ture 4.3 g. of the *cis*-ketone II. After 12 hours at room temperature, the reaction product was refluxed for 90 minutes and decomposed with ice and dilute sulfuric acid. The aqueous layer was extracted with ether, and the combined ethereal solutions were washed with 5% sodium hydroxide solution, dried and concentrated. The residue was heated for 20 minutes with a little iodine at 160°, dissolved in ether and after treatment with 5% sodium bisulfite solution, 5% sodium hydroxide solution and water and drying was distilled *in vacuo;* b.p. 145° (0.4 mm.), yield 4.4 g. (73%), n^{19}_D 1.5662, n^{25}_D 1.5610, d^{25}_4 1.012.

Anal. Calcd. for $C_{16}H_{20}$: C, 90.6; H, 9.4; *MR*, 67.54. Found: C, 91.0; H, 9.4; *MR*, 67.84.

***trans*-6-Phenylbicyclo[5.3.0]-6-decene (III).**—From 0.7 g. of the *trans*-ketone II, 0.57 g. (68%) of the hydrocarbon was obtained, b.p. 120° (0.4 mm.), n^{20}_D 1.4928.

Anal. Calcd. for $C_{16}H_{20}$: C, 90.6; H, 9.4. Found: C, 90.7; H, 8.8.

6-Phenylazulene (I).—In the dynamic system described by Plattner, *et al.*,[25] 1 g. of the *cis*-hydrocarbon III was passed at 300° over 100 mg. of 10% palladium–charcoal in an atmosphere of dry nitrogen. The blue reaction product was condensed in a trap cooled with solid carbon dioxide. It was dissolved in petroleum ether and the phenylazulene extracted with 85% phosphoric acid. The unchanged starting material was recovered from the petroleum ether and subjected to the same treatment; this operation was repeated 8 times. By dilution of the phosphoric acid solutions and extraction with ether, 350 mg. of phenylazulene was obtained. The hydrocarbon does not give an addition product with trinitrobenzene; obviously, the phenyl group in the 6-position as well as in the 2-position[7] reduces the basicity of the azulene system. The crude phenylazulene was, therefore, purified by adsorption on activated alumina and elution, benzene serving as solvent. The deep blue benzene solution was concentrated *in vacuo* and the solid residue recrystallized from methanol as deep blue leaflets, m.p. 150°.

Anal. Calcd. for $C_{16}H_{12}$: C, 94.1; H, 5.9. Found: C, 93.4; H, 6.5.

The *trans*-hydrocarbon III gave an identical product; the dehydrogenation appeared to proceed somewhat more easily than in the case of the *cis* isomer.

Alternative Route to Ethyl Cyclopentanone-2-acetate. N-Cyclopentenyl-pyrrolidine.—The azeotropic condensation between 42 g. of cyclopentanone and 71 g. of pyrrolidine in 300 ml. of benzene was complete in 4 hours; yield 58 g. (85%), b.p. 81.5–82° (5 mm.), n^{16}_D 1.5144.

Anal. Calcd. for $C_9H_{15}N$: C, 78.8; H, 10.9. Found: C, 79.1; H, 10.6.

N-Cyclopentenylmorpholine.—From 42 g. of cyclopentanone and 87.1 g. of morpholine in 300 ml. of benzene, there was obtained within 3 hours, 55 g. (72%) of the enamine, b.p. 97° (7.5 mm.), $n^{16.5}_D$ 1.5098.

Anal. Calcd. for $C_9H_{15}NO$: C, 70.6; H, 9.8. Found: C, 70.3; H, 9.7.

Ethyl Cyclopentanone-2-acetate.—(a) At room temperature and during 45 minutes, 71 g. of ethyl bromoacetate was added to a solution of 58 g. of N-cyclopentenyl-pyrrolidine in 200 ml. of anhydrous dioxane (with benzene, the same results were obtained). The solution turns red and a white precipitate appears. Upon refluxing for 3 hours, the precipitate disappeared; the solution was cooled and 200 ml. of water was added. The mass was stirred for 45 minutes at room temperature and extracted with benzene. The benzene layer was washed with water, dried and distilled; b.p. 105–106° (7 mm.), yield 15 g. (15%).

Anal. Calcd. for $C_9H_{14}O_3$: C, 63.5; H, 8.2. Found: C, 63.1; H, 8.2.

(b) By the same method, one obtains from 51 g. of N-cyclopentenylmorpholine, 56 g. of ethyl bromoacetate and 250 ml. of benzene, a solution which is treated with 100 ml. of water, washed with 10% hydrochloric acid, 10% sodium bicarbonate solution and water, dried and fractionated; b.p. 104° (6.5 mm.), yield 10 g. (13%).

JERUSALEM, ISRAEL

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[25] P. A. Plattner, A. Fuerst and K. Jirasek, *Helv. Chim. Acta*, **29**, 740 (1946).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE FLORIDA STATE UNIVERSITY]

Azulenes. VII. A Novel Rearrangement in the Synthesis of Azulenes

BY WERNER HERZ

RECEIVED AUGUST 25, 1955

The alkylation of ethyl cyclopentanonecarboxylate with several γ-bromo α,β-unsaturated esters has been studied. Chemical and spectroscopic evidence demonstrates that the products (I) have the expected structure, but attempts to utilize them as starting materials for the synthesis of 4- or 5-alkylazulenes invariably resulted in the formation of 1(or 2)-alkylazulenes. Degradation of the intermediate ε-ketoacids II obtained from I by reduction and hydrolysis showed that hydrolysis was accompanied by rearrangement, thus accounting for the structure of the azulenes finally obtained.

In order to achieve the total synthesis of azulenes derived from natural sources, a number of workers have devoted considerable effort to the development of general methods for the preparation of azulenes substituted simultaneously in the 4- and 7-positions. Application of the usual diazoacetic ester methods[1] to the ring expansion of suitably substituted indans leads to difficultly separable mixtures of azulenes[2,3] or to substances whose purity is still in question.[4] More recently Šorm and co-workers[5] have published unequivocal, if tedious, syntheses of S- and Se-guaiazulene in which appropriately substituted dicarboxylic acids were prepared by oxidation of vicinal dihydroxyhexahydroindans and cyclized to 6,10-dialkylbicyclo[5,3,0]-3-decanones.

In theory at least, the preparation of 4,7-disubstituted azulenes might be achieved by modifying an azulene synthesis developed by Šorm[6] in such a way as to afford a 2-alkylbicyclo[5,3,0]-5-decanone as the key intermediate. However, the initial alkylation of cyclopentanonecarboxylic ester by γ-bromoesters in which the bromine atom is secondary (a necessary condition for the introduction of alkyl groups in position 2) would not be expected to proceed in satisfactory yield. Similar objections might be raised to a sequence of reactions suggested by Dev.[6a]

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[1] M. Gordon, *Chem. Revs.*, **50**, 127 (1952).

[2] H. Hippchen, *Z. Naturforsch.*, **1**, 325 (1946).

[3] Pl. A. Plattner, A. Fürst, L. Marti and H. Schmid, *Helv. Chim. Acta*, **32**, 2137 (1949); Pl. A. Plattner, A. Fürst and L. Marti, *ibid.*, **32**, 2452 (1949).

[4] Th. Wagner-Jauregg, H. Arnold and F. Hüter, *Ber.*, **75**, 1293 (1942); see also H. Pommer, *Ann.*, **579**, 47 (1953).

[5] F. Šorm, J. Gut, H. Hlavnička, J. Kučera and L. Sedivy, *Coll. Czech. Chem. Communs.*, **16**, 158 (1951); F. Šorm, J. Kučera and J. Gut, *ibid.*, **16**, 184 (1951); J. Novak, F. Šorm and J. Sicher, *ibid.*, **19**, 1264 (1954).

[6] F. Šorm, *ibid.*, **12**, 251 (1947).

[6a] S. Dev, *Science and Culture*, **16**, 31 (1950). The proposed synthesis of apo-S-guaiazulene outlined in this paper apparently has not been realized experimentally.

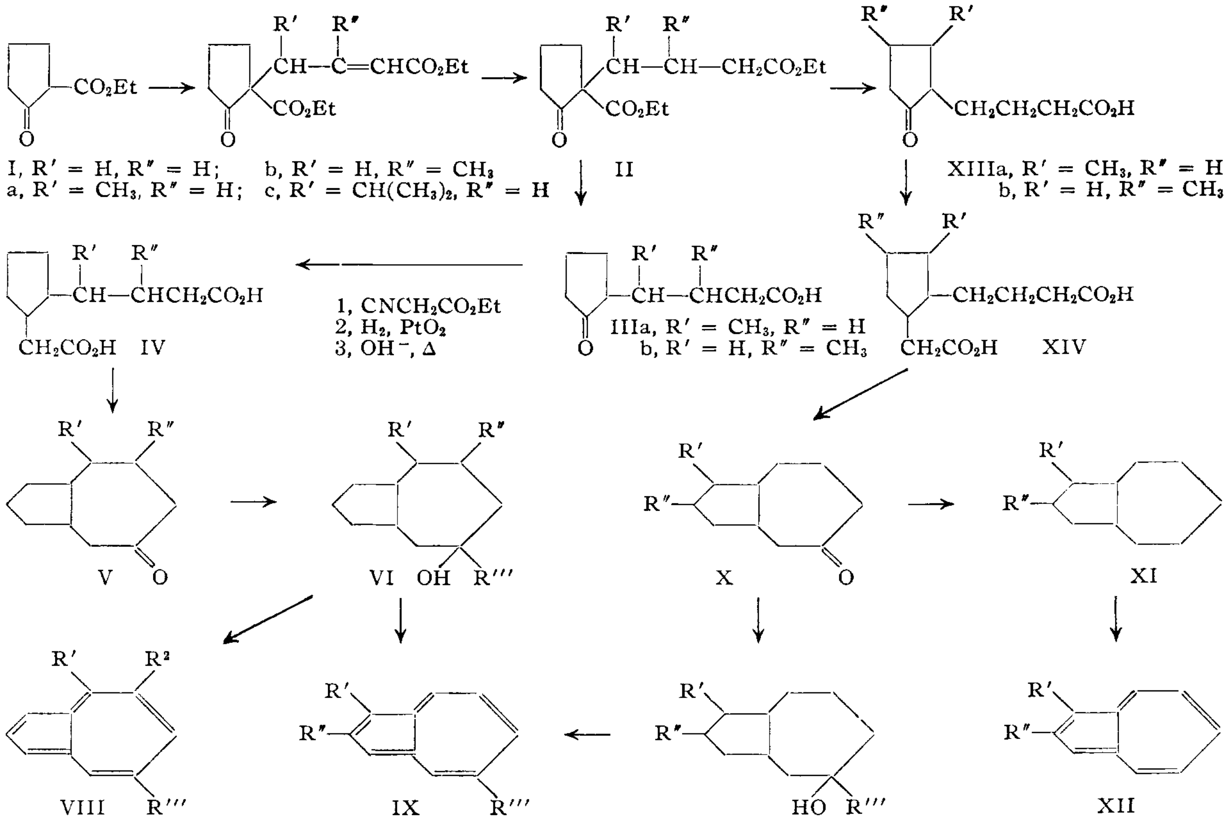
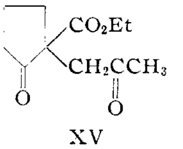


Fig. 1.

