges.*, 20, 1194 (1887).
[4] Brühl, J. W., *Z. phys. Chem.*, 22, 383 (1897); *ibid.*, 79, 4 and 509 (1912).
[5] Gabriel, S., and Sonn, A., *Ber. deut. chem. Ges.*, 40, 4851 (1907).
[6] Padoa, M., *Atti Reale Acc. Lincei*, [5], 12, I, 393 (1903).
[7] Hinsberg, O., *J. prakt. Chem.*, [2], 94, 182 (1916).
[8] Chattaway, F. D., and Humphrey, W. G., *J. Chem. Soc.*, 648 (1929).
[9] Bergstrom, F. W., and Ogg, jun., R. A., *J. Amer. Chem. Soc.*, 53, 246 (1931).
[10] Kuhn, R., and Bär, F., *Ber. deut. chem. Ges.*, 67, 903 (1934).
[11] Maurer, K., Schiedt, B., and Schroeter, H., *Ber. deut. chem. Ges.*, 68, 1721 (1935).
[12] Sausville, J. W., and Spoerri, P. E., *J. Amer. Chem. Soc.*, 63, 3153 (1941).
[13] Billman, J. H., and Rendall, J. L., *J. Amer. Chem. Soc.*, 66, 541 (1944).
[14] Hinsberg, O., and Pollak, J., *Ber. deut. chem. Ges.*, 29, 784 (1896).
[15] Motylewski, S., *Ber. deut. chem. Ges.*, 41, 804 (1908).
[16] Maurer, K., and Boettger, B., *Ber. deut. chem. Ges.*, 71, 2092 (1938).

Antimalarial Action of Cinnoline Derivatives

A NOTEWORTHY feature of the published synthetic work relevant to the chemotherapy of malaria is the extent to which attention has been concentrated on the preparation of active agents derived from either quinoline or acridine, of which the two outstanding examples are, respectively, pamaquin and mepacrine. By comparison, little information is available concerning the effectiveness of other structural types, with the important exception of paludrine, the discovery of which was announced recently[1].

In an attempt to discover antimalarial activity in the quinazoline field, various 4-basicalkylaminoquinazolines (formula I; $R = NO_2$ or Cl) were prepared by Magidson and Golovchinskaya[2], but the compounds were stated to be devoid of such activity. Activity is,