Anal. Calcd. for $C_{11}H_{20}O$: C, 78.51; H, 11.97. Found: C, 78.65; H, 11.81.

Acknowledgment.—We thank the Public Health Service for support of this work through a research grant (AI-04965) from the National Institute of Allergy and Infectious Diseases. We are indebted to Professor A. S. Hussey for a sample of decalol 25 and to Mr. Joel Williams and Dr. Frederick Schappel for their generous assistance with gas chromatographic analyses.

Synthetic Studies in The Resin Acids Series. VI[1]

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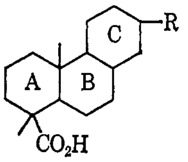
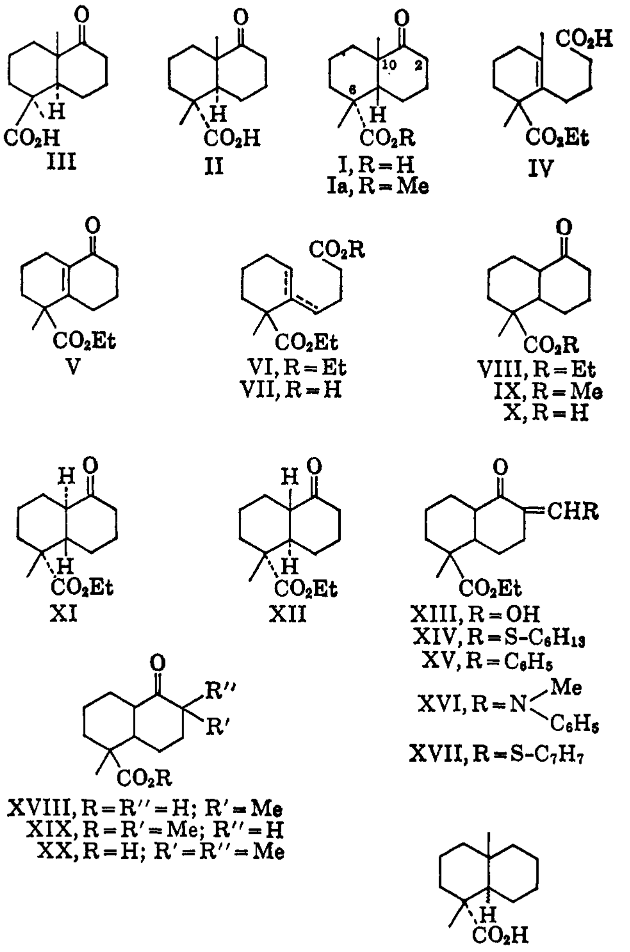
A synthesis of a stereoisomer of the bicyclic keto acid I is described, and this compound has been utilized for developing new syntheses for two isomers of methyl desisopropyldehydroabietate. A novel method for converting an A/B *cis* isomer to the corresponding A/B *trans* isomer of tricarbocyclic resin acids through treatment with palladium on charcoal at elevated temperature has been developed.

Several pathways for the synthesis of resin acids have been reported from this[3,4] and other laboratories.[5] While some investigators have constructed bicyclic intermediates with ring A and C bearing suitable substituents for the closure of ring B, others have constructed rings C and B at the start, leaving ring A to be built up in the latter stages of the synthesis. None of the methods reported so far have followed the sequence of constructing rings A, B, and C in that order. In addition, all reported syntheses have invariably utilized compounds with an aromatic ring which ultimately becomes ring C of the acids. No approach has been reported which utilizes a tricarbocyclic intermediate with a hydroaromatic ring C. After a short communication on our present work had been published,[1b] Spencer[6] reported the synthesis of methyl desisopropyldehydroabietate through the route just discussed.



Our immediate aim was to construct a bicyclic system with all the required structural details so that it would be possible to develop it into a tricarbocyclic system. Compounds II and III (Chart I) seemed to satisfy all these requirements. Having failed to achieve the cyclization of IV[7] which would ultimately have afforded II or III, attention was turned to the possibility of synthesizing V and introducing the angular methyl group at a later stage. Dehydration of the saturated hydroxy ester[8] corresponding to VI was effected with phosphorus pentoxide, potassium bisulfate being found unsatisfactory. This was partially hydrolyzed and afforded VII. Cyclization of VII with polyphosphoric acid[5a] proceeded smoothly furnish-

CHART I



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[1] (a) Paper V: M. Sharma, U. R. Ghatak, and P. C. Dutta, *Tetrahedron*, **19**, 985 (1963); (b) C. T. Mathew and P. C. Dutta, *Proc. Chem. Soc.*, 135 (1963); (c) C. T. Mathew, G. Sengupta, and P. C. Dutta, *ibid.*, 336 (1964).

[2] To whom all communications regarding this paper may be made.

[3] (a) U. R. Ghatak, D. K. Datta, and S. C. Ray, *J. Am. Chem. Soc.*, **82**, 1728 (1960); (b) N. N. Saha, B. K. Ganguly, and P. C. Dutta, *ibid.*, **81**, 3670 (1959).

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[5] (a) F. E. King, T. J. King, and T. G. Topliss, *Chem. Ind.* (London), 113 (1956); *J. Chem. Soc.*, 573 (1957); (b) B. K. Bhattacharyya, *J. Indian Chem. Soc.*, **22**, 165 (1945); (c) R. D. Haworth and B. P. Moore, *J. Chem. Soc.*, 633 (1946); (d) J. A. Barltrop and N. A. J. Rogers, *ibid.*, 2566 (1958); (e) E. Wenkert and A. Tahara, *J. Am. Chem. Soc.*, **82**, 3229 (1960); E. Wenkert, A. Afonso, T. B. Bredenberg, C. Kaneko, and A. Tahara, *ibid.*, **86**, 2038 (1964); (f) G. Stork and J. W. Schulenberg, *ibid.*, **84**, 284 (1962); (g) R. E. Ireland and R. C. Kierstead, *J. Org. Chem.*, **27**, 703 (1962); (h) S. N. Mahapatra and R. M. Dodson, *Chem. Ind.* (London), 253 (1963); (i) J. Barltrop and A. C. Day, *Tetrahedron*, **14**, 310 (1961).

