nitric acid was used for the adjustment of *p*H with the silver solutions.

Purification.—Acidic tracer yttrium solutions were centrifuged, filtered through ultrafine Misco Metallic Filters, or filtered through ultrafine Selas Bacteriological Filters in an attempt to remove suspended impurities. All these experiments were performed in a dust-free atmosphere and all apparatus was washed with centrifuged or filtered water. After centrifugation or filtration, the *p*H values of the solutions were adjusted with centrifuged or filtered sodium hydroxide solution, and then the solutions were centrifuged for 30 minutes. Samples taken from the solutions before this final centrifugation and after centrifugation were counted and used to determine the percentage of yttrium removed.

Results

Centrifugation of yttrium solutions which had not been purified gave results in agreement with previously reported values using filtration.[5] Up to a *p*H value of 5.0, no yttrium is centrifuged, then the removal increases almost linearly with *p*H up to a *p*H value of 7.0, at which 100% of the yttrium is removed. The percentage removed remains at 100% for higher *p*H values. No differences were noted when the previously purified yttrium solutions were used. Adsorption of tracer yttrium onto Norit A carbon goes from 0% at a *p*H value of 0.0 to 100% at a *p*H value of 5.0, the percentage adsorption then remaining at 100% up to a *p*H value of 12.0. The presence of carbonate had little effect upon the adsorption.

The antimony solutions were filtered and centrifuged at *p*H values from 1.0 to 12.0. From a *p*H value of 1.0 to 8.0 the percentage antimony filtered rose from 15 to 30% then dropped to 20% at a *p*H value of 12.0. The centrifugation curve was almost identical in shape, but was about 10 percentage points lower. Adsorption of antimony on Norit A increased from 60% to a *p*H value of 0.0 to 95% at a *p*H value of 5.0, then dropped to 34% at a *p*H value of 10.0, remaining here up to a *p*H value of 12.0.

Filtration and centrifugation of labeled silver solutions at a *p*H value of 8.0 showed that 55 and 20%, respectively, of the silver was removed at 10^{-6} *M* and below and that practically all the silver was separated at 10^{-5} *M* and above.

Conclusions

The use of previously purified yttrium solutions in filtration and centrifugation experiments yielded results similar to those obtained with solutions which had not been purified. Adsorption of tracer yttrium onto Norit A carbon as a function of *p*H differed from the trend shown in centrifugation or filtration. The presence of carbonate does not alter the adsorption behavior to any marked degree, but has a profound influence upon removal by filtration.[1] These observations lead to the conclusion that adsorption of yttrium upon impurities suspended in solution is probably not the major factor involved in the formation of radiocolloids.

Some removal of tracer antimony from its solutions can be realized by centrifugation or filtration, maximum removal occurring in the neutral region. The antimony probably existed partly as a radiocolloid and partly as chloro- or chlorohydroxocomplexes at all *p*H values. Adsorption results showed no similarity to the centrifugation experiments, leading to the conclusion that there is probably no relation.

The results in the silver experiments are what one would expect on the basis of true colloid formation and not for adsorption of silver ions onto suspended impurities.

Acknowledgment.—The authors wish to express their gratitude to the U. S. Atomic Energy Commission for Research Grant AT-(40-1)-1058 which supported this work.

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF TENNESSEE
KNOXVILLE 16, TENNESSEE

[5] J. D. Kurbatov and M. H. Kurbatov, *J. Phys. Chem.*, **46**, 441 (1942); G. K. Schweitzer, B. R. Stein and W. M. Jackson, THIS JOURNAL, **75**, 793 (1953).

COMMUNICATIONS TO THE EDITOR

A NOVEL REARRANGEMENT IN THE SYNTHESIS OF AZULENES

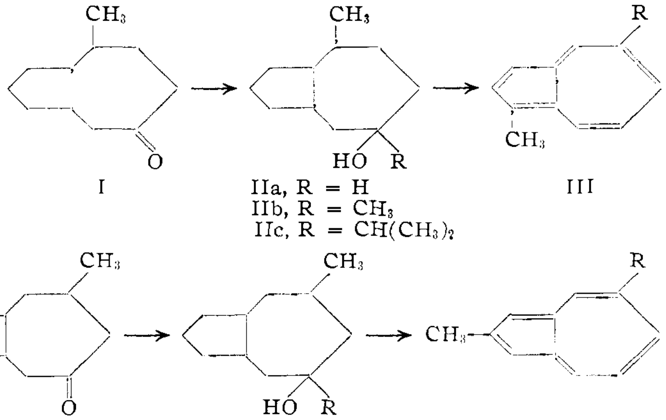
Sir:

