All attempts to treat the ketone with methylmagnesium bromide in ether or with methyllithium in ether led only to the isolation of starting compound in moderate yield.

3-Carboethoxy-2-methyl-5-*p*-tolylfuran.—To a solution of 8.7 g. of sodium metal dissolved in 700 ml. of dry ethanol was added 50 g. of ethyl acetoacetate followed by a solution of 80 g. of *p*-methylphenacyl bromide in 200 ml. of warm ethanol. The reaction mixture was refluxed overnight. Most of the solvent was then distilled off and the residue was diluted with water. The product was extracted with several portions of ether; the extracts were washed with water and dried over anhydrous magnesium sulfate. The oil obtained after evaporating the solvent was refluxed for 30 min. with a solution of 40 g. of sodium hydroxide dissolved in 2 l. of water. After cooling, the product was extracted from the solution with several portions of ether. After washing the extracts with water and drying over anhydrous magnesium sulfate, the solution was distilled under reduced pressure. The product, 16 g. of b.p. 135–145° (2.5 mm.), was a greenish yellow liquid which soon solidified. Several recrystallizations from methanol gave 8 g. of pale yellow prisms, m.p. 82–83°. The ultraviolet spectrum in methanol solution had λ_{max} 278 mμ (ϵ 18,000). The infrared spectrum contained a carbonyl band at 1725 cm.$^{-1}$. The n.m.r. spectrum in deuteriochloroform solution at 60 Mc. had six types of protons: at −78.5° a triplet with area 3 (methyl in ester group), at −136 a singlet with area 3 (*p*-tolyl methyl), at −154 a singlet with area 3 (methyl on the furan ring), at −254 a quartet with area 2 (methylene of the ester group), at −405 a singlet of area 1 (hydrogen on the furan ring), and at −426 to −448 c.p.s. an AB quartet of area 4 (aromatic protons) with reference to tetramethylsilane as an internal standard.

Anal. Calcd. for $C_{15}H_{16}O_3$: C, 73.75; H, 6.60. Found: C, 73.69; H, 6.73.

A 1.0-g. sample of the compound was hydrolyzed by refluxing it with 10 ml. of 1.0 *M* potassium hydroxide in ethanol and 2 ml. of water for 5 hr. The addition of water and dilute hydrochloric acid precipitated the product. After filtering and drying overnight in air, it was recrystallized from chloroform. Pale yellow crystals of m.p. 234–235° were obtained. The ultraviolet spectrum in methylene chloride solution had λ_{max} 280 mμ (ϵ 23,100).

Anal. Calcd. for $C_{13}H_{21}O_3$: C, 72.21; H, 5.60; equiv. wt., 216. Found: C, 72.37; H, 5.79; equiv. wt., 234.

3-Hydroxymethyl-2-methyl-5-*p*-tolylfuran.—To a slurry of 1.0 g. of lithium aluminum hydride in 100 ml. of dry ether was added dropwise under nitrogen a solution of 4.8 g. of the above ester in 50 ml. of ether. After the addition, the solution was refluxed for 2 hr. and cooled. Then, 5 ml. of ethyl acetate was added followed by cold dilute hydrochloric acid. The aqueous layer was separated and then extracted again with ether. The combined extracts were washed once with water and then with aqueous sodium bicarbonate. After the solution was dried over anhydrous magnesium sulfate, the solvent was evaporated on a steam bath and the residue was recrystallized several times from ether–pentane solution at 0°. There was obtained from 1 g. of colorless crystals, m.p. 98–99°. The ultraviolet spectrum in methanol solution had λ_{max} 288 mμ (ϵ 23,500). The n.m.r. spectrum at 60 Mc. in deuteriochloroform had the following peaks: at −114 a singlet with area 1 (hydroxy proton), at −139 a singlet with area 6 (both methyl groups), at −265 a singlet with area 2 (methylene group), at −388 a singlet with area 1 (proton on the furan ring), and at −424 to −448 c.p.s. an AB quartet of area 4 (aromatic protons) with reference to tetramethylsilane as an internal standard.

Anal. Calcd. for $C_{13}H_{14}O_2$: C, 76.81; H, 7.41. Found: C, 77.09; H, 7.07.

Acknowledgment.—The n.m.r. spectra were measured by Dr. M. M. Anderson of these laboratories.