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[8] W. E. Bachmann and A. S. Drieding, *J. Org. Chem.*, **13**, 317 (1948).

ing the keto ester V, after purification through the semicarbazone. The structure of V was confirmed by reduction with sodium borohydride. The resulting hydroxy ester was dehydrogenated with selenium and furnished a yellow picrate identical with that obtained from 1-methylnaphthalene. Attempts to introduce the angular methyl group in V according to Birch[9] or Jones[10] were unsuccessful. Conversion of V to the saturated keto ester VIII, and protection of the free α-methylene group followed by methylation of the protected keto ester was considered. Hydrogenation of V over palladium on charcoal readily afforded a saturated keto ester VIII as a crystalline solid, m.p. 67°; the corresponding acid X melted at 138°. This ester accounted for about 90% of the total product. The remaining oily fraction showed ultraviolet characteristics of the unsaturated ester V and it was not further investigated.

Thus the process of hydrogenation has taken place stereospecifically. It has been widely recognized that the role of substituents in deciding the stereochemical course of hydrogenation is important and rather decisive.[11] Perhaps the presence of the carbethoxyl group in V is important in this stereospecific reduction. With respect to the role of carbethoxyl groups in hydrogenation processes in octalin systems, opposite views have been put forth by Dauben[12a] and Mcquillin[12b] on one side and House, *et al.*,[12c] on the other. Augustine[12d] has stated that the steric course of hydrogenation is unpredictable. Chemical reduction of V with lithium and ammonia, subsequent hydrolysis to decarboxylate any unreduced V, and esterification of the acid fraction with diazomethane furnished the product IX, m.p. 84°; the corresponding acid X melted at 138°. The observation that chemical reduction[13] furnished the same product as catalytic hydrogenation sheds some light on the stereochemistry of the over-all reaction and suggests that the product has structure XI or XII. Presumably *cis* addition of hydrogen followed by epimerization at the angular carbon next to the carbonyl has occurred, ultimately leading to a *trans* ring junction. The product was later found to be XI, but, at this stage of our investigation, no definite conclusion could be reached in favor of either XI or XII. The greater resistance of VIII toward alkaline hydrolysis compared with that of the methylated product III (*vide infra*) is worthy of note, and suggests a 1,3-diaxial interaction. This would be due to a *cis* relationship between the angular hydrogen next to the carbonyl and the carbethoxyl function. This experiment tentatively supports the structure XI for the saturated keto ester.

The α-methylene group of VIII was protected with the *n*-hexylthiomethylene group.[14] The protected keto ester XIV was methylated using potassium *t*-butoxide and methyl iodide. The product was hydrolyzed to the corresponding acid, obtained as a crystalline solid, m.p. 141°, in a yield of about 30%. The structure of this acid was originally considered to be II, but is now known to be I. The original hypothesis that this acid has the structure II was based on the following evidence. Elemental analyses corresponded to a monomethylated acid, $C_{13}H_{20}O_3$. The methyl ester of this acid condensed readily with diethyl oxalate as well as with ethyl formate indicating that the new methyl is not at C-2. The n.m.r. spectrum[15] of the acid, m.p. 141°, showed two three-proton methyl singlets at τ 8.70 for C-6 methyl and 8.81 for C-10 methyl confirming the structure I or II but giving no indication of the stereochemistry of this acid.

It may be worthwhile to record here the experience gained during efforts to standardize the conditions for angular methylation of VIII with the help of different blocking groups. First the benzylidene derivative XV was prepared[16] and methylation was attempted with potassium *t*-butoxide and methyl iodide. The method was not pursued further owing to the difficulty involved in the removal of the benzylidene group. It appeared that the desired methylation product was formed in a very poor yield. Next, methylation[17] was attempted on the methylanilino derivative XVI. After removing the blocking group and hydrolyzing the product, an acid, m.p. 160°, was formed. This acid produced a methyl ester, m.p. 68°, and the yield was low. From elemental analysis and from the fact that it exhibited in the n.m.r. spectrum sharp three-proton doublets at τ 8.94 and 9.0, due to a methyl group attached to –CH–, in addition to the three-proton singlet at τ 8.71 arising from the methyl group at C-6, this acid was assigned the structure XVIII and the ester the structure XIX. When the whole of the acidic fraction from methylation of XVI and subsequent hydrolysis was esterified with diazomethane and chromatographed on neutral alumina, small amounts of the ester, m.p. 68°, along with another ester, m.p. 56°, were obtained. These two esters failed to condense with ethyl oxalate, indicating that they do not have a free methylene group next to the ketone, and hence possess the structure XIX. The ester, m.p. 68°, was prepared directly from VIII through monomethylation according to Kalvoda and Loeffel.[18] The structure of the other isomeric ester, m.p. 56°, obtained in very poor yield, is not clear. When the crude hexylthiomethylene derivative of XVII was methylated, two undesirable overmethylated acids could also be obtained, while under altered conditions the desired acid, m.p. 141°, was obtained in low yield. The two overmethylated acids, m.p. 174 and 119°, showed in the n.m.r. spectrum three sharp methyl singlets at τ 8.70, 8.82, and 8.91 and 8.69, 8.77, and 8.93, respectively. This evidence, along with the elementary analyses, revealed that these acids are probably stereoisomers of compound XX. The acid XX, m.p. 174°, was the only

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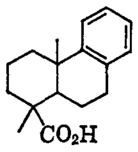
(15) N.m.r. spectra were taken in $CDCl_3$ solution in Varian A-60 spectrometer. We wish to thank the Instrument Division of Varian Associates, Palo Alto, Calif., and Professor L. M. Jackman, University of Melbourne, Australia, for determining these spectra.

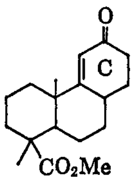
(16) W. S. Johnson, *J. Am. Chem. Soc.*, **65**, 1317 (1943).

(17) A. J. Birch and R. Robinson, *J. Chem. Soc.*, 501 (1944).

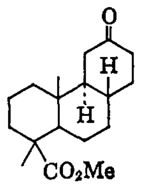
(18) J. Kalvoda and H. Loeffel, *Helv. Chim. Acta*, **40**, 2340 (1957).



