hydride. A solution of 2.0 g. of cycloheptatriene and 2.1 g. of maleic anhydride in 15 ml. of anhydrous ether was allowed to stand at room temperature for 24 hr. The solvent was partially evaporated to one-third the original volume, and 1.7 g. of solid, m.p. 95–98°, was collected. Recrystallization of the product from carbon tetrachloride afforded colorless crystals, m.p. 102–103°, that proved on the basis of m.m.p. and infrared spectra to be identical with the adduct prepared in refluxing xylene.[5,7]

Diels-Alder reaction of cycloheptatriene with tetracyanoethylene. A solution of 0.1 g. of tetracyanoethylene in 12 ml. of tetrahydrofuran was mixed with 1 ml. of cycloheptatriene. A deep red color developed on mixing and faded on standing. After 12 hr. the product was precipitated by carbon tetrachloride as 0.22 g. of pale yellow crystals, m.p. 157–160° (dec.). Recrystallization from ethanol afforded colorless crystals, m.p. 160–161° (dec.); λ_{max}^{Nujol} 4.49, 9.82, 11.61, and 13.55 μ.

Anal. Calcd. for $C_{13}H_8N_4$: C, 70.88; H, 3.66; N, 25.46. Found: C, 70.90; H, 3.73; N, 24.99.

Diels-Alder reaction of tropylacetylacetone with tetracyanoethylene. To a solution of 0.3 g. of tetracyanoethylene in 10 ml. of tetrahydrofuran was added 0.3 g. of tropylacetylacetone in 10 ml. of tetrahydrofuran. The solution was allowed to stand overnight, and 0.42 g. of colorless crystals m.p. 174–175° (dec.) was obtained. For analysis the sample was recrystallized from acetonitrile. The infrared spectrum shows bands at 4.50, 5.79, 9.80, 11.60, and 13.45 μ.

Anal. Calcd. for $C_{18}H_{14}N_4O_2$: C, 67.90; H, 4.44; N, 17.61. Found: C, 68.50; H, 4.78; N, 17.93.

Attempted Reactions of Tropylacetylacetone. (a) *Chelation with copper*(II) *salts.* When cupric acid and tropylacetylacetone were heated in dimethylformanide or in a mixture of acetic acid sodium acetate no evidence of chelate formation was obtained. An attempted reaction by the method of Garg[16] failed to afford a chelate of the substituted β-diketone.

(*b*) *Attempted condensation of tropylacetylacetone with benzamidine.* Tropylacetylacetone (0.1 g.) and 0.1 g. of benzamidine were dissolved in 15 ml. of ethanol and warmed for 5 min. Five milliliters of acetic acid was added, and the solution was boiled 10 min. and allowed to stand overnight. The solution was filtered, and the precipitate (0.9 g.) colsected and air dried, m.p. 123–125°. Recrystallization from ethanol afforded white crystals, m.p. 124–125°. Infrared analysis and a mixed m.p. showed the product to be identical with tropylacetylacetone. Subsequent trials, using basic catalysis, were similarly unsuccessful.

(*c*) *Reaction of tropylacetylacetone with urea.* Three grams of tropylacetylacetone and 1.5 g. of urea in ethanol using sodium hydroxide as catalyst were refluxed for 5 hr. On cooling a small amount of colorless solid, m.p. 300°, was obtained. The filtrate was concentrated, and crystals were obtained that slowly melted when they were collected on the funnel. The oily residue was redissolved in ethanol and further unsuccessful attempts to obtain crystals were made.

In one run urea (0.1 g.) and tropylacetylacetone (0.1 g.) were dissolved in pyridine and heated for 0.5 hr.; only unchanged starting materials were obtained by fractional crystallization.

(*d*) *Reaction of tropylacetylacetone with thiourea.* A solution of 1.0 g. of thiourea, 0.8 g. of tropylacetylacetone and 0.1 g. of sodium hydroxide in ethanol were heated intermittently, slowly driving off the alcohol. The total heating time was about 4 hr., and the concentrated solution on cooling deposited a small portion of inorganic salts. The second crop of crystals proved to be unchanged thiourea (0.9 g.) by m.p. and infrared identification.

