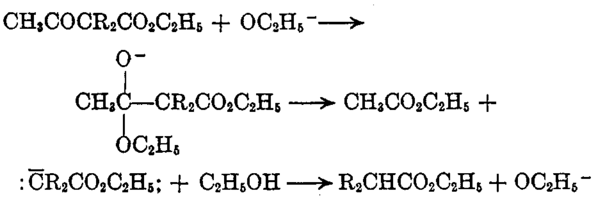
# Notes

## An Improvement in the Preparation of Acids *via* Acetoacetic Ester

John J. Ritter[1] and Thaddeus J. Kaniecki[2,3]

*Received August 31, 1961*

The preparation of acids $RCH_2CO_2H$ by the acetoacetic ester route is known to result usually in only fair or even poor yields because of the competing and usually preferred reaction to form methyl ketones. Dieckmann[4] reported the alcoholysis of *di*alkyl acetoacetic esters in presence of ethoxide to result in high yields of the products of acid cleavage:



$$CH_3COCR_2CO_2C_2H_5 + OC_2H_5^- \longrightarrow$$

$$CH_3\overset{O^-}{\underset{OC_2H_5}{C}}-CR_2CO_2C_2H_5 \longrightarrow CH_3CO_2C_2H_5 +$$

$$:\bar{C}R_2CO_2C_2H_5; + C_2H_5OH \longrightarrow R_2CHCO_2C_2H_5 + OC_2H_5^-$$

We have now found that the alcoholysis of monoalkyl acetoacetic esters, reported by Dieckmann and others to have failed, may be accomplished in excellent yields by heating with catalytic amounts of alkoxide in excess of absolute ethanol. The complete absence of products of ketonic cleavage in either case is to be anticipated, as alkoxide attack on the ester carbonyl group would result only in ester exchange and would lead to no significant chemical alteration of this group.

The success of the method reported here appears to depend upon scrupulous care in the preparation of the antecedent materials, which must be dry and free of acetoacetic ester. Reaction is accomplished under reflux with continuous removal of ethyl acetate as the ethanol–ethyl acetate azeotrope. The reaction time varied in ten cases examined (Table I) from ten to twenty-four hours. Continuous removal of ethyl acetate was performed in early experiments under the assumption that this would aid in equilibrium shift and also possibly minimize obvious side reactions. However, a control experiment using $\alpha$-allylacetoacetic ester without removal of ethyl acetate resulted in fair (70%) yield of ethyl 4-pentenoate in contrast to 88% obtained with continuous removal. It would appear that the principal value of ethyl acetate removal is simply that of avoiding temperature drop in the reaction vessel. This procedure was used throughout.

It seems evident that the reaction begins with alkoxide attack at the keto-carbonyl group, as shown above. The presence of water or acetoacetic ester would be expected to interfere by destruction of the alkoxide catalyst. The survival of the catalyst in the presence of monosubstituted acetoacetic esters might be due to the diminution of acidity of the alpha-hydrogen atom resulting from alpha-alkyl substitution. It may be noted also that alkylideneacetoacetic esters, $CH_3COC(=CHR)CO_2C_2H_5$,

TABLE I

$$CH_3COCHRCO_2C_2H_5 + C_2H_5OH \xrightarrow{OC_2H_5^-} CH_3CO_2C_2H_5 + RCH_2CO_2C_2H_5$$

| R | Ester[a] | $C_2H_5OH$[a] | Na[a] | Moles Used Ester | Yield, % | B.P./P. |
|---|---|---|---|---|---|---|
| $C_2H_5$ | 1 | 3.5 | 0.13 | 0.50 | 70[b] | 120–121/atm. |
| $n$-$C_3H_7$ | 1 | 3.5 | 0.13 | 0.50 | 82 | 145–146/atm. |
| $C_3H_5$ | 1 | 2.5 | 0.10 | 0.72 | 88 | 142–144/atm. |
| $C_4H_5$ (methallyl) | 1 | 3.9 | 0.15 | 0.45 | 83 | 165–167/atm. |
| $n$-$C_4H_9$ | 1 | 2.9 | 0.15 | 0.43 | 81 | 166–168/atm. |
| $i$-$C_5H_{11}$ | 1 | 3.5 | 0.15 | 0.50 | 88 | 181–182/atm. |
| $n$-$C_{10}H_{21}$ | 1 | 7.0 | 0.12 | 0.25 | 84 | 104–106/1.5 mm. |
| $C_6H_5CH_2$ | 1 | 3.9 | 0.15 | 0.50 | 84 | 93–95/2 mm. |
| $C_6H_5C_3H_4$ (cinnamyl) | 1 | 3.9 | 0.13 | 0.23 | 92 | 115–116/1 mm. |
| $C_4H_7O_2$ (carbethoxymethyl) | 1 | 4.5 | 0.16 | 0.40 | 84 | 215–217/atm. |