In the course of work which had as its goal the preparation of 4,7-disubstituted azulenes by a method designed eventually to lead to azulenes derivable from natural sources, 2-methylbicyclo-(5,3,0)-5-decanone (I), b.p. 92–96° (2.5 mm.) (Calcd. for $C_{11}H_{18}O$: C, 79.46; H, 10.92. Found: C, 79.64; H, 11.02); semicarbazone, m.p. 143–143.5° (Calcd. for $C_{12}H_{21}N_3O$: C, 64.54; H, 9.48; N, 18.82. Found: C, 64.58; H, 9.48; N, 19.0) was prepared as follows: Cyclopentanone carboxylic ester was condensed with ethyl γ-bromo-γ-methylcrotonate; rearrangement at this stage is excluded by consideration of the infrared spectrum of I (bands at 1705 and 1385 cm.$^{-1}$).[1] The non-enolic character of the condensation product, demonstrated by chemical tests and infrared spectrum, eliminates another, though unlikely, isomerization occurring *via* reversal of the Dieckmann reaction and recyclization in the other direction. Reduction, hydrolysis and decarboxylation furnished an acid whose ethyl ester was condensed with ethyl cyanoacetate. The condensation product was reduced, hydrolyzed and decarboxylated and the resulting dibasic acid cyclized to I through the barium salt.

---

[1] An S_N2 type rearrangement, would have led to a bicyclo(3,3,0)-octanone derivative possessing a band near 1735–1750 cm.$^{-1}$. A shift from α,β- to β,γ-type unsaturation in the crotonic ester during bromination, which might have led to a δ-bromo compound, would have resulted in the formation of bicyclo(6,3,0)undecanone and elimination of the C–CH_3 band at 1385 cm.$^{-1}$ which appears in all compounds.

I was treated with lithium aluminum hydride and with methyl- and isopropylmagnesium halide. The resulting alcohols (II) were dehydrated with potassium acid sulfate. Much to our surprise, dehydrogenation of the olefins with sulfur yielded *blue* azulenes obviously not identical with the expected 4-methyl-,[2] 4,7-dimethyl-[3] and 4-methyl-7-isopropylazulenes; no other azulenes were isolated. The visible spectrum and trinitrobenzene complex identified III-a as 1-methylazulene[4] (3%) (λ_{max} 742, 703, 669, 635, 611, 587, m.p.[5] of TNB complex 160°). III-b (isolated in 4% yield) had properties identical with those reported for 1,5-dimethylazulene[3,6] (λ_{max} 765, 715, 681, 650, 622, 602, 565, 545 mμ; m.p. of TNB complex 151–152.5°). III-c, whose spectrum is virtually undistinguishable from IIIb, is therefore assumed to be 1-methyl-5-isopropylazulene,[7] m.p. of TNB complex 137.5–138° (Calcd. for $C_{20}H_{19}N_3O_6$: C, 60.45; H, 4.82; N, 10.58. Found: C, 60.60; H, 5.07; N, 10.7).



I

IIa, R = H
IIb, R = CH_3
IIc, R = $CH(CH_3)_2$

III

IV

Va, R = H
Vb, R = CH_3
Vc, R = $CH(CH_3)_3$

VI

The generality of this rearrangement has been demonstrated by subjecting to a similar series of reactions 3-methylbicyclo(5,3,0)-5-decanone (IV), prepared in essentially the same way from cyclopentanone carboxylic ester and ethyl γ-bromodimethylacrylate, b.p. 79–80° (1 mm.) (Calcd. for $C_{11}H_{18}O$: C, 79.46; H, 10.92. Found: C, 79.57; H, 10.92); semicarbazone, m.p. 182–183° (Calcd. for $C_{12}H_{21}N_3O$: C, 64.54; H, 9.48; N, 18.82. Found: C, 64.35; H, 9.67; N, 18.7). V-a yielded 2-methylazulene[4,8] (VI, 6%)[9] (λ_{max} 678, 652, 634, 625, 615, 601, 591, 568, 562, 551, 533, 523, 460 mμ, m.p. of TNB complex 135–136°), V-b gave only the previously unreported 2,5-dimethylazulene (VI-b, 5%), (λ_{max} 693, 668, 655, 628, 603, 578, 558, 545, 480 mμ; m.p. of TNB complex 149–150.5°. Calcd. for $C_{18}H_{15}N_3O_5$: C, 58.53; H, 4.09; N, 11.38. Found: C, 58.67; H, 4.21; N, 11.2), and V-c gave exclusively 2-methyl-5-isopropylazulene[1,11] (λ_{max} 688, 663, 655, 625, 600, 575, 545, 485; m.p. of TNB complex 112.5–114°. Calcd. for $C_{20}H_{19}O_6N_3$: C, 60.45; H, 4.82; N, 10.58. Found: C, 60.58; H, 5.05; N, 10.6).