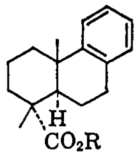
XXII



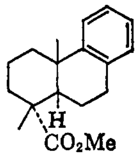
XXIII



XXIV



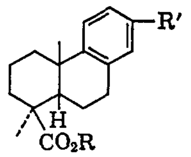
XXV, R = Me
XXVI, R = H



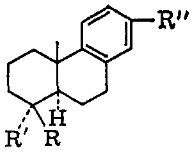
XXVII

product isolated after intensive methylation of VIII. Returning to the stereochemistry of the acid, I or II, the following conversions were carried out. On Wolff–Kishner reduction an acid, m.p. 132°, was obtained. A polymorphic form[1b] of this acid, m.p. 120°, had been synthesized in this laboratory[4b] and was assigned the stereochemistry shown in XXI, from its mode of formation. Doubt remained in the stereochemistry of the ring junction. Approach of the entering methyl, axial with respect to the carbonyl-bearing ring, is not only in conformity with the generalization of Johnson,[19] but also eliminates the 1,3-diaxial interaction arising from the *gem*-methylcarboxyl group. Therefore a *cis* ring junction has probably been generated in this reaction. This is supported by the fact that only one acid was isolated in this methylation step. To establish the complete stereochemistry of the acid I or II, its conversion into one of the stereoisomers of the tricarbocyclic acid XXII, all four of which have already been synthesized in this laboratory,[3a,b] was contemplated. The methyl ester Ia was converted to the Mannich base and this, as its methiodide, was condensed with ethyl acetoacetate in the presence of sodium ethoxide to afford XXIII as a crystalline solid. Hydrogenation as well as chemical reduction of XXIII gave rise to the same saturated ketone, m.p. 140°. This has been assigned the structure XXIV. Among other attempts which turned out to be unsuccessful in an effort to make XXIII, mention may be made of the attempts to condense with β-chloroethyl methyl ketone under varied conditions. Sondheimer[20] and Wenkert[21] have reported the failure of methyl vinyl ketone to condense with analogous systems. While Sondheimer succeeded in achieving this end with 1-iodo-3-chloro-but-2-ene according to Prelog,[22] this method failed in our hands. Efforts to aromatize ring C of XXIII were then launched. The hydroxy compound produced by reduction with sodium borohydride afforded methyl desisopropyldehydroabietate XXV on heating with palladium on charcoal. However, the compound was obtained in poor yield. The latter was characterized through its ultraviolet absorption[23] spectrum and mixture melting point determination with an authentic sample.[24] It was converted to the acid XXVI, which in turn was compared with authentic sample.[3a] The immediate conclusion was that the acid, m.p. 141°, possessed the stereochemistry shown in II. Another attempt to bring about aromatization through dehydration of the hydroxy compound with potassium bisulfate followed by bromination with N-bromosuccinimide and dehydrobromination with collidine did not succeed.

With the publication[1b] of our findings, Professor T. A. Spencer informed us of his results (*vide infra*) in a private communication. To reconcile these two contradictory views, it became necessary to avoid the high temperature dehydrogenation step using palladium on charcoal. For partial aromatization, XXIII was converted to the enol acetate by treatment with acetic anhydride, acetyl chloride, and pyridine.[25] Bromination of the acetate with N-bromosuccinimide in carbon tetrachloride in the presence of fused potassium carbonate[26] and dehydrobromination with collidine afforded a glassy solid. On mild alkaline hydrolysis this afforded the corresponding phenol. Removal of the phenolic hydroxyl group was carried out by treatment with diethyl phosphite followed by lithium and ammonia.[27] On evaporative distillation of the product, XXVII was obtained as a white crystalline solid, m.p. 89–90°; its identity was established through mixture melting point determination with an authentic sample of methyl desisopropyldehydro-*cis*-abietate, m.p. 89–90°, synthesized earlier in this laboratory.[3b] Consequently, the previous concept of stereochemistry of the acid I or II had to be revised. The sequence of reactions employed for aromatization obviously did not involve any process which would bring about isomerization, and this meant that, in the earlier palladium on charcoal treatment, isomerization of XXV to XXVII had occurred. Spencer has communicated[6a] the synthesis of a keto acid, m.p. 184°, isomeric with our acid, m.p. 141°, and to which he has assigned the stereoformula II. This assignment was further confirmed through the conversion of II to XXV.



XXVIII, R = Me; R′ = H
XXX, R = Me; R′ = *i*-Pr
XXXII, R = R′ = H
XXXIII, R = H; R′ = *i*-Pr



XXIX, R = CO₂Me; R′ = Me; R″ = H
XXXI, R = CO₂Me; R′ = Me; R″ = *i*-Pr
XXXIV, R = Me, R′ = CN; R″ = *i*-Pr

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(19) W. S. Johnson, D. S. Allen, Jr., R. B. Hindersinn, G. N. Sansen, and R. Pappo, *J. Am. Chem. Soc.*, **84**, 2181 (1962).

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(23) E. Wenkert and B. G. Jackson, *J. Am. Chem. Soc.*, **80**, 211 (1958).

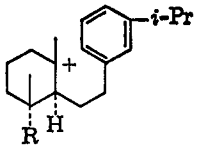
(24) Professor Wenkert of Indiana University and Dr. Barltrop of Oxford University carried out mixture melting point determinations with their authentic samples of methyl desisopropyldehydroabietate.

(25) L. Velluz, B. Goffinet, J. Wornant, and G. Amiard, *Bull. soc. chim. France*, 1289 (1957).

(26) R. E. Corbett and R. N. Speden, *J. Chem. Soc.*, 3711 (1958).

(27) G. W. Kenner and N. R. Williams, *ibid.*, 522 (1955).

That heating with palladium on charcoal brings about isomerization of an A/B *cis* system to an A/B *trans* system in tricarbocyclic resin acid esters, epimerization having occurred at the ring junction next to the carboxyl function, is a novel observation. This was further verified in the following cases. The *cis* ester XXVIII,[3a] m.p. 85-86°, was heated with palladium on charcoal as above. The product was separated into acidic and neutral fractions through hydrolysis with 1-butanolic potassium hydroxide. The neutral fraction melted at 131–132°, alone or with an authentic sample of XXIX,[3a] and accounted for about 60% of the starting material. The acidic fraction melted at 206° after purification through crystallization and this showed no depression in mixture melting point with an authentic sample of XXXII.[3a] The presence or absence of any other isomeric acid could not be established at this stage. Similarly, XXX[1a] could be isomerized to XXXI in about 60–65% yield under identical conditions. However, when the *trans* compound XXXIV was treated under identical conditions, no isomerization was observed, indicating that the *trans* systems are stable under such conditions. This confirms the observations of Spencer.[6a] Similar studies with *cis*-decalin derivatives have also been carried out, and isomerization has also been observed to occur in such systems.[4b,28] Wenkert[23,29] and Ohta[30] independently observed that treatment of tricyclic systems belonging to the *trans*-abietic acid series with anhydrous aluminum chloride brings about isomerization at the ring junction. The main point of difference between these two cases and the present one is that in the former the site of isomerization is the carbon carrying the angular methyl, whereas in the latter case it involves the hydrogen β to the ester function. The mechanism proposed for the aluminum chloride induced conversion is of an ionic type with cleavage and recyclization of the carbonium ion XXXV leading to two isomers in different proportions.[29] Such a mechanism does not seem to be plausible here.