We have attempted to circumvent this difficulty by alkylating cyclopentanonecarboxylic ester with γ-bromo-α,β-unsaturated esters readily available by treating the unsaturated esters with N-bromosuccinimide. Model experiments with γ-bromocrotonic ester gave a 60% yield of I; ethyl γ-methyl-γ-bromocrotonate and ethyl β-methyl-γ-bromocrotonate gave 60% yields of the condensation products Ia and Ib. On the other hand, the low yield (26%) in the condensation of the keto ester with ethyl γ-isopropyl-γ-bromocrotonate precluded use of Ic as an intermediate for further work. Catalytic hydrogenation furnished excellent yields of the reduced substances II.

That the alkylation had proceeded without rearrangement was established unequivocally in one instance. Ozonolysis of Ib gave as major product a diketoester $C_{11}H_{16}O_4$ which was identical in all respects with a substance obtained by alkylation of ethyl cyclopentanone carboxylate with chloroacetone, *i.e.*, XV.



XV

The double bond of Ib is therefore in the side chain, as postulated. That I, Ia, Ib and Ic possess analogous structures is indicated by the following facts. (1) The infrared and ultraviolet spectra of the four substances are very similar, as detailed in the Experimental Part; in particular, no spectrum contains a band in the range 1580–1620-cm.⁻¹ characteristic of 2-cyclopenten-1-ones.[7] (2) The four compounds do not give a ferric chloride test. (3) The infrared spectra of the four compounds II are very similar and do not exhibit bands at 1667 and 1624 cm.⁻¹ which are typical of enolizable cyclopentanonecarboxylic esters.[8] (4) The ferric chloride test of compounds II is negative. (5) I and Ib can be isomerized to enolic β-keto esters.[9]

These observations render untenable the hypothesis that compounds I, Ia or Ic might have undergone a reversal of the Dieckmann reaction and subsequent recyclization to the isomeric β-ketoesters A or B, formulations which would account satisfactorily for the azulenes isolated in the last step (*vide infra*).[10]

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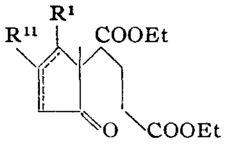
[7] H. Conroy, THIS JOURNAL, **74**, 491 (1952); R. H. Eastman and A. Oken, *ibid.*, **75**, 1029 (1953); L. H Sarett, W. F. Johns, R. E. Beyler, R. M. Lukes, G. I. Poos and G. E. Arth, *ibid.*, **77**, 559 (1955).

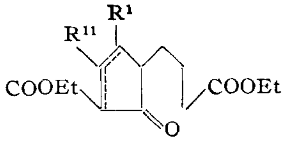
[8] N. J. Leonard, H. S. Gutowsky, W. J. Middleton and E. M. Petersen, *ibid.*, **74**, 4970 (1952). Our measurements on cyclopentanonecarboxylic ester in carbon tetrachloride solution show bands at 1760, 1725, 1667 (conjugated C=O) and 1624 cm.⁻¹ (conjugated C=C). The fairly strong bands at 1667 and 1624 cm.⁻¹ are entirely absent from the spectrum of 2-methyl-1-cyclopentanone-2-carboxylate and from the spectra of compounds of type II.

[9] H. T. Openshaw and R. Robinson, *J. Chem. Soc.*, 941 (1937); N. N. Chatterjee, B. K. Das and G. N. Barpujari, *J. Indian Chem. Soc.*, **17**, 161 (1940); N. J. Leonard and W. J. Middleton, THIS JOURNAL, **74**, 5114 (1952).

[10] These isomerizations, however, require prolonged refluxing of the alkylated β-ketoester with sodium alkoxide[9] and the spontaneous rearrangement during the alkylation process required by the above hypothesis has not been observed previously. H. Staudinger and L. Ruzicka, *Helv. Chim. Acta*, **7**, 446 (1924), reported partial cleavage of a β-ketoester during the alkylation of cyclopentanonecarboxylic ester with allyl bromide under conditions analogous to those employed by us, but no isomerization.



A



B

B and the conjugated structure A are excluded by observations 1, 2, 3 and 4. The unconjugated structure A whose suggested mode of formation is quite implausible[11] is ruled out by observation 5 which shows that it cannot be the end product of an isomerization even if cleavage of the primary condensation product is assumed.

The constitution of the alkylation products thus had been established and the remainder of the synthesis was planned to follow the path outlined in the flow sheet. On the basis of earlier work[12] the dibasic acids IV might be expected to have the *cis*-configuration; however, one of them, the compound presumed to be IVa, was obviously a mixture of stereoisomers. One of these was isolated in apparently pure form. Cyclization of the dibasic acids gave ketones which boiled over a 3° range and may also be mixtures of stereoisomers although their semicarbazones melted sharply.[13] These ketones were originally assigned[14] structure V because the possibility of a rearrangement in the formation of I and II had been ruled out and the succeeding steps appeared straightforward.

As described in an earlier communication[14] the ketones were treated with lithium aluminum hydride, methyl- and isopropylmagnesium halides and the resulting alcohols were dehydrated with potassium acid sulfate. However, dehydrogenation of the olefins with sulfur yielded not the expected azulenes of type VIII, but substances which because of their color and the melting points of their derivatives obviously possessed structure IX. It was suggested[14] that a *trans*-annular rearrangement during the acid-catalyzed dehydration of VI would satisfactorily account for these observations.[15] We now present evidence which indicates that a rearrangement took place *prior* to cyclization and that the structures of the bicyclic ketones must be represented by X instead of by V.

In our efforts to investigate the reality of the postulated *trans*-annular rearrangement, the olefins obtained by dehydration of VI (or X, $R''' = H$) were reduced catalytically and the products compared with the bicyclic hydrocarbons prepared directly by Wolff–Kishner reduction of the presumed ketones V. Physical properties and infrared spectra of the two types of products differed somewhat; this lent weight to the supposition of a rearrangement during dehydration. On the other hand, it was considered that any such differences might well be due to the presence of different proportions of *cis* and *trans* isomers or to methyldecalins which might have been formed as by-products during the acid-catalyzed dehydration of the bicyclo[5,3,0]-decanols.[16] The hydrocarbon resulting from the Wolff–Kishner reduction of Va (or Xa) was therefore subjected to dehydrogenation. Sulfur did not yield any azulenes whatsoever, but use of palladium-on-charcoal or selenium furnished very small yields of an azulene which was identified spectroscopically as 1-methylazulene (XII). Since alkyl group migration from the seven- to the five-membered ring of azulenes has not been observed, this observation suggested that the hydrocarbons possessed structures XI and the bicyclic ketones structures X instead of V.[17]

The degradation of these ketones was not expected to provide compounds which could be related easily to substances of known structure for verification of this hypothesis. The keto acids obtained by hydrolysis of II offered themselves as more convenient starting materials. The keto acid originally formulated as IIIa was reduced by the Wolff–Kishner reaction. The properties of the resulting acid XVI indicated that it was a mixture which would be difficult to understand on the basis of formula IIIa. On the other hand, if formula XIIIa were ascribed to the keto acid, equilibration of *cis* and *trans* isomers under the conditions of the Wolff–Kishner reduction might result in formation of a mixture. XVI was degraded twice by the Barbier–Wieland method, but the apparent presence of stereoisomers interfered with the planned comparison of XVI and its degradation product with authentic samples of acids whose synthesis is described elsewhere.[18] The properties of XVI and its degradation products were, however, quite different from those of 4-cyclopentylvaleric acid and its two lower homologs (3-cyclopentylbutyric and 2-cyclopentylpropionic acid) and more in keeping with the properties to be expected of mixtures of acids of the *cis*- and *trans*-2-methylcyclopentylacetic acid series.[18,19]

On the other hand, removal of the keto group from the acid obtained by hydrolysis of IIb ($R' = H$, $R'' = CH_3$) furnished a substance which appeared to be homogeneous and whose properties differed from those of authentic 3-methyl-4-cyclopentylbutyric acid (XVII) whose synthesis is outlined below. Moreover, two Barbier–Wieland degradations of this substance gave an *acid* of

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[11] For a recent discussion with literature references, see D. Stauffacher and H. Schinz, *Helv. Chim. Acta*, **37**, 1223 (1954).

[12] R. P. Linstead and E. M. Meade, *J. Chem. Soc.*, 935 (1934); A. H. Cook and R. P. Linstead, *ibid.*, 946 (1934); J. W. Barrett and R. P. Linstead, *ibid.*, 436 (1935); F. Šorm, *Coll. Czech. Chem. Communs.*, **12**, 251 (1947).

[13] For similar observations, see the article by H. Pommer cited in ref. 3.

[14] W. Herz, THIS JOURNAL, **76**, 3350 (1954).

[15] Molecular models indicate, however, that carbon atoms 1 and 5 of the bicyclo(5,3,0)decane ring system do not approach each other sufficiently to render this hypothesis very plausible.

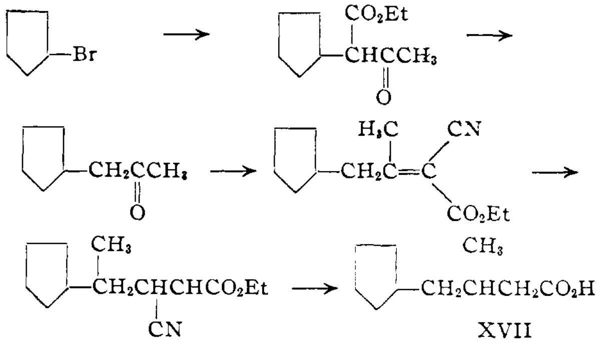
[16] E. Kováts, A. Fürst and Hs. A. Günthard, *Helv. Chim. Acta*, **37**, 534 (1954).

[17] The possibility that 1-methylazulene arose by dehydrogenation of a small amount of rearranged olefin formed during the Wolff–Kishner reduction could not be excluded at this juncture.

[18] W. Herz, *J. Org. Chem.*, **20**, 1062 (1955).

[19] The possibility that XVI is a mixture of 4-methylcyclopentylvaleric acid and 3-(2-methylcyclopentyl)-butyric acid (*cis* or *trans*) was considered remote because the azulenes isolated subsequently were apparently quite pure. The referee has suggested that nevertheless the experimental results indicate (in view of the proposed mechanism for the rearrangement of II to XIII) that crude XIIIa may really be a mixture of XIIIa and IIIa. From a consideration of amide m.p.'s, yields in subsequent steps, etc., he has proposed that the ratio of XIIIa to IIIa is probably 2 to 1 or larger and that the disappearance of the minor constituent *en route* to the final azulenes may be due to manipulative losses. Further investigations now in progress may help to elucidate this point.

