A subsequent reduction was carried out with 7.452 g. (0.0445 mole) of the ketone **13c**, 6.9 g. (0.30 g.-atom) of sodium, 50 g. (0.83 mole) of isopropyl alcohol, and 150 ml. of toluene, small aliquots (*ca.* 0.25 ml.) of the reaction mixture being removed periodically and analyzed as previously described. After the sodium had been consumed (128 min.), 720 mg. (3.95 mmoles) of benzophenone was added and refluxing was continued. The amino alcohol composition in the reaction mixture after various periods of time was as follows: 8 min., 9% of **15c** and 91% of **16c**; 128 min., 9% of **15c** and 91% of **16c**; 25.5 hr., 24% of **15c** and 76% of **16c**; 120 hr., 44% of **15c** and 56% of **16c**; 216 hr., 55% of **15c** and 45% of **16c**; 262 hr., 57% of **15c** and 43% of **16c**.

After a total reaction time of 262 hr., the crude mixture of amino alcohols was separated in the usual way and treated with 10.5 g. (0.056 mole) of *p*-nitrobenzoyl chloride in 120 ml. of chloroform. The resulting mixture was allowed to stand for 3 days and then worked up as previously described. The crude amino ester hydrochloride **20c**–*p*-nitrobenzoic acid mixture which crystallized from ethanol was shaken with a mixture of 100 ml. of aqueous sodium bicarbonate and 100 ml. of methylene chloride until solution was complete. The methylene chloride solution was washed with aqueous sodium bicarbonate, dried over potassium carbonate, and concentrated to leave 5.779 g. (40.7% based on the starting ketone) of the ***p*-nitrobenzoate of the amino alcohol 15c** (*i.e.*, the free base corresponding to the amine hydrochloride **20c**), m.p. 112–113°. Recrystallization from an ether–petroleum ether mixture afforded the pure amino ester as yellow plates, m.p. 114.5–115°. The material has infrared absorption[34] at 1720 cm.$^{-1}$ (conj. ester C=O) with no absorption in the 3-μ region attributable to an N–H or O–H function. The product has an ultraviolet maximum[25] at 250 mμ (ϵ 14,100) and n.m.r. absorption at 1.68 τ (aryl C–H), at 4.75 τ (broad >CH–O), and at 7.76 τ (singlet, N–CH$_3$).

Anal. Calcd. for $C_{17}H_{22}N_2O_4$: C, 64.13; H, 6.97; N, 8.80. Found: C, 64.08; H, 6.99; N, 8.82.

The ethanol mother liquors remaining after the separation of crude **20c** were concentrated and diluted with acetone to separate 2.535 g. (27.7%) of the crude hydrochloride of amino alcohol **16c**, m.p. 225–230°. Recrystallization from an ethanol–acetone mixture separated various fractions of the hydrochloride of **16c** contaminated with the hydrochloride of **15c**. The samples of free base liberated from these various fractions were found to contain[30] **16c** contaminated with 13 to 27% of **15c**.

4-*t*-Butyl-1-methylpiperidin-4-ol (**22**).—A solution of 11.7 g. (0.103 mole) of 1-methyl-4-piperidone in 20 ml. of pentane was added, dropwise and with stirring under a nitrogen atmosphere, to a solution containing 0.140 mole of *t*-butyllithium in 75 ml. of pentane.[35] After the addition was complete, the reaction mixture was stirred at room temperature for 3 hr. and then hydrolyzed with water. The pentane layer was separated and the aqueous phase was saturated with sodium chloride and extracted with ether. The combined organic solutions were dried over sodium sulfate, concentrated and fractionally distilled to separate 2.96 g. (25.1% recovery) of unchanged 1-methyl-4-piperidone, b.p. 63–65° (15 mm.), and the crude amino alcohol **22**, b.p. 110–130° (13 mm.), which solidified. Recrystallization from ligroin and subsequent sublimation (80° at 14 mm.) gave 3.684 g. (21.0%) of the **amino alcohol 22**, m.p. 79.5–80.5°. An additional crystallization from ligroin gave the pure amino alcohol as colorless plates, m.p. 80–81°. The material has infrared absorption[26] at 3600 cm.$^{-1}$ (unassoc. O–H), at 3200 cm.$^{-1}$ (broad, assoc. O–H) and at 2795, 2760, 2740 and 2680 cm.$^{-1}$ (two C–H bonds adjacent, *trans* and coplanar to the unshared electron pair on nitrogen), with n.m.r. singlets[28] at 7.72 τ (3H, N–CH$_3$) and 9.07 τ (9H, C–CH$_3$).

