2-Pyrones from Condensation of β-Keto Esters with 1,3 Diketones in Trifluoroacetic Acid. A Correction of the Literature

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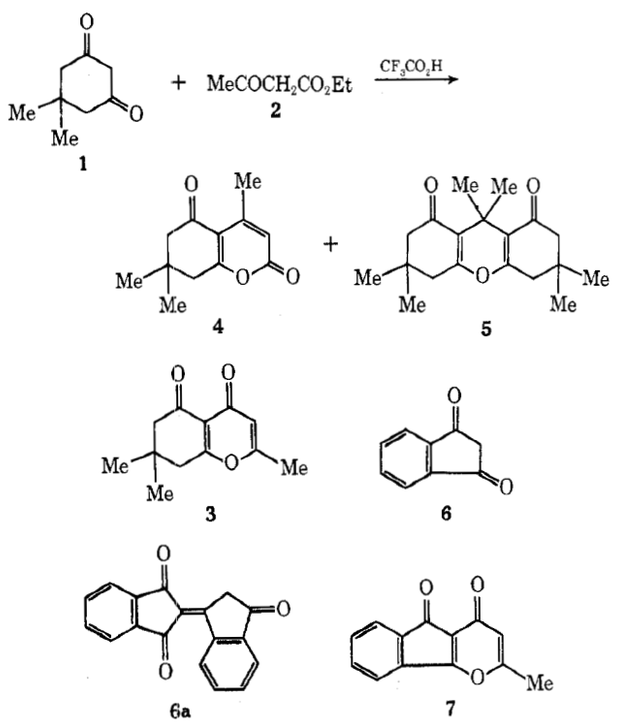
The reaction of 5,5-dimethyl-1,3-cyclohexanedione (**1**) with ethyl acetoacetate (**2**) in CF_3CO_2H gives the 2-pyrone **4** and a xanthene-1,8-dione **5** instead of the reported 4-pyrone **3**. Sodium diethyl oxalacetate (**13**) and **1** react in a similar manner giving ester **14**, isomeric with ester **10** prepared by condensing **8** with ethyl oxalate. Acid **15**, prepared by hydrolysis of **14**, gives 2-pyrone **16** on decarboxylation, isomeric with 4-pyrone **9** prepared by condensation of **8** with ethyl formate. Ultraviolet spectra comparisons of **4**, **9**, and **16** substantiates the structure of **4**. Indan-1,3-dione (**6**) and **2** did not give a pyrone on condensation in CF_3CO_2H; instead, dimer **6a** is isolated.

Condensation of 5,5-dimethyl-1,3-cyclohexanedione (**1**) with ethyl acetoacetate (**2**) has been described[1] as

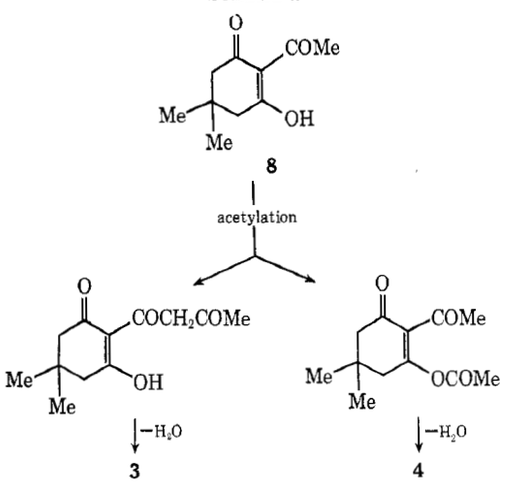


yielding 7,8-dihydro-2,7,7-trimethyl-4*H*-1-benzopyran-4,5(6*H*)-dione (**3**). We needed **3** for uv spectral comparison purposes and repeated the original preparation.[1] Instead of **3**, however, we isolated 7,8-dihydro-4,7,7-trimethyl-2*H*-1-benzopyran-2,5(6*H*)-dione (**4**) and 3,4,6,7-tetrahydro-3,3,6,6,9,9-hexamethylxanthene-1,8-(2*H*,5*H*)-dione (**5**).[2] The structure of **4** was substantiated by uv spectral correlations with several synthesized model 2- and 4-pyrones.

After considering the incongruities involved with the attempted preparation of **3**, we repeated the original preparation[1] involving the condensation of 1,3-indandione (**6**) and **2**. The nmr spectra indicated that none or only a very small amount of the proposed product **7** was present. Instead, we found that, when the reaction was worked up as described, mostly **6** was recovered, along with [$\Delta^{1,2'}$-biindan]-1′,3,3′-trione (**6a**)[3] and another high melting product. Apparently the original investigator's efforts resulted in the isolation of **6** and he described it as a new compound **7**. The originally described melting points (129 and 129–131°) agree with that reported for **6** (130–131°).[4] The originally reported found analysis (C, 73.70, 73.85; H, 3.94, 4.04),[1] presumably applicable to **7** ($C_{13}H_8O_3$), also agrees with that calculated for **6** ($C_9H_6O_2$) (C, 73.96; H, 4.14).