XXXV

The question as to whether this type of isomerization proceeds as a result of homolytic cleavage and subsequent recyclization in a fashion similar to the ionic cleavage above or sequential dehydrogenation–hydrogenation processes[31] on the surface of the catalyst is under investigation. It may be interesting to mention here that the 10-methyloctahydrophenanthrenes with an A/B *cis* junction appear to be stable[32] under equilibrating conditions.

Returning to the acid, m.p. 141°, it has now become certain that this acid possesses the stereochemistry shown in I and that Spencer's acid, m.p. 184°, is rightly represented as II. In retrospect, we are able to assign rather firmly the stereoformula XI for the hydrogenation product VIII, m.p. 67°, addition of hydrogen having occurred from the side opposite to the carbethoxyl function in conformity with the views of Dauben[12a] and Mcquillin.[12b] This has also finally confirmed the *cis* stereochemistry[33] of the acid XXI.

Experimental[34]

Ethyl γ-(6-Methyl-6-carbethoxycyclohexene)butyrate (VI).—Ethyl 2-methylcyclohexanone-2-carboxylate (40 g.), ethyl γ-bromocrotonate (112 g.), and zinc wool (70 g.) were allowed to react in ether (100 ml.) and benzene (100 ml.), furnishing the unsaturated hydroxy ester (45 g.). The product was hydrogenated in ethanol in the presence of palladium on charcoal (500 mg., 10%). The saturated hydroxy ester (45 g.) dissolved in dry benzene (300 ml.) was mixed with phosphorus pentoxide (41 g.) and the mixture was heated under reflux over a water bath for 3 hr. with vigorous shaking. The dark brown mass was cooled, and the benzene layer was decanted. The solid residue was decomposed carefully with crushed ice, and the aqueous portion was extracted repeatedly with ether. The ethereal extract, mixed with benzene solution, was washed with 5% sodium carbonate solution and then with water. The solvents were distilled off and the residue was distilled at 160° (0.8 mm.) to afford a colorless liquid (40 g.).

Anal. Calcd. for $C_{16}H_{26}O_4$: C, 68.0; H 9.2. Found: C, 67.6; H, 9.1.

6-Methyl-6-carbethoxy-$\Delta^{5,10}$-octalone (V).—The unsaturated diester VI (40 g.) was partially hydrolyzed by refluxing with 1% aqueous ethanolic potassium hydroxide solution (800 ml.) for 5 hr. The acidic part was separated by extraction with ether from a small quantity of neutral fraction and was obtained as a yellowish viscous mass (29 g.), b.p. 185–190° (0.6 mm.).

Polyphosphoric acid from phosphorous pentoxide (70 g.) and sirupy phosphoric acid (45 ml.) was kept heated on a water bath and stirred vigorously, and the crude half ester VII (25 g.) was added all at once. Heating and stirring were continued for 1 hr. The reaction was cooled and diluted with cold water and the product was extracted with ether. The ethereal solution was washed with 5% sodium carbonate solution and then with water. After drying over sodium sulfate, the ether was distilled off and the brownish residue thus obtained weighed 16 g. The crude ketonic product (16 g.) was mixed with semicarbazide hydrochloride (26 g.), pyridine (33 ml.), and alcohol (300 ml.) and heated under reflux over a water bath for 2 hr. It was then poured into a large quantity of cold water and left overnight in the cold. The next day, the semicarbazone was collected by filtration and washed with petroleum ether (b.p. 40–60°) in order to remove any oily organic material, and the product was dried. The semicarbazone (20 g.) was mixed with a 10% aqueous solution of oxalic acid (200 ml.) and heated under reflux for 3 hr., whereupon the solid went into solution producing a brownish oil. It was cooled and thoroughly extracted with ether. The organic layer was washed with 5% sodium carbonate solution followed by water and then dried over sodium sulfate. The residue left on removing ether was distilled at 160° (7 mm.) to furnish V as a colorless mobile liquid (10.5 g.): $\lambda_{\max}^{\text{alc}}$ 245 mμ (log ε 4.1); $\nu_{\max}^{\text{CHCl}_3}$ 1720 (s), 1660 (m), and 1630 (m) cm.$^{-1}$.

Anal. Calcd. for $C_{14}H_{20}O_3$: C, 71.1; H, 8.5. Found: C, 70.8; H, 8.3.

The **semicarbazone**, on crystallization from ethanol, melted at 194–195°.

Anal. Calcd. for $C_{15}H_{23}N_3O_3$: C, 61.4; H, 7.9; N, 14.3. Found: C, 61.5; H, 8.0; N, 14.0.

The **2,4-dinitrophenylhydrazone**, crystallized from ethyl acetate, melted at 177°.

Anal. Calcd. for $C_{20}H_{24}N_4O_6$: C, 57.6; H, 5.8. Found: C, 57.7; H, 5.8.

The unsaturated ketone V (0.4 g.) dissolved in methanol (10 ml.) containing 1 drop of water was treated with sodium borohydride (0.1 g.) and left overnight. The next day it was de-

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(28) A. Ross, P. A. S. Smith, and A. S. Dreiding, *J. Org. Chem.*, **20**, 905 (1955).

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(32) *Cf.* ref. 3b, footnote 6c, p. 3671.

(33) The forthcoming communication in this series.

(34) Microanalyses were performed by Mrs. Chhabi Dutta. Melting points and boiling points are uncorrected. Merck acid-washed alumina was used for chromatography.

composed in the cold with dilute hydrochloric acid and worked up as usual. The crude alcohol (0.4 g.) was mixed with selenium (0.5 g.) and heated for 6 hr. at 300° in a metal bath. The product finally afforded an orange-yellow picrate. This was crystallized from ethanol, m.p. and m.m.p. 140–141° with an authentic sample of 1-methylnaphthalene picrate.