Anal. Calcd. for $C_{10}H_{21}NO$: C, 70.12; H, 12.36; N, 8.18; mol. wt., 171. Found: C, 70.04; H, 12.37; N, 8.21; mol. wt., 171 (mass spectrum).

Acknowledgment.—We are indebted to Dr. Malcolm R. Bell of the Sterling-Winthrop Research Institute for samples of the 2- and 3-tropanols.

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[34] Determined in carbon tetrachloride solution.

[35] This lithium reagent was obtained from the Lithium Corporation of America.

Bicyclic Ketones. I. Reaction of Cyclopentadiene with *cis*- and *trans*-Benzalacetone and Acetylphenylacetylene[1]

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Received November 13, 1962

Diels–Alder addition of *cis*-benzalacetone to cyclopentadiene yielded the expected *endo–cis* adduct X. *trans*-Benzalacetone produced a mixture of the two *trans* isomers in proportions which depended on the temperature of reaction. Acetylphenylacetylene formed the expected norbornadiene derivative XV. The stereochemistry of these compounds was established by haloform degradation to the acids, followed by iodolactonization.

Our need for pure samples of isomers in the 2-acetyl-3-phenyl-5-norbornene series and their saturated analogs prompted us to investigate the Diels–Alder reactions of cyclopentadiene with the geometrical isomers of benzalacetone (I and II) and acetylphenylacetylene (III, 4-phenylbut-3-yn-2-one) as a preparative method.

It was hoped at the outset of this work that the mixtures derived from the Diels–Alder reactions could be separated by any one of the conventional methods, *i.e.*, fractional distillation, vapor phase chromatography (v.p.c.), fractional crystallization, etc.; however, this was not the case. Therefore, it was decided to analyze the mixtures by conversion of the ketones to their derived acids *via* the haloform reaction and then utilize the procedures previously reported for determination of the isomer ratios of the acids.[2–4]

Reaction of cyclopentadiene with *trans*-benzalacetone (I) at 139°, 155°, and at 155–220° yielded in each case a mixture of *endo*-2-acetyl-*exo*-3-phenyl-5-norbornene (IV) and *exo*-2-acetyl-*endo*-3-phenyl-5-norbornene (V). Treatment of IV and V under the conditions of the haloform reaction gave a mixture of *exo*-3-phenyl-5-norbornene-*endo*-2-carboxylic acid (VI) and *endo*-3-phenyl-5-norbornene-*exo*-2-carboxylic acid (VII). The procedure of Rondestvedt and Ver Nooy,[3] was used to prepare the iodolactone VIII of the *endo* acid VI,

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[1] Presented at the 14th annual Southeastern Regional Meeting of the American Chemical Society, Gatlinburg, Tenn., November 1–3, 1962.

[2] K. Alder, W. Gunzl, and K. Wolff, *Ber.*, **93**, 809 (1960).

[3] C. S. Rondestvedt and C. D. Ver Nooy, *J. Am. Chem. Soc.*, **77**, 4878 (1955).

[4] G. I. Poos, J. Kleis, R. R. Wittekind, and J. D. Rosenau, *J. Org. Chem.*, **26**, 4898 (1961).