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The Pyrolysis of Barium 1,4-Cyclohexanedicarboxylate

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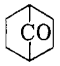
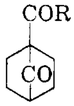
Sixty years ago, Zelinsky[1b] reported that, upon the distillation of the barium salt of 1,4-cyclohexanedicarboxylic acid, a fraction of the distillate gave a semicarbazone which melted at 209–210°; the carbonyl compound was not regenerated. However, the assumption was made that the semicarbazone was derived from the carbonyl bridged compound I. It seemed advisable to repeat this work and to identify the substance containing the carbonyl group.



I



IIa. R = OH
b. R = OCH$_3$
c. R = Cl

Benzaldehyde and *o*-tolualdehyde, rather than 7-oxo-1,4-methanocyclohexane (I) as claimed by Zelinsky, are the carbonyl compounds obtained by the dry distillation of the barium salt of 1,4-cyclohexanedicarboxylic acid. By the use of infrared spectra, the *absence* of a band at 5.64 mμ, characteristic for a carbonyl group across a six-membered ring, was noted.[2] However, there was a strong band for an aromatic aldehyde carbonyl. The crude oil obtained from the dry distillation was fractionated *in vacuo*, and a portion of the fraction giving a dinitrophenylhydrazone was converted to this derivative and submitted to paper chromatography. Two of the 2,4-dinitrophenylhydrazones were identified as those of benzaldehyde and *o*-tolualdehyde, and there were small amounts of three others, apparently derived from products of ring cleavage.

It is highly probable that the dicarboxylic acid (as barium salt) first loses formic acid to give a cyclohexenemonocarboxylate, the usual aldehyde synthesis from a carboxylate and a formate, thus accounting for the aldehyde. The time of dehydrogenation is unknown, but the occurrence of methane suggests that a greater part of the salt is decarboxylated and reduced. A slight reduction of carboxyl to methyl is indicated by the presence of the tolualdehyde; such a behavior has been noted in a zinc dust reduction.[3]

In the mass spectrum, a band of mass 126 cor-

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[1] (a) Present address: Rochester Institute of Technology, Rochester, N. Y. (b) N. D. Zelinsky, *Ber.*, **34**, 3798 (1901).

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responded to tetrahydrobenzoic acid. Comparison with a synthetic sample of the 1,2,5,6- isomer indicated that not more than a third could be this isomer.

Attempts to decarboxylate the keto acid (IIA)[4] were unsuccessful, as would be expected.

EXPERIMENTAL

The dry distillations were carried out in three ways: (1) the barium salt was heated in a copper flask (assumed to have been Zelinsky's method); (2) the salt was heated in a long-necked, Pyrex glass flask with a stainless-steel stirrer; (3) the free acids were heated at 230° in the inlet of the mass spectrometer. Method 1 required 2.5 hr. for 200 g., but method 2 only 45 min. per 100-g. run. Qualitatively, the products were alike. The highest yield of aldehyde came from the second procedure. The *trans* acid gave much less volatile material in the mass spectrometer.

In methods 1 and 2 the apparatus used was set up with a distillation head connected to a series of three dry ice–cooled traps, and terminated with a gas sampling tube. A typical procedure is as follows: the finely ground barium salt (100 g.) was placed in a flask. After the apparatus had been flushed with nitrogen, the flask was heated directly with two large burners. Nearly all the distillate which came over between 280° and 320° (thermometer in the vapor) collected in the first trap. The effluent gas was led through bromine water (5–10 bubbles per second) which only slowly diminished in color. After the pyrolysis and gas evolution was complete, the first trap and its contents were warmed with steam, causing a small amount of condensate to collect in the second trap. The residual liquid in the first trap from five runs after separation consisted of 36 g. of water and 108 g. of yellow oil. Following removal of a sample for infrared examination, the oil was fractionated *in vacuo;* those fractions (52 g. total) that gave dinitrophenylhydrazones were collected separately.

