than reaction 3 must account for the high percentage of carbon monoxide found in experiments having a relatively high concentration of foreign gas. A reaction such as

$$CHOCHO' \longrightarrow CO + HCHO$$

would meet the requirements but why it would predominate only at high pressures is not obvious. However, it is evident from the large variation of gaseous products that the primary process for glyoxal is the formation of an activated molecule which does not spontaneously dissociate into formyl radicals.

From the limited results obtained, it appears that the same chemical processes occur at λ 3660, 3130 and 2537, the variation being only one of degree.

DEPARTMENTS OF CHEMISTRY
STANFORD UNIVERSITY AND
UNIVERSITY OF CALIFORNIA AT LOS ANGELES
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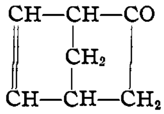
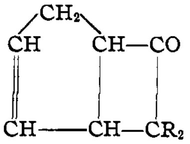
The Reaction of Cyclopentadiene and Ketene

BY BENJAMIN T. BROOKS AND GODFREY WILBERT

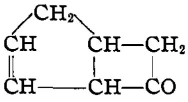
The now well-known Diels–Alder reaction was discovered by these authors[1] in a study of the reactions of cyclopentadiene with acrolein, acrylic acid and the anhydrides of maleic, citraconic and itaconic acids. All of these reactions give endomethylene products, acrolein giving endomethylene tetrahydrobenzaldehyde. It is obvious that ketene and cyclopentadiene would give an unsaturated ketone (1) which upon hydrogenation would give norcamphor, if the reaction follows the type Diels–Alder reaction. Norcamphor has been synthesized by Hinticka and Komppa[2] and by Diels and Alder[3] by other methods.

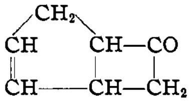
None of the ketenes appear to react with cyclopentadiene in the Diels–Alder fashion. Diphenylketene with cyclopentadiene gives a product (2) having the cyclobutanone structure[4,5] as originally suggested by Staudinger[6] and his co-workers. In view of these results, it appeared desirable to study the reaction of ketene itself upon cyclopentadiene.

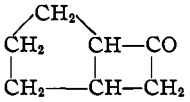

(1)


(2)

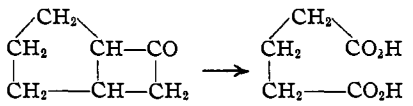
Recently Smith, Agre, Leekley and Prichard[5] were unable to obtain a reaction product of ketene and cyclopentadiene. We have found that ketene reacts with cyclopentadiene in a manner analogous to the reaction with diphenylketene, and not to give the product (1) to be expected from the Diels–Alder reaction. The resulting unsaturated ketone (3) or (4) was hydrogenated to the saturated ketone (5) which proved to be not identical with norcamphor.


(3)


(4)


(5)

The unsaturated ketones (3) and (4) obviously give the same hydrogenated product. That the saturated ketone (5) is not identical with norcamphor is indicative of this structure which was further confirmed by oxidation to glutaric acid.



All attempts to isolate the intermediate product cyclopentane-1,2-dicarboxylic acid were negative.

Experimental

Ketene.—This was prepared in the customary manner, passing acetone vapor rapidly through a 1/4″ (6-mm.) copper tube maintained at about 700°. Unchanged acetone was condensed and the ketene absorbed from the gas stream by passing through toluene cooled to about −70° by solid carbon dioxide in isopropyl alcohol.

Cyclopentadiene.—This was prepared as needed by slowly distilling dicyclopentadiene through a packed four-foot (122-cm.) glass column, all of the product used distilling at 39–41°.

Reaction between Cyclopentadiene and Ketene.—Ketene was absorbed in two wash-bottles in series, each containing 300 g. of toluene, cooled as described. When the ketene dissolved in the toluene amounted to about 75 g., the toluene solutions were combined and 145 g. of freshly distilled cyclopentadiene were added and the solution placed in two small steel cylinders. The solution of ketene and cyclopentadiene in toluene was then heated under pressure at about 100° for one hour. The product was separated by fractional distillation, the material distilling at 150–160° being retained as the crude ketone. The crude unsaturated ketone, yield 78 g., a nearly colorless oil, thus obtained contained some cyclopentadiene

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[1] O. Diels and K. Alder, *Ann.*, **460**, 98 (1928).

[2] Hinticka and Komppa, *Chem. Zentr.*, **89**, II, 369 (1918).

[3] O. Diels and K. Alder, *Ann.*, **470**, 98 (1928).

[4] J. R. Lewis, G. R. Remage, J. L. Simonsen and W. G. Wainwright, *J. Chem. Soc.*, 1837 (1937).

[5] L. I. Smith, P. L. Agre, R. M. Leekley and W. W. Prichard, THIS JOURNAL, **61**, 9 (1939).

[6] H. Staudinger, "Die Ketene," Stuttgart, p. 59, 1912; *Ann.*, **356**, 51 (1907).

resulting from breakdown of the dimer. It was further purified by redistilling, and through the sodium bisulfite compound, made in a minimum of aqueous methyl alcohol solution. The washed bisulfite compound in water was treated with sodium bicarbonate and gently warmed to regenerate the ketone. Thus purified the unsaturated ketone distilled at 157.5–159°, sp. gr. (20°C.) 0.9813, analysis C, 77.62; H, 7.51; calcd. C, 77.74; H, 7.46. The semicarbazone recrystallized from alcohol melted at 222° and showed N, 24.76; calcd., N, 25.45.