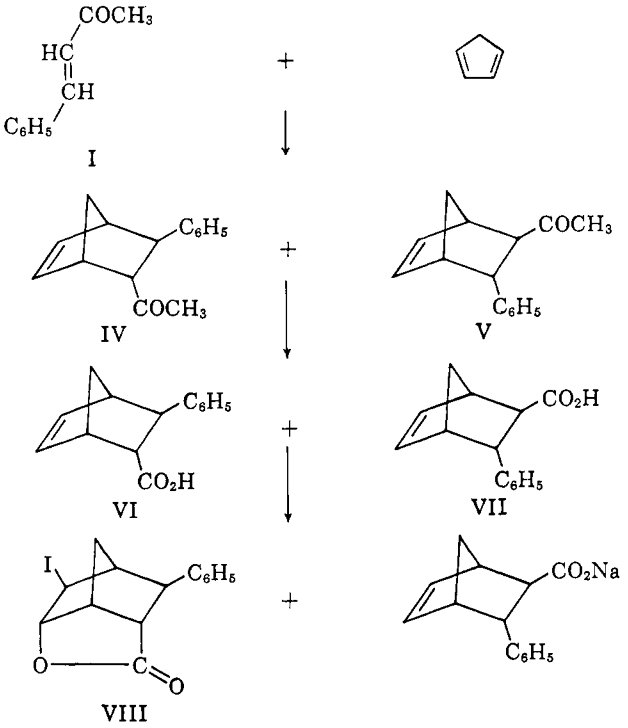
TABLE I

EFFECT OF TEMPERATURE ON THE RATIO OF ISOMERS IN THE REACTION OF I WITH CYCLOPENTADIENE

Temp., °C.	IV, %	V, %
139	49	51
155	22	78
155–220	81	19

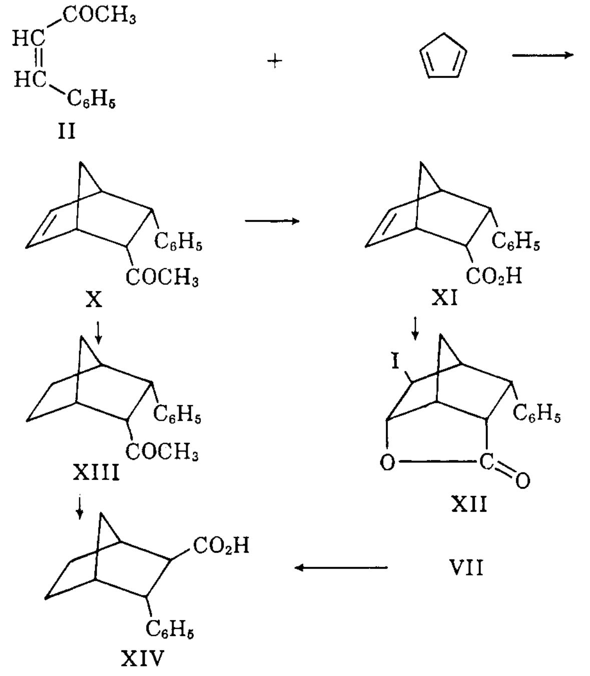
which was separated from the unchanged sodium salt of VII.[5] The results are summarized in Table I.

It is the normal trend[6] for the per cent of the *endo*-carbonyl isomer in a *trans* arrangement to decrease as the temperature increases. The values obtained for the ratio of IV and V at 139° and at 155° are in agreement with this trend and also agree well with values obtained with *trans*-cinnamoyl chloride[2,3] and *trans*-cinnamic acid.[3,7] The ratio obtained for the reaction at 155–220° is in disagreement with the trend but not completely surprising. At this high temperature the thermodynamically more stable isomer would be expected since the reaction is reversible.[8] The phenyl group is larger than the acetyl group and, therefore, would be more stable in the *exo* configuration.[6]

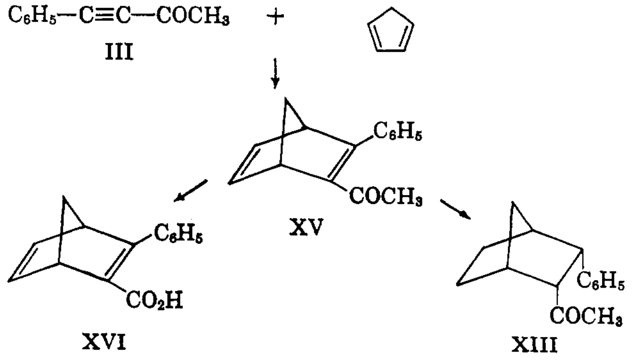


Upon standing for about two days in a stoppered Pyrex flask, a mixture of IV and V polymerized to form a white solid IX of unknown structure. Elemental analysis and molecular weight determination indicated the product was a dimer. The resistance of this dimer to hydrogenation indicates a saturated compound, which may be a cyclobutane derivative or possibly a nortricyclic structure[9] of the type proposed by Kleinfelter and von R. Schleyer.[10]