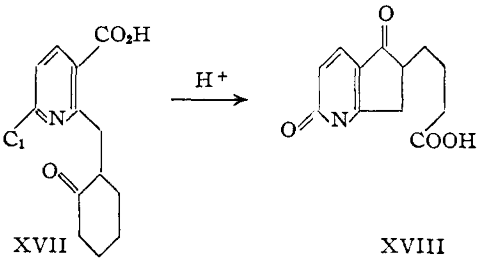
formula $C_8H_{14}O_2$ whereas IIIb should have given rise to cyclopentylacetone.



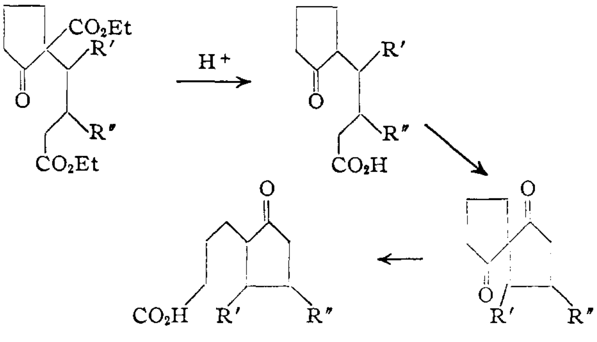
If one considers the structure of the azulenes obtained in the final step of the synthesis, it follows that the keto acids must be formulated as XIII and the bicyclic ketones as X.

As a corollary of this conclusion the acid $C_8H_{14}O_2$ should be *cis*- or *trans*-3-methylcyclopentylacetic acid or a mixture thereof. Indeed its physical properties closely resembled those of a 3-methylcyclopentylacetic acid fraction which has been isolated from petroleum[20,21] and synthesized[20] from 3-methylcyclopentanol[22] and it was not identical with *cis*- or *trans*-2-methylcyclopentylacetic acid or 2-cyclopentylpropionic acid.[18]

Since all the available evidence points to I as the structure of the products which result when cyclopentanonecarboxylic ester is alkylated by γ-bromo-α,β-unsaturated esters, a rearrangement II → XIII is apparently effected when compounds of type II are hydrolyzed with hydrochloric acid. This finds a parallel in the conversion of 2-(2′-oxocyclohexyl)-methyl-6-chloronicotinic acid (XVII) to 6-(4′-carboxy)-butyl-2-hydroxy-5-oxo-6,7-dihydro-1,5H-pyrindine (XVIII) which has been reported recently.[24] The mechanism proposed by Ramirez and Paul would be equally applicable to other ε-keto acids, as shown below, although the degree of substitution and other factors might be expected to exert a certain influence on the equilibria involved. Work now in progress suggests that this may be the case.



XVII XVIII



Acknowledgment.—This work was aided by a grant from the Research Council of the Florida State University and, in the later stages, by a grant from the National Science Foundation.

Experimental[25]

Ethyl 4-Bromo-2-pentenoate.—To a solution of 62 g. of ethyl 2-pentenoate[26] in 500 ml. of dry carbon tetrachloride was added in small portions a mixture of 85 g. of N-bromosuccinimide and 1 g. of benzoyl peroxide. After 12 hours at reflux the reaction mixture was chilled and filtered, the residual succinimide was washed with fresh carbon tetrachloride and the combined filtrate and washings were concentrated *in vacuo*. The fraction boiling at 65–75° (2 mm.), wt. 84 g. (84%), was collected. The analytical sample distilled at 60–62° (1 mm.), $n^{25}D$ 1.4838.

Anal. Calcd. for $C_7H_{11}O_2Br$: C, 40.40; H, 5.36. Found: C, 40.70; H, 5.64.

Ethyl 4-Bromo-5-methyl-2-hexenoate.—Bromination of 75 g. of ethyl 5-methyl-2-hexenoate[35] in the manner described above yielded 84 g. (61%) of a fraction distilling in the range 91–98° (3 mm.). The analytical sample boiled at 78–79° (1 mm.), $n^{25}D$ 1.4815.[27]

Anal. Calcd. for $C_9H_{15}O_2Br$: C, 45.97; H, 6.43. Found: C, 45.93; H, 6.45.

Ethyl 4-Bromo-3-methyl-2-butenoate.—Bromination of 256 g. of ethyl β,β-dimethylacrylate with N-bromosuccinimide yielded 256 g. (62%) of ester boiling in the range 78–82° (4 mm.) (lit.[28] 105–108° (20 mm.)).

Ethyl 4-(1-Carbethoxy-2-oxocyclopentyl)-crotonate (Ia).—To a dispersion of 4.8 g. of powdered sodium in 250 ml. of hot toluene was added 31 g. of 2-carbethoxycyclopentanone. After three hours at reflux 39 g. of ethyl γ-bromocrotonate was added dropwise with stirring. The mixture was refluxed for an additional six hours, cooled and diluted with water. The organic layer was washed with water, the water was extracted with ether and the combined toluene and ether layers were dried, concentrated at reduced pressure and distilled. The product was collected at 156–161° (2 mm.), yield 33 g. (60%). Its infrared spectrum (carbon tetrachloride solution) exhibited a weak band at 1755 (C=O), and stronger bands at 1722 (C=O) and 1658 (C=C) cm.$^{-1}$. The corresponding bands of ethyl crotonate occur at 1725 and 1665 cm.$^{-1}$. It gave a negative test

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(20) C. D. Nenitzescu, D. A. Isacescu and T. Volrap, *Ber.*, **71**, 2056 (1938).

(21) W. O. Ney, W. W. Crouch, C. E. Rannefeld and H. L. Lochte, THIS JOURNAL, **65**, 770 (1943).

(22) The configuration of this fraction is not known. However, the method of synthesis adopted by the Roumanian workers would scarcely be expected to yield a pure *cis*- or *trans*-acid (see ref. 18). An earlier synthesis by R. Desai, *J. Chem. Soc.*, 1216 (1931), gave a product of unspecified configuration, but no derivatives were reported. Repetition of this work, described in the Experimental Part, furnished material whose derivatives melted slightly below the derivatives of the acid $C_8H_{14}O_2$ but which could not be differentiated from it spectroscopically or by the method of mixed m.p.'s. A 3-methylcyclopentylacetic acid prepared by Sebe and Naito[23] was optically active and cannot therefore be used for comparison.

(23) Y. Sebe and T. Naito, *J. Taiwan Pharm. Assoc.*, **2**, No. 1, 23 (1950); *C. A.*, **45**, 6163 (1951).

(24) F. Ramirez and A. P. Paul, THIS JOURNAL, **77**, 1035 (1955). I wish to thank Dr. Howard E. Zimmerman for drawing my attention to this paper.

(25) Melting points, except those taken on the Kofler block, and boiling points are uncorrected. Analyses by Drs. Weiler and Strauss, Oxford. Infrared spectra were determined by Mr. Dean S. Keeley and Mr. Daniel Raden on a Perkin–Elmer model 21 instrument. Ultraviolet spectra were run on a Beckman model DK recording spectrophotometer.

(26) K. V. Auwers, *Ann.*, **432**, 46 (1923).

(27) The preparation of the acid corresponding to this ester was reported recently by E. B. Reid and W. Sause, *J. Chem. Soc.*, 516 (1954).

(28) H. D. Huisman, A. Smit, S. Vromen and L. G. M. Fisscher, *Rec. trav. chim.*, **71**, 899 (1952).

with ferric chloride solution. Its ultraviolet spectrum had a maximum below 220 mμ which could not be located accurately, and a second, weaker maximum at 294–296 mμ.

Anal. Calcd. for $C_{14}H_{20}O_5$: C, 62.67; H, 7.51. Found: C, 62.40; H, 7.57.

The semicarbazone solidified on trituration with petroleum ether and was recrystallized by taking up in a small amount of benzene, adding ligroin dropwise, seeding when still clear and allowing to stand for several days. This was repeated several times until a constant m.p. 92.5–93.5° was reached. Its ultraviolet spectrum in ethanol exhibited a shoulder at 232.5 mμ (ϵ_{max} 15500) indicating the absence of conjugation.[29]

Anal. Calcd. for $C_{15}H_{23}N_3O_5$: C, 55.37; H, 7.13; N, 12.91. Found: C, 55.50; H, 7.43; N, 12.7.

Isomerization of the unsaturated ester by means of sodium ethoxide[11] furnished a liquid of b.p. 165–170° (5 mm.) which gave a strong ferric chloride test. The double bond region of this material had bands at 1745 (very strong), 1722, 1660 and 1615 cm.$^{-1}$. This compound is probably ethyl 4-(3-carbethoxy-2-oxocyclopentyl)-crotonate.

Anal. Calcd. for $C_{14}H_{20}O_5$: C, 62.67; H, 7.51. Found: C, 62.55; H, 7.42.

Ethyl 4-(1-Carbethoxy-2-oxocyclopentyl)-butyrate (IIa).—Reduction of 30 g. of Ia with 5% palladium–charcoal in alcohol furnished 24.5 g. of a fraction, b.p. 165–170° (3.5 mm.), n^{24}D 1.4572, which gave no color with ferric chloride. Its infrared spectrum had a band at 1735 (shoulder at 1755) cm.$^{-1}$.

This compound has been prepared previously by a different method.[30]

Ethyl 4-(3-Carbethoxy-2-oxocyclopentyl)-butyrate.—Isomerization of 21 g. of the previous keto ester with sodium ethoxide[9] gave 12.5 g. of product, b.p. 175–179° (3.5 mm.), n^{24}D 1.4572, which gave a strong test with ferric chloride. Its infrared spectrum had a strong band centered at 1735 cm.$^{-1}$ (shoulder near 1755 cm.$^{-1}$) and weaker bands at 1670 and 1630 cm.$^{-1}$.

Anal. Calcd. for $C_{14}H_{22}O_5$: C, 62.20; H, 8.20. Found: C, 62.19; H, 8.39.

Ethyl 4-(1-Carbethoxy-2-oxocyclopentyl)-2-pentenoate (Ia).—Alkylation of 31 g. of 2-carbethoxycyclopentanone with 42 g. of ethyl 4-bromo-2-pentenoate gave 34 g. of product, b.p. 158–163° (2 mm.), yield 34 g. (60%). The analytical sample boiled at 140–142° (0.5 mm.), n^{26}D 1.4766.

Anal. Calcd. for $C_{15}H_{22}O_5$: C, 63.81; H, 7.85. Found: C, 63.65; H, 7.98.

The infrared spectrum in carbon tetrachloride solution exhibited a very strong band at 1722 cm.$^{-1}$ (shoulder at 1750) and a C=C band at 1652 cm.$^{-1}$. The ultraviolet spectrum was similar to that of I. The ferric chloride test was negative. The semicarbazone could not be crystallized satisfactorily; its ultraviolet spectrum indicated the absence of conjugation.