The demonstration of this apparently transannular rearrangement implies that thermal migration of alkyl groups from position 1 to position 2 of the azulene nucleus is not the only source of error in locating alkyl groups in azulenogens and that reëxamination of certain structures which rest on the dehydration of bicyclodecane derivatives containing hydroxyl groups, particularly hydroxyls in the 5-position, may be in order.

The homogeneity of the azulenic products and their structure suggests that the rearrangement occurs during the dehydration rather than during the dehydrogenation step by a mechanism which involves two 1,3-shifts (or a series of 1,2-shifts). Isomerization during dehydrogenation might have been expected to result in mixtures and to lead to 2- rather than 1-substituted azulenes in the reaction sequence based on I. Studies intended to elucidate this are in progress.

Thanks are due Mr. Lin Tsai for stimulating discussions and to the Research Council of the Florida State University for a grant in support of this work.

DEPARTMENT OF CHEMISTRY
THE FLORIDA STATE UNIVERSITY WERNER HERZ
TALLAHASSEE, FLORIDA

RECEIVED APRIL 9, 1954

---

[2] Pl. A. Plattner, E. Heilbronner and A. Fürst, *Helv. Chim. Acta*, **30**, 1100 (1947).

[3] H. Pommer, *Ann.*, **579**, 47 (1953).

[4] Pl. A. Plattner and J. Wyss, *Helv. Chim. Acta*, **24**, 483 (1941); Plattner and G. Büchi, *ibid.*, **29**, 1608 (1946).

[5] Melting points determined on Kofler block.

[6] H. Arnold and H. Schachtner, *Ber.*, **86**, 1445 (1953).

[7] Yield not reported because the reaction of I and IV with isopropylmagnesium bromide or isopropyllithium resulted in a mixture of I and II and IV and Vc consisting largely of starting material. This was used directly for further work.

[8] Pl. A. Plattner and E. Heilbronner, *Helv. Chim. Acta*, **30**, 910 (1947).

[9] This experiment also yielded a small amount of a blue azulene which could not be characterized but whose spectrum was identical with that of 5-methylazulene,[10] the "expected" product.

[10] F. Sorm, *Coll. Czech. Chem. Commun.*, **12**, 251 (1947).

[11] Pl. A. Plattner, A. Fürst, A. Müller and W. Keller, *ibid.*, **37**, 271 (1954).

OXYGEN EXCHANGE DURING THE ACIDIC AND BASIC HYDROLYSES OF AMIDES AND THE ENZYMATIC HYDROLYSIS OF ESTERS[1]

Sir:

Oxygen exchange has been found to occur between benzamide-O^{18} and water during the basic hydrolysis of benzamide, but no exchange was observed during its acidic hydrolysis. Oxygen exchange was not observed during the α-chymotrypsin catalyzed hydrolysis of methyl β-phenylpropionate-*carbonyl*-O^{18}. These results are in contrast to those obtained during the basic and acidic hydrolyses of ethyl benzoate.[2] In both ethyl benzoate hydrolyses, exchange between the carbonyl oxygen of the ester and the water occurred. This phenomenon was attributed to the reversible formation of a symmetrical addition intermediate, $RC(OH)_2OR$.[3]

Benzamide-O^{18} was prepared from benzoic acid-

---

[1] This investigation has been supported by grants from the Research Corporation and the U. S. Public Health Service. III in the series, Intermediates in the Reactions of Carboxylic Acid Derivatives.

[2] M. L. Bender, THIS JOURNAL, **73**, 1626 (1951).

[3] Infrared evidence for stable addition compounds related to this structure is given in M. L. Bender, *ibid.*, **75**, 5986 (1953).