Bromomethylenecycloalkanes

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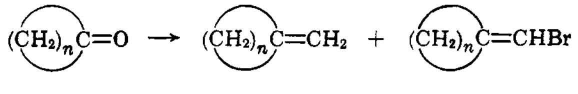
Methods for the preparation of bromomethylenecycloalkanes are described. The application of the Wittig reaction is shown to involve appreciable abstraction of bromine as well as hydrogen from bromomethyltriphenylphosphonium bromide to produce ultimately a mixture of methylenecycloalkane and bromomethylenecycloalkane. The decarboxylative debromination of α-bromo-1-bromocycloalkylacetic acids is shown to give high yields of pure bromomethylenecycloalkanes. Alternatively, pure vinyl bromides can be obtained by the addition of bromine to methylenecycloalkanes in the presence of a small amount of pyridine, followed by dehydrobromination of the resulting dibromide with potassium *t*-butoxide in *t*-butyl alcohol.

The need for a convenient general method of preparing bromomethylenecycloalkanes[2] prompted a study of the various synthetic routes available for these compounds. As the most direct route to exocyclic vinyl bromides the Wittig reaction[3] is the most likely choice. However, attempts to adapt the Wittig procedure to the synthesis of bromomethylenecycloalkanes by employing bromomethyltriphenylphosphonium bromide invariably led to the recovery of large quantities of cycloalkanone, even when an excess of organolithium reagent was employed, and to the production of methylenecycloalkanes together with a low yield (5–30%) of the desired vinyl bromide. Similar results have been reported by Seyferth.[4]

When phenyllithium was employed to generate the ylide, not only was benzene recovered, but a large amount of bromobenzene was produced. With either *p*-tolyllithium or *p*-chlorophenyllithium appreciable quantities of *p*-bromotoluene and *p*-bromochlorobenzene, respectively, were obtained and little, if any, benzene and bromobenzene were detected. These observations demonstrate that initial bromine abstraction by the base competes favorably with proton abstraction to give a mixture of methylene- and bromomethylenephosphoranes. The fact that additional side reactions take place was indicated by the failure of the phosphonium salt to react completely with the organolithium compounds and by the formation of small amounts of bromobenzene and benzene when methyllithium and butyllithium were used to generate the ylide. The latter observation suggests that the

$$[Ph_3\overset{+}{P}—CH_2Br]Br^- + ArLi \longrightarrow ArH + ArBr + Ph_3P{=}CH_2 + Ph_3P{=}CHBr$$



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[1] Gulf Oil Co. Fellow, 1963–1964.

[2] K. Erickson and J. Wolinsky, *J. Am. Chem. Soc.*, **87**, 1142 (1965).

[3] S. Trippett, *Quart. Rev.* (London), **17**, 406 (1963).

[4] D. Seyferth, J. K. Heeren, and S. O. Grim, *J. Org. Chem.*, **26**, 4783 (1961).

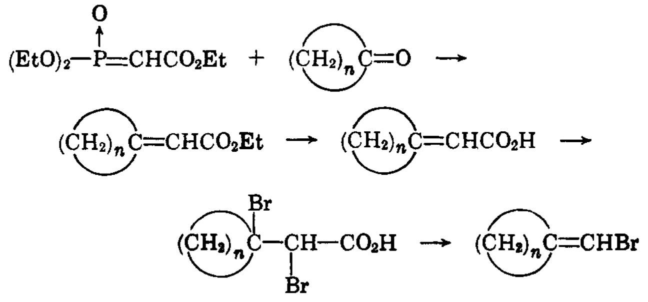
addition of the organolithium reagent to the ylides to form pentavalent phosphorus intermediates is an important side reaction.[5]

Attempts to circumvent the bothersome side reactions in this modification of the Wittig reaction by manipulation of reaction conditions were to no avail. Efforts to avoid the problem of bromine abstraction by the use of Grignard reagents, sodium hydride, or sodium methoxide generally gave little or no ylide and negligible amounts of vinyl bromides. In our hands the use of lithium piperidide, which has been claimed to circumvent the problem of bromine abstraction,[6] did not improve the yield of vinyl bromide or decrease the amount of recovered cycloalkanone. At present it does not appear that the Wittig reaction can be effectively adapted for the synthesis of large quantities of *pure* vinyl bromides.

