

The benzene filtrate from recrystallization contained more soluble material presumed to be a mixture of phenylacetamide and α -phenylpropionamide.

Reaction with Ethylbenzene.—When a mixture of 53 g. of ethylbenzene (0.5 mole), 64 g. of sulfur (2 moles) and 150 ml. of concentrated aqueous ammonia (2.2 moles) was heated at 250–260° for 2 hours, the initial pressure went from 115 to 225 atm. The solid filtered directly from the reaction mixture was recrystallized and decolorized with charcoal in water. This product, 11.7 g., melted from 106–111° and contained 11.3% nitrogen—a value suggesting a mixture of benzamide (11.56% N) and phenylacetamide (10.37% N).

Reaction with *p*-Xylene.—This reaction was carried out to see whether a diamide could be prepared. A mixture of 26 g. of *p*-xylene (0.5 mole), 64 g. of sulfur (2 moles) and 150 ml. of aqueous ammonia (2.2 moles) was treated at 300° for one hour. A light yellow solid was filtered from the reaction mixture which was insoluble in boiling water. The solid weighed 10.5 g. after being extracted three times with boiling, 200-ml. portions of water. Further extraction of the solid (8 times with a total of 200 ml. of boiling carbon disulfide) yielded 8.0 g. of tan-colored product. This material did not melt below 260°, gave off NH₃ when warmed with caustic and compared with terephthalamide as follows:

Anal. Calcd. for C₈H₈N₂O₂: C, 58.53; H, 4.91; N, 17.05. Found: C, 58.52, 58.81; H, 4.90, 5.31; N, 16.63, 16.72.

For further identification of the above product as terephthalamide, 2.00 g. of the material was boiled 1 hour with 30 ml. of 20% sodium hydroxide. Dilution of the resulting slurry to 100 ml. gave a yellow solution containing a trace of black solid. Decolorization with charcoal resulted in a

colorless solution from which a white solid was filtered after acidifying with concd. HCl. This precipitate was boiled with water, filtered, and washed several times with water and methanol. The solid product (1.98 g.) compared with terephthalic acid as follows:

Anal. Calcd. for C₈H₆O₄: C, 57.77; H, 3.64. Found: C, 58.08, 58.12; H, 3.71, 3.80.

The filtrate from the original reaction mixture was combined with the 500 ml. of water used to extract and wash the terephthalamide. Evaporation to dryness on a steam-cone gave 53.8 g. of dark yellow solid. Two extractions of this material with 300 ml. of boiling water left 24.1 g. of sulfur. Cooling of this filtrate to 0° gave a total 2.1 g. of tan solid which did not melt below 300° and was not characterized further.

Reaction with Benzyl Chloride.—One-half mole of benzyl chloride (63.3 g.) was treated as above at 190° for 3.75 hours. The product was evaporated to dryness. The residue was extracted three times with hot water, and 35.2 g. of benzamide was obtained on crystallization from the water. After several recrystallizations from water, the product melted at 125–126°.

Anal. Calcd. for C₇H₇NO: N, 11.56. Found: N, 11.61.

We plan to publish data on the application of the Willgerdt reaction to saturated aliphatic hydrocarbons in a future paper.

Acknowledgment.—The authors wish to thank Mr. W. P. Pickhardt for the elemental analyses reported here.

WILMINGTON, DEL.

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

The Low Temperature Halogenation of Isobutylenes

BY RICHARD T. ARNOLD AND WILLIAM W. LEE¹

RECEIVED MARCH 10, 1953

The direct chlorination of pure methylenecyclohexane (I) in the presence of anhydrous sodium bicarbonate at 0° has been examined. Two products, 1-chloromethylcyclohexene (II) and 1-chloromethyl-1-chlorocyclohexane (III), were isolated in yields of 38–48% and 12–19%, respectively. A cyclic transition state is proposed for the formation of the allylic monochloride and an ionic mechanism for the dichloride. Bromination of methylenecyclohexane gives the simple addition compound (XVII) as the major product.

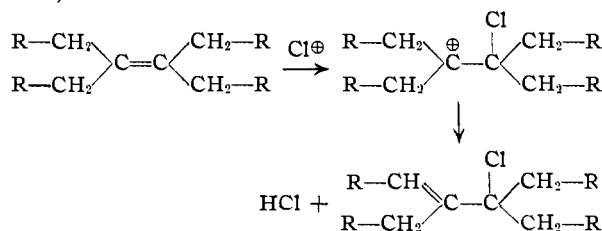
That simple olefins can react with chlorine to give substitution products was first observed by Sheshukov,² but for fifty years this reaction received little attention.