Reaction of *cis*-benzalacetone (II) with cyclopentadiene in boiling toluene afforded *cis-endo*-2-acetyl-3-phenyl-5-norbornene (X) which was shown to be free of its *cis–exo* isomer by conversion to the acid XI with sodium hypobromite, and iodolactonization to *endo*-3-phenyl-*exo*-5-iodo-*endo*-6-hydroxynorbornane-*endo*-2-carboxylic acid lactone (XII). None of the free *cis–exo* acid was found present. Alder, Gunzl, and Wolff[2] claimed less than 5% of the *cis–exo* isomer from the reaction of *cis*-cinnamic acid with cyclopentadiene.



Acetylphenylacetylene (III), upon reaction with cyclopentadiene, gave a good yield of 2-acetyl-3-phenyl-2,5-norbornadiene (XV),[11] which was oxidized to the known unsaturated acid XVI.[4,12] Catalytic reduction of both X and XV gave *cis-endo*-2-acetyl-3-phenylnorbornane (XIII). The conditions used in the haloform oxidation of XIII caused isomerization at the



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[5] The procedure is sufficiently mild so as not to cause any structural changes except iodolactonization of the *endo*-acid function; *cf.* (a) E. E. van Tamelen and M. Shamma, *J. Am. Chem. Soc.*, **76**, 2315 (1954); (b) C. S. Rondestvedt and C. D. Ver Nooy, *ibid.*, **77**, 3583 (1955).

[6] J. G. Martin and R. K. Hill, *Chem. Rev.*, **61**, 537 (1961).

[7] F. Winternitz, W. Mousseron, and G. Rouzier, *Bull. soc. chim. France*, 170 (1955).

[8] For a mechanistic approach to this type reaction, see J. D. Roberts and J. E. Baldwin, *J. Am. Chem. Soc.*, **85**, 115 (1963).

[9] The infrared of compound IX taken in a potassium bromide disk on a Perkin-Elmer Model 221 instrument showed the absence of any significant band in the 12.2–12.5-μ region (see ref. 12); however, this evidence alone does not rule out a nortricyclenic structure.

[10] D. C. Kleinfelter and P. von R. Schleyer, *J. Org. Chem.*, **26**, 3740 (1961).

[11] D. Nightingale and F. Wadsworth, *J. Am. Chem. Soc.*, **67**, 416 (1945), attempted this reaction; however, they reported their product was inhomogeneous and did not give the required analytical data.

[12] S. J. Cristol and R. T. LaLonde, *ibid.*, **81**, 5417 (1959).

position alpha to the carbonyl giving *endo*-3-phenylnorbornane-*exo*-2-carboxylic acid (XIV). Catalytic hydrogenation of VII gave the same acid XIV. It is seen, with the use of models, that the hindrance to the carboxyl group from the phenyl group and the *endo*-hydrogen of C-6 would be sufficient to promote isomerization in strongly basic media to the more stable *trans* form. Alder, Gunzl, and Wolff have reported a similar isomerization.[2]

Experimental[13]

Reaction of *trans*-Benzalacetone (I) with Cyclopentadiene. A.—A solution of 3.0 g. (0.021 mole) of I and 15 g. (0.23 mole) of cyclopentadiene in 50 ml. of *m*-xylene was refluxed for 20 hr. Concentration *in vacuo* and chromatography on Merck acid-washed alumina gave 2.64 g. (64%) of a yellow oil, a mixture of *endo*-2-acetyl-*exo*-3-phenyl-5-norbornene (IV), and *exo*-2-acetyl-*endo*-3-phenyl-5-norbornene (V). The infrared spectrum had as major bands, $\lambda_{\max}^{\text{neat}}$ 3.29, 3.41, 5.90, 6.26, 7.41, 13.33, 14.3 μ. An analytical sample was prepared by chromatography again on alumina eluting with hexane.