We next turned our attention to the decarboxylative debromination of the dibromides of cycloalkylideneacetic acids and have found that high yields of pure vinyl bromides can be prepared in this manner.

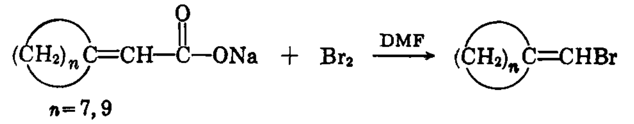
The decarboxylative debromination of α,β-dibromo acids is a method developed by Bachman[7] in the acyclic series and found to be useful in the preparation of vinyl bromides in those cases where the β carbon atom bears two alkyl substituents. It can be seen that this criterion is met with the dibromides of cycloalkylideneacetic acids.

With the exception of cyclohexylideneacetic acid, which was made by Wallach's method through the Reformatsky sequence,[8] all of the cycloalkylideneacetic acids used in this work were prepared by the condensation of the corresponding cycloalkanone with triethyl phosphonoacetate[9-11] followed by saponification of the resulting α,β-unsaturated esters to the α,β-unsaturated acids.



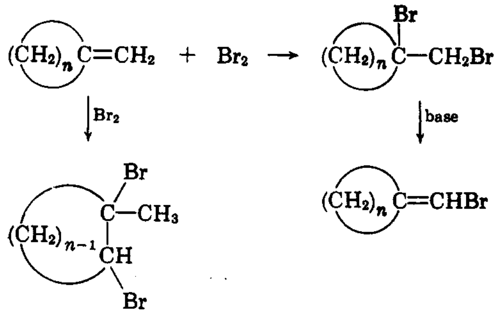
The hydrolysis of the esters to the cycloalkylidene acids proceeded smoothly only in the case of the seven- and twelve-membered ring compounds. In all other cases, the hydrolyses were effected with boiling aqueous sodium carbonate in order to avoid the isomerization to the 1-cycloalkenylacetic acids.[12] The use of aqueous sodium carbonate led to a good deal of recovered ester which was generally recycled. The conversion to acid per hydrolysis ranged from 35% for cyclopentylideneacetic acid to 6% for cyclodecylideneacetic acid.

The addition of bromine to the cycloalkylideneacetic acid presented no problem for the five-, six-, and seven-membered ring compounds. However, cyclododecylideneacetic acid, being quite insoluble in all common organic solvents, had to be brominated in hot acetic acid. The addition of bromine to cyclooctylidene- and cyclodecylideneacetic acids under normal conditions led to recovered starting materials or unidentified products. Addition of bromine to their sodium salts in aqueous solution gave oxygen-containing compounds. With these two acids it was necessary to prepare the anhydrous sodium salts and then conduct the bromine addition in dimethylformamide. Decarboxylative dehydrobromination occurred as the bromine addition took place and led directly to the desired bromomethylenecycloalkanes.



The decarboxylative debromination of α,β-dibromo acids with sodium carbonate or pyridine is an extremely simple and clean reaction. The reaction is nearly instantaneous and the bromomethylenecycloalkanes are produced in high yield and in high purity.

In the event that methylenecycloalkanes are available then the bromination–dehydrobromination scheme outlined below provides an excellent method for the preparation of bromomethylenecycloalkanes. Dehydrobromination of the dibromides with KOH in aqueous ethanol or with potassium *t*-butoxide in *t*-butyl alcohol affords high yields of the vinyl bromide. Difficulties are generally experienced in adding bromine to the methylenecycloalkane. We have found that considerable amounts of 1,2-dibromo-1-methylcycloalkanes are produced when bromine is added to certain methylenecycloalkanes in $CHCl_3$ or methylene chloride at 0°. In the case of methylenecyclopentane the abnormal addition product is the major product. This important side reaction can be eliminated by conducting the bromine addition in the presence of a small amount of pyridine.[13]



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[5] M. Schlosser, *Angew. Chem.*, **74**, 291 (1962); D. Seyferth, J. K. Heeren, and W. B. Hughes, *J. Am. Chem. Soc.*, **84**, 1764 (1962); G. Wittig and W. Boell, *Chem. Ber.*, **95**, 2526 (1962).