[a] Ester: $C_2H_5OH$: Na is on 1 mole ester basis. [b] Methyl and ethyl acetoacetic ester gave poorer yields than the higher homologs, apparently because of the difficulty of their separation from acetoacetic ester by distillation.

---

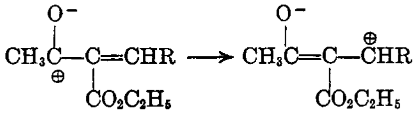
(1) Present address: Evans Research and Development Corp., New York, N. Y.

(2) Abstracted from a portion of the thesis submitted by Thaddeus J. Kaniecki to the Graduate Faculty of New York University in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

(3) Present address: Lever Brothers, Edgewater, N. J.

(4) W. Dieckmann, *Ber.*, **33**, 2670 (1900); W. Dieckmann and A. Kron, *Ber.*, **41**, 1260 (1908). See also: W. M. Kutz and H. Adkins, *J. Am. Chem. Soc.*, **52**, 4391 (1930); R. Connor and H. Adkins, *J. Am. Chem. Soc.*, **54**, 3420 (1932); L. J. Beckham and H. Adkins, *J. Am. Chem. Soc.*, **56**, 1119 (1934); J. Finkelstein and R. C. Elderfield, *J. Org. Chem.*, **4**, 365 (1939); W. B. Renfrow and G. B. Walker, *J. Am. Chem. Soc.*, **70**, 245 (1956).

obtained by Knoevenagel condensation of crotonaldehyde and benzaldehyde with acetoacetic ester yielded only polymeric materials instead of the anticipated sorbic and cinnamic esters. It is suggested that allylic resonance may account for the failure of such esters to undergo the cleavage:



$$\mathrm{CH_3\overset{O^-}{\underset{\oplus}{C}}-\underset{CO_2C_2H_5}{C}=CHR \longrightarrow CH_3\overset{O^-}{C}=\underset{CO_2C_2H_5}{C}-\overset{\oplus}{C}HR}$$

### EXPERIMENTAL

*General procedure.* The same procedure was used for all compounds shown in Table I, except for variations in time required for completion of the reaction. Preparative details are given only for the alcoholysis of ethyl α-allylacetoacetate to *ethyl 4-pentenoate:* To a solution of 1.5 g. (0.065 g.-atom) of oxide-free sodium in 81 g. (1.76 moles) of absolute ethanol in a 500-ml. round bottomed flask was added 122 g. (0.72 mole) of freshly distilled ethyl α-allylacetoacetate. The resulting light yellow solution was refluxed under a 5-ft. distilling column packed with glass helices and fitted with an automatic liquid-divider head. When the vapor temperature at the column head had dropped from 78° to 72° (the boiling point of the ethanol–ethyl acetate azeotrope), slow distillation was begun and the take-off ratio was adjusted to maintain the vapor temperature at 72–73°. After the calculated amount of azeotrope had been collected (22 hr.), the distillation was stopped and the excess ethanol was removed on the water bath. The flask contents were cooled, transferred to a separatory funnel, and washed with 100 ml. of cold 5% sulfuric acid. After separation of the ester layer the aqueous portion was washed twice with 25-ml. portions of ether, and the ether extracts were combined with the main portion of the ester. The resulting ether solution was washed successively with 50 ml. of water, 50 ml. of 2% sodium bicarbonate solution, and 50 ml. of water, and dried over anhydrous magnesium sulfate. The dry ethereal solution was filtered from the drying agent, the ether was removed and the product, ethyl 4-pentenoate, was distilled at ordinary pressure and collected at 142–144°; yield, 81 g. (88%). The still residue consisted mainly of unchanged ethyl α-allylacetoacetate.