Anal. Calcd. for $C_{15}H_{16}O$: C, 84.86; H, 7.59; Found: C, 84.97; H, 7.34.

The mixture would not volatilize at 225° on a 2-m. column packed with silicone grease (Perkin-Elmer column O_x) and attempted distillation at reduced pressure resulted in much decomposition. The product was oxidized as a mixture.

B.—A solution of 5.0 g. (0.034 mole) of I, 4.53 g. (0.034 mole) of dicyclopentadiene,[14] and 25 ml. of bromobenzene was refluxed for 10 hr. The volatile components were removed *in vacuo* on a steam bath leaving a yellow oil, which was used for further steps without purification. The infrared spectrum showed the same major bands previously mentioned.

C.—A solution of 42 g. of I in 300 ml. of dicyclopentadiene was heated at reflux (~155°) for about 8 hr., the temperature then gradually rising to 220° as the excess cyclopentadiene polymerized. After a total reaction time of 22 hr., the reaction mixture was cooled with formation of a white waxy solid. Several extractions with acetone[15] were required to separate the desired product from the polymer. A benzene solution of the product was passed through two 40 × 450 mm. columns of acid-washed alumina giving, after removal of the solvent, 21.2 g. (35%) of the mixture of IV and V, which was used in subsequent steps without separation.

Oxidation of *endo*-2-Acetyl-*exo*-3-phenyl-5-norbornene (IV) and *exo*-2-Acetyl-*endo*-3-phenyl-5-norbornene (V).—The mixtures of IV and V resulting from the Diels-Alder reaction in boiling *m*-xylene, in boiling bromobenzene, and in excess cyclopentadiene at 155° to 220° were oxidized with sodium hypobromite in dioxane-water solution to yield crystalline mixtures of *exo*-3-phenyl-5-norbornene-*endo*-2-carboxylic acid (VI) and *endo*-3-phenyl-5-norbornene-*exo*-2-carboxylic acid (VII).[16] The yield was approximately 90% in each case.

Iodolactonization of *exo*-3-Phenyl-5-norbornene-*endo*-2-carboxylic Acid (VI). A.—A 2.25-g. sample of the acid mixture obtained from the oxidation of IV and V was dissolved in 60 ml. of 5% sodium bicarbonate and the solution added with swirling to 5.0 g. of iodine and 10 g. of potassium iodide in 30 ml. of water. After standing for 15 min., the dark colored solution was extracted with ether. Both the aqueous and ethereal extracts were treated with sodium bisulfite to reduce any excess iodine. The ether solution was treated with Norit and concentrated, yielding a light brown solid which was recrystallized from ether–ethanol to give 1.09 g. (33%) of the iodolactone VIII. A second recrystallization gave white crystals, m.p. 118–119°. When mixed with an authentic sample[17] of *exo*-3-phenyl-*exo*-5-iodo-*endo*-6-hydroxynorbornane-*endo*-2-carboxylic acid lactone (VIII), no depression in melting point was observed.

Acidification of the aqueous phase and extraction with ether gave, after treatment with Norit, drying over magnesium sulfate, and concentration, 0.79 g. (35%) of a white crystalline solid. Two recrystallizations from cyclohexane gave the purified sample of *endo*-3-phenyl-5-norbornene-*exo*-2-carboxylic acid (VII), m.p. 113–114°; lit.[2] m.p. 113–113.5°. A mixture melting point with an authentic sample[17] of VII showed no depression.

B.—Using the same procedure, the mixture of acids VI and VII resulting from the oxidation of the product of the Diels–Alder reaction in boiling bromobenzene gave 11.2% of VIII, m.p. 118–119°, from ether–ethanol, m.m.p. 118–119°[17]; and 39.8% of VII, m.p. 112–113°, from ether–hexane, m.m.p. 112–113.5°.[17] The over-all yield based on I was 51%.

C.—Again using the iodolactonization procedure, the mixture of acids VI and VII from the oxidation of product of the Diels–Alder reaction in excess cyclopentadiene yielded 75% of the lactone VIII and 18.3% of the *exo* acid VII. Melting points and mixture melting points of these samples were identical with those of previous samples.

