4-Methyl-2-pentanone dimethyl acetal. b.p. 58° (35 mm.), n_D^{25} 1.4042, d_{26} 0.850.

Anal. Calcd. for $C_8H_{18}O_2$: C, 65.71; H, 12.41. Found: C, 66.07; H, 12.35.

Yields. The acetone-methanol reaction system was the only case where attempts were made to account for all of the starting materials. It was possible to distill the unreacted acetone and methanol from the alkaline wash solution with recovery of more than 90% of the unreacted acetone and methanol. Therefore, for this system the conversion of acetone was 25–30% and the yield based on unrecovered acetone and methanol was consistently over 90%. No effort was made to account for all of the materials used in the other reaction systems, but it is believed that most of the unreacted materials could be recovered because no appreciable discoloration of the solutions was observed and no high boiling distillation residues or other by-products were obtained.

Effect of temperature on the reaction of ketones with alcohols. Stock solutions of 4 moles of alcohol per mole of ketone were passed slowly through the reactor at the desired temperature to ensure thorough displacement of all foreign fluids by the reaction solution. The flow was then stopped and the stock solution was kept in contact with the catalyst for a period of time. When the flow was again started, the effluent was collected in increments of 10 ml. each and the refractive index of each increment was measured. This procedure was repeated with successively longer contact times until there was no further increase in the maximum index observed in each set of effluent increments. Since the refractive index increases with conversion, the sample with the highest refractive index was taken as the one most nearly approaching equilibrium. The amount of ketone acetal present was then determined from its absorbance in the infrared. Methanol and ethanol were at equilibrium after 1 hr. in their reactions with every ketone except cyclohexanone. In the methanol-cyclohexanone system, the conversion of the cyclohexanone increased from 79% after 5 hr. to 86% after an 8-hr. contact period. Both propanol and butanol were at equilibrium in the reaction with acetone after a 5-hr. contact period. The values in Table I give the conversion of the ketones at equilibrium as determined in this manner.

Acknowledgment. We are indebted to J. Ambuhl and R. L. Yeakley for infrared measurements and to B. L. Self for his assistance in the laboratory.

FREEPORT, TEX.

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

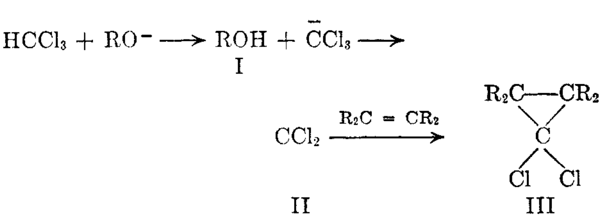
An Improved Synthesis of Dichlorocarbene from Ethyl Trichloroacetate[1]

WILLIAM E. PARHAM AND EDWARD E. SCHWEIZER

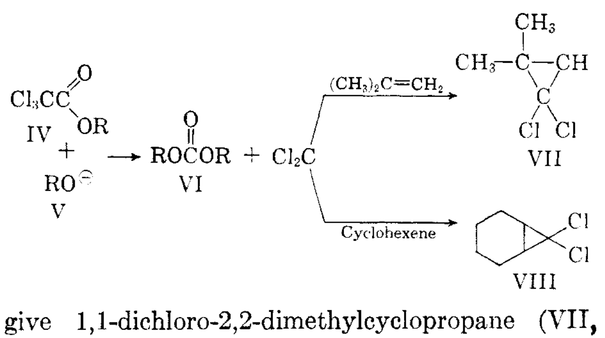
Received May 29, 1959

The reaction of ethyl trichloroacetate(IV) with sodium methoxide (commercial), sodium ethoxide, or potassium *t*-butylate in the presence of the olefins cyclohexene and isobutylene were studied both in the presence and absence of solvent (pentane). Similar results were obtained with all bases used, and yields of 72–88% of the derived cyclopropanes resulted. This reaction affords significantly higher yields of cyclopropanes than analogous reactions in which chloroform is used as the carbene precursor.

The reaction of chloroform, potassium *t*-butylate, and olefin constitutes an excellent synthesis of certain cyclopropane derivatives.[2] The yield of cyclopropane(III), obtained from such reactions, is generally 55–65%[2] and is unquestionably lowered by a side reaction occurring between dichlorocarbene and the alcohol (I) formed in the reaction.[2a,3] The superiority of *t*-butylate[2b] over other alkoxides in this reaction may be related, at least in part, to decreased reactivity of the more highly hindered *t*-alcohol with the derived carbene.