Tishchenko,³ as a result of an extensive investigation, proved that the chlorine atom of the allylic chloride so formed is bonded directly to one of the original unsaturated carbon atoms of the olefin molecule and that a shift of the carbon-carbon double bond takes place.

The chlorination of isobutylene and related hydrocarbons is now carried out on a commercial scale, and the reaction has received a great deal of attention in the research laboratories of the Shell Development Company.⁴

In a recent paper, Taft⁵ has given an excellent bibliography, has summarized the evidence which serves to exclude a radical mechanism, and has

proposed a two-step mechanism for the chlorination, as follows.



It is generally accepted that the first and rate-determining step in the reaction of many A-B type molecules with olefins involves the addition of an active cation to the double bond. In such reactions with α - and β -pinene, a Wagner-Meerwein rearrangement occurs, and products having a camphane skeleton are produced. Thus, with each of these terpenes, hydrogen chloride yields⁶ bornyl chloride (IV), and α -pinene reacts with bromine to give 2,6-dibromocamphane (V).⁷

(6) J. L. Simonsen, "The Terpenes," Vol. II, Cambridge Univ. Press, Cambridge, 1949, pp. 170 and 202.

(7) J. L. Simonsen, ref. 6, p. 168.

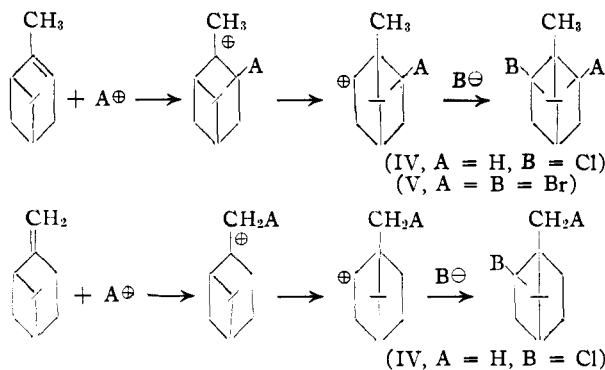
(1) Taken from the Ph.D. Thesis of William W. Lee, July, 1952.

(2) Sheshukov, *J. Russ. Phys. Chem. Soc.*, **18**, 478 (1884).

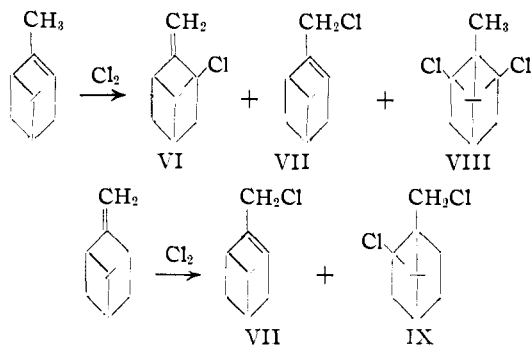
(3) D. V. Tishchenko, *J. Gen. Chem. (U.S.S.R.)*, **3**, 1326 (1938); *C. A.*, **33**, 4190 (1939).

(4) J. Burgin, W. Engs, H. P. A. Gross and G. Hearne, *Ind. Eng. Chem.*, **31**, 1413 (1939).

(5) R. W. Taft, Jr., *THIS JOURNAL*, **70**, 3364 (1948).

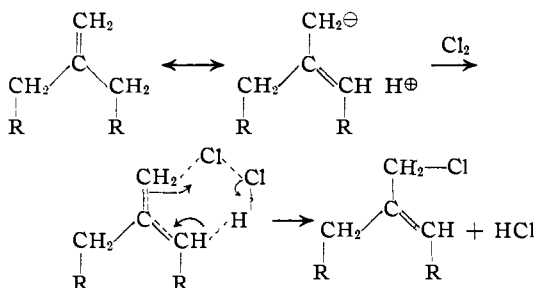


One would assume on the basis of the above ionic mechanism that both α - and β -pinene would yield camphane derivatives upon chlorination. This is true, however, only to a minor degree. The major products are allylic chlorides in which no expansion of the four-membered ring occurs. Thus, α -pinene, when subjected to chlorination at 0° , yields pinocarveol chloride (VI), mertenyl chloride (VII), and 2,6-dichlorocamphane (VIII).⁸ β -Pinene, under similar experimental conditions, yields mertenyl chloride as the major product, accompanied by a liquid dichloride⁸ to which we have assigned formula IX.



Presumably, compounds VI and VII cannot be formed *via* an attack by a chloronium ion (Cl^+) in the first step, since this would lead to a Wagner-Meerwein rearrangement. The formation of the camphane derivatives VIII and IX in relatively small quantities, however, is best explained in this way.