Dimerization of the Mixture of *endo*-2-Acetyl-*exo*-3-phenyl-5-norbornene (IV) and *exo*-2-Acetyl-*endo*-3-phenyl-5-norbornene (V).—Upon standing out on the lab bench in a stoppered Pyrex flask for about 48 hr., a mixture of IV and V formed a thick gum which when boiled in ethanol produced a white solid IX which decomposed at about 170°.

Anal. Calcd. for $C_{30}H_{32}O_2$: C, 84.86; H, 7.59; mol. wt., 425. Found: C, 85.26; H, 7.41; mol. wt., 435.

The dimer IX gave a positive iodoform test and was resistant to hydrogenation with 10% palladium-on-charcoal catalyst at 31-p.s.i. hydrogen pressure.

Reaction of *cis*-Benzalacetone (II) with Cyclopentadiene.—Three grams of II, prepared by the method of Schinz[18] using Lindlar catalyst obtained from Engelhard Industries, Inc., 15 g. of cyclopentadiene, and 75 ml. of toluene were heated to reflux for 30 hr. Removal of the excess cyclopentadiene and toluene under reduced pressure left a light yellow oil. Elution from acid washed alumina with 20:80 benzene–petroleum ether (30–60°) gave 2.41 g. (55%) of *cis*-2-acetyl-3-phenyl-5-norbornene (X), $\lambda_{\max}^{\text{neat}}$ 3.29, 3.40, 5.90, 7.50, 13.3, 13.8, 14.25 μ.

Anal. Calcd. for $C_{15}H_{16}O$; C, 84.86; H, 7.59. Found: C, 85.08; H, 7.33.

Treatment of an ethanolic solution of X with 2,4-dinitrophenylhydrazine produced an oil which was crystallized by dissolving it in ethyl acetate and adding ethyl alcohol until turbidity. Recrystallization by this procedure gave the pure 2,4-dinitrophenylhydrazone, m.p. 123–124°.

Anal. Calcd. for $C_{21}H_{20}N_4O_4$: C, 64.26; H, 5.13; N, 14.27. Found: C, 64.17; H, 5.36; N, 14.42.

***endo*-3-Phenyl-*exo*-5-iodo-*endo*-6-hydroxynorbornane-*endo*-2-carboxylic Acid Lactone (XII).**—A solution of 0.55 g. (0.0026 mole) of X in 25 ml. of dioxane was added to a cooled solution of 0.63 g. (0.0039 mole) of bromine and 0.32 g. of sodium hydroxide (0.0080 mole) in 30 ml. of water. The mixture was stirred for 4 hr. at 0° and then extracted with ether to remove any unchanged materials. Addition of sodium bisulfite destroyed the excess sodium hypobromite. The solution was acidified with dilute hydrochloric acid and extracted with ether. Evaporation of the solvent left a small amount of residue containing the *cis* acid XI. The residue was dissolved in 14.3 ml. of 5% sodium bicarbonate and added with swirling to a solution of 1.23 g. of iodine and 2.38 g. of potassium iodide in 8 ml. of water. After standing for 15 min., the solution was extracted with two 20-ml. portions of ether. Both the ethereal and aqueous extracts were treated with sodium bisulfite to reduce the excess iodine. The ether solution was treated with Norit and filtered. Removal of the ether gave 0.10 g. of the lactone XII, which was recrystallized from ether–ethanol, m.p. 119–122°. A second recrystallization gave white crystals, m.p. 122.5–123.5°; lit.[2] m.p. 124°; $\lambda_{\max}^{\text{KBr}}$ 3.40, 5.63, 13.3, 14.3 μ.

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(13) Melting points were determined either in capillary tubes or on a Fisher-Johns block and are uncorrected. Infrared spectra, unless otherwise stated, were taken on a Perkin-Elmer Model 137 Infracord. The microanalyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn. A Perkin-Elmer Model 154D vapor fractometer was used for vapor phase chromatographic work.

(14) Dicyclopentadiene was used since at this temperature the monomer is readily produced.

(15) The polymer was found to be fairly soluble in hot chloroform, but nearly insoluble in acetone. The mixture of ketones IV and V are very soluble in acetone.

(16) In some early runs these acids were purified further by recrystallization, m.p. 89–96°; however, since any manipulation of these intermediates could possibly cause a change of the isomer ratio, it was decided not to purify them prior to iodolactonization.

