*Anal.* Calcd for $C_{16}H_{20}O_2$: C, 78.65; H, 8.25. Found: C, 78.55; H, 8.60.

**Registry No.**—**6**, 18634-49-6; **7**, 18634-50-9; **8**, 18634-51-0; **9**, 18634-52-1; **11**, 18634-53-2; **13**, 18634-54-3; **14**, 18634-55-4; **15**, 18634-56-5; **16**, 18634-57-6.

## Reaction of Lead Tetraacetate with Isophorone[1]

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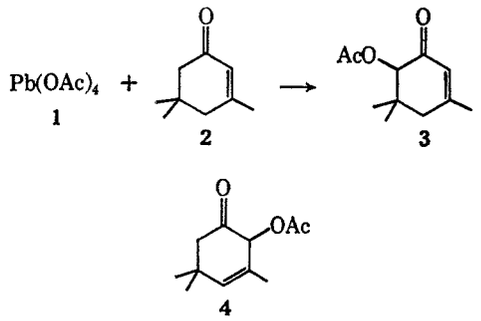
*Received September 1, 1968*

The reaction of lead tetraacetate (**1**) with isophorone (**2**) was studied and an improved procedure for the preparation of 6-acetoxyisophorone (**3**) is reported. As indicated,[2] when acetic acid was used as a solvent, acetate **3** could be isolated in only 38% yield. Using benzene as a solvent in the presence of $CaH_2$ or $BF_3$,[3] only slightly better yields were observed. Benzene and $CaCO_3$ [4] gave yields of 74% but the best yields were obtained using benzene alone where the product was isolated by crystallization in 78% yield. The yields




could be increased by distillation of the mother liquors.[2] As with saturated ketones,[5] the reaction was faster in acetic acid, or in the presence of acids[3] or bases.

It is of interest that acetate **3** was the only product observed. Gas chromatograms of the crude reaction mixtures and mother liquors remaining after crystallization of the product showed only starting material, acetate **3**, and with the crude reaction mixtures, usually 1% or less other materials. These minor components could be other products, or oxidation products of the trace impurities (<1%) in the starting material. In the case of the uncatalyzed reaction in benzene, approximately 99% of the organic starting material was accounted for either as acetate **3** or unreacted starting material. Other products might have been expected since rearrangements are known to occur,[6,7] and, since isophorone is known to enolize approximately equally in both directions[8,9] and the enol form is apparently the species that is attacked,[10] products such as **4** might also have been expected. However, **4** could have rearranged to **3** under the conditions of the reaction since a similar rearrangement is known.[11] The structural assignment of **3** was confirmed by its ir and nmr spectra.

### Experimental Section

Melting points were taken on a Thomas–Hoover apparatus and are uncorrected. Infrared spectra were taken on a Perkin-Elmer 337 spectrometer; nmr spectra were recorded on a Varian HA-60 spectrometer using $DCCl_3$ as a solvent and tetramethylsilane as an internal standard. Gas chromatograms were obtained with a Perkin-Elmer 154L instrument using a thermal conductivity detector and a column of 0.25 in. × 5 ft 5% neophentylglycol sebacate on nonacid washed Chromosorb W with the He flow rate at 60 ml/min. Peak areas were determined by the height times width at half-height method and the peak areas due to **3** were multiplied by 1.2 to correct for detector response differences. Microanalyses were performed by M-H-W Laboratories of Garden City, Mich. The lead tetraacetate was dried over KOH under reduced pressure. Tests for completion were made with KI–starch indicator paper.

**Reaction of Isophorone with $Pb(OAc)_4$ in Benzene.**—A mixture of 150 ml of benzene, 10.0 g (0.0725 mol) of **2**, and 35.0 g (0.0787 mol) of $Pb(OAc)_4$ was refluxed with stirring for 90 hr. The mixture was cooled, washed once with water, saturated NaCl, saturated $NaHCO_3$, and saturated NaCl; the organic layer was dried ($MgSO_4$) and filtered; and solvent was removed at 45° under reduced pressure giving 14.0 g of light yellow solid. Vpc analysis at 200° of the crude product dissolved in ether showed 3% starting material, 1% minor component, and 96% acetate **3**. The ether solution was concentrated by evaporation to give 8.99 g of **3**, mp 76–78°, (lit.[2] mp 77–77.5°). A second crop of 2.08 g brought the total to 11.07 g (78%). A vpc analysis at 198° showed the 2.69 g of material in the mother liquor to be 69% **3**, 28% **2**, and approximately 1% each of three minor components. Vpc analysis at 240° of the crude reaction mixture and the mother liquors remaining after crystallization of **3** showed no additional products to be present.

The product **3** exhibited the following properties: bp 136–137° (9 mm) [lit.[2] 141–145° (12 mm)]; ir (KBr) 1740 (ester C=O), 1675 (C=O), 1635 (C=C), 1238 $cm^{-1}$ (C—O—C); nmr δ 5.92 (m, 1, with line spacings of 1.1 Hz, olefinic proton), 5.22 (s, 1, CHOAc), 2.20 (s, 3), 1.97 (s, 3), 1.1 (s, 3), 0.98 (s, 3).

*Anal.* Calcd for $C_{11}H_{16}O_3$: C, 67.32; H, 8.22. Found: C, 67.21; H, 8.53.

**Registry No.**—**1**, 546-67-8; **2**, 78-59-1; **3**, 19019-49-9.

(1) Support from the Council of Faculty Research, Eastern Illinois University is gratefully acknowledged.

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## Ring Expansion of Tetramethyl-1,3-cyclobutanedione with Difluoramine[1]

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*Received August 5, 1968*

Recent advances in the chemistry of difluoramine have demonstrated its utility in the synthesis of a

(1) This research was supported by the Advanced Research Projects Agency, Propellant Chemistry Office, and was monitored by Army Ordinance under Contract No. DA 30-069-ORD-2487.

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