(−)-*2-Heptylmethylmalonic acid.* The hydrolysis procedure used with the *dl* ester was followed using 15.1 g. of butyl (−)-2-heptylmethylmalonate, 26.5 g. potassium hydroxide, and 100 ml. of 80% ethanol. The crude acid weighed 10.7 g. (108%). One crystallization from pentane furnished 4.45 g. (50%) of the active acid, 99–101°. A second crystallization gave pure acid; m.p. 100–102°; $[\alpha]^{25}\text{D}$ −23.35° (95% ethanol, *c* 4, 2 d.).

Anal. Calcd. for $C_{11}H_{20}O_4$: C, 61.09; H, 9.32; neut. equiv., 108.14. Found: C, 61.04; H, 9.43; neut. equiv., 108.2.

The amide had m.p. 135–136°, $[\alpha]^{25}\text{D}$ −18.5° (95% ethanol).

Anal. Calcd. $C_{11}H_{22}N_2O_2$: N, 13.07. Found: N, 13.34.

dl-2,3-Dimethyloctanoic acid. Twenty-seven grams of crude 2-heptylmethylmalonic acid from the saponification of 36 g. of butyl *dl*-2-heptylmethylmalonate was heated at 165–180° to decarboxylate. Distillation furnished 24.2 g. of product; b.p. 126–150° (19 mm.); $n^{25}\text{D}$ 1.4330, neut. equiv. 295 (calcd., 172.6). Since the acid was contaminated with butyl ester, this crude acid (23.3 g.) was heated under reflux for 4 hr. with 75 ml. of absolute ethanol and 2.5 ml. of concd. hydrochloric acid. The reaction mixture was diluted, was extracted with ether and 22.3 g. of ester was eventually distilled; b.p. 94–104° (2 mm.); $n^{25}\text{D}$ 1.4230; sapon. equiv., 207.8 (calcd., 200.3).

The ethyl 2,3-dimethyloctanoate (17.9 g.) was saponified by boiling for 3 hr. in 100 ml. of 20% alcoholic potassium hydroxide. The reaction mixture was diluted and extracted with hexane. Acidification of the aqueous phases followed by extraction with ether gave a solution of the acid which was distilled to give two fractions: (1) 4.0 g., b.p. 125° (5 mm.); and (2) 6.8 g. (28%, based on butyl ester), b.p. 131.5° (5 mm.), $n^{25}\text{D}$ 1.4338.

Anal. Calcd. for $C_{10}H_{20}O_2$: Neut. equiv., 172.6. Found: Neut. equiv. 169.5. The amide had a m.p. 85–86°.

(−)-*2,3-Dimethyloctanoic acid.* Three grams of pure (−)-2-heptylmethylmalonic acid was heated at 180–220° for 2 hr. and distilled; b.p. 115° (1 mm.); 1.92 g. (80%); $n^{25}\text{D}$ 1.4341; d^{25} 0.9079; $\alpha^{25}\text{D}$ −12.73° (homogeneous); $[\alpha]^{25}\text{D}$ −14.1°.

Anal. Calcd. for $C_{10}H_{20}O_2$: C, 69.72; H, 11.70; neut. equiv., 172.6. Found: C, 69.82; H, 11.90; neut. equiv. 172.5.

The amide melted at 76–78°; $[\alpha]^{25}\text{D}$ −29.1° (95% ethanol).

Anal. Calcd. for $C_{10}H_{21}ON$: N, 8.28. Found: N, 7.86.

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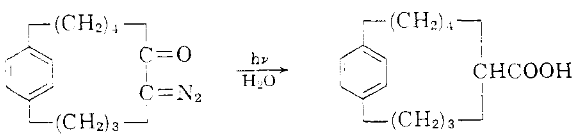
Communications TO THE EDITOR

The Synthesis of Highly Strained Medium Rings.[1] [8]Paracyclophane-4-carboxylic Acid

Sir:

The photolysis of an α-diazoketone is a type of Wolff rearrangement which has recently been shown to yield ring contraction of small rings, even when the product being formed is highly strained.[2] We have applied the reaction to the synthesis of a strained medium ring system, the [8]-paracyclophane. This compound is of theoretical interest because of the fact that models indicate that the benzene ring is deformed from planarity, and such a deformation should have an effect on the ultraviolet spectrum.[3] This compound long defied synthesis,[4] but was recently reported[5] as obtained by an ingenious reaction sequence, which lacks generality, however. The synthesis reported herein was developed as what is believed will be a general method applicable in particular to strained medium and large rings.[6]



The known 4,5-diketo-[9]paracyclophane monohydrazone[7] was treated with excess activated manganese dioxide and a trace of potassium hydroxide in ether–dioxane at 25° for two hours.[8] Filtration of the solution and evaporation of the ether left the diazoketone in dioxane, infrared absorption at 2030 cm.$^{-1}$ and 1640 cm.$^{-1}$. A little water was added and the solution was irradiated with a 250-watt Sylvania sun lamp at 100° for 3 hours. The product, [8]paracyclophane-4-carboxylic acid, was isolated and twice recrystallized

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[1] This work was supported by a grant from the Petroleum Research Fund administered by the American Chemical Society. Grateful acknowledgment is hereby made to the donors of this fund.