It is of interest that essentially all of the data reported to date relating to the conversion of isobutylenes to allylic chlorides by direct chlorination can be readily accounted for on the basis of a concerted mechanism involving a transition state containing a quasi six-membered ring. According to

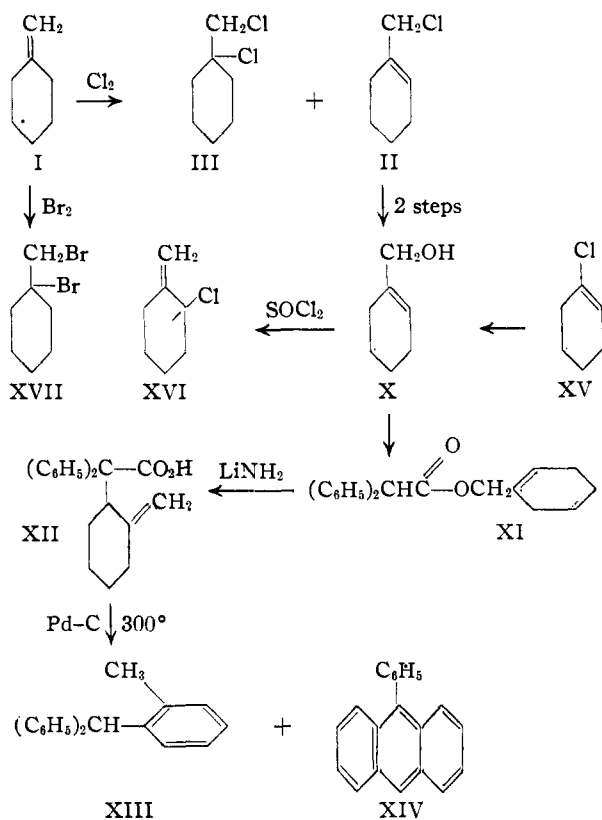


(8) D. Tishchenko and B. Matveev, *J. Gen. Chem. (U.S.S.R.)*, **20**, 8961 (1950); *C. A.*, **44**, 9381 (1950).

this view, the attachment of the chlorine atom to carbon, the rearrangement of the double bond, and the elimination of hydrogen chloride proceed simultaneously.⁹

Unfortunately, the results obtained from the chlorination of C^{14} -labeled¹⁰ isobutylene are not decisive, since they can be interpreted readily either by the ionic or cyclic transition state mechanisms.

In this Laboratory, pure methylenecyclohexane has been chlorinated at 0° to give 1-chloromethylcyclohexane (II) and 1-chloromethyl-1-chlorocyclohexane (I) in yields of 38–48% and 12–19%, respectively. These data, of course, may be explained by either of the two mechanisms discussed above.



Considerable evidence was accumulated to prove that the monochloride formed from methylenecyclohexane had the structure II and not XVI, which could have resulted from a direct attack of chlorine at the α -carbon atom. Hydrolysis of II by methods which should not lead to rearrangement^{11,12} gave 1-cyclohexenylcarbinol (X), which was synthesized independently from chlorocyclohexene (XV). The alcohol X, when treated with thionyl chloride, produced 2-chloromethylcyclohexane (XVI) and 1-chloromethylcyclohexane (II) in a ratio of 6:1, with the former predominating. Further proof for the structure assigned to X follows from its conversion to the acid XII by

(9) This mechanism assumes that pinocarveol chloride (VI) is the only allylic chloride derived from the direct chlorination of α -pinene and that mertenyl chloride (VII) is formed by isomerization.

(10) W. Reeve and D. H. Chambers, *THIS JOURNAL*, **73**, 4499 (1951).

(11) W. G. Young and L. J. Andrews, *ibid.*, **66**, 421 (1944).

(12) W. G. Young and I. D. Webb, *ibid.*, **73**, 780 (1951).

means of a thoroughly dependable transformation¹³ in which the allylic ester XI undergoes an intramolecular rearrangement.

When ozonized, the acid XII gave significant quantities of formaldehyde and was dehydrogenated to a mixture of *o*-tolylidiphenylmethane (XIII) and 9-phenylanthracene (XIV).¹⁴ The conflicting reports^{15,16} relative to the properties of 1-cyclohexenylcarbinol now appear to have been rectified.

An examination of the infrared spectra of the compounds in question supports the structures assigned on the basis of chemical evidence. Of the bands shown by compounds having methylene groups, the two that fall in the region 1639–1661 cm^{-1} and 3077–3096 cm^{-1} are present in 2-chloromethylenecyclohexane (1645 and 3050 cm^{-1}) and methylenecyclohexane (1645 and 3100 cm^{-1}), but these are absent from 1-chloromethylcyclohexene and 1-methylcyclohexene. Of the bands ascribed to trisubstituted olefins, the two falling in the range 908–926 cm^{-1} and 1667–1692 cm^{-1} ¹⁷ are quite similar in 1-methylcyclohexene (923 and 1670 cm^{-1}), 1-chloromethylcyclohexene (922 and 1665 cm^{-1}), and 1-cyclohexenylcarbinol (920 and 1670 cm^{-1}).