Ethyl 4-(1-Carbethoxy-2-oxocyclopentyl)-valerate (IIa).—Reduction of 26 g. of the unsaturated ester Ia, dissolved in 150 ml. of absolute ethanol, at 2–3 atmospheres pressure using 5% palladium-on-charcoal, was complete after four hours. Frequently, however, the reduction proceeded very slowly and required the addition of several batches of platinum oxide catalyst to go to completion. Distillation yielded 21.5 g. (83%) of product boiling in the range 158–170° (3 mm.). For analysis the sample was redistilled and a cut taken at 143–147° (1.2 mm.), n^{24}D 1.4635. The ferric chloride test was negative. The infrared spectrum (CCl_4 solution) had a very strong band at 1725 cm.$^{-1}$ (shoulder at 1745–1750 cm.$^{-1}$), but no other bands in the double bond region.

Anal. Calcd. for $C_{15}H_{24}O_5$: C, 63.36; H, 8.51. Found: C, 63.80; H, 8.56.

In subsequent work, this ester was not isolated, but hydrolyzed immediately to the keto acid.

Ethyl 4-(1-Carbethoxy-2-oxocyclopentyl)-3-methyl-2-butenoate (Ib).—Alkylation of 78 g. of 2-carbethoxycyclopentanone with 103.5 g. of ethyl 4-bromo-3-methyl-2-butenoate yielded 89 g. (64%) of ester, b.p. 162–168° (2 mm.), n^{23}D 1.4808.

Anal. Calcd. for $C_{15}H_{22}O_5$: C, 63.81; H, 7.85. Found: C, 63.98; H, 8.15.

The ferric chloride test was negative. The infrared spectrum in CCl_4 solution had bands at 1752 (relatively weak), 1720 and 1645 cm.$^{-1}$. The corresponding bands of ethyl β,β-dimethylacrylate were found at 1720 and 1660 cm.$^{-1}$. The ultraviolet spectrum was similar to that of I.

The semicarbazone was prepared by the method of Shriner and Fuson,[31] but separated only after dilution with water as an oil which was difficult to crystallize. It was purified in the same manner as the semicarbazone of I. It decomposed at 124–125.5°, when heated gradually, but melted instantaneously with gas evolution when immersed in a bath kept at 100° or higher. This behavior apparently is due to loss of water at elevated temperatures and explains the analytical results. The ultraviolet spectrum of the semicarbazone dried at room temperature had λ_{max} 222.5 (ϵ_{max} 19300).

Anal. Calcd. for $C_{16}H_{25}N_3O_5$: C, 56.62; H, 7.43; N, 12.4. Calcd. for $C_{16}H_{23}N_3O_4$: C, 59.79; H, 7.21; N, 13.1. Found: C, 59.57; H, 7.45; N, 13.6.

Isomerization of the unsaturated ester with sodium ethoxide[9] yielded a product, b.p. 160–167° (1 mm.), n^{22}D 1.4796, which gave a strong ferric chloride test and had an infrared spectrum similar to that of isomerized I (bands at 1730 and 1655, shoulders at 1750, 1635 and 1610).

Anal. Calcd. for $C_{15}H_{22}O_5$: C, 63.84; H, 7.85. Found: C, 63.75; H, 8.03.

Ethyl 4-(1-Carbethoxy-2-oxocyclopentyl)-3-methylbutyrate (IIb).—A solution of 26.5 g. of the unsaturated ester in 100 ml. of ethanol was reduced with platinum oxide catalyst until hydrogen uptake ceased. There was obtained 23.5 g. of product, b.p. 145–155° (1.3 mm.). The analytical sample boiled at 145–147° (1.2 mm.), n^{24}D 1.4581. The infrared spectrum showed a band at 1725 cm.$^{-1}$, but none at 1667 and 1624 cm.$^{-1}$. The ferric chloride test was negative.

Anal. Calcd. for $C_{15}H_{24}O_5$: C, 63.36; H, 8.51. Found: C, 63.35; H, 8.53.

Ethyl 4-(1-Carbethoxy-2-oxocyclopentyl)-5-methyl-2-hexenoate (Ic).—Alkylation of 31 g. of 2-carbethoxycyclopentanone with 48 g. of ethyl 4-bromo-5-methyl-2-hexenoate required a reflux period of 24 hours. The yield of ester, b.p. 158–168° (3 mm.), was 16.5 g. (26%). The analytical sample boiled at 138° (0.8 mm.), n^{25}D 1.4675. The ferric chloride test was negative.

Anal. Calcd. for $C_{17}H_{26}O_5$: C, 65.77; H, 8.44. Found: C, 65.72; H, 8.53.

Ethyl 4-(1-Carbethoxy-2-oxocyclopentyl)-5-methylhexanoate (IIc).—Catalytic reduction of 15 g. of Ic gave on fractionation 10.5 g. of saturated ester, b.p. 150–160° (1.5 mm.). The ferric chloride test was negative. The infrared spectrum had a strong band at 1720 cm.$^{-1}$ (shoulder near 1745 cm.$^{-1}$).

Anal. Calcd. for $C_{17}H_{28}O_5$: C, 65.36; H, 9.03. Found: C, 65.31, H, 9.11.

Ozonolysis of Ic.—A solution of 4 g. of Ic in 40 ml. of ethyl acetate was ozonized at 0° (2–3% ozone) until ozone absorption was complete. The solution was transferred to a Parr low-pressure hydrogenator and reduced (catalyst 5% palladium-on-calcium carbonate) at a pressure of 50 lb. until hydrogen absorption stopped. Distillation furnished a small amount of low-boiling material, 1.7 g. of a middle fraction of b.p. 95–115° (1.5 mm.) and some higher-boiling material which was not investigated further. The main fraction was refractionated and yielded a middle cut, b.p. 102–108° (1.5 mm.), n^{22}D 1.4570. It gave a positive iodoform test, but only after standing for several hours. The ferric chloride test was negative. The infrared spectrum had two bands in the carbonyl region at 1750 and 1720 cm.$^{-1}$. The disemicarbazone was recrystallized twice from dimethylformamide and melted at 232–233° (dec. with gas evolution).

Anal. Calcd. for $C_{13}H_{22}N_4O_6$: C, 47.30; H, 7.04. Found: C, 47.84; H, 6.80.

Alkylation of 2-Carbethoxycyclopentanone with Chloroacetone.—To 5.8 g. of sodium sand in 250 ml. of hot toluene was added, with stirring and heating, 39 g. of ethyl cyclo-

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[29] L. K. Evans and A. E. Gillam, *J. Chem. Soc.*, 565 (1943).

[30] W. E. Bachmann and W. S. Struve, This Journal, **63**, 2589 (1941).

[31] R. L. Shriner and R. C. Fuson, John Wiley and Sons, Inc., New York, N. Y., Third Ed., 1948, p. 170.

pentanonecarboxylate. After two hours at reflux 23 g. of chloroacetone was added and stirring and heating was continued for an additional six hours. The cooled mixture was diluted with water, washed thoroughly, dried and fractionated. There was recovered 11.5 g. of β-ketoester, 15 g. of an intermediate fraction, b.p. 100–140° (5 mm.) and there was a considerable amount of semi-solid residue. The second fraction was fractionated repeatedly and finally yielded 7.8 g. (21%) of product, b.p. 105–110° (1.5 mm.), which still retained a trace of cyclopentanonecarboxylic ester as shown by a weak ferric chloride test. The infrared spectrum was identical in all respects with the infrared spectrum of the ozonolysis product.

The disemicarbazone melted at 232-233°. The mixed m.p. with the semicarbazone of the ozonolysis product was not depressed.

4-(5-Methyl-2-oxocyclopentyl)-butyric Acid (XIIIa).—Hydrolysis of 130 g. of the crude ester IIb was accomplished by refluxing with 500 ml. of concentrated hydrochloric acid for seven hours. The excess acid was removed *in vacuo;* the residue was made basic with sodium carbonate, extracted with ether, reacidified and again extracted with ether. The acid extract was dried and yielded 76 g. of crude acid after removal of ether *in vacuo*. A small portion of the acid was distilled for analysis, b.p. 165° (1.5 mm.), $n^{24}\text{D}$ 1.4760.

Anal. Calcd. for $C_{10}H_{16}O_3$: C, 65.19; H, 8.75. Found: C, 65.16; H, 8.47.

The semicarbazone was prepared by dissolving 1.5 g. of crude acid in 5 ml. of water containing 0.6 g. of sodium carbonate and adding a solution of 1.2 g. of semicarbazide hydrochloride in 3 ml. of water. The oily precipitate solidified on standing and melted at 200° dec. after repeated recrystallization from methanol.

Anal. Calcd. for $C_{11}H_{19}O_3N_3$: C, 54.75; H, 7.94; N, 17.4. Found: C, 54.71; H, 8.01; N, 17.3.

The remaining crude acid (73 g.) was esterified by dissolving in 300 ml. of absolute ethanol, saturating with dry hydrogen chloride in the cold and allowing to stand for several days. The solvent was removed at reduced pressure and the residue was mixed with ice-cold saturated potassium carbonate solution and extracted with ether. The dried ether extract was fractionated and the fraction boiling at 118–125° (2 mm.) was collected, wt. 61 g. (66% based on the β-ketoester). The analytical sample boiled at 112–114° (1.5 mm.), $n^{24}\text{D}$ 1.4560.

Anal. Calcd. for $C_{12}H_{20}O_3$: C, 67.89; H, 9.50. Found: C, 67.36; H, 9.44.

4-(4-Methyl-2-oxocyclopentyl)-butyric Acid (XIIIb).—Hydrolysis of 23 g. of the ester IIc in the manner described previously yielded 13 g. (86%) of crude acid. A sample was distilled, b.p. 160-161° (1.2 mm.), $n^{24}\text{D}$ 1.4708.

Anal. Calcd. for $C_{10}H_{16}O_3$: C, 65.19, H, 8.75. Found: C, 65.09; H, 8.92.

The semicarbazone was recrystallized several times from methanol, in which it was more soluble than the previous isomer. It decomposed at 162–164° (gas evolution).

Anal. Calcd. for $C_{11}H_{19}O_3N_3$: C, 54.75; H, 7.94; N, 17.4. Found: C, 54.69; H, 7.86; N, 17.7.

A solution of 101 g. of distilled acid, b.p. 170–180° (3 mm.), in 500 ml. of absolute ethanol was esterified by bubbling in gaseous hydrogen chloride in the cold for five hours and allowing to stand for three days. On working up in the manner described earlier there was obtained 98 g. (83%) of ester, b.p. 125–135° (3 mm.). The analytical sample boiled at 119–121° (2 mm.), $n^{24}\text{D}$ 1.4538.

Anal. Calcd. for $C_{12}H_{20}O_3$: C, 67.89; H, 9.50. Found: C, 67.43; H, 9.43.