The formation of dichlorocarbene,[4] in the absence of alcohol, from *t*-butyl trichloroacetate (IV. R = *t*-butyl) and potassium *t*-butylate (V. R = *t*-butyl), and its further reaction with isobutylene to give 1,1-dichloro-2,2-dimethylcyclopropane (VII, 55% yield) suggested that the reaction of esters of



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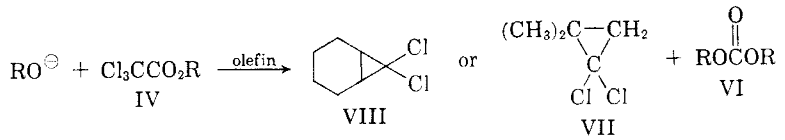
[1] This work was supported by a grant (G-7382) from the National Science Foundation.

[2] (a) W. von E. Doering and A. K. Hoffmann, *J. Am. Chem. Soc.*, **76**, 6162 (1954); (b) W. von E. Doering and W. A. Henderson, Jr., *J. Am. Chem. Soc.*, **80**, 5274 (1958); (c) W. E. Parham, H. E. Reiff, and P. Swartzentruber, *J. Am. Chem. Soc.*, **78**, 1437 (1956); (d) A. P. Ter. Borg and A. F. Bickel, *Proc. Chem. Soc.*, 283 (1958); (e) S. M. McElvain and P. L. Weyna, Abstracts of Papers, 134th Meeting of the American Chemical Society, Chicago, Ill., September 1958, p. 1P.

[3] J. Hine, E. L. Pollitzer, and H. Wagner, *J. Am. Chem. Soc.*, **75**, 5607 (1953).

[4] W. E. Parham and F. C. Loew, *J. Org. Chem.*, **23**, 1705 (1958).

TABLE I



Run	Base	Moles Base	Addition Time IV in Min.	Solvent ml. Pentane	ml. Olefin	% Yield VIII[a]	% Yield VII[b]	% Yield VI[b]
1	Potassium *t*-butylate	0.32	96	0	250	43		
2	Potassium *t*-butylate	0.32	90	150	75	72		76
3	Potassium *t*-butylate	0.25	0.25	0	250	53[d]		
4	Potassium *t*-butylate	0.25	0.25	150	100	56[d]		
5	Sodium methoxide	0.25	0.25	0	250	78		
6	Sodium methoxide	0.32	0.25	0	250	79		
7	Sodium methoxide	0.32	0.25	150	75	79		
8	Sodium methoxide	0.32	0.25	150	25.4[c]	88		
9	Potassium *t*-butylate	0.25	72	100	75		86	89
10	Potassium *t*-butylate	0.32	30	125	150		74	72
11	Sodium ethoxide	0.32	120	150	150		73	69
12	Sodium ethoxide	0.32	0.25	150	150		78	86
13	Sodium ethoxide	0.25	0.25	150	150		74	93
14	Sodium ethoxide	0.25	0.25	0	250		82	94
15	Sodium methoxide	0.25	0.25	0	250		76	73

[a] Yield compound VIII by isolation. [b] Yield compound VII and VI by gas chromatography. [c] Measured as 20.54 g. (0.25 mole) of cyclohexene, 0.3 mole of ethyl trichloroacetate used. [d] Uncontrollable large exotherm experienced.

trichloroacetic acid with alkoxides may represent an improved and more convenient synthesis of dichlorocarbene and the corresponding cyclopropanes derived by further reaction of the carbene with an olefin. This has been shown to be the case. This report describes the reactions of ethyl trichloroacetate (IV) with sodium ethoxide, potassium *t*-butylate and with commercially available sodium methoxide. The reactions were carried out both in the presence and absence of solvent (pentane), and with the olefins isobutylene and cyclohexene. The conditions and yields of the experiments resulting in the formation of 1,1-dichloro-2,2-dimethylcyclopropane(VII), from isobutylene, and 7,7-dichlorobicyclo[4,1,0]heptane(dichloronorcarane, VIII), from cyclohexene, are summarized in Table I.