[6] G. Kobrich, *Angew. Chem.*, **74**, 33 (1962).

[7] G. B. Bachman, *J. Am. Chem. Soc.*, **55**, 4279 (1933); J. K. Farrell and G. B. Bachman, *ibid.*, **57**, 1281 (1935).

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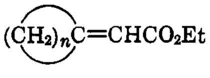
[12] For references to this isomerization, see R. M. Beesley, C. K. Ingold, and J. F. Thorpe, *J. Chem. Soc.*, **107**, 1080 (1915); W. F. Hugh, G. A. R. Kon, and T. Mitchell, *ibid.*, 1435 (1929); R. P. Linstead, *ibid.*, 1603 (1930), and references cited therein.

[13] The exact nature of the addition of bromine to terminal olefins will be discussed in a future publication.

TABLE I

ETHYL CYCLOALKYLIDENEACETATES


$(CH_2)_nC{=}CHCO_2Et$

n	Reaction time, hr.	% yield	B.p., °C. (mm.)	n_D (°C.)	% carbon Calcd.	% carbon Found	% hydrogen Calcd.	% hydrogen Found
4	1	93	71–72.5 (1)	1.4705 (20)	...	...	...	...
6	10	89	94–95 (1)	1.4809 (18)	72.49	72.46	9.95	10.23
7	72	72	81–83 (0.58)	1.4920 (18)	73.43	73.63	10.27	10.21
9	168	39	102–109 (0.8)	1.4957 (24)	74.95	75.06	10.78	10.99
11	84	70	133–134 (1)	1.4950 (24)	76.14	75.84	11.18	10.86

Experimental[14]

Bromomethyltriphenylphosphonium Bromide. A. From Triphenylphosphine and Methylene Bromide.—A solution of 60.0 g. (0.228 mole) of triphenylphosphine and 89.2 g. (0.460 mole) of methylene bromide in 500 ml. of dry toluene was refluxed for 24 hr. The mixture was cooled to 0° and the salt crystals were collected by filtration and washed with toluene. The filtrate was refluxed for another 24 hr., and a second crop of crystals was collected. The combined solids were dried *in vacuo* and weighed 77.4 g. (75%), m.p. 232–235° (lit.[15] m.p. 240–241° for bromomethyltriphenylphosphonium bromide).

Anal. Calcd. for $C_{19}H_{17}Br_2P$: C, 52.32; H, 3.93. Found: C, 52.03; H, 3.80.

When triphenylphosphine of lesser purity was used, a brown oil initially separated after about 4 hr. of heating. In such cases, the solution was decanted from the oil. Continued heating of the solution then gave the colorless crystalline salt in somewhat lower yield.

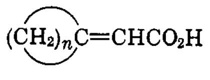
B. From Hydroxymethyltriphenylphosphonium Bromide and Phosphorus Pentabromide.—Anhydrous hydrogen bromide was passed for 3 hr. through a stirred mixture of triphenylphosphine (26.2 g., 0.10 mole) and paraformaldehyde (3.0 g., 0.10 mole based on CH_2O) in ether. A white precipitate formed immediately and gradually coagulated during the course of the reaction. The precipitate, 38.9 g., was collected by filtration and displayed m.p. 150–156°.

To a suspension of freshly prepared phosphorus pentabromide [from 16.9 g. (0.106 mole) of bromine and 28.5 g. (0.105 mole) of phosphorus tribromide] in methylene chloride was added a solution of 38.0 g. (0.102 mole) of hydroxymethyltriphenylphosphonium bromide in methylene chloride. During the addition the phosphorus pentabromide disappeared from the sides of the flask. The resulting solution was refluxed for 30 min. and most of the solvent was removed. Ether was added to precipitate the product which was collected and recrystallized from ethanol–ethyl acetate to give large white hexagons, m.p. 234–237°.

General Procedure for the Wittig Reaction in the Preparation of Bromomethylenecycloalkanes.—Various conditions were employed in an effort to attain maximum yields of bromomethylenecycloalkanes from the reaction of cyclic ketones with the ylide derived from bromomethyltriphenylphosphonium bromide. In general, a slight excess of an organolithium compound in ether was added to a suspension of bromomethyltriphenylphosphonium bromide in ether or tetrahydrofuran. The cycloalkanone was then added. After standing or heating for periods ranging from several hours to several days the reaction was generally worked up by filtration of the solids and distillation of the filtrate. In a few instances the solids were not removed, the reaction mixture being subjected to direct distillation. All volatile products were examined by vapor phase chromatography on a 20% Carbowax 20 M on firebrick column, with helium as the carrier gas. When necessary, samples of each product were collected for identification.