Identification of the aldehydes was based on a comparison of their dinitrophenylhydrazones with known samples, using infrared spectra and mixed melting points (no depression). Based on the weight of dinitrophenylhydrazones, the yield of aldehyde was 10%. An aliquot was converted to the dinitrophenylhydrazone for paper chromatography. By this technique[5] five 2,4-dinitrophenylhydrazone fractions were separated, benzaldehyde and *o*-tolualdehyde[6] being present in the largest amounts, while the other three occurred in very small quantities. From the quantities involved, it was calculated that 15 g. of aldehyde was formed per 400 g. of barium salt. The three unknown dinitrophenylhydrazones were none of the following with which direct comparisons on paper were made: saturated straight-chain aliphatic aldehydes, C_1–C_3, C_5–C_9; tetrahydro- and hexahydrobenzaldehydes; 6-methyl-3-cyclohexenecarboxaldehyde; α-methyl- and α-methyl-β-ethylacrolein; 3-methylcyclohexanone; 3-methyl-2-cyclohexenone; *m*- and *p*-tolualdehydes. Although small amounts gave bands on paper, larger quantities could not be separated by column chromatography.

During the dry distillation, a large amount of gas was given off fairly steadily. Samples taken at the beginning and the end had practically the same composition. Roughly quantitative analysis of the effluent, using a mass spectrometer, showed large amounts of hydrogen and methane, with small amounts of carbon dioxide, and very small amounts of ethane, ethylene, propylene, a butene, butadiene, and a hydrocarbon of mass 108 (1,4-dimethylcyclohexadiene ?) which was not dimethylenecyclohexane.[7] From the infrared absorption curve, it seems likely that the unresolved oily residue is a mixture of hydrocarbons and an unidentified ester. From the analytical figures, Zelinsky[1b] concluded that the low-boiling hydrocarbon fractionation was a mixture of benzene, cyclohexene, and cyclohexadiene.

During attempted pyrolysis the acid (IIA) sublimed unchanged under all conditions at about 350°. In a sealed capillary, IIA sublimed at about 500° and blackened. The silver salt was unchanged on heating alone or in quinoline, as was the free acid in the latter with and without copper salt. The methyl ester IIB is new; it was obtained by the action of methanol on the acid chloride. 2,4-Dinitrophenylhydrazones and semicarbazones of the acid and methyl ester were prepared as reference compounds.

7-Oxobicyclo[2.2.1]heptan-1-carbonyl chloride (IIC), b.p. 95–98°/4 mm., n^{25}D 1.4998, was prepared in a 48% yield; absolute dryness is essential. By the usual procedures, the corresponding acid IIA gave a 2,4-dinitrophenylhydrazone, m.p. 210°, and semicarbazone, m.p. 201°, with bubbling. The methyl ester was obtained in a yield of 48% by addition of 1.6 g. of methanol in 25 ml. of methylene chloride, with stirring, to 9.4 g. of IIC, followed by washing the mixture with sodium bicarbonate solution and distilling it. The ester, b.p. 85–86°/1.5 mm., after recrystallization from petroleum ether, had a melting point of 41°; the yield was 4 g. Two grams of a by-product, b.p. 91–92°/1.5 mm., and 2 g. of residue accounted for the remainder. In the infrared, carbonyl bands came at 5.65 and 5.85 mμ. The 2,4-dinitrophenylhydrazone, m.p. 148–149°, and semicarbazone, m.p. 209–210°, were prepared as reference compounds. The analyses are collected in the accompanying table.

TABLE I

ANALYTICAL RESULTS

		Calcd. (Found)		
Substance	Formula	C	H	N
Acid DNPH	$C_{14}H_{14}N_4O_6$	50.0	4.2	16.7
		(50.1)	(4.4)	(16.7)
Acid semicarbazone	$C_9H_{13}N_3O_3$	51.2	6.1	19.9
		(51.5)	(6.5)	(19.8)
Ester	$C_9H_{12}O_3$	64.3	7.1	—
		(63.8)	(7.0)	(—)
Ester DNPH	$C_{15}H_{16}N_4O_6$	51.1	4.6	16.1
		(51.4)	(4.8)	(16.1)
Ester semicarbazone	$C_{10}H_{15}N_3O_3$	53.3	6.7	18.7
		(52.9)	(6.7)	(18.3)

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[5] E. Sundt and M. Winter, *Anal. Chem.*, **30**, 1620 (1958).

[6] We are indebted to D. M. Burness, of these laboratories, for authentic samples of the three tolualdehyde 2,4-dinitrophenylhydrazones. The aldehydes were made from the toluic acids *via* the MacFayden-Stevens reaction.

[7] We thank G. F. Wright, of the University of Toronto, for an authentic sample of this hydrocarbon to use for comparison.