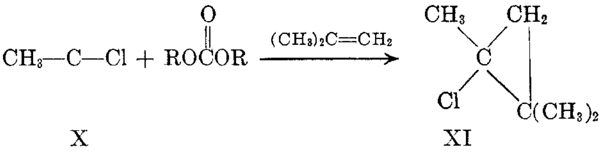
From the table one may see that the yields of the derived cyclopropanes were quite high (generally 72–88%). It is interesting to note that the yields of 1,1-dichloro-2,2-dimethylcyclopropane(VII) were quite similar regardless of the base used (potassium *t*-butylate, 86%; sodium ethoxide, 82%; commercial sodium methoxide, 76%). Similar results were obtained in the preparation of 7,7-dichlorobicyclo-[4,1,0]heptane(VIII) (potassium *t*-butylate, 72%; commercial sodium methoxide, 79%). The maximum yield of compound VIII (88%) was obtained (run No. 8) when an excess of sodium methoxide and ethyl trichloroacetate(IV) in pentane was used. The yield was based on the olefin used.

In reactions employing sodium methoxide or sodium ethoxide, the presence of solvent or the speed of addition of the ester had little effect on the yield of the derived cyclopropanes (runs 6, 7, and 11–14). However, when potassium *t*-butylate was employed, yields were greatly enhanced by the presence of solvent (runs 1 and 2) and by a slower addition of the ethyl trichloroacetate (runs 2 and 4). The use of commercial sodium methoxide has a number of advantages over the use of potassium *t*-butylate: (1) ready availability; (2) little exotherm is evidenced due to the lessened nucleophilicity of the methoxide ion over the *t*-butylate ion, and/or due to the lower solubility of of the methoxide over the *t*-butylate in the solution.

Initial experiments[5] with *t*-butyl α,α-dichloropropionate(IX) have failed to yield di-*t*-butyl carbonate and the corresponding addition product (XI) of the carbene(X) and isobutylene.

$CH_3—CCl_2CO_2R + RO^- \longrightarrow$

IX



X XI

The investigation is being extended to other haloesters and carbene acceptors.

EXPERIMENTAL[6]

Metal alkoxides. Powdered sodium methoxide, obtained commercially,[7] was always transferred to the dry reaction flask in a dry box under an atmosphere of dry nitrogen. Powdered potassium *t*-butylate and sodium ethoxide were prepared by the method used by Doering and Hoffman[2] to produce potassium *t*-butylate.

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(5) W. E. Parham and F. C. Loew, unpublished results.

(6) Boiling points are uncorrected.

(7) Matheson Coleman and Bell Division, The Matheson Co., Inc., East Rutherford, N. J.

Analyses of products. The 1,1-dichloro-2,2-dimethylcyclopropane (VII) and carbonates produced were analyzed by vapor-phase chromatography using a column[8] of polyethylene glycol on diatomaceous earth with helium as the eluent. The weight per cent composition of each component was obtained by determining the ratio of the individual peak areas which were calculated from the product of the peak height and the half-band width. These areas were weighted according to the areas found for standard predetermined amounts of standard samples. The yield of 2,2-dichlorobicyclo[4,1,*0*]heptane(VIII) was obtained by isolation. All samples of compound VIII had boiling points ranging over a one-degree range between b.p. 78–82.5° (15–16 mm.) and refractive indices ranging between n_D^{25} 1.5001–1.5005 (reported[2a] b.p. 78–79° (15 mm.), n_D^{23} 1.5014).

Ethyl trichloroacetate(IV) was prepared from trichloroacetic acid by the Fischer method using A.R. trichloroacetic acid[9] and absolute ethanol, with concentrated sulfuric acid as catalyst. The ethyl trichloroacetate(IV) used had b.p. 50.5–51.5° (8 mm.), n_D^{25} 1.4477. (Reported[10] b.p. 58–59° (13 mm.), n_D^{20} 1.4505.)

2,2-Dichlorobicyclo[4,1,0]heptane(VIII). Ethyl trichloroacetate(IV), 47.86 g. (0.25 mole), was added (under dry N_2) all at once to a cold (2.5°) mixture of commercial sodium methoxide (17.3 g., 0.32 mole) and dry cyclohexene (250 ml.). The mixture was cooled in an ice water bath and stirred (under N_2) for a period of 8 hr. After allowing the mixture to stand overnight, water (200 ml.) was added. The layers were separated and the aqueous phase was extracted twice with two 100-ml. portions of pentane. The organic layers were combined and dried ($MgSO_4$). The dried solution was filtered and concentrated. Distillation of the residue yielded 32.6 g. (79%, based on ethyl trichloroacetate) of 2,2-dichlorobicyclo[4,1,0]heptane(VIII), b.p. 81.5–82.5° (16 mm.), n_D^{25} 1.5004 (reported[2a] b.p. 78–79° (15 mm.), n_D^{23} 1.5014).