TABLE II

CYCLOALKYLIDENEACETIC ACIDS


$(CH_2)_nC{=}CHCO_2H$

n	Method of preparation	M.p., °C.	% carbon Calcd.	% carbon Found	% hydrogen Calcd.	% hydrogen Found
4	Procedure B	63[a]	...	...	...	...
5	...	89[b]	...	...	...	...
6	Procedure A	54–55	...	...	...	...
7	Procedure B	89–89.5[c]	71.39	71.71	9.59	9.28
9	Procedure B	132–132.5[d]	73.43	73.74	10.27	10.60
11	Procedure A	165–166	74.84	74.47	10.79	10.44

[a] 1-Cyclopentenylacetic acid, m.p. 50–51°. [b] Prepared by Wallach's method.[13] [c] 1-Cyclooctenylacetic acid, m.p. 32–33°. [d] 1-Cyclodecenylacetic acid, m.p. 44–45°.

The following is a typical example of the procedure followed. An ether solution of phenyllithium, prepared from 2.3 g. (0.015 mole) of bromobenzene and 0.40 g. (0.057 g.-atom) of lithium, was added under nitrogen to a rapidly stirred suspension of 5.0 g. (0.011 mole) of bromomethyltriphenylphosphonium bromide in ether. The mixture was stirred for 10 min. after the phenyllithium was added. An ether solution of 1.1 g. (0.011 mole) of cyclohexanone was added to the orange-red solution. The color of the solution faded long before all the cyclohexanone had been added. The mixture was stirred overnight at room temperature. The solid was removed by filtration and the filtrate was distilled *in vacuo*. Benzene, methylenecyclohexane, bromobenzene, and bromomethylenecyclohexane (See Table III) were obtained, the latter in approximately 15% yield.

Triethyl Phosphonoacetate.—Freshly distilled ethyl bromoacetate (70 g., 0.42 mole) was added dropwise to 70 g. (0.42 mole) of triethyl phosphite. After a 0.5-hr. induction period the temperature rose and ethyl bromide began to distil. The remainder of the ethyl bromoacetate was then added at a rate to maintain the reaction. After complete addition, the mixture was heated at 170° for 9 hr. Distillation afforded 74.5 g. (88%) of triethyl phosphonoacetate: b.p. 109–109.5° (0.80 mm.), n^{18}_{D} 1.4316; lit.[16] b.p. 152–153° (20 mm.).

Ethyl Cycloalkylideneacetates.—The properties of ethyl cycloalkylideneacetates, prepared by the condensation of triethyl phosphonoacetate with cycloalkanones, are summarized in Table I. The following procedure is typical for the preparation of these esters.

To a stirred mixture of 200 ml. of anhydrous monoglyme (refluxed over sodium and distilled from lithium aluminum hydride) and 8.4 g. (0.35 mole) of sodium hydride under a nitrogen atmosphere was added dropwise 80.64 g. (0.36 mole) of triethyl phosphonoacetate in monoglyme at a rate to keep the temperature below 35°. This mixture was stirred until hydrogen evolution ceased (24–48 hr.) and then 30 g. (0.36 mole) of freshly distilled cyclopentanone was added at a rate to keep the temperature below 35°. The mixture was stirred for 1 hr. The precipitation of a thick gelatinous semisolid indicated the reaction was complete. The mixture was poured into a large excess of water and extracted with ether. The ether extracts were washed with water and dried over magnesium sulfate. Distillation gave a forerun of monoglyme and 51.5 g. (93%) of pure ethyl cyclopentylideneacetate: b.p. 71–72.5° (1 mm.), n^{20}_{D} 1.4705; lit.[17] b.p. 80° (5 mm.), n^{20}_{D} 1.4731.

It was necessary to use a slight excess of triethyl phosphonoacetate in order to ensure complete reaction of the sodium hydride.