6-Methyl-6-carbethoxydecalone (VIII). A.—The unsaturated keto ester V (30 g.) in acetic acid (50 ml.) was mixed with palladium on charcoal (500 mg., 10%) and stirred in hydrogen. The uptake of hydrogen was complete within 8 hr. The catalyst was removed by filtration, and the filtrate was neutralized with saturated sodium bicarbonate solution. The product was taken up in ether. On distilling at 160–165° (8 mm.) the product immediately solidified. It was crystallized from petroleum ether: m.p. 67° (27 g.), $\nu_{\max}^{\mathrm{CHCl_3}}$ 1720 (s) and 1702 (s) cm.$^{-1}$.

Anal. Calcd. for $C_{14}H_{22}O_3$: C, 70.5; H, 9.3. Found: C, 70.7; H, 9.4.

The yellow **2,4-dinitrophenylhydrazone** of the corresponding methyl ester IX (diazomethane) was crystallized from ethanol–ethyl acetate, m.p. 186–187°.

Anal. Calcd. for $C_{19}H_{24}N_4O_6$: C, 56.4; H, 6.0. Found: C, 56.4; H, 6.1.

6-Methyl-6-carboxydecalone (X).—The crystalline ester (1 g.) was mixed with an aqueous methanolic solution of potassium hydroxide (10 ml., 5%) and refluxed for 4 hr. It was cooled, acidified with cold dilute hydrochloric acid solution (6 *N*), and extracted with ether. The acidic fraction was separated from the ethereal solution by washing with sodium bicarbonate solution (5%), acidifying the washing, and extracting again with ether. On evaporation of the solvent, a yellowish solid was obtained, which, when crystallized from ethyl acetate–petroleum ether, melted at 138–139° (220 mg.). The neutral fraction was worked up as usual and on removal of ether and distillation of the residue afforded a colorless liquid, which solidified on purification through distillation and melted at 67°. This was found to be identical with the starting material.

Anal. Calcd. for $C_{12}H_{18}O_3$: C, 68.5; H, 8.6. Found: C, 68.3; H 8.6.

B.—In a 2-l. three-necked flask fitted with a stirrer was collected liquid ammonia (1500 ml.). The unsaturated keto ester V (8 g.) dissolved in dry ether (50 ml.) and anhydrous tetrahydrofuran (50 ml.) was added with stirring. Lithium (2 g.) was added in small pieces at intervals with continuous stirring. The color changed to dark blue. After addition was complete, the mixture was stirred until the ammonia evaporated off. It was then diluted with cold water (200 ml.) and extracted with ether. After washing with water, the extract was dried over sodium sulfate and the solvents were removed. The residue was distilled at 155–165° (5 mm.) to afford a colorless oily liquid (5.7 g.). The redistilled product (4.7 g.) was dissolved in pure acetone (100 ml.) in a three-necked flask and to this was added with stirring Jones reagent (15 ml.) until the orange color persisted for about 20 min. It was then diluted with water and extracted with ether. After washing with water, the extract was dried over sodium sulfate and the solvent was distilled off. The residue was distilled at 155–160° (4 mm.) giving 3.9 g. This was hydrolyzed with 15% ethanolic potassium hydroxide solution (35 ml.) for 30 hr. and worked up as usual. The acidic part was esterified with diazomethane and a colorless liquid (2.7 g.), b.p. 150° (5 mm.), was obtained.

The methyl ester readily afforded a yellow 2,4-dinitrophenylhydrazone, m.p. 186–187° alone or mixed with the sample prepared in part A.

6,10-Dimethyl-*cis*-decalone-6-carboxylic Acid (I).—Dry sodium ethoxide was prepared from sodium dust (4.8 g.) suspended in benzene (200 ml.) and anhydrous ethanol (17 ml.) and this was suspended in benzene (200 ml.) and kept cooled in an ice bath under nitrogen. A mixture of VIII (25 g.) and pure ethyl formate (22 ml.) was slowly dropped in with shaking, and the whole was left overnight. The semisolid mass was then decomposed with crushed ice, the benzene layer was separated and washed with ice-cold 5% sodium hydroxide solution, and the washing was mixed with the aqueous part. The aqueous mixture was carefully acidified with cold dilute hydrochloric acid (1:1), saturated with sodium chloride, and extracted with ether. The extract was washed with water and dried over sodium sulfate. On removal of ether, **6-methyl-6-carbethoxy-2-hydroxymethylene-decalone** (XIII, 23 g.) was obtained as a light brown viscous material which gave a deep violet coloration with alcoholic ferric chloride solution. XIII (20 g.) was mixed with *n*-hexyl thioalcohol (10.5 g.), dry benzene (150 ml.), and *p*-toluenesulfonic acid (0.1 g.) and heated under reflux in a flask fitted with a Dean-Stark water separator. After 6 hr. water ceased to separate; the mixture was cooled and the product was washed with saturated sodium bicarbonate solution and then with water. On removing benzene under reduced pressure, a brown viscous residue was obtained (16.5 g.), b.p. 220–230° (0.8 mm.). In subsequent operations the crude residue was heated at 180° (8 mm.) for 1 hr. with the flask completely immersed in the oil bath in order to remove all low-boiling materials and this was directly used for methylation.

Potassium *t*-butoxide from potassium (18 g.) in *t*-butyl alcohol (400 ml.) was cooled in ice under nitrogen and the crude thio compound XIV (25 g.) dissolved in *t*-butyl alcohol (25 ml.) was added with stirring. After 10 min. the whole mixture turned brown and viscous, and with further cooling and vigorous stirring methyl iodide (90 ml.) was added. After 15 min. the ice bath was removed and stirring was continued at room temperature for a further 2 hr. Finally, it was heated under reflux over a water bath for 2 hr. *t*-Butyl alcohol was then distilled off under reduced pressure and the residue was diluted and extracted with ether. The residue, after removal of ether, was dried at the pump and the process of methylation was repeated once more with the product (25 g.) in the same manner. The crude product (25 g.) was mixed with a solution of potassium hydroxide (20 g.) in water (20 ml.) and diethylene glycol (130 ml.) and heated under reflux under nitrogen for 12 hr. After cooling, it was acidified with cold hydrochloric acid (1:1), the product was taken up in ether, and the ethereal solution was washed with 5% sodium carbonate solution until the washings were colorless. The alkaline washings were acidified with cold hydrochloric acid (1:1) and worked up as above. On removal of ether the residue solidified, and this on crystallization from ethyl acetate afforded I (6.5 g.), m.p. 141°.

Anal. Calcd. for $C_{13}H_{20}O_3$: C, 69.6; H, 8.9. Found: C, 69.5; H, 9.1.