All the reactions were run in essentially the same manner as this experiment. Reactions with isobutylene were started in a dry ice bath and once the ester IV had been introduced, the mixture was allowed to reflux (at −6°).

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[8] Perkin-Elmer Co., Norwalk, Conn. Vapor Fractometer, Model 154-C, column K.

[9] Mallinckrodt Chemical Works, St. Louis 7, Mo.

[10] M. H. Palomaa, E. J. Salmi, and R. Korte, *Ber.*, **72**, 790 (1939).

[CONTRIBUTION NO. 258 FROM THE DEPARTMENT OF CHEMISTRY, TUFTS UNIVERSITY]

Pyrolysis of Allylic Acetates

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Received June 8, 1959

2-Acetoxy-*trans*-3-heptene and 4-acetoxy-*trans*-2-heptene have been pyrolyzed; the former pyrolyzed satisfactorily at 350°, whereas the latter required 363° for comparable pyrolysis. Both esters produced a mixture of 1,3- and 2,4-heptadiene. The evidence showed that the esters underwent thermal isomerization, and that in this isomerization the *trans*-configuration of the carbon-carbon double bond was essentially retained. The facts can be interpreted as supporting an intramolecular mechanism for the thermal rearrangement of allylic esters.

The pyrolysis of allylic acetates has been rarely used as a method for the preparation of conjugated dienes. In one of the early examples of this reaction van Pelt and Wibaut[1] found that the pyrolysis of 4-acetoxy-2-hexene gave a 66% yield of a diene which was designated as 2,4-hexadiene. Marvel and Williams[2] successfully employed the pyrolysis of 3-acetoxy-2-alkyl-1-butenes for the preparation of 2-alkyl-1,3-butadienes. And in the same laboratory 3-cyano-1,3-butadiene was obtained[3] by the pyrolysis of 3-acetoxy-3-cyano-1-butene. More recent work has indicated that where possible the pyrolysis of allylic acetates may give rise to a mixture of conjugated dienes as products. Grummitt and co-workers[4] have shown that the pyrolysis of either 1-cyclohexyl-3-acetoxybutene or 1-cyclohexyl-1-acetoxy-2-butene produced as product a mixture of 1-cyclohexyl-1, 3-butadiene and 1-cyclohexylidene-2-butene. The mixture of dienes was explained by isomerization of either of the acetates to the other prior to pyrolysis.

Isomerization of the allylic ester during pyrolysis had been observed by Marvel and Brace.[3] Bailey and Barclay[5] reported isomerization of 1,4-diacetoxy-2-butene during pyrolysis, and Bailey and Goossens[6] have explained the obtention of 3-methylenecyclohexene from the pyrolysis of 1-cyclohexenylmethyl acetate by isomerization of the ester to 2-methylenecyclohexyl acetate before pyrolysis. Grummitt and Mandel[4] have shown that either of a pair of allylic acetates will undergo thermal rearrangement to the other. This type of isomerization also occurs with propargylic acetates, for the Landors[7] have reported the rearrangement

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[1] A. J. van Pelt, Jr., and J. P. Wibaut, *Rec. trav. chim.*, **60**, 55 (1941).

[2] C. S. Marvel and J. L. R. Williams, *J. Am. Chem. Soc.*, **70**, 3842 (1948).

[3] C. S. Marvel and N. O. Brace, *J. Am. Chem. Soc.*, **70**, 1775 (1948).

[4] O. Grummitt and J. Splitter, *J. Am. Chem. Soc.*, **74**, 3924 (1952); O. Grummitt and Z. Mandel, *J. Am. Chem. Soc.*, **78**, 1054 (1956).

[5] W. J. Bailey and R. Barclay, Jr., *J. Org. Chem.*, **21**, 328 (1956).

[6] W. J. Bailey and J. C. Goossens, *J. Am. Chem. Soc.*, **78**, 2804 (1956).

[7] P. D. Landor and S. R. Landor, *J. Chem. Soc.*, 1015 (1956).