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[14] All boiling and melting points are uncorrected. N.m.r. spectra were measured at 60 Mc. with the Varian Associates A-60 spectrometer. Chemical shifts are given with reference to tetramethylsilane. Infrared spectra were determined with the Perkin-Elmer Model 221 and Infracord spectrometers. Microanalyses were conducted by Dr. C. S. Yeh and associates.

[15] F. Ramirez, N. B. Desai, B. Hansen, and N. McKelvie, *J. Am. Chem. Soc.*, **83**, 3539 (1961).

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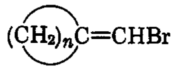
[17] J. H. S. Wieland and J. F. Arens, *Rec. trav. chim.*, **75**, 1358 (1956).

TABLE III

BROMOMETHYLENECYCLOALKANES



	%			Infrared, μ		N.m.r., p.p.m.		% carbon		% hydrogen		% bromine	
n	yield	B.p., °C. (mm.)	nD (°C.)	—C=CHBr	—CH2—	—C=C—CH2—	—C=CHBr	Calcd.	Found	Calcd.	Found	Calcd.	Found
3[a]		63 (60)	1.4987 (20)	6.06	2.02	2.67	5.72	...	...	...	...	...	...
4	90	70 (31)	1.5074 (18)	6.10	1.70	2.27	5.87	44.74	44.81	5.63	5.55	...	...
5	89	64–66 (10)	1.5142 (20)	6.15	1.54	2.23	5.80	48.02	48.26	6.33	6.27	...	...
6	95	62–63 (2.2)	1.5141 (21)	6.21	1.56	2.33	5.93	50.80	50.96	6.93	6.95	52.24	42.42
7	47	...	1.5210 (21)	6.20	1.46	2.28	5.90	53.21	53.37	7.39	7.43	...	...
9	12	88–92 (0.85)[b]	1.5244 (19)	6.12	1.44	2.29	5.81	57.10	57.84	8.28	8.31	34.57	32.48
11	83	116–118 (0.65)	1.5196 (20)	6.22	1.50	2.20	5.90	60.23	60.60	8.94	9.21	30.83	30.74

[a] Prepared by bromination–dehydrobromination of methylenecyclobutane; data is that obtained on a sample approximately 95% pure. [b] This boiling point was determined for a mixture containing 64% of the vinyl bromide.

When excess sodium hydride was present, isomerization of the conjugated ester to the internal, unconjugated isomer occurred.

Cycloalkylideneacetic Acids. Procedure A.—Cycloheptylidene- and cyclododecylideneacetic acids were obtained by hydrolysis of their respective ethyl esters with sodium hydroxide (see Table II). Ethyl cycloheptylideneacetate (56.0 g.) was heated with 29.0 g. of sodium hydroxide in aqueous ethanol for 3 hr. The solution was cooled and most of the alcohol was removed. The resulting solution was acidified with 10% hydrochloric acid and the solid which precipitated was collected and recrystallized from aqueous ethanol to give 42 g. (88%) of white needles, m.p. 54–55° (lit.[18] m.p. 55° for cycloheptylideneacetic acid).

When this procedure was applied to other ethyl cycloalkylideneacetates only the internal, unconjugated acid or a mixture of conjugated and unconjugated acids was obtained.

Procedure B.—Cycloalkylideneacetic acids (Table II), besides the two described above, were prepared by the following general procedure. A mixture of ethyl cyclooctylideneacetate (21.7 g., 0.11 mole) and an aqueous solution of 12.7 g. (0.12 mole) of sodium carbonate was kept at reflux for 5 days. The cooled mixture was extracted with ether to give 15.7 g. (73%) of ethyl cyclooctylideneacetate. The aqueous phase was cooled in an ice bath and carefully acidified with cold 5% hydrochloric acid to pH 5. Filtration of the white precipitate gave 4.2 g. (22%) of crystalline cyclooctylideneacetic acid. Acidification beyond pH 5 led to the coprecipitation of the internal, unconjugated acid. The recovered ester was recycled to give eventually a high yield of the desired acid.

When it was necessary to reflux the ester with aqueous sodium carbonate for 1 week or more, as with ethyl cyclodecylideneacetate, substantial sodium carbonate attack on the glass occurred, and sizeable quantities of sodium silicate were produced. Most of the silicate was held in solution until acidification, when it coprecipitated with the desired acid. The best method for removing the silicate was to dry the solid mixture *in vacuo* and then to extract the acid with ether. When a direct extraction of the wet mixture was attempted, unworkable emulsions formed.