(17) The authentic sample was prepared by the method of Alder, Gunzl, and Wolff, ref. 2.

(18) H. Schinz, *Drug Cosmetic Ind.*, **76**, 332 (1955); H. Schinz, G. Gamboli, and V. Theus, *Helv. Chim. Acta*, **38**, 255 (1955).

The aqueous phase was acidified and extracted with ether. Evaporation of the ether left no weighable quantity of the *cis–exo* acid.

Reaction of Acetylphenylacetylene (III) with Cyclopentadiene.—Ten grams of III[11] and 50 g. of cyclopentadiene in 75 ml. of *m*-xylene were refluxed for 36 hr. The solvents were distilled under reduced pressure. Distillation of the residue gave 11.6 g. (79%) of 2-acetyl-3-phenyl-2,5-norbornadiene (XV), b.p. 86–93° (0.08–0.1 mm.); λ_{max}^{neat} 3.28 (sh), 3.35, 6.08, 7.37, 7.74, 8.11, 13.20, 13.81, 14.28 μ. The 2,4-dinitrophenylhydrazone was prepared as red crystals from ethyl acetate–ethanol, m.p. 164–165°.

Anal. Calcd. for $C_{21}H_{18}N_4O_4$: C, 64.61; H, 4.65; N, 14.35. Found: C, 64.55; H, 4.54; N, 14.27.

3-Phenyl-2,5-norbornadiene-2-carboxylic Acid (XVI).—To a cooled solution of 10 g. (0.25 mole) of sodium hydroxide and 1.5 ml. (0.0275 mole) of bromine in 50 ml. of water was added 1.1 g. (0.0053 mole) of XV in 35 ml. of dioxane. After stirring at 0° for 10 hr., the excess sodium hypobromite was destroyed by addition of sodium bisulfite. Extraction with ether, drying of the ethereal extract over magnesium sulfate, and concentration of the solution *in vacuo* gave 0.98 g. (89%) of XVI. Recrystallization from ether–petroleum ether gave white crystals, m.p. 135–136°; lit.[4,12] m.p. 135–136°.

***endo*-2-Acetyl-*endo*-3-phenylnorbornane (XIII). I. From X.**—A suspension of 0.1 g. of 10% palladium on charcoal, 0.60 g. of X, and 25 ml. of benzene was hydrogenated at 40 p.s.i. for 4 hr. Filtration of the catalyst and removal of the solvent left a light yellow oil, λ_{max}^{neat} 3.31 (sh), 3.40, 5.91, 6.28, 13.36, 14.25 μ; $n^{20}D$ 1.5543.

II. From XV.—A suspension of 1.0 g. of 10% palladium on charcoal in 40 ml. of methanol was stirred in an atmosphere of hydrogen until uptake was negligible. A solution of 5.5 g. of XV in 50 ml. of methanol was added and the mixture was allowed to take up hydrogen until uptake ceased. Filtration of the catalyst and removal of the solvent gave a theoretical yield of XIII, $n^{20}D$ 1.5547. The infrared spectrum of this sample was identical with that obtained from reduction of X. The 2,4-dinitrophenylhydrazone prepared in the normal way was an oil. Crystallization was obtained by using the same procedure as for the 2,4-dinitrophenylhydrazone of X, m.p. 110–111°. Two further recrystallizations from ethyl acetate–ethanol gave the pure derivative, m.p. 115–116°.

Anal. Calcd. for $C_{21}H_{22}N_4O_4$: C, 63.95; H, 5.62; N, 14.20. Found: C, 64.01, H, 5.80; N, 14.11.