Methyl 6,10-Dimethyl-*cis*-decalone-6-carboxylate (Ia).—An ethereal solution of diazomethane prepared from nitrosomethylurea (7 g.) and dried over potassium hydroxide pellets was added to the keto acid (6 g.) in ether (150 ml.) cooled in ice bath. The solution was then worked up and distilled at 160° (6–7 mm.), affording 6 g. of a colorless liquid.

Anal. Calcd. for $C_{14}H_{22}O_3$: C, 70.5; H, 9.3. Found: C, 69.9; H, 9.4.

The **2,4-dinitrophenylhydrazone** was crystallized from ethyl acetate–ethanol, m.p. 161°.

Anal. Calcd for $C_{20}H_{26}N_4O_6$: C, 57.4; H, 6.2. Found: C, 57.1; H, 6.1.

The liquid methyl ester (200 mg.) was refluxed with an aqueous–methanolic potassium hydroxide solution (4 ml., 5%) for 4 hr. This was worked up as usual and, from sodium bicarbonate washings, a crystalline solid (160 mg.) was isolated which, on one crystallization from ethyl acetate, melted at 141°, alone or mixed with the sample described before. From the neutral ethereal solution, no residue was left on removal of the solvent.

2,6-Dimethyl-*cis*-decalone-6-carboxylic Acid (XVIII).—The hydroxymethylene compound XIII from the keto ester VIII (2 g.) was dissolved in dry pyridine (30 ml.). With cooling in ice, pure acetic anhydride (90 ml.) was added slowly with shaking and the solution was left aside for 24 hr. The mixture was next treated with crushed ice, saturated with sodium chloride, and extracted with ether. The ethereal extract was washed successively with sodium bicarbonate solution, water, dilute hydrochloric acid solution, and again with water. After drying with sodium sulfate, ether was distilled off, and the residue on distillation furnished a colorless liquid (1.1 g.), b.p. 185–190° (0.6 mm.).

The enol acetate (1.1 g.) was dissolved in acetic acid (25 ml.), mixed with palladium on charcoal (400 mg., 10%), and stirred in an atmosphere of hydrogen. After 1 hr., when the hydrogen uptake was complete, the catalyst was filtered off and the filtrate was neutralized with sodium bicarbonate solution and extracted with ether. On removal of the solvent and on distillation, the residue afforded 700 mg. of a colorless liquid, b.p. 150–155° (3 mm.). The keto ester (700 mg.) was mixed with a solution of potassium hydroxide (500 mg.) dissolved in water (0.5 ml.) and diethylene glycol (6.5 ml.) and the solution was refluxed under nitrogen for 12 hr., cooled, diluted, acidified with hydrochloric acid (1:1), and extracted with ether. The ethereal extract was washed with sodium carbonate solution. From alkaline washing after acidifications and extractions with ether, a solid, m.p. 160° (400 mg.), was obtained. This was crystallized from ethyl acetate.

Anal. Calcd. for $C_{13}H_{20}O_3$: C, 69.6; H, 9.0. Found: C, 69.4; H, 8.9.

The methyl ester XIX (diazomethane) was crystallized from petroleum ether, m.p. 68°.

Anal. Calcd. for $C_{14}H_{22}O_3$: C, 70.5; H, 9.3. Found: C, 70.2; H, 9.2.

2,2,6-Trimethyl-*cis*-decalone-6-carboxylic Acid (XX).—Potassium (3 g.) was dissolved in *t*-butyl alcohol (70 ml.) and the solution was cooled in an ice bath under nitrogen. A solution of the keto ester VIII (5 g.) in *t*-butyl alcohol (10 ml.) was added with stirring. After 10 min. and with further cooling in ice, methyl iodide (15 ml.) was added and the solution was stirred vigorously for another 10 min. Ice was removed and the stirring was continued for 2 hr. at room temperature and then with heating under reflux for another 2 hr. The mixture was cooled, butanol was removed under reduced pressure, and the residue was diluted with water and extracted with ether. The ethereal solution was washed with water and dried over sodium sulfate. On removing the ether, a brownish residue was obtained. This was dried under vacuum and remethylated twice more under the same conditions. The crude product (5 g.) was heated under reflux with an aqueous methanolic potassium hydroxide solution (30 ml., 10%) for 4 hr. under nitrogen. On working up in the usual way, a solid acid was obtained which was crystallized from ethyl acetate, m.p. 174°. The neutral part (2 g.) was further heated under reflux with aqueous 1-butanol–potassium hydroxide solution (10 ml., 10%) under nitrogen, and a further quantity of the acid was obtained; yield 1.6 g.

Anal. Calcd. for $C_{14}H_{22}O_3$: C, 70.5; H, 9.3. Found: C, 70.5; H, 9.2.

4,10-Dimethyl-4-carbomethoxy-12-keto-1,2,3,4,5,6,7,8,10,12,13,14-dodecahydrophenanthrene (XXIII).—Methyl 6,10-dimethyldecalone-6-carboxylate (6 g.) was mixed with diethylamine hydrochloride (3 g.) and paraformaldehyde (1.2 g.) in ethanol (10 ml.). The mixture was heated on a water bath for 5 hr. and cooled. On dilution with water, it was extracted with ether to remove neutral materials. The ice-cold aqueous solution was made basic with solid potassium carbonate, whereupon the free base separated at the top. On extracting it with ether, it was washed once with a cold saturated solution of sodium chloride. After drying over anhydrous potassium carbonate, ether was distilled off. The light brown viscous residue having a characteristic pungent odour weighed 6 g. A solution of the Mannich base (6 g.) in dry ether (15 ml.) was cooled to 0°. To this was added dropwise with shaking a solution of methyl iodide (5 ml.) in dry ether (15 ml.). After the addition was complete, it was shaken for a few minutes more in the cold and left overnight. The next day ether and the excess of methyl iodide were removed under reduced pressure. Dry ether (10 ml.) was added and removed similarly. Finally it was thoroughly dried under vacuum at room temperature, furnishing the methiodide as white powder; yield 8.5 g. Freshly distilled ethyl acetoacetate (6 ml.) was mixed with the methiodide and stirred under nitrogen with cooling in ice. After 5 min. it was treated with a solution of sodium ethoxide from sodium (0.6 g.) in ethanol (12 ml.) added dropwise and with shaking, and after a further 10 min. it was refluxed for 6 hr. over a water bath under nitrogen. The alcohol was distilled off under reduced pressure, and the residue was diluted with water and extracted with ether. The ethereal solution, after washing with water, was dried over sodium sulfate. On removal of ether, a very viscous yellowish brown residue was obtained (7.5 g.). This was distilled and two fractions were collected.