α-Bromo-1-bromocyclopentylacetic Acid.—Bromine (17.1 g., 0.107 mole) was added dropwise to an ice-cooled solution of 13.4 g. (0.106 mole) of cyclopentylideneacetic acid in methylene chloride. After the addition was complete the solution was stirred for 3 hr. The solution was washed with sodium bisulfite solution and water. The solution was dried and the solvent was removed. The residue was crystallized from petroleum ether (b.p. 35–37°) to give 28.5 g. (94%) of colorless hexagons, m.p. 103–104°.

Anal. Calcd. for $C_7H_{10}Br_2O_2$: C, 29.40; H, 3.51; Br, 55.69. Found: C, 29.69; H, 3.79; Br, 55.59.

α-Bromo-1-bromocyclohexylacetic acid was obtained from cyclohexylideneacetic acid in 83% yield by the procedure described above and after crystallization from ether–petroleum ether showed m.p. 134–135°, lit.[17] m.p. 135–136°.

α-Bromo-1-bromocycloheptylacetic acid was obtained from cycloheptylideneacetic acid in 75% yield by the procedure described above and after crystallization from chloroform–petroleum ether displayed m.p. 119–124°.

α-Bromo-1-bromocyclododecylacetic Acid.—A solution of 4.56 g. (0.0285 mole) of bromine in acetic acid was added to a hot solution of 6.40 g. (0.0285 mole) of cyclododecylideneacetic acid in 100 ml. of acetic acid. The resulting solution was kept at 70–80° for 4 hr. The solution was cooled and poured into a large volume of water. The mixture was extracted with ether. The ether extracts were washed with water and dried and the ether was removed. The residue was crystallized from ethanol to give 10.5 g. (96%) of white plates, m.p. 119–120°.

Anal. Calcd. for $C_{14}H_{24}Br_2O_2$: C, 43.76; H, 6.29; Br, 41.69. Found: C, 43.43; H, 6.29; Br, 42.34.

Bromomethylenecycloalkanes.—The following procedure is typical for the preparation of the five-, six-, seven-, and twelve-membered ring bromomethylenecycloalkanes.

α-Bromo-1-bromocyclopentylacetic acid (29.1 g., 0.070 mole) was added to an aqueous solution containing 10.6 g. (0.106 mole) of sodium carbonate. Immediate evolution of carbon dioxide occurred. When the reaction subsided, the mixture was distilled. The distillate was extracted with ether and the ether extracts were dried. Distillation afforded 10.2 g. (90%) of bromomethylenecyclopentane whose properties are described in Table III. The bromide was stored under nitrogen in the cold. Exposure to air rapidly discolored the sample.

Bromomethylenecyclooctane.—The sodium salt of cyclooctylideneacetic acid was prepared by dissolving the acid in an aqueous solution of an equivalent amount of sodium carbonate. Dissolution was slow but was eventually achieved. The water was removed and the salt was dried *in vacuo*.

The sodium salt was suspended in 500 ml. of anhydrous dimethylformamide and with vigorous stirring, 7.38 g. (0.047 mole) of bromine in dimethylformamide was added dropwise at room temperature. The color discharged slowly, and the addition of bromine was allowed to proceed overnight. Solid sodium bisulfite was added and the mixture was stirred until the bromine color disappeared. The DMF was distilled at 30° *in vacuo*. The DMF distillate was poured into a large volume of water and the mixture was extracted with ether. The ether extracts were washed with water and dried. Distillation gave 4.0 g. (47%) of bromomethylenecyclooctane which was 95% pure according to v.p.c. analysis.

Bromomethylenecyclohexane.—1-Bromomethyl-1-bromocyclohexane[19] (2.4 g.) was kept overnight at room temperature with an equivalent of potassium *t*-butoxide in *t*-butyl alcohol. The mixture was poured into water and extracted with ether. Distillation gave 1.0 g. (60%) of the vinyl bromide: b.p. 62–64° (6 mm.), $n^{20}D$ 1.5143; lit.[20] b.p. 77° (25 mm.), $n^{24}D$ 1.5120.

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