*Acknowledgment.* The authors wish to express their thanks to the Food Machinery and Chemical Corp. for financial support of this investigation and also for providing generous quantities of necessary materials.

Department of Chemistry
New York University
New York, N. Y.

---

## Allylic Bromination by *N*-Bromo-*t*-butylamine[1]

C. E. Boozer and J. W. Moncrief

*Received August 14, 1961*

Currently allylic bromination is most frequently accomplished through the use of *N*-bromosuccinimide.[2] We have discovered that *N*-bromo-*t*-butylamine also reacts with olefins to give bromination at the allylic position. The yields in the *N*-bromo-*t*-butylamine reaction under certain conditions are comparable to those of the *N*-bromosuccinimide reaction.[2]

In the study of the allylic brominating ability of *N*-bromo-*t*-butylamine, cyclohexene was used as the olefin, the concentrations of the reagents and the type of solvent were varied, and the effect of azobisisobutyronitrile (AIBN) was studied. Light seemed to be inferior to AIBN as an initiator, and therefore was not investigated further. Our results appear in Table I.

TABLE I

The Effects of Variables on the Reaction of *N*-Bromo-*t*-Butylamine as an Allylic Brominating Agent

| Solvent | Ratio of Moles *N*-Bromo-*t*-butylamine/ Moles Olefin/ Ml. Solvent | Catalyst or Initiator | Time (Hr.) | Yield of 3-Bromocyclohexene %[a] |
|---|---|---|---|---|
| Carbon tetrachloride | 1/1.5/750 | None | 6 | none[b] |
| Isohexane | 1/1.5/750 | Light[c] | 6.5 | 18[d] |
| Isohexane | 1/1.5/750 | 0.2 g. AIBN | 3 | 23 |
| Isohexane | 1/2/750 | 1 g. AIBN | 5.5 | 38 |
| Isohexane | 1/3/750 | 1 g. AIBN | 5 | 37 |
| Isohexane | 1/3/375 | 1 g. AIBN | 3 | 59 |
| Isohexane | 1/3/187.5 | 1 g. AIBN | 1.5 | 31 |
| Isohexane | 1/1.5/375 | 1 g. AIBN | 5 | 40 |
| Benzene | 1/3/750 | 1 g. AIBN | 5 | 30 |
| Benzene | 1/3/375 | 1 g. AIBN | 5 | 42 |
| Benzene | 3/1/750 | 1 g. AIBN | 5 | 17[e] |

Yield of 3-bromocyclohexene based on *N*-bromo-*t*-butylamine. [b] There appeared to be a competing reaction involving the carbon tetrachloride. [c] Light was supplied by sun lamp. Light seemed to favor the formation of *t*-butylamine hydrobromide. [d] All yields of 3-bromocyclohexene were corrected for the amount of product lost in working up the sample, using a technique similar to that of H. J. Dauben, Jr., and L. L. McCoy.[2] [e] 22% 3,6-Dibromocyclohexene was produced; collected 95–100° (10 mm.).

### EXPERIMENTAL

*Preparation of N-bromo-t-butylamine.*[3] *t*-Butylamine, 0.2 mole, (freshly distilled) was mixed with 20 ml. of 10*N* sodium hydroxide and 100 ml. of water. Bromine, 0.2 mole, was added dropwise over a period of 50–70 min. The reaction was kept at 0–5° and was stirred constantly. After the bromine was added, the sample was extracted with ether, and the ether layer dried over magnesium sulfate. The ether then was removed by means of an aspirator. The *N*-bromo-*t*-butylamine remained in almost quantitative yield, about 30 g. It is a deep red-orange liquid with a strong unpleasant odor. It should be prepared immediately before use since it decomposes on standing with the formation of *t*-butylamine hydrobromide, a white crystalline solid.

---

(1) This work was supported by an undergraduate research grant (G-15672) from the National Science Foundation.

(2) See H. J. Dauben, Jr., and L. L. McCoy, *J. Am. Chem. Soc.*, 81, 4863 (1959).

(3) See N. Kijner, *J. prakt. Chem.*, 172, 64 (1901).