Condensations with Ethyl Cyanoacetate.—A mixture of 97 g. of the ester XIIIa, 52 g. of cyanoacetic ester, 7.1 g. of ammonium acetate, 22 g. of acetic acid and 300 ml. of benzene in a flask fitted for azeotropic distillation was refluxed for 17 hours until the volume of evolved water remained constant. Fractional distillation resulted in recovery of 23 g. of ketoester, b.p. 110–140° (2.5 mm.), 9 g. of an intermediate fraction, b.p. 140–185° (2.5 mm.), and 65 g. (61% based on recovered starting material) of product, b.p. 185-195° (2.5 mm.). Recycling of fractions 1 and 2 yielded an additional 25 g. of product and raised the total to 90 g. (64%). The analytical sample boiled at 172–174° (1 mm.), $n^{24}\text{D}$ 1.4831.

Anal. Calcd. for $C_{17}H_{25}O_4N$: C, 66.42; H, 8.20. Found: C, 66.49; H, 7.98.

Condensation of 98 g. of the ketoester XIIIb with ethyl cyanoacetate in the usual way, followed by recycling of the recovered starting material gave a total of 116 g. (82%) of condensation product, b.p. 185–195° (2.5 mm.), and 13 g. of crude starting material, b.p. 110–185° (3 mm.). The yield per cycle amounted to 60–67%. Redistillation yielded a product of b.p. 180–185° (1.5 mm.), $n^{24}\text{D}$ 1.4775.

Anal. Calcd. for $C_{17}H_{25}O_4N$: C, 66.42; H, 8.20. Found: C, 66.02; H, 8.39.

Ethyl 4-(5-Methyl-2-α-cyanocarbethoxymethylcyclopentyl)-butyrate.—The reduction of 48 g. of the cyanoester with platinum oxide in ethanol solution required several days and repeated additions of fresh catalyst. The product was collected at 180–190° (3.5 mm.). The analytical sample boiled at 175–177° (1.7 mm.), $n^{24}\text{D}$ 1.4640.

Anal. Calcd. for $C_{17}H_{27}O_4N$: C, 65.99; H, 8.80. Found: C, 65.99; H, 8.92.

4-(5-Methyl-2-carboxymethylcyclopentyl)-butyric Acid.—Hydrolysis of 39.5 g. of the preceding compound with 400 ml. of concentrated hydrochloric acid yielded 25 g. of viscous brown acid which was purified by taking up in 3 l. of hot water, treating with charcoal and allowing to cool. An oil separated which solidified on chilling for several days, wt. 16.3 g. (56%), m.p. in the range 90–94°, a difficultly separable mixture of stereoisomers. The more soluble of these was isolated in small quantity by concentrating the original acid mother liquor to small volume and allowing to stand for two weeks. The crystals, wt. 1.1 g., which had separated were taken up in 100 ml. of hot water. The solution was allowed to cool to 50° and decanted from some oil. Crystals separated on standing. The procedure was repeated once more and yielded colorless plates, m.p. 102–104°.

Anal. Calcd. for $C_{12}H_{20}O_4$: C, 63.13, H, 8.83. Found: C, 63.38; H, 8.64.

Ethyl 4-(4-Methyl-2-α-cyanocarbethoxymethylcyclopentyl)-butyrate.—Repeated additions of fresh catalyst (PtO_2) were needed to reduce the unsaturated ester completely. From 10 g. of ester there was obtained 8 g. (80%) of reduced material, b.p. 175–185° (2 mm.). The analytical sample boiled at 165–170° (1.5 mm.), $n^{25}\text{D}$ 1.4607.

Anal. Calcd. for $C_{17}H_{27}O_4N$: C, 65.99; H, 8.80. Found: C, 65.34; H, 8.42.

4-(4-Methyl-2-carboxymethylcyclopentyl)-butyric Acid.—In a subsequent run, 116 g. of the condensation product was reduced catalytically and hydrolyzed without prior purification by refluxing with 750 ml. of concentrated hydrochloric acid for 18 hours. The acid crystallized on cooling, wt. 84 g. (98%). Several recrystallizations from water afforded colorless crystals, m.p. 133-133.5°.

Anal. Calcd. for $C_{12}H_{20}O_4$: C, 63.13; H, 8.83. Found: C, 62.84; H, 8.86.

8-Methylbicyclo(5,3,0)-3-decanone (Xa).—A carefully ground mixture of 14.5 g. of the dibasic acid prepared from XIIIa, 14 g. of iron powder and 0.7 g. of barium hydroxide was heated in a 125-ml. distilling flask fitted with a thermometer whose bulb extended into the reactants. When the temperature reached 225°, a mixture of water and product began to distil. Heating was continued until the temperature rose above 350°. The product was taken up in ether and dried. Distillation yielded 7.5 g. (71%) of the ketone, b.p. 92–96° (2.5 mm.). Contamination by an apparently azulenic impurity caused a light blue coloration which could not be removed by distillation. The infrared spectrum (carbon tetrachloride solution) exhibited a strong band at 1705 $cm.^{-1}$ characteristic of aliphatic six- or seven-membered cyclic ketones.

Anal. Calcd. for $C_{11}H_{18}O$: C, 79.46; H. 10.92. Found: C, 79.64; H, 11.02.

The semicarbazone was recrystallized from methanol-water. It melted at 143–143.5°.

Anal. Calcd. for $C_{12}H_{21}N_3O_3$: C, 64.54; H, 9.48; N, 18.82. Found: C, 64.58; H, 9.48; N, 19.0.

8-Methylbicyclo(5,3,0)-decane (XIa).—A mixture of 5.5 g. of Xa, 4 g. of potassium hydroxide, 30 ml. of triethylene glycol and 5 ml. of hydrazine hydrate was heated at 110° for one hour. The condenser was removed, the temperature of the mixture was allowed to rise to 190° and refluxing was continued for three hours. Dilution with water followed by extraction with ether yielded 3.2 g. of a hydrocarbon, b.p. 47–50° (2 mm.), $n^{24}\mathrm{D}$ 1.4703.

Anal. Calcd. for $C_{11}H_{20}$: C, 86.76; H, 13.24. Found: C, 86.93; H, 13.11.

8-Methylbicyclo(5,3,0)-3-decanol.—A solution of 5.5 g. of Xa in 30 ml. of absolute ether was added dropwise with stirring to a solution of 1 g. of lithium aluminum hydride in 100 ml. of anhydrous ether. A brisk reaction ensued. After six additional hours of stirring and refluxing, the product was decomposed with water and 10% sulfuric acid. The neutral ether extract was dried and distilled. The product, wt. 4.7 g., boiled at 104–105° (4 mm.), $n^{24}\mathrm{D}$ 1.4911.

Anal. Calcd. for $C_{11}H_{20}O$: C, 78.51; H, 11.98. Found: C, 78.71; H, 11.83.

8-Methylbicyclo(5,3,0)-decene.—Six grams of freshly fused potassium acid sulfate was heated with 4.5 g. of the preceding alcohol at 190° for one-half hour. The product was taken up in ether, dried and distilled. There was obtained 1.3 g. of an olefin, b.p. 50–60° (2.5 mm.), and 1.9 g. of undehydrated alcohol, b.p. 95–105° (2.5 mm.), which could be recycled to yield more olefin. Lithium aluminum hydride reduction of 11 g. of Xa thus furnished a total of 4.8 g. of dehydrated material. Redistillation furnished a sample boiling at 45–47° (1 mm.), $n^{23}\mathrm{D}$ 1.4829.

Anal. Calcd. for $C_{11}H_{18}$: C, 87.92; H, 12.08. Found: C, 87.93; H, 12.23.

No attempt was made to locate the position of the double bond, which may be at the 2- or 3-position.[16]

A solution of 1 g. of the olefin in methanol was reduced catalytically (5% palladium–charcoal) until hydrogen uptake ceased. The infrared spectrum of the product, b.p. 47–50° (2 mm.), $n^{23}\mathrm{D}$ 1.4750, differed somewhat from the material obtained by Wolff–Kishner reduction of XIIIa in that a band at 798 cm.$^{-1}$ was missing.

1-Methylazulene.—A mixture of 2.2 g. of the olefin and 1.8 g. of sulfur was heated in an oil-bath at 230–240° for 25 minutes. The black product was extracted thoroughly with petroleum ether. The extract was filtered and passed through an alumina column. The first zone to be eluted contained a blue azulene; subsequent fractions (green and yellow) were discarded. The eluate was concentrated and mixed with a solution of 0.2 g. of trinitrobenzene in 15 ml. of warm ethanol. The precipitate which separated on standing weighed 93 mg. It was recrystallized repeatedly from ethanol. The violet-black needles melted at 160–160.5° (Kofler block), lit.[32] 160–161°, $\lambda_{\max}$ (after decomposition on alumina) in isoöctane solution 742, 703, 669, 635, 611, 587 mμ; lit.[33] 738, 705, 669, 638, 607, 582 mμ.

Dehydrogenation of the Wolff–Kishner reduction product XIa gave a very small amount of a blue azulene which was chromatographed repeatedly over alumina. Its spectrum ($\lambda_{\max}$ 742, 701, 668, 612, 588, 571 mμ) indicated that it was contaminated 1-methylazulene.

3,8-Dimethylbicyclo-(5,3,0)-decene.—A solution of 4 g. of Xa in 25 ml. of dry ether was added to methylmagnesium iodide prepared from 16 g. of methyl iodide and 2 g. of magnesium. A vigorous reaction ensued. The mixture was refluxed with stirring for two hours and decomposed by pouring over ice–ammonium chloride. The ether extracts were dried, concentrated and heated with 2.5 g. of freshly fused potassium acid sulfate at 180–190° for 15 minutes. The product was taken up in ether, dried, and distilled. The fraction boiling at 62–64° (2.3 mm.), was collected, yield 2.3 g. The analytical sample boiled at 56° (1.6 mm.), $n^{24}\mathrm{D}$ 1.4821. The infrared spectrum exhibited a band at 1645 with a shoulder at 1670 cm.$^{-1}$ (C=C).

Anal. Calcd. for $C_{12}H_{20}$: C, 87.73; H, 12.27. Found: C, 87.52; H, 12.50.

1,5-Dimethylazulene.—Two grams of the preceding olefin was mixed with 1.5 g. of sulfur and heated at 225–230° for one-half hour. The product was taken up in much petroleum ether and purified by passing through an alumina column. The blue azulene portion passed through first, followed by a green and then a yellow fraction which were discarded. The eluate containing the azulene was concentrated, taken up in 10 ml. of alcohol and mixed with a solution of 0.75 g. of trinitrobenzene in 50 ml. of warm ethanol. On cooling there precipitated a mixture of trinitrobenzene complex and trinitrobenzene, which was purified by passing again through an alumina column (eluent cyclohexane). The azulene was taken up in 10 ml. of ethanol, and mixed with 0.1 g. of trinitrobenzene in 10 ml. of warm ethanol. On standing there precipitated 77 mg. of trinitrobenzene complex. Two recrystallizations from ethanol furnished the analytical sample, m.p. 151–152.5° (Kofler block); lit.[34,35] 151–152°, 150–151°.