Bicyclo-(0,2,3)-heptanone-7.—The unsaturated ketone was reduced, in dilute alcohol solution, by colloidal palladium and hydrogen at substantially atmospheric pressure. The saturated ketone distills at 164–165°, sp. gr. 0.9958 (20°C.), $n^{20}_{\rm D}$ 1.5030. It forms a semicarbazone melting at 216° (semicarbazone of norcamphor melts at 196.5–197.5°).

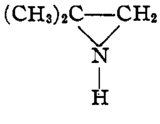
Oxidation of Bicyclo-(0,2,3)-heptanone-7.—The ketone was oxidized by refluxing for three hours with dilute nitric acid, equal parts of concentrated nitric and water. On gently evaporating the resulting solution nearly to dryness, the product crystallized on cooling and on purification proved to be glutaric acid, melting point 98°.

NEW YORK, N. Y. RECEIVED DECEMBER 5, 1940

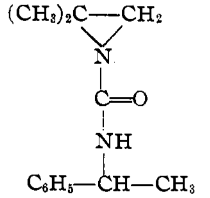
The Preparation and Attempted Resolution of 2,2-Dimethylethyleneimine

BY THEODORE L. CAIRNS

Previous investigations[1] of the possible asymmetry of the nitrogen atom in substituted ethyleneimines have all failed because it was not possible to synthesize the desired compounds. A method for the preparation of 2,2-dimethylethyleneimine (I) has now been developed. This compound gave a sulfonamide, insoluble in alkali, identical with one previously prepared[1a] by a different method. Compound I did not reduce permanganate and when treated with dilute sulfuric acid the ring opened to give 1-amino-2-methyl-2-propanol.



I



II

The substituted urea derivative (II) derived from compound I and *l*-α-phenylethylisocyanate was subjected to fractional crystallization, but no evidence of separation into diastereoisomers was obtained. Compound II exhibited mutarotation in boiling benzene, but the change in rotation could always be accounted for by decomposition.

There are certain objections to a compound having a carbonyl group directly attached to the nitrogen atom.[2] However, the whole problem is provided with a theoretical basis by the calculations of Kincaid and Henriques[3] and the synthesis of more suitable derivatives is now being investigated.

Experimental[4]

2,2-Dimethylethyleneimine.—To a solution of 100 g. of 2-methyl-2-amino-1-propanol (Commercial Solvents Corporation) in 200 cc. of water was added with shaking 110 g. of sulfuric acid in 200 cc. of water. The solution was distilled at atmospheric pressure until the temperature of the reaction mixture reached 115°, and then at 25–30 mm. and a temperature of 150–170° for one hour. The flask was cooled and broken and the brown crystalline mass crushed. This was treated with an excess of 40% aqueous sodium hydroxide and the mixture distilled until about 120 g. of distillate was obtained. The distillate was saturated with potassium hydroxide and the organic layer separated and dried with potassium hydroxide and finally with sodium. Distillation gave 30–40 g. of a mobile, colorless liquid of ammoniacal odor; b. p. 69–70°, $n^{25}_{\rm D}$ 1.4052.

Anal. Calcd. for C_4H_9N: C, 67.55; H, 12.76. Found: C, 67.59; H, 12.70.

***l*-α-Phenylethyl Isocyanate.**—A solution of 20 g. *d*-α-phenylethylamine[5] in 200 cc. of toluene was saturated with dry hydrogen chloride. A heavy white precipitate was formed. An additional 100 cc. of toluene was added and phosgene passed into the mixture for a few minutes. The mixture was then heated to boiling and phosgene bubbled through for four hours. The solution was cooled to room temperature, decanted from a very small amount of a white crystalline solid, and fractionated under reduced pressure; yield 16.5 g.; b. p. 82–83° at 12–14 mm.

Rotation. 0.3541 g. made up to 10 cc. with benzene gave $\alpha^{24}_{\rm D}$ −0.09°, $l = 1$, $[\alpha]^{24}_{\rm D}$ −2°.

***d*-N-(α-Phenylethyl)-urea.**—Treatment of a few drops of *l*-α-phenylethyl isocyanate in benzene solution with anhydrous ammonia gave white crystals, which, after crystallization from water, had m. p. 121–122°.

Rotation. 0.2225 g. made up to 10 cc. in absolute alcohol gave $\alpha^{25}_{\rm D}$ 1.086, $l = 1$, $[\alpha]^{25}_{\rm D}$ +48.8°.

Anal. Calcd. for $C_9H_{12}ON_2$: C, 65.83; H, 7.31. Found: C, 65.75; H, 7.16.

The literature[6] gives m. p. 122–123° and $[\alpha]_{\rm D}$ 46.2.

***d*-(1-α-Phenylethylcarbamyl)-2,2-dimethylethyleneimine.**—A solution of 10.35 g. *l*-α-phenylethyl isocyanate

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[1] (a) Adams and Cairns, THIS JOURNAL, **61**, 2464 (1939). (b) Meisenheimer and Chou, *Ann.*, **539**, 70 (1939). (c) Mole and Turner, *Chem. and Ind.*, 582 (1939). (d) Maitland, *Ann. Repts. Chem. Soc.*, **36**, 243 (1939).

[2] Gilman, "Organic Chemistry," John Wiley and Sons, New York, N. Y., 1938, Vol. I, p. 334.

[3] Kincaid and Henriques, THIS JOURNAL, **62**, 1474 (1940).

[4] Analyses by Dr. L. Weisler.

[5] "Organic Syntheses," Vol. XVII, 1937, p. 80.

[6] Marckwald and Methe, *Ber.*, **38**, 801 (1905).