By contrast to what has been said above, it is of interest that addition, and not substitution, is the major reaction between isobutylenes and bromine at low temperature. As anticipated, methylenecyclohexane reacted with bromine to give the corresponding dibromide (XVII) and an allylic bromide in yields of 54 and 10%, respectively. The dibromide can be purified by vacuum distillation but gives off copious quantities of hydrogen bromide when heated at 190°. By contrast, the corresponding dichloride may be heated at its boiling point (198° (760 mm.)) for one hour with only slight decomposition.

Experimental

Methylenecyclohexane.—This hydrocarbon was prepared according to the procedure described by Arnold and Dowdall.¹⁸ The bulk sample was stored at 0° over hydroquinone to prevent autooxidation.

Chlorination of Methylenecyclohexane.—Into a 500-ml. 3-necked flask, fitted with a glass stirrer, condenser and delivery tube, were placed 105 g. (1.25 moles) of anhydrous sodium bicarbonate, 150 ml. of dry carbon tetrachloride and 78.3 g. (0.81 mole) of methylenecyclohexane which had been freshly distilled from hydroquinone. The mixture was cooled to 0° with stirring, and 12.4 l. of chlorine gas (0.5 mole at $p = 743$ mm., $t = 23^\circ$) was bubbled through the stirred mixture over a period of 100 minutes. The reaction mixture was filtered to remove the solid inorganic salts, washed with three 50-ml. portions of sodium bicarbonate solution (5%), once with water, dried over anhydrous magnesium sulfate, and then filtered to remove the drying agent. After the solvent and unreacted olefin had been removed rapidly by vacuum distillation below 60° on a steam-bath, the residual liquid was fractionated through a 45-cm. column

of glass helices to give 30.6 g. (47%) of 1-chloromethylcyclohexene, b.p. 75–80° (32 mm.) (mainly at 77–79° (32 mm.)), and 15.9 g. (19%) of methylenecyclohexane dichloride, b.p. 95–100° (32 mm.). Redistillation of the solvent and excess olefin through the above column gave 26.6 g. (35% of starting amount) of methylenecyclohexane, b.p. 100–103°.

The above sample of 1-chloromethylcyclohexene was carefully fractionated to give an analytical sample, b.p. 78° (32 mm.), n_{D}^{20} 1.4912. This material reacted immediately with alcoholic silver nitrate and decolorized both potassium permanganate and bromine dissolved in carbon tetrachloride.

Anal. Calcd. for $\text{C}_7\text{H}_{11}\text{Cl}$: C, 64.36; H, 8.49. Found: C, 64.35; H, 8.74.

Methylenecyclohexane dichloride, as obtained above, was redistilled, b.p. 97° (32 mm.), n_{D}^{20} 1.4910. Its analysis was not completely satisfactory.

Anal. Calcd. for $\text{C}_7\text{H}_{10}\text{Cl}_2$: C, 50.32; H, 7.24. Found: C, 51.4; H, 7.46.

1-Cyclohexenylcarbinol. Method (A).—The apparatus and general procedure are those described by Gilman and Catlin.¹⁹

Gaseous formaldehyde, formed by the depolymerization of 37.5 g. (1.25 moles) of paraformaldehyde at 180–200°, was swept by a slow stream of nitrogen into the vigorously stirred and cooled (0°) ethereal solution of cyclohexenyl-lithium (prepared from 118 g., 1.0 mole, of chlorocyclohexene in 800 ml. of ether). After 1.5 hours, the reaction was complete, as indicated by a negative color test with Michler ketone.¹¹ Several grams of paraformaldehyde still remained.

The reaction mixture was poured into a 4-l. beaker containing 1.5 l. of saturated ammonium chloride solution at 0°. After vigorous stirring, the ethereal layer was separated, the aqueous layer was extracted with 300 ml. of ether, and the two ether solutions were combined. The combined solution was washed with 200 ml. of water and dried over anhydrous magnesium sulfate–potassium carbonate. Distillation through a 45-cm. glass helices-packed column gave 11.7 g. (10%) of unreacted chlorocyclohexene, b.p. 58–61° (47 mm.), and 55.6 g. (50% based on chlorocyclohexene) of 1-cyclohexenylcarbinol, b.p. 89–90° (15–16 mm.), n_{D}^{20} 1.4910, n_{D}^{25} 1.4890. A redistilled portion of 1-cyclohexenylcarbinol, b.p. 84° (10 mm.), n_{D}^{20} 1.4910, was analyzed.