Anal. Calcd. for $C_{18}H_{15}N_3O_6$: C, 58.53; H, 4.09; N, 11.4. Found: C, 58.87; H, 4.31; N, 10.9.

The visible spectrum was determined by decomposing 5.7 mg. of the trinitrobenzene complex over alumina (eluent spectral grade isoöctane) and concentrating the eluate to 5 ml. It exhibited maxima at 765, 715 (shoulder), 681, 650 (shoulder), 622, 602, 565 (shoulder) and 545 (shoulder) mμ; $\epsilon_{\max}$ 126, 158, 316, 318, 374, 320, 264, 184.

1-Methyl-5-isopropylazulene.—To a solution of isopropylmagnesium bromide prepared from 12.5 g. of isopropyl bromide and 2 g. of magnesium was added dropwise a solution of 5 g. of 2-methylbicyclo(5,3,0)-5-decanone in 25 ml. of anhydrous ether. The mixture was stirred and refluxed for two hours and poured over ice–ammonium chloride. The ether layer was washed, dried, concentrated and heated with 5 g. of fused potassium acid sulfate at 180° for 20 minutes. Distillation furnished 3.9 g. of a product, b.p. 70–82° (2 mm.) whose infrared spectrum indicated that it consisted largely of unchanged Xa. An attempt to improve the yield of olefin by adding Xa to isopropyllithium did not appear to alter the composition of the product. For this reason, 2.2 g. of the olefin-ketone mixture was dehydrogenated directly by heating with 1.5 g. of sulfur at 220–235° for 30 minutes. The blue azulene was purified in the usual manner, yield 43 mg. of crude trinitrobenzene complex. Several recrystallizations from ethanol furnished violet-black needles, m.p. 137.5–138°.

Anal. 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.

The spectrum was determined on 5 ml. of an isoöctane solution obtained by decomposing 6.2 mg. of the complex over alumina. It exhibited maxima at 765, 705, 680, 645 (shoulder), 621, 602 (shoulder), 596 and 566 mμ (shoulder); $\epsilon_{\max}$ 110, 146, 264, 305, 353, 320, 320, 275.

9-Methylbicyclo(5,3,0)-3-decanone (Xb).—A mixture of 30 g. of the dibasic acid, prepared from XIIIb, 30 g. of iron powder and 1.5 g. of barium hydroxide was cyclized as previously described. Redistillation after drying furnished 14.1 g. (65%) of a liquid possessing a penetrating odor, b.p. 84–87° (1.8 mm.). A middle cut was distilled for analysis, b.p. 79–80° (1 mm.), $n^{23}\mathrm{D}$ 1.4820. Its infrared spectrum (carbon tetrachloride solution) exhibited the expected carbonyl band at 1703 cm.$^{-1}$.

Anal. Calcd. for $C_{11}H_{18}O$: C, 79.46; H, 10.92. Found: C, 79.57; H, 10.92.

The semicarbazone was recrystallized several times from aqueous methanol and melted at 182–183° dec.

Anal. Calcd. for $C_{12}H_{21}N_3O$: C, 64.54; H, 9.48; N, 18.82. Found: C, 64.35; H, 9.62; N, 18.7.

9-Methylbicyclo[5,3,0]decane (XIb).—A mixture of 5.5 g. of the previous ketone, 5 ml. of hydrazine hydrate, 30 ml. of triethylene glycol and 4 g. of potassium hydroxide was heated at 100° for one hour. After removal of the condenser the temperature was allowed to rise to 190°, the condenser was replaced and the heating continued for three hours. Dilution with water followed by ether extraction and distillation yielded 3.1 g. of the hydrocarbon, b.p. 53–54° (2.8 mm.), $n^{26}\mathrm{D}$ 1.4680.

Anal. Calcd. for $C_{11}H_{20}$: C, 86.76; H, 13.24. Found: C, 86.77; H, 13.24.

Attempts to dehydrogenate this hydrocarbon with sulfur or palladium did not furnish an azulene.

9-Methylbicyclo(5,3,0)-5-decanol and 9-Methylbicyclo(5,3,0)decene.—A solution of 5 g. of 9-methylbicyclo(5,3,0)-5-decanone in 25 ml. of anhydrous ether was added dropwise with stirring to a solution of 1 g. of lithium aluminum hydride in 100 ml. of ether. Stirring and refluxing was con-

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

[33] Pl. A. Plattner, *ibid.*, **24**, 283E (1941)

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

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

tinued for five hours and the mixture was worked up in the usual manner. The neutral fraction was heated for 35 minutes with 8 g. of freshly fused potassium acid sulfate at 180–190°. The organic material was taken up in ether, dried and distilled. Two fractions were obtained: I, b.p. 55–70° (2.5 mm.), wt. 0.9 g.; II, b.p. 95–100° (2.5 mm.), wt. 2.9 g.

Fraction II was redistilled, b.p. 85–88° (1.5 mm.), n^{23}D 1.4887. The infrared spectrum indicated that it was undehydrated alcohol containing a trace of ketone (nonbonded OH at 3645 cm.$^{-1}$, bonded OH centered at 3400, very weak C=O at 1703 cm.$^{-1}$).

Anal. Calcd. for $C_{11}H_{20}O$: C, 78.51; H, 11.98. Found: C, 78.42; H, 11.73.

Redehydration of the alcohol yielded more of fraction I (3.9 g. of alcohol gave 1.5 g. of fraction I and 1.7 g. of recovered material; the latter was recycled once more). The material was redistilled and analyzed, b.p. 45° (0.8 mm.), n^{24}D 1.4867. The infrared spectrum exhibited no bands characteristic of OH and C=O frequencies, but weak bands at 1690, 1650 and 1605 cm.$^{-1}$ probably due to C=C and indicating that the olefin was a mixture of isomers.

Anal. Calcd. for $C_{11}H_{18}$: C, 87.92; H, 12.08. Found: C, 87.76; H, 11.86.

2-Methylazulene.—A mixture of 2.6 g. of fraction I and 1.5 g. of sulfur was heated in an oil-bath at 235° for 30 minutes. The black product was extracted thoroughly with petroleum ether. The extract was filtered and percolated through an alumina column. A violet-blue product (A) passed through first; a second zone (B) was held more tenaciously and was eluted with petroleum ether–benzene. The color of eluate B was pure blue. Green and yellow zones were discarded.

Eluate A was concentrated on the steam-bath. The residue was taken up in 10 ml. of ethanol and treated with a solution of 0.5 g. of trinitrobenzene in 40 ml. of ethanol. There was obtained a total of 0.35 g. of rust-colored complex which was recrystallized several times from ethanol and exhibited a constant m.p. of 135–136° (Kofler block), lit.[32,36] 140–141°.

Anal. Calcd. for $C_{17}H_{13}N_3O_6$: C, 57.46; H, 3.69; N, 11.83. Found: C, 57.38; H, 3.80; N, 11.9.

The spectrum was determined by decomposing 15.4 mg. of the complex on a small column of alumina, using spectral grade isoöctane as eluent, and concentrating the eluate to 10 ml., λ_{max} 678, 652, 634 (shoulder), 625 (shoulder), 615 (shoulder), 591, 568, 562, 551, 533, 523, 475 mμ; ϵ_{max} 111, 130, 133, 180, 240, 220, 236, 255, 253, 227, 185, 162, 48; lit.[36] 676, 650, 634, 623, 613, 601, 592, 579, 570, 561, 551, 543 mμ. Although the m.p. was slightly lower than reported, the analysis and the visible spectrum furnished evidence for the identity of our material with 2-methylazulene.

Elutate B did not furnish a crystalline trinitrobenzene complex and therefore was not investigated further.

3,9-Dimethylbicyclo(5,3,0)decene.—A solution of 8 g. of ketone Xb in 30 ml. of anhydrous ether was added dropwise to methylmagnesium iodide prepared from 21 g. of methyl iodide and 3 g. of magnesium. The mixture was refluxed for two hours and then decomposed. The neutral fraction was heated at 180° for 20 minutes with 4 g. of freshly fused potassium acid sulfate. The organic material was extracted with ether, dried and distilled, b.p. 55–58° (1.5 mm.), yield 5.1 g. The analytical sample had n^{23}D 1.4817 (C=C band at 1640 cm.$^{-1}$).

Anal. Calcd. for $C_{12}H_{20}$: C, 87.73; H, 12.27. Found: C, 87.68, 12.28.

2,5-Dimethylazulene.—A mixture of 2.4 g. of the preceding olefin and 1.5 g. of sulfur was heated at 230° for 30 minutes. The dark green petroleum ether extract was chromatographed over alumina and the violet-blue eluate (a small amount of a blue fraction stayed on the column) was concentrated, taken up in ethanol, mixed with a solution of 0.3 g. of trinitrobenzene in 20 ml. of ethanol, concentrated to 30 ml. and allowed to stand. The violet-black needles of the trinitrobenzene complex weighed 0.268 g. Several recrystallizations from benzene resulted in a constant m.p. of 149–150.5° (Kofler).

Anal. Calcd. for $C_{18}H_{15}N_3O_6$: C, 58.53; H, 4.09. Found: C, 58.49; H, 4.01.

Spectral measurements were carried out by decomposing 15.9 mg. of complex and making up to 10 ml. with spectral grade isoöctane. The azulene exhibited maxima at 693, 668, 655 (shoulder), 628, 603, 578, 558, 545 and 480 mμ; ϵ_{max} 112, 131, 153, 266, 260, 291, 253, 223 and 63.

2-Methyl-5-isopropylazulene.—A solution of 6 g. of 9-methylbicyclo(5,3,0)-3-decanone in 30 ml. of anhydrous ether was added to isopropylmagnesium bromide prepared from 20 g. of isopropyl bromide and 3 g. of magnesium. The mixture was refluxed for two hours, decomposed, dried and dehydrated with 3.5 g. of fused potassium acid sulfate for 30 minutes at 180°. Distillation yielded material which was arbitrarily divided into two fractions: b.p. up to 68° (0.8 mm.), wt. 0.98, and b.p. 68–75° (0.8 mm.), wt. 3.1 g. The infrared spectrum of the lower boiling fraction indicated that it was a mixture of olefin and starting material. The use of isopropyllithium did not offer any advantage.

The low boiling fraction, wt. 0.9 g., was mixed with 0.55 g. of sulfur and heated to 235° for 20 minutes. The petroleum ether extract was chromatographed several times to remove a bluish fraction from the violet-blue eluate, concentrated, taken up in 10 ml. of ethanol, mixed with a solution of 0.1 g. of trinitrobenzene in 10 ml. of ethanol, concentrated to 10 ml. and allowed to stand. Several recrystallizations from a small amount of ethanol furnished long needles, m.p. 113–114.5° (Kofler), lit.[37] 110–111°.