(2) J. Meinwald and P. G. Gassman, *J. Am. Chem. Soc.*, **82**, 2857 (1960), and references therein.

(3) D. J. Cram and H. Steinberg, *ibid.*, **73**, 5691 (1951).

(4) D. J. Cram, N. L. Allinger, and H. Steinberg, *ibid.*, **76**, 6132 (1954).

(5) D. J. Cram, and G. R. Knox, *J. Am. Chem. Soc.*, **83**, 2204 (1961).

(6) Subsequent to completion of this work A. T. Blomquist and F. W. Schlaefer, *J. Am. Chem. Soc.*, **83**, 4547 (1961), reported the application of this method to the preparation of other medium rings, and mentioned that [8]-paracyclophane-4-carboxylic acid was also obtained by this method.

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(8) H. Morrison, S. Danishefsky, and P. Yates, *J Org. Chem.*, **26**, 2617 (1961).

from aqueous ethanol, m.p. 79–80°, yield (over-all) 25%. Found: C, 77.53; H, 8.85. The compound showed typical carboxylic acid infrared bands at 3300, 2560, 1703 cm.$^{-1}$. The ultraviolet spectrum showed the expected[4,5] shifts and distortion; $\lambda_{\max}$ 230, ϵ 7,480; λ_{should} 270 mμ, ϵ 268; $\lambda_{\max}$ 276 mμ, ϵ 343; $\lambda_{\max}$ 283, ϵ 295. The distortion of the ultraviolet absorption curve from that of a *p*-dialkylbenzene is exactly as would be predicted for the [8]paracyclophane by comparison with the spectra of the higher homologs.[4] The PMR spectrum showed a band at 9.35 τ consistent with the assigned structure.[9]

A detailed Pariser-Parr treatment of the ultraviolet spectrum will be reported in the full publication.

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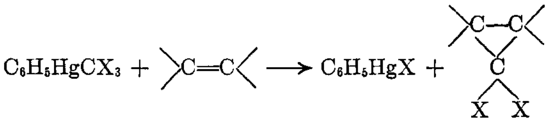
(9) J. S. Waugh and R. W. Fessenden, *J. Am. Chem. Soc.*, **79**, 846 (1957).

A New Preparation of Dihalocarbenes by an Organometallic Route

Sir:

The usual preparatively useful procedures for the generation of dihalocarbenes involve treatment of chloroform,[1] ethyl trichloroacetate,[2] or hexachloroacetone[3] with an alkali metal alkoxide in an inert solvent, or of bromotrichloromethane with organolithium reagents.[4] An alternative method which avoids basic conditions uses the slow thermal decomposition of sodium trichloroacetate in refluxing 1,2-dimethoxyethane to generate dichlorocarbene.[5] The yield of the carbene, as indicated by the isolated yield of its olefin adduct, did not exceed 65% in the latter procedure.

We report here a new, simply effected synthesis of dichloro- and dibromocarbene which may be carried out under very mild conditions, and which gives excellent yields of the dihalocarbenes. Russian workers[6,7] have reported recently two different syntheses of compounds of the types $RHgCCl_3$ and $RHgCBr_3$. Furthermore, it was reported that heating phenyl(trichloromethyl)mercury either alone at 150°[6] or in ethanol solution[7] produces phenylmercuric chloride in high yield. The recent work of Haszeldine and co-workers,[8] in which the pyrolysis of trichloromethyltrichlorosilane at 250° was shown to proceed *via* a dichlorocarbene intermediate, suggested to us that the decomposition of the trichloromethyl- and tribromomethyl-substituted mercurials also might involve formation of the respective dihalocarbenes. We have found this to be the case. When a benzene solution of either phenyl(trihalomethyl)mercury compound (easily prepared by the method described by Reutov and Lovtsova[7]) was refluxed with an olefin (the latter preferably in excess), phenylmercuric halide slowly precipitated from solution, and the dihalocarbene formed reacted with the olefin.



The yields of the dihalocyclopropane derivative in general were excellent, and the preparation of 7,7-dibromobicyclo[4.1.0]heptane is described to illustrate the very simple procedure used.

A suspension of 0.105 mole of phenyl(tribromomethyl)mercury in 50 ml. of benzene and 0.315 mole of cyclohexene was heated with stirring under reflux for 2 hr. During this time the starting mercurial dissolved and phenylmercuric bromide precipitated. The latter, m.p. 285–286°, was isolated in quantitative yield. Fractional distillation of the filtrate resulted in 22.5 g. (88%) of 7,7-dibromobicyclo[4.1.0]heptane, b.p. 60–63° at 0.5–0.7 mm. The product was identified by comparison of its infrared spectrum with that of an authentic sample,[1] and by its refractive index (n^{25}_{D} 1.5582; lit.,[1] n^{22}_{D} 1.5578). Phenyl(trichloromethyl)mercury is much more stable, and reaction times of *ca.* 36–48 hr. were required to realize comparable yields of dichlorocyclopropane compounds under the same conditions.

The procedure described above has the advantage that basic conditions are avoided and that very high yields are attainable, in contrast to the sodium trichloroacetate route. The phenylmercuric halide formed in this reaction is of good purity and can easily be reconverted[7] to new starting material in good yield. We report our initial findings at this

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