Anal. Calcd. for $\text{C}_7\text{H}_{12}\text{O}$: C, 74.95; H, 10.79. Found: C, 74.70; H, 10.95.

Method (B).—Into a 500-ml. 3-necked flask, fitted with stirrer, reflux condenser and drying tube, were placed 20 g. (0.153 mole) of 1-chloromethylcyclohexene, b.p. 75–80° (32 mm.), 15.5 g. (0.16 mole) of freshly fused potassium acetate and 150 ml. of redistilled acetic anhydride. The reaction mixture was heated on a steam-bath with stirring for 192 hours. At the end of this period, the condenser was turned down for distillation, and the mixture was distilled to remove all liquids boiling below 68° (23 mm.). The residue was poured onto ice, allowed to stand with occasional stirring for one hour, in order to hydrolyze any acetic anhydride, and neutralized with alkali. From this mixture, the ester was extracted with ether, and the ethereal solution was dried over anhydrous potassium carbonate. Removal of the drying agent and ether left 14.4 g. (61%) of crude 1-cyclohexenylmethyl acetate which was hydrolyzed directly. The crude 1-cyclohexenylmethyl acetate, 14.4 g. (0.93 mole) was poured into a flask containing 170 ml. of 10% potassium hydroxide in ethanol–water (9:1). The resultant solution was homogeneous but darkened immediately. It was heated under reflux for one hour. The ethanol was then removed by distillation through a 12-inch Vigreux column. The residue was washed into a separatory funnel with 75 ml. of ether and 75 ml. of 15% sodium chloride solution. The layers were separated, the aqueous layer was extracted with two 15-ml. portions of ether, and all the ether layers were combined. This was washed with 15 ml. of water, dried over anhydrous magnesium sulfate, and distilled carefully through an efficient 60-cm. concentric tube column manufactured by Podbielniak, Inc. There was obtained 8.4 g. (81%) of 1-cyclohexenylcarbinol, b.p. 92–93° (14–15 mm.), n_{D}^{20} 1.4898. No lower-boiling material which

(13) R. T. Arnold and S. Searles, Jr., *This Journal*, **71**, 1150 (1949).

(14) We are indebted to Prof. F. Vingiello of Virginia Polytechnic Institute, Blacksburg, Virginia, for an authentic sample of 9-phenylanthracene.

(15) E. P. Kohler, M. Tishler, H. Potter and H. T. Thompson, *This Journal*, **61**, 1057 (1939).

(16) M. Mousseron and Nguyen Phouc Du, *Bull. soc. chim.*, **91** (1948).

(17) L. H. McMurray and V. Thornton, *Anal. Chem.*, **24**, 318 (1952).

(18) R. T. Arnold and L. F. Dowdall, *This Journal*, **70**, 2590 (1948).

(19) H. Gilman and W. E. Catlin, "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., 2nd ed., 1941, p. 188.

might correspond to the isomeric secondary alcohol was isolated.

That the above samples of 1-cyclohexenylcarbinol are identical was established by preparing the same phenylurethan from each. Three-tenths (0.3) gram of carbinol and 0.4 g. of phenyl isocyanate were mixed together and tested on the steam-bath for 10 minutes. Upon cooling, the mixture solidified. After five recrystallizations from petroleum ether, b.p. 95–115°, beautiful white needles were obtained, m.p. 96.2–97.5°.

Anal. Calcd. for $C_{14}H_{17}O_2N$: C, 72.70; H, 7.41; N, 6.06. Found: C, 72.66; H, 7.81; N, 6.64.

Similarly, the carbinols prepared by methods (A) and (B) gave the same α -naphthylurethan; m.p. 125–125.6°.

Anal. Calcd. for $C_{18}H_{19}O_2N$: C, 76.87; H, 6.81; N, 4.98. Found: C, 77.08; H, 7.07; N, 5.07.

Reaction of Thionyl Chloride with 1-Cyclohexenylcarbinol.—Thirty-five grams (0.295 mole) of carefully purified thionyl chloride and 30 ml. of anhydrous ether were cooled in an ice-salt-bath. To this cooled solution was added, over a period of 30 minutes, 30 g. (0.268 mole) of 1-cyclohexenylcarbinol dissolved in 30 ml. of anhydrous ether. The reaction mixture turned brown during the addition. After standing for three hours at room temperature, the reaction mixture was diluted with 60 ml. of ether, shaken well with two 100-ml. and one 50-ml. portions of 5% sodium bicarbonate solution. No effervescence or foaming was observed during the shaking with the last portion. The ethereal layer was separated and dried over anhydrous magnesium sulfate and potassium carbonate. Distillation of the ethereal solution through a 15-cm. column of glass helices gave the following fractions

Fraction	B.p., °C. (32 mm.)	Wt., g.	n_D^{25}
Forerun	To 63	0.4	1.4860
1	63–66	2.0	1.4846
2	66–68	16.3	1.4850 n_D^{20} 1.4870
3	68–70	2.0	1.4858
4	70–72	0.9	1.4873
5	72–75	2.8	1.4893
Residue		Ca. 2 ml.	