Anal. Calcd. for $C_{20}H_{19}N_3O_6$: C, 60.45; H, 4.82; N, 10.58. Found: C, 60.58; H, 5.05; N, 10.6.

The spectrum was obtained by using a solution prepared by decomposition of 14.0 mg. of the trinitrobenzene complex. Maxima were observed at 688, 663, 655 (shoulder), 625, 600, 575, 545 (shoulder) and 485 (shoulder) mμ; ϵ_{max} 108, 122, 126, 275, 218, 307, 236 and 80; lit.[37] 689, 662, 624, 600, 578, 553 and 536.

4-(2-Methylcyclopentyl)-butyric Acid (Mixture of *cis* and *trans* Isomers.—Reduction of 69 g. of XIIIa by the procedure of Huang-Minlon for ketoacids gave 56 g. of a viscous liquid boiling at 125–130° (2.5 mm.). The analytical sample boiled at 120° (1.2 mm.).

Anal. Calcd. for $C_{10}H_8O_6$: C, 70.54; H, 10.66. Found: C, 70.31; H, 10.49.

The amide melted in the range 65–72°, the highest m.p. observed being 68–72°. A mixed m.p. with the amide of authentic *trans*-4-(2-methylcyclopentyl)-butyric acid[18] (m.p. 72.5–73°) was 68–70°. The m.p. of the amide of authentic 4-cyclopentylvaleric acid is 112°.[18]

In a later run a smaller amount of this acid was prepared by reduction of a sample of XIIIa which had been regenerated from its ethyl ester by basic hydrolysis, thus affording more opportunity for equilibration. This fraction boiled at 130–134° (3 mm.) and gave an amide of m.p. 86–96° (three crystallizations from ligroin). Further crystallizations from cyclohexane raised the m.p. to 94–97.5°. The *p*-bromophenacyl ester prepared from this material melted at 66–68°; mixed m.p. with *p*-bromophenacyl ester of *trans*-4-(2-methylcyclopentyl)-butyric acid[18] (m.p. 70–71°) 67–70°. The *p*-bromophenacyl ester of 4-cyclopentylvaleric acid melts at 75.5–77°.[18]

Degradation of the Acid Mixture.—(A) The mixture of *cis* and *trans* isomers, wt. 53 g., was esterified by refluxing with 80 ml. of dry ethanol, 200 ml. of benzene and 8 ml. of sulfuric acid in an apparatus fitted with a Dean–Stark trap. The ester, yield 59.5 g. (96%), boiled at 79–80° (1.5 mm.), n^{22}D 1.4448.

Anal. Calcd. for $C_{12}H_{22}O_2$: C, 72.68; H, 11.18. Found: C, 72.84; H, 11.17.

(B) A solution of 48 g. of ester in 150 ml. of dry ether was added dropwise to a solution of phenylmagnesium bromide prepared from 118 g. of bromobenzene and 18 g. of magnesium. The mixture was refluxed for three hours and decomposed with ammonium chloride. The residue obtained from the ether layer was dehydrated by refluxing with 70 ml. of acetic acid and 30 ml. of acetic anhydride. The solvents were removed ***in vacuo*** and the residue was distilled, furnishing 53 g. of an olefin boiling at 191–198° (3 mm.), n^{22}D 1.5650. The carbon value of this material was somewhat low, possibly due to the presence of some alcohol.

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

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

Anal. Calcd. for $C_{22}H_{26}$: C, 90.98; H, 9.02. Found: C, 89.90; H, 9.11.

(C) Oxidation of 21 g. of the olefin, dissolved in 50 ml. of isoöctane and 200 ml. of acetic acid, with a solution of 28 g. of CrO_3 in 20 ml. of water and 150 ml. of acetic acid at 65° furnished 6.9 g. (61%) of an acid fraction, b.p. 102–105° (1.5 mm.), n^{21}D 1.4602.

Anal. Calcd. for $C_9H_{16}O_2$: C, 69.19; H, 10.32. Found: C, 69.59; H, 10.25.

The *p*-bromophenacyl ester melted at 57.5–58.5°.

Anal. Calcd. for $C_{17}H_{21}O_3Br$: C, 57.85; H, 5.99. Found: C, 57.47; H, 6.17.

A mixed m.p. with the *p*-bromophenacyl ester of authentic *trans*-3-(2-methylcyclopentyl)-propionic acid (m.p. 68°)[18] was 57–67°.

The amide melted at 101–102.5° after five successive recrystallizations, none of which gave a constant m.p. The amide of authentic *trans*-3-(2-methylcyclopentyl)-propionic acid melts at 93°[18]; the m.p. of the amide of 3-cyclopentylbutyric acid is 119–120.5°.

(D) Esterification of 9 g. of the preceding acid with diazomethane furnished 8 g. of a methyl ester, b.p. 65–70° (2 mm.), n^{25}D 1.3348.

Anal. Calcd. for $C_{10}H_{18}O_2$: C, 70.54; H, 10.66. Found: C, 70.05; H, 10.85.

This was converted to an olefin by reaction with phenylmagnesium bromide and dehydration in the manner described previously. The olefin, wt. 8.4 g., boiled at 175–180° (3.5 mm.); its carbon analysis was low, as was that of the higher homolog.

Anal. Calcd. for $C_{21}H_{24}$: C, 91.25; H, 8.75. Found: C, 90.09; H, 8.93.

(F) Oxidation of 8 g. of the olefin with 11.5 g. of chromic oxide gave 1.6 g. of an acid fraction, b.p. 105–108° (4 mm.), n^{23}D 1.4538, whose amide melted at 132–133.5°, mixed m.p. with amide of 2-cyclopentylpropionic acid (m.p. 140.5–141°) 120–127°, mixed m.p. with amide of *cis*-2-methylcyclopentylacetic acid (m.p. 149–149.5°) 142–147°, mixed m.p. with amide of *trans*-2-methylcyclopentane-acetic acid (m.p. 140.5–141.5°) 135–140°.

Anal. Calcd. for $C_8H_{15}NO$: C, 68.04; H, 10.71. Found: C, 68.29; H, 10.93.

The *p*-bromophenacyl ester of the mixed *cis*- and *trans*-acids melted at 62.5–64°. The esters of the pure *cis*- and *trans*-acids melt at 60.5–61.5° and 65–66.5°, respectively, and there was no evidence of depression below 60° on taking m.p.'s of various compositions.

4-(3-Methylcyclopentyl)-butyric Acid.—Reduction of 10 g. of acid XIIIb by the procedure of Huang-Minlon for ketoacids resulted in 6.1 g. of an acid, b.p. 120–122° (2 mm.), n^{23}D 1.4550.

Anal. Calcd. for $C_{10}H_{18}O_2$: C, 70.54; H, 10.66. Found: C, 70.76; H, 10.71.

The amide was recrystallized from ligroin and melted at 100–101°. The mixed m.p. with the amide of 3-methyl-4-cyclopentylbutyric acid (*vide infra*) was 98.5–100°.

Anal. Calcd. for $C_{10}H_{19}NO$: C, 70.96; H, 11.32. Found: C, 71.13; H, 11.27.

The *p*-bromophenacyl ester melted at 67.5–68° after recrystallization from ethanol–water. The *p*-bromophenacyl ester of 3-methyl-4-cyclopentylbutyric acid melts at 56–57° (*vide infra*).

Anal. Calcd. for $C_{18}H_{23}O_3Br$: C, 58.86; H, 6.31. Found: C, 58.87; H, 6.33.

The ethyl ester, b.p. 78–80° (1.5 mm.), n^{22}D 1.4418, was prepared in 73 g. yield (89%) by refluxing 70 g. of the acid with 100 ml. of absolute ethanol, 300 ml. of benzene and 10 g. of sulfuric acid in an apparatus fitted with a Dean–Stark trap.

Anal. Calcd. for $C_{12}H_{22}O_2$: C, 72.68; H, 11.18. Found: C, 72.73; H, 11.06.

2-Bromo-4-(3-methylcyclopentyl)-butyric Acid.—In an effort to degrade the acid by two carbon atoms at once, it was brominated by the method of Schwenk and Papa,[38] but 25 g. yielded only 11 g. of a fraction, b.p. 122–125° (3.5 mm.), n^{22}D 1.4731, whose analysis showed that it was the desired bromo acid.

Anal. Calcd. for $C_{12}H_{21}O_2Br$: C, 51.99; H, 7.64. Found: C, 52.13; H, 7.58.

An attempt to dehydrohalogenate this material by heating with dimethylaniline did not result in a pure product.

1,1-Diphenyl-4-(3-methylcyclopentyl)-propionic Acid.—A solution of 73 g. of the preceding ester in 200 ml. of dry ether was added to phenylmagnesium bromide prepared from 180 g. of bromobenzene and 27 g. of magnesium. After three hours of stirring at reflux, the mixture was worked up in the usual manner. The neutral fraction was refluxed with 450 ml. of acetic acid and 200 ml. of acetic anhydride for four hours. Distillation gave 90 g. (84%) of product, b.p. 170–174° (1 mm.), n^{22}D 1.5643. Analysis of this material indicated that it was not completely dehydrated.

Anal. Calcd. for $C_{22}H_{26}$: C, 90.98; H, 9.02. Found: C, 89.88; H, 9.01.

3-(3-Methylcyclopentyl)-propionic Acid.—Chromic acid oxidation of the olefin gave only 8.1 g. of an acid fraction (apparently due to over-heating during solvent removal), b.p. 105–110° (1.5 mm.).

Anal. Calcd. for $C_9H_{16}O_2$: C, 69.19; H, 10.32. Found: C, 69.11; H, 10.37.

The ethyl ester was prepared by azeotropic distillation, b.p. 62–66° (1 mm.), yield 8.4 g. (88%), n^{22}D 1.4364.

Anal. Calcd. for $C_{11}H_{10}O_2$: C, 71.69; H, 10.94. Found: C, 71.61; H, 10.89.

1,1-Diphenyl-3-(3-methylcyclopentyl)-1-propene.—Reaction of 8.2 g. of the ethyl ester with excess phenylmagnesium bromide in the manner described above gave, prior to dehydration, 11.5 g. (88%) of tertiary alcohol, b.p. 170–175° (1 mm.).

Anal. Calcd. for $C_{21}H_{26}O$: C, 85.66; H, 8.90. Found: C, 85.61; H, 8.88.

The alcohol was dehydrated by refluxing with 70 ml. of acetic acid and 30 ml. of acetic anhydride, yield 8.9 g. (82%) n^{22}D 1.5702, b.p. 155–160° (1 mm.).

Anal. Calcd. for $C_{21}H_{24}$: C, 91.25; H, 8.75. Found: C, 90.51; H, 8.94.