***endo*-3-Phenylnorbornane-*exo*-2-carboxylic Acid (XIV).**—A 0.20-g. portion of XIII in 15 ml. of dioxane was added to a cooled solution of 4 g. (0.1 mole) of sodium hydroxide and 0.75 ml. (0.0185 mole) of bromine in 20 ml. of water. The solution was stirred at 0° for 4 hr., then at room temperature for 30 hr. Sodium bisulfite was added to reduce the excess hypobromite. Acidification with dilute hydrochloric acid, extraction with ether, drying over magnesium sulfate, and concentration of the ethereal solution gave a crystalline residue. Recrystallization from ethanol–water gave white crystals, m.p. 109–118°. A second recrystallization from ether–petroleum ether (90–120°) gave XIV, m.p. 138–139°; lit.[2] m.p. 139°. This compound showed no depression in melting point when mixed with an authenic sample.[17]

The Synthesis and Reactions of N,N'-Dicarbalkoxy-N,N'-dialkoxyhydrazines and Some Observations on Carbalkoxylium Ions

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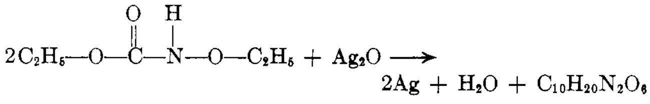
Received April 11, 1963

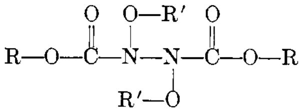
N-Carbalkoxy-O-alkylhydroxylamines react readily with silver oxide in diethyl ether to give N,N'-dicarbalkoxy-N,N'-dialkoxyhydrazines in almost quantitative yields. These hydrazines are very sensitive towards strong acids and bases and do not undergo the normal type of ester hydrolysis. The products from the decomposition with *p*-toluenesulfonic acid in diethyl ether and 1-propanol provided evidence for the formation of carbonium ions and carbalkoxylium ions. A new type of mixed anhydride, carbomethoxy *p*-toluenesulfonate, is reported.

Attempts to alkylate N-carbethoxy-O-ethylhydroxylamine[2] with ethyl iodide in the presence of silver oxide led to the discovery of an interesting coupling reaction, which proceeded equally well in the absence of ethyl iodide.[3]



$$2C_2H_5-O-\overset{\overset{O}{\|}}{C}-\overset{\overset{H}{|}}{N}-O-C_2H_5 + Ag_2O \longrightarrow 2Ag + H_2O + C_{10}H_{20}N_2O_6$$

The product, isolated in a 91% yield, was found to have a molecular weight of 261 and to fit the empirical formula $C_{10}H_{20}N_2O_6$ (mol. wt., 264). The infrared spectrum of the compound displayed strong absorption at 1750 cm.$^{-1}$ and the absence of any absorption above 3000 cm.$^{-1}$ dismissed the possibility of any NH or OH groups. The compound's n.m.r. spectrum showed two methylene quartets (at 5.76 and 5.95 τ) of equal intensity and two methyl triplets (at 8.67 and 8.77 τ) also of equal intensity. From the ratios of the peaks, methylene to methyl ratio was 2:3, the n.m.r. spectrum indicated the presence of two different ethoxy groups. Assuming a minimum of rearrangements the three structures anticipated for the material are I to III.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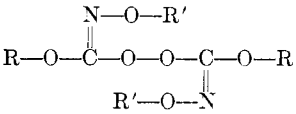
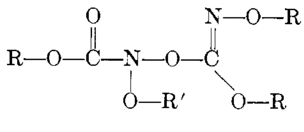
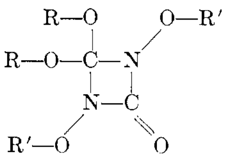

II


III


IV

Structure II is essentially a peroxide and it is not expected to absorb above 1700 cm.$^{-1}$ for the carbon–nitrogen double bond.[4] The compound was stable on distillation at 110° (0.7 mm.) and did not give the products that one would expect from II upon hydrolysis.

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[1] Holder of a Province of Alberta Graduate Fellowship, 1962–1963.

[2] We have chosen to name these compounds as derivatives of hydroxylamine, because of the ambiguity and redundancy of the previously used names, *e.g.*, O-ethylcarbethoxyhydroxamic acid and α-ethylhydroxyurethane.

[3] The silver salt of N-carbethoxy-O-benzylhydroxylamine was isolable and was converted to the coupling product at room temperature in ether, thus indicating that the silver salt is indeed an intermediate in the reaction.

[4] The infrared spectrum of $(C_2H_5O)_2C{=}N{-}OCH_3$ shows an intense band at 1646 cm.$^{-1}$; unpublished work of R. Raap.