The yield of 2-chloromethylenecyclohexane, b.p. 66–68° (32 mm.), n_D^{25} 1.4850, is 16.3 g. (47%). The yield of 1-chloromethylenecyclohexane, b.p. 72–75° (32 mm.), n_D^{25} 1.4893, is 2.8 g. (8%).

Two redistillations of fractions 1 to 3 gave a heart cut, b.p. 67–67.5° (32 mm.), n_D^{25} 1.4842, which was submitted for analysis and infrared spectral determination.

Anal. Calcd. for $C_7H_{11}Cl$: C, 64.36; H, 8.49. Found: C, 64.53; H, 8.21.

1-Cyclohexenylmethyl Diphenylacetate.—The procedure described by Arnold and Searles was employed.¹³

Diphenylacetyl chloride, 45.3 g. (0.196 mole), was dissolved in 100 ml. of carbon tetrachloride, and the resultant solution was cooled to 0°. To this was added 20 g. (0.178 mole) of 1-cyclohexenylcarbinol in 19.5 ml. (0.24 mole) of pyridine. A solid precipitate formed. The reaction mixture, after standing overnight at room temperature, was washed with portions of 5% sodium hydroxide solution until the last portion yielded no precipitate upon being acidified. In this way, 4.1 g. of diphenylacetic acid was recovered. The chloroform solution was finally washed with 30 ml. of water and dried over anhydrous sodium sulfate. Distillation gave three fractions of ester: frac. 1, 8.1 g., b.p. 145–155° (0.05 mm.), n_D^{20} 1.5660; frac. 2, 16.6 g., b.p. 155–170° (0.05–0.04 mm.), n_D^{20} 1.5668; and frac. 3, 19.9 g., b.p. 170–175° (0.04–0.03 mm.), n_D^{20} 1.5666. Fraction 2 was redistilled to give an analytical sample of 1-cyclohexenylmethyl diphenylacetate. The three fractions were combined to give a total yield, 44.6 g. (82%) of 1-cyclohexenylmethyl diphenylacetate, b.p. 145–175° (0.05–0.03 mm.), n_D^{20} 1.5660–1.5668.

Anal. Calcd. for $C_{21}H_{22}O_2$: C, 82.32; H, 7.24. Found: C, 82.25; H, 7.29.

2-Methylenecyclohexyldiphenylacetic Acid (XII).—Into a dry 500-ml. flask, fitted with stirrer and reflux condenser, were placed 31 g. (0.1 mole) of 1-cyclohexenylmethyl diphenylacetate, 200 ml. of anhydrous toluene and 11 g.

(0.48 mole) of lithium amide. The reaction mixture was heated under reflux with stirring for 42 hours. Then 50 ml. of 95% ethanol was added to decompose the excess lithium amide. The mixture was washed into a separatory funnel with alternate portions of ether and water. The organic layer was separated and washed with 30-ml. portions of water until the last portion gave no precipitate when acidified. The combined aqueous washes were acidified to give the crude acid. This acid, on drying overnight in a vacuum desiccator, weighed 28.4 g. (92%) and melted at 193–202°. Recrystallization from benzene-methanol (5:1) gave 14.7 g. of 2-methylenecyclohexyldiphenylacetic acid, m.p. 208–209.5°. Evaporation of the mother liquor gave a second crop of 10.9 g. of acid, m.p. 207–209°. Total yield, m.p. 207° and above, equalled 25.6 g. (83% yield). No trace of any isomeric acid was found.

Anal. Calcd. for $C_{21}H_{22}O_2$: C, 82.32; H, 7.24; neut. equiv., 306. Found: C, 82.64; H, 7.36; neut. equiv., 307.

Ozonization of the above acid in ethyl acetate at 0–5° gave 35% of formaldehyde in the form of its dimerone derivative, m.p. 189–191°.

Dehydrogenation of 2-Methylenecyclohexyldiphenylacetic Acid.—A mixture of 0.3 g. of palladium-on-charcoal (30%) and 1.4 g. of the acid was heated while a stream of carbon dioxide was passed slowly through the system and out into a gas buret containing 50% potassium hydroxide solution. The evolution of hydrogen began at 240° and became rapid at 270°. The temperature was raised gradually to 300° as the evolution of hydrogen became slower. After 12 hours, 60% of the theoretical amount of hydrogen was collected, and the reaction appeared to come to a standstill. The reaction mixture was cooled, extracted with benzene, and filtered.