Fraction i, b.p. up to 120° (3–4 mm.), 3 g., consisted mainly of unreacted ethyl acetoacetate as an identifiable product.

Fraction ii, b.p. 130–170° (0.2 mm.), 4.5 g., readily solidified and, on crystallization from ethyl acetate–petroleum ether furnished 3.2 g. of the tricyclic unsaturated keto ester, m.p. 101°, $\lambda_{\max}^{\text{alc}}$ 241 mμ (log ε 4.3), $\nu_{\max}^{\text{CHCl}_3}$ 1723 (s) and 1658 (s) cm.$^{-1}$.

Anal. Calcd. for $C_{18}H_{26}O_3$: C, 74.4; H, 9.0. Found: C, 74.1; H, 9.1.

It afforded readily a red **2,4-dinitrophenylhydrazone**, which was crystallized from ethyl acetate, m.p. 209°.

Anal. Calcd. for $C_{24}H_{30}N_4O_6$: C, 61.2; H, 6.4. Found: C, 60.7; H, 6.3.

Methyl Desisopropyldehydroabietate (XXV).—The keto ester (1 g.) was dissolved in methanol (15 ml.) and 1 drop of water was added. To this cooled solution was added an excess of sodium borohydride (600 mg.) in small portions with shaking after each addition. After addition was complete, it was left overnight. The next day, it was cooled in ice and decomposed with cold hydrochloric acid (1:1). The product was extracted with ether and the ethereal extract was washed with water and dried. The hydroxy ester was obtained as an almost colorless, highly viscous residue (1 g.). In a hard glass dehydrogenation flask fitted with a long tube was put a mixture of the above hydroxy ester (300 mg.) and palladium on charcoal (300 mg., 10%) and the mixture was heated in a metal bath at 235–240° for 1 hr. under nitrogen. During heating water droplets were seen at the neck of the flask. After cooling, the residue was triturated with benzene and transferred to a small column of neutral alumina (5 g.). It was next eluted with benzene (total 150 ml.). On evaporation of the solvent, an oily material remained, which soon solidified to afford crystals melting at 80–85°. By repeated crystallization from petroleum ether the melting point of the solid was raised to 100–106°. It was next sublimed at 120–130° (5 mm.), and the melting point rose to 107–109°. Finally it was recrystallized from methanol repeatedly to furnish thin flakes (60 mg.), m.p. 112–113°, $\lambda_{\max}^{\text{alc}}$ 260 mμ (log ε 2.64) and 266 mμ (log ε 2.74).

Anal. Calcd. for $C_{18}H_{24}O_2$: C, 79.3; H, 8.9. Found: C, 79.4; H, 9.0.

The mixture melting point with the sample (m.p. 114–115°) kindly supplied by Dr. Barltrop was 113–114° and with another sample (m.p. 110–112°) from Professor Wenkert was 110–112°.

Desisopropyldehydroabietic Acid (XXVI).—The above methyl ester (40 mg.) was mixed with an aqueous 1-butanolic solution of potassium hydroxide (2 ml., 10%) and refluxed for 9 hr. under nitrogen. This was cooled, acidified with cold hydrochloric acid (1:1), and then subjected to steam distillation to remove butanol as much as possible. The aqueous residue was cooled and extracted with ether. The ethereal extract was washed with sodium carbonate solution (5%), followed by water, and finally dried over sodium sulfate. On removing the ether, practically no residue was obtained. The sodium carbonate washings were carefully acidified with cold hydrochloric acid (1:1) and thoroughly extracted with ether. The ethereal solution was washed with water and dried. When ether was distilled off, a white solid was obtained. This was sublimed at 120–140° (0.4 mm.) to afford shining white flakes (20 mg.), m.p. 174°.

The mixture melting point with an authentic sample of desisopropyldehydroabietic acid (m.p. 174–175°) from this laboratory was 174°.

Methyl Desisopropyl-*cis*-dehydroabietate (XXVII).—The keto-ester XXIII (1.4 g.), dissolved in acetic anhydride (25 ml.), was mixed with pyridine (1 ml.) and, with cooling and shaking, acetyl chloride (10 ml.) was slowly added. When the addition was complete, the mixture was heated over a water bath under nitrogen for 2.5 hr. Low-boiling material was distilled off under reduced pressure, and the residue was distilled at 170–180° (bath temperature) (0.4 mm.) to furnish the colorless, highly viscous enol acetate (1.2 g.), $\lambda_{\max}^{\text{alc}}$ 268 mμ (log ε 3.8). The enol acetate (1.2 g.), without further purification, was dissolved in carbon tetrachloride (25 ml.) and mixed with N-bromosuccinimide (1.5 g.), fused potassium carbonate (600 mg.), and a crystal of benzoyl peroxide and heated under reflux over an electric lamp for 3 hr. The mixture was cooled thoroughly and the solid was separated by filtration. The filtrate on evaporation furnished a brown solid (1.5 g.), which readily responded to the test for halogen. The crude bromo compound (1.5 g.) was mixed with collidine (15 ml.) and heated at 180–185° in a preheated oil bath under nitrogen for 30 min. On working up in the usual manner and evaporatively distilling the product at 140–160° (bath temperature) and 0.5 mm., the phenol acetate was obtained as a glassy solid (700 mg.). The acetate (700 mg.) was mixed with potassium hydroxide (300 mg.) in water (0.3 ml.) and methanol (30 ml.) and left overnight. The next day the solution was heated under reflux for 1 hr. and then worked up. The product was obtained as a deep brown solid (450 mg.). A mixture of the crude phenolic ester (450 mg.), anhydrous tetrahydrofuran (4 ml.), carbon tetrachloride (20 ml.), diethyl phosphite (1.2 ml.), and freshly distilled triethylamine (1.3 ml.) was heated under reflux for 6 hr. After cooling, the mixture was washed with 5% hydrochloric acid solution followed by 5% sodium hydroxide solution and water. It was then dried over sodium sulfate and the solvents were removed, whereupon a brown solid (800 mg.) was obtained. The crude diethyl phosphate derivative (800 mg.) in anhydrous tetrahydrofuran (10 ml.) was added to liquid ammonia (100 ml.). Lithium wire (500 mg.) was added in small pieces with stirring. When the metal had dissolved completely, ammonium chloride (1 g.) was added and the mixture was stirred until the ammonia had evaporated. The residue was dissolved in a mixture of chloroform and 5% hydrochloric acid solution. After separating the chloroform layer the aqueous part was again extracted with chloroform and the chloroform solution was washed with 5% sodium hydroxide solution. On removing chloroform, a light brown residue was obtained, and this, on evaporative distillation at 150–170° (bath temperature) and 8 mm., afforded a white crystalline solid, m.p. 83–84°. After crystallization once from petroleum ether, it melted at 89–90°, alone or mixed with an authentic sample of XXVII.