3-Methylcyclopentylacetic Acid.—Oxidation of 8.5 g. of the olefin with 11.5 g. of chromic oxide furnished 2.2 g. (50%) of an acid fraction, b.p. 93–95° (2 mm.), n^{22}D 1.4503.

Anal. Calcd. for $C_8H_{14}O_2$: C, 67.57; H, 9.93. Found: C, 67.28; H, 9.97.

The amide was recrystallized from benzene–ligroin (b.p. 65–110°), m.p. 140.5–141°, mixed m.p. with amide of *trans*-2-methylcyclopentylacetic acid (m.p. 140.5–141.5°),[18] 132.5–137°.

Anal. Calcd. for C_8H_0NO: C, 68.04; H, 10.71. Found: C, 67.66; H, 11.07.

The *p*-bromophenacyl ester was recrystallized from ethanol–water and melted at 67.5°; mixed m.p. with the *p*-bromophenacyl ester of *trans*-2-methylcyclopentylacetic acid 56–61°.

Anal. Calcd. for $C_{16}H_{19}O_3Br$: C, 56.65; H, 5.65. Found: C, 56.64; H, 5.92.

The 3-methylcyclopentylacetic acid synthesized by Nenitzescu and co-workers[20] had b.p. 236°, n^{20}D 1.4504, amide m.p. 142°. The 3-methylcyclopentylacetic acid isolated by Ney, *et al.*,[21] had b.p. 239, n^{20}D 1.4487, amide m.p. 141–142°. The 3-methylcyclopentylacetic acid prepared by Desai[20] had b.p. 141° (25 mm.), n^{20}D 1.4463. This work was repeated in the following way. 3-Methylcyclopentanone was condensed with ethyl cyanoacetate in 72% yield by the method of Cope and co-workers.[39] The observation of Vogel[40] that the condensation product existed in a liquid and solid form was confirmed, but since the English worker obtained the same product from both forms on reduction no attempt was made to reduce them separately. The infrared spectrum of the solid (m.p. 67–68°) indicated that the double bond was exocyclic, contrary to the speculation of Desai[32] (conjugated ester at 1725 cm.$^{-1}$, conjug. C≡N at 2230 cm.$^{-1}$, C=C at 1620 cm.$^{-1}$). Reduction with aluminum amalgam in moist ether for a period of three days furnished the saturated ester, b.p. 103–107°, n^{22}D 1.4513,

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[38] E. Schwenk and D. Papa, THIS JOURNAL, **70**, 3626 (1948).

[39] A. C. Cope, C. M. Hoffmann, C. Wyckoff and E. Hardenbergh, *ibid.*, **63**, 3453 (1941).

[40] A. I. Vogel, *J. Chem. Soc.*, 1795 (1931).

yield 69%, which was hydrolyzed and decarboxylated to 3-methylcyclopentylacetic acid, probably a mixture of *cis* and *trans* isomers, b.p. 93–95° (1.4 mm.), $n^{22}\text{D}$ 1.4499, m.p. of the amide 139–140.5°, mixed m.p. with degradation product 138–140.5°; m.p. of *p*-bromophenacyl ester 65°, mixed m.p. with degradation product 64–66°.

It was hoped that catalytic hydrogenation of 3-methylcyclopentylidene cyanoacetic ester might furnish the *cis* isomer due to interference of the methyl group with the catalyst surface (for a similar case see ref. 18). Hydrogenation in ethanol, 5% palladium-on-charcoal as catalyst, stopped after the absorption of 1.3 moles of hydrogen and distillation furnished 30 g. of a fraction, b.p. 103–106° (2 mm.), $n^{22}\text{D}$ 1.4520. Hydrolysis and decarboxylation gave an acid, virtually identical with the acid obtained by aluminum amalgam reduction, b.p. 89–91° (1.2 mm.), $n^{22}\text{D}$ 1.4494, m.p. of amide 138–139°, mixed m.p. with the other reduction product 137.5–139°, mixed m.p. with degradation product 138–140.5°, m.p. of *p*-bromophenacyl ester 66–67°, mixed m.p. with the other reduction product 64–66°, mixed m.p. with degradation product 66–67°. The infrared spectra of all fractions were identical. Apparently the relatively great distance of the methyl group from the reaction site operates to reduce the degree of steric control during reduction, but more work is needed to establish this point.

Cyclopentylacetone.—Ethyl cyclopentylacetoacetate was prepared by the method of Rydon[41] which gave better yields than the procedure described by Burschkies and Scholl.[42] A mixture of 110 g. of the ketoester, 60 g. of potassium hydroxide and 800 ml. of water was refluxed overnight and then steam distilled. The distillate was extracted with ether and the ether extracts were dried and distilled. The ketone was collected at 84–86° (31 mm.), yield 49.5 g. (71%). This method appears to be more convenient than the one described in the literature.[43] The 2,4-dinitrophenylhydrazone melted at 84° (lit.[43b] 78–79°).

Ethyl 2-Cyano-3-methyl-4-cyclopentylcrotonate.—A mixture of 49 g. of cyclopentylacetone, 45 g. of ethyl cyanoacetate, 16 g. of acetic acid, 5.9 g. of ammonium acetate and 200 ml. of benzene was refluxed in an apparatus fitted with a Stark–Dean trap until water was no longer evolved. The solution was washed with water, dried and distilled. The product distilled at 135–138° (2.5 mm.), $n^{22}\text{D}$ 1.4890, wt. 74.5 g. (87%).

Anal. Calcd. for $C_{13}H_{19}NO_2$: C, 70.65; H, 8.65. Found: C, 70.70; H, 8.73.

Ethyl 2-Cyano-3-methyl-4-cyclopentylbutyrate.—A solution of 74.5 g. of the unsaturated ester in 175 ml. of absolute alcohol was shaken with 5% palladium-on-charcoal in an atmosphere of hydrogen (3–4 atmospheres) until hydrogen uptake ceased. Distillation furnished 66 g. of product, b.p. 120–126° (2 mm.), $n^{22}\text{D}$ 1.4559.

Anal. Calcd. for $C_{13}H_{21}NO_2$: C, 69.92; H, 9.48. Found: C, 70.00; H, 9.57.

3-Methyl-4-cyclopentylbutyric Acid.—A mixture of 66 g. of the preceding ester, 100 g. of potassium hydroxide, 100 ml. of water and 350 ml. of water was refluxed for 16 hours. The alcohol was removed and the residue was diluted with water, extracted with ether and acidified. An oil separated which solidified on standing. It did not decarboxylate on distillation. A small amount was recrystallized several times from a benzene-petroleum ether mixture. Analysis of the colorless crystals, m.p. 99°, showed that the solid was 2-cyano-3-methyl-4-cyclopentylbutyric acid.

Anal. Calcd. for $C_{11}H_{17}NO_2$: N, 7.17. Found: N, 7.25.

In order to complete the hydrolysis, the remaining material was refluxed with 300 ml. of concd. hydrochloric acid. The mixture was cooled and extracted with ether. The dried ether extracts were distilled, furnishing 34 g. (67%) of the desired acid, b.p. 119–121° (2 mm.), $n^{22}\text{D}$ 1.4579. Its preparation has been reported previously[44] but no properties were given.

Anal. Calcd. for $C_{10}H_{18}O_2$: C, 70.54; H, 10.66. Found: C, 70.82; H, 10.69.

The amide was recrystallized several times from ligroin and melted at 99.5–101°.

Anal. Calcd. for $C_{10}H_{19}NO$: C, 70.96; H, 11.32. Found: C, 71.16; H, 11.42.

The *p*-bromophenacyl ester was recrystallized three times from ethanol containing a little water and melted at 56–57°.

Anal. Calcd. for $C_{18}H_{23}O_3Br$: C, 58.86; H, 6.31. Found: C, 59.12; H, 6.48.

TALLAHASSEE, FLA.

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[41] H. N. Rydon, *J. Chem. Soc.*, 1544 (1939)

[42] K. Burschkies and J. Scholl, *Arch. Pharm.*, **281**, 328 (1943).

[43] (a) E. Rohrmann, U. S. 2,520,015; *C. A.*, **45**, 647 (1951); (b) Ming-Chien Chiang, *J. Chin. Chem. Soc.*, **18**, 65 (1951); *C. A.*, **46**, 4471 (1952).

[44] J. v. Braun, W. Rudolph, H. Kröper and W. Pinkernelle, *Ber.*, **67**, 269 (1934).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, PURDUE UNIVERSITY]

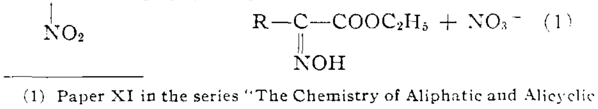
A New Reaction of α-Nitroesters[1,2]

BY NATHAN KORNBLUM AND JOHN H. EICHER

RECEIVED AUGUST 5, 1955

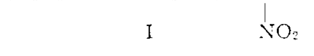
α-Nitroesters react with a solution of sodium nitrite in aqueous ethanol at room temperature giving α-oximinoesters in 70–78% yields. Ethyl nitroacetate reacts vigorously to give a mixture of nitrous oxide, nitrogen and carbon dioxide. If the α-nitroester does not have a hydrogen atom on the carbon holding the nitro group it is quantitatively recovered. The mechanism of this new reaction is discussed.

α-Nitroesters react with sodium nitrite according to eq. 1. This reaction, which takes place at room temperature, gives 70–78% yields of the α-oximinoesters.[3]

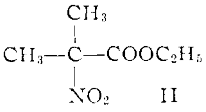


$$\underset{\displaystyle NO_2}{\underset{|}{R\text{—}CHCOOC_2H_5}} + NO_2^- \longrightarrow \underset{\displaystyle NOH}{\underset{\|}{R\text{—}C}}\text{—}COOC_2H_5 + NO_3^- \quad (1)$$

On the other hand, α-nitroesters I and II, which have no α-hydrogen atoms, are recovered in 94–96% yields after eleven days exposure to the action of aqueous ethanolic sodium nitrite.[4]



$$(C_2H_5OOC\text{—}CH_2CH_2)_2\text{—}\underset{\displaystyle NO_2}{\underset{|}{C}}\text{—}COOC_2H_5 \quad \text{I}$$



$$CH_3\text{—}\overset{\displaystyle CH_3}{\overset{|}{\underset{\displaystyle NO_2}{\underset{|}{C}}}}\text{—}COOC_2H_5 \quad \text{II}$$

The rather striking oxidation–reduction of eq. 1 becomes readily intelligible on the following basis

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[1] Paper XI in the series "The Chemistry of Aliphatic and Alicyclic Nitro Compounds" for X see THIS JOURNAL, **77**, 6654 (1955).

[2] This research was supported by the United States Air Force under Contract No. AF18(600)-310 monitored by the Office of Scientific Research, Air Research and Development Command.

[3] The stereochemistry of these oximes is not known. The presence of nitrate ion in the reaction product has been established.

[4] We thank Dr. D. C. Iffland for the experiment with ethyl α-nitroisobutyrate.