Evaporation of the benzene filtrate gave 0.9 g. of residue, which was chromatographed through a 15-cm. alumina column, using 60–68° petroleum ether as the eluant. Fractions of 30 ml. were collected. After evaporation of the solvent, there was obtained 0.4 g. of residue from fractions 1 to 6. Several recrystallizations from methanol gave white crystals, m.p. 78–80°. This melting point was not depressed upon admixture with authentic *o*-tolylidiphenylmethane, m.p. 81–82°.

The evaporation of fractions 10–15 gave 0.07 g. of yellow solid residue which melted from 145–149°. Sublimation did not improve the melting point of this material. This compound gave strongly fluorescent solutions which fluoresced under ultraviolet light in exactly the same way as an authentic sample of 9-phenylanthracene, m.p. 150–151°. The ultraviolet spectra of this yellow solid (1.52 mg.) and 9-phenylanthracene (1.44 mg.), each in a 500-ml. solution of 95% ethanol, gave peaks at identical wave lengths and with the same relative intensities.

Bromination of Methylenecyclohexane.—Faworsky and Borgmann²⁰ have reported the addition of bromine to methylenecyclohexane, using ether as solvent at low temperature (*i.e.*, salt-ice-bath). Since these investigators said nothing of the thermal instability of the dibromide and since their experimental conditions and results differ from ours, the following directions are presented in some detail.

Methylenecyclohexane, 20 g. (0.208 mole), anhydrous sodium bicarbonate, 26.2 g. (0.312 mole), and 400 ml. of carbon tetrachloride were cooled to 0° in a 1-l. 3-necked flask fitted with stirrer, reflux condenser and dropping funnel. While this mixture was cooled and stirred, a solution of 33.2 g. (0.208 mole) of bromine in 200 ml. of carbon tetrachloride was added over a period of 100 minutes. After the addition was complete, the reaction mixture was filtered to remove the sodium salts. The filtrate was flash-distilled to remove the solvent and then distilled under reduced pressure through a 2" column of glass helices. Two fractions were obtained: fraction 1, b.p. 90–105° (16 mm.), weighed 4.8 g., and fraction 2, b.p. 106–115° (16 mm.), weighed 36.5 g.

The dibromide gave essentially no reaction with bromine in carbon tetrachloride and potassium permanganate solutions but reacted rapidly (though less so than the monobromide) with alcoholic silver nitrate. On attempting to distil a sample of methylenecyclohexane dibromide at atmospheric pressure, copious fuming was observed when the bath temperature reached 190°. The fumes were acidic to moist litmus and gave a precipitate on being passed into a

(20) A. Faworsky and I. Borgmann, *Ber.*, **40**, 4863 (1907).

solution of silver nitrate. A sample of methylenecyclohexene dibromide, b.p. 112° (16 mm.), n_D^{20} 1.5442, was analyzed. The properties previously reported²⁰ are b.p. 121.5–123° (27 mm.), d_4 1.7156.

Anal. Calcd. for $C_7H_{12}Br_2$: C, 32.85; H, 4.73. Found: C, 33.34; H, 4.77.

The monobromide reacted immediately with alcoholic

silver nitrate to give a copious precipitate and also decolorized bromine in carbon tetrachloride solution and potassium permanganate solution. A heart cut, b.p. 80° (16 mm.), n_D^{20} 1.5267, was analyzed.

Anal. Calcd. for $C_7H_{11}Br$: C, 48.02; H, 6.33. Found: C, 47.42; H, 6.40.

MINNEAPOLIS 14, MINNESOTA

[CONTRIBUTION FROM THE RESEARCH LABORATORIES OF A. BOAKE, ROBERTS AND COMPANY LIMITED]

The Reactions of Diketene with Ketones¹

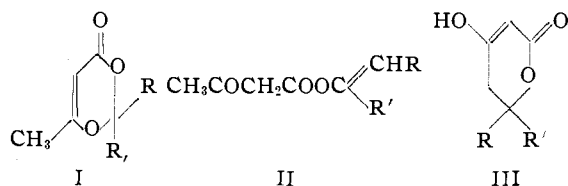
BY MICHAEL F. CARROLL AND ALFRED R. BADER²

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The acid-catalyzed reactions of diketene with ketones yield 2,2-disubstituted-4-methyl-6-keto-1,3-dioxenes (I), many reactions of which parallel those of diketene.