Isomerization of Methyl Desoxy-*cis*-podocarpate (XXVIII) with Palladium on Charcoal.—The methyl ester XXVIII (80 mg.) was mixed with palladium on charcoal (80 mg., 10%) in a dehydrogenation tube and heated under nitrogen in a metal bath (preheated to 235°). The temperature was maintained in the range of 235–240° for 1 hr., the tube was then cooled to room temperature, and the mixture was triturated with benzene (10 ml.). It was then poured onto a small column of neutral alumina (3 g.) and washed down with benzene (400 ml.). From the eluate benzene was distilled off under reduced pressure and the product was obtained as a colorless oil. On dissolution in methanol, crystals slowly separated, m.p. 118–120°.

The solid (75 mg.) was mixed with a solution of potassium hydroxide (200 mg.) in water (0.2 ml.) and 1-butanol (2 ml.) and heated under reflux for 10 hr. under nitrogen. It was cooled, diluted with water, and extracted with chloroform. The chloroform solution was washed with water and the solvent was then distilled off. The residue furnished crystals from methanol, m.p. 131–132° (50 mg.). The mixture melting point with an authentic sample of XXIX (m.p. 131–132°) showed no depression. The aqueous alkaline solution from hydrolysis was acidified with dilute hydrochloric acid and extracted with chloroform. The organic extract was washed with water and chloroform was distilled off. The residue was crystallized several times from methanol and this furnished the acid XXXII, m.p. 206°, alone or mixed with an authentic sample.

Isomerization of Methyl 7-Isopropyldesoxy-*cis*-podocarpate (XXX).—The *cis* ester XXX (60 mg.), mixed with palladium on charcoal (60 mg., 10%) was heated under exactly the same conditions as before. The product was separated from the catalyst as above, and the colorless oily product slowly afforded crystals, m.p. 76–78°. The whole product was hydrolyzed with 10% aqueous 1-butanolic potassium hydroxide solution as above and the acidic and neutral fractions were separately isolated through extraction with chloroform. The neutral part, on crystallization from methanol, afforded the *trans* ester XXXI (40 mg.) and this melted at 98–99° alone or mixed with an authentic sample (m.p. 98–99°). The acidic fraction furnished crystals (10 mg.), m.p. 155°, and this was found to be identical with XXXIII, through a mixture melting point determination with an authentic sample (m.p. 155°).

Treatment of Dehydroabietonitrile (XXXIV) with Palladium on Charcoal.—Dehydroabietonitrile (1 g.) was mixed with palladium on charcoal (1 g., 10%) and heated in a metal bath at 235–240° as before. The product, when eluted through alumina (5 g.) with benzene, crystallized readily, m.p. 84°. This was crystallized once from petroleum ether and the melting point rose to 88° and exhibited no depression in melting point with the starting material, m.p. 88°.

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Fused Organic Salts. III.[1a] Chemical Stability of Molten Tetra-*n*-alkylammonium Salts. Medium Effects on Thermal $R_4N^+X^-$ Decomposition. $RBr + I^- = RI + Br^-$ Equilibrium Constant in Fused Salt Medium

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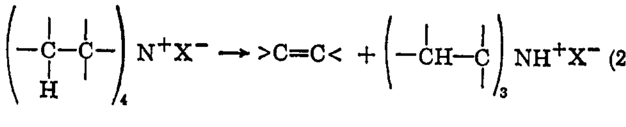
A selected set of low-melting tetra-*n*-alkylammonium salts, Q^+X^- (X = Br, I, SCN, NO_3, picrate, ClO_4), were shown to be stable during short periods at temperatures just above their freezing points (50–100°), thus demonstrating the feasibility of making meaningful physical measurements in such melts. At 140° four of the salts (X = Br, I, SCN, NO_3) decomposed to $RX + R_3N$ and/or olefin + $R_3NH^+X^-$ to varying degrees. The olefin appears to arise from secondary reaction of R_3N and RX. Relative reactivities in the reverse Menschutkin decomposition in a variety of media are compared with the fused salt results and all of the available information is re-evaluated in terms of recent studies of medium effects on anion nucleophilicities. The equilibrium constant for the reaction, $Q^+I^- + n\text{-HexBr} = Q^+Br^- + n\text{-HexI}$, in molten tri-*n*-hexyl-*n*-heptylammonium iodide-bromide ($X_{I^-} \sim 0.97$) was found to be 0.029.

Part IV of this series[1c] describes a collection of low-melting quaternary ammonium salts and provides information on phase relations in binary salt–salt and salt–organic nonelectrolyte systems. Another property of fundamental importance which governs the utility of these melts is their chemical stability. This report describes measurements on the chemical stability of fused quaternary ammonium salts, Q^+X^-, containing six common anions. The results help to define the temperature ranges available to decomposition-free experimentation in melts of these materials, and also provide useful information on the chemical reactions involved and some characteristics of the fused salt medium. Closely related to the Q^+X^- decomposition reactions are equilibria of the type $RX' + Q^+X^- \rightleftharpoons RX + Q^+X'^-$; measurements of the equilibrium constant for one such system are included in the present report.

Fused Salt Decomposition Products.—Two modes of thermal quaternary ammonium salt decomposition are

$$R_4N^+X^- \longrightarrow RX + R_3N \qquad (1)$$



$$\left(\begin{matrix} | & | \\ -C- & C- \\ | & | \\ H & \end{matrix}\right)_4 N^+X^- \longrightarrow {>}C{=}C{<} + \left(\begin{matrix} & | \\ -CH- & C \\ & | \end{matrix}\right)_3 NH^+X^- \qquad (2)$$

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[1] (a) Part II: J. E. Gordon, *J. Am. Chem. Soc.*, **87**, 1499 (1965); (b) Woods Hole Oceanographic Institution, Woods Hole, Mass. 02543; (c) to be published.