Although the preparation of ketene and diketene in acetone is a commercial process, the reaction of diketene has not been investigated in any detail.³ When acetone and diketene are heated on the steam-bath with a catalytic amount of *p*-toluenesulfonic acid, a crystalline solid, $C_7H_{10}O_3$, melting at 12–13°, can be isolated in 91% yield. Reactions with other unhindered ketones proceed similarly, and pure adducts are obtained from methyl ethyl ketone, acetophenone and dibenzyl ketone. Ketones which are more hindered sterically react more sluggishly and diisobutyl ketone, benzophenone and also acetoacetates do not appear to react at all.

Three structures, I, II and III were considered.



That of the enol acetoacetate II was rejected because of the adducts' non-reactivity with carbonyl reagents and because the adducts' ultraviolet spectra are inconsistent with II. Acetoacetates, even of complex alcohols, are known to react readily with carbonyl reagents⁴ whereas the adducts do not. Intensities of absorption maxima of acetoacetates increase sharply on passage to non-polar solvents because chelated enols are favored by non-solvating media. The adducts' ultraviolet spectra show identical intensities in water, ethanol and isoöctane.⁵ Furthermore the spectra of acetoacetates of the enols of acetophenone and dibenzyl ketone would be the composite of the spectra of substituted styrenes and acetoacetates. The spectra of the

adducts of these ketones, however, are very similar to that of the acetone adduct.

The enol III can be considered as the lactone of an aldol condensation product of acetoacetic acid and ketones. Similar 4-hydroxy-5,6-dihydro-2-pyrones have been prepared as analogs of the enol lactone form of auxin b. The methyl analog⁶ (III, R = -CH₃, R' = -H) reacts readily with dinitrophenylhydrazine and semicarbazide, and absorbs in the ultraviolet at somewhat lower wave lengths than do the diketene adducts. The phenyl analog⁷ (III, R = -C₆H₅, R' = -H) also reacts with semicarbazide and in contrast to the spectra of the diketene adducts shows in the infrared a strong enolic hydroxyl band at *ca.* 4.0 μ and no carbonyl band below 6.1 μ .

2,2-Disubstituted-4-methyl-6-keto-1,3-dioxenes (I) should be unstable in aqueous acid and alkali, should not react with carbonyl reagents and should react as do diketene and acetoacetic acid with alcohols and amines. The adducts' ultraviolet and infrared spectra are in accord with structure I. Their ultraviolet maxima in ethanol at 247–252 $m\mu$ are at longer wave lengths than those of β -alkoxycrotonates,⁸ an exaltation attributable to resonance contributions of structures Ia \leftrightarrow Ib \leftrightarrow Ic analogous to the exaltation of cyclohexadiene.⁹

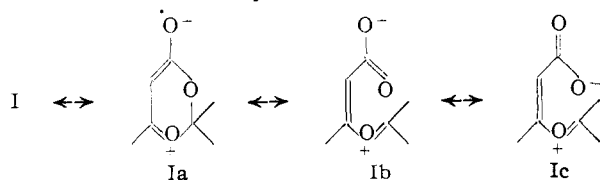


Figure 1 shows the infrared spectra of the acetone and acetophenone adducts. The pronounced associated hydroxyl band present in the spectra of cyclic 1,3-diketones such as dimedone at 3.4 μ , and in six-membered enol lactones such as III at *ca.* 4.0 μ is absent, and the carbonyl bands, at *ca.* 5.8 μ , are at significantly lower wave lengths than the carbonyl band of III. Thus we favor structure I for these diketene ketone adducts.

(6) E. R. H. Jones and M. C. Whiting, *J. Chem. Soc.*, 1419 (1949).

(7) E. B. Reid and W. R. Ruby, *THIS JOURNAL*, **73**, 1054 (1951).

(8) K. Bowden, E. A. Braude and E. R. H. Jones, *J. Chem. Soc.*, 948 (1946).

(9) R. S. Mulliken, *J. Chem. Phys.*, **7**, 339 (1939).

(1) For a preliminary communication, *cf.* *THIS JOURNAL*, **74**, 6305 (1952).

(2) The Research Laboratories, The Pittsburgh Plate Glass Co., Milwaukee, Wisconsin.

(3) In the reaction of ketene with acetone, which is catalyzed by zinc chloride, R. F. Naylor (*J. Chem. Soc.*, 244 (1948)), observed the formation in low yield of a product, $C_7H_{10}O_3$, thought to be isopropenyl acetoacetate. This may have been the diketene-acetone adduct here described.

(4) M. F. Carroll, *J. Applied Chem.*, 443 (1951).

(5) The log ϵ 's reported in ref. 3 were 3.93 in water and 4.0 in cyclohexane. Our values for the acetone adduct are 3.94 in water and 3.93 in isoöctane.