Efforts to provide a structural proof for **3** started with 2-acetyl-5,5-dimethyl-1,3-cyclohexanedione (**8**).[5] It became obvious that any acid- or base-catalyzed acetylation of **8**, followed by ring closure, could lead to the ambiguities shown in Scheme I. In fact, **4** was isolated from the neutral fraction separated from the preparation of **8**.

SCHEME I



Instead of synthesizing **3** or **4**, the problem was approached by preparing chromophorically identical 4- and 2-pyrones as uv spectral models. Two 4-pyrones easily prepared from **8** are 7,8-dihydro-7,7-dimethyl-4*H*-1-benzopyran-4,5(6*H*)-dione (**9**) and 5,6,7,8-tetrahydro-7,7-dimethyl-4,5-dioxo-4*H*-1-benzopyran-2-carboxylic acid ethyl ester (**10**). Compounds **9** and **10** were formed, respectively, by formylation and ethoxylation of the disodium salt of **8**, followed by dehydrative cyclization. The uv spectra of **9** and **10** (Table I) indicate that they have identical chromophores, but there is no similarity to the chromophore of **4**, which must be a 2-pyrone. Intermediate **11** was isolated and characterized en route to preparation of **9**.

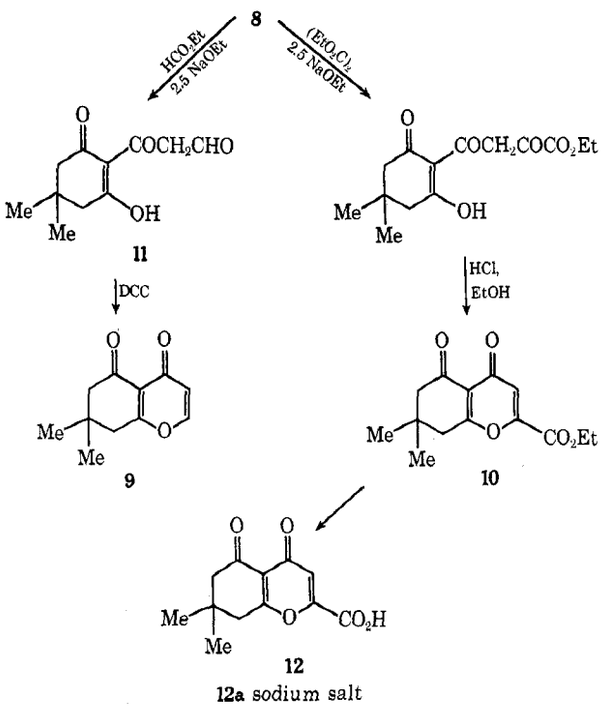
(1) L. L. Woods, *J. Org. Chem.*, **34**, 2796 (1969).
(2) D. Vorländer and F. Kalkow, *Justus Liebigs Ann. Chem.*, **309**, 374 (1899); *Beilstein*, 17:509.
(3) W. Wislicenus, *Chem. Ber.*, **20**, 589 (1887).
(4) W. O. Teeters and R. L. Shriner, *J. Amer. Chem. Soc.*, **55**, 3026 (1933).
(5) W. Dieckmann and R. Stein, *Chem. Ber.*, **37**, 3370 (1904); A. W. Crossley and N. Renouf, *J. Chem. Soc.*, **101**, 1524 (1912).

TABLE I

ULTRAVIOLET SPECTRA IN 95% ALCOHOL

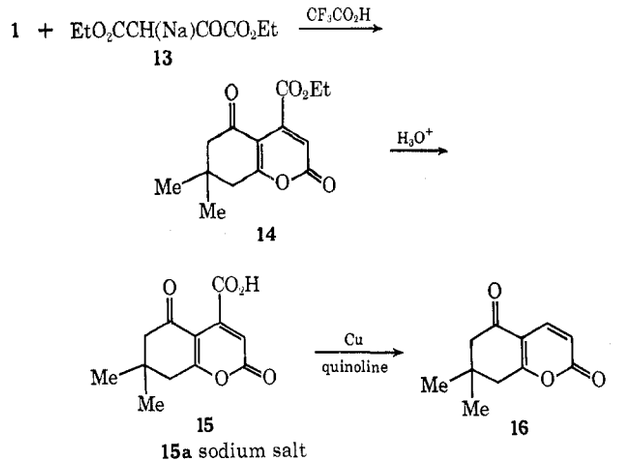
2-Pyrones		4-Pyrones	
Compd	mμ (ε)	Compd	mμ (ε)
4	262 (12,100), 290[a] (5960)	**5**	232 (15,450), 309 (5490)
14	263 (11,400), 296[a] (6530)	**9**	245 (8840)
15	263 (11,100), 296[a] (6240)	**10**	221 (22,800), 248 (7220)
15a	264 (10,250), 295[a] (5930)	**12**	217 (24,800), 247 (8830)
16	261 (12,230), 294[a] (6380)	**12a**	216 (28,800), 247 (10,160)

[a] Inflection points.



Ester **10** was hydrolyzed and characterized as the free acid **12** and sodium salt **12a**. Several attempts to decarboxylate **12** to **9** met only with extensive decomposition.

To complete the sequence, a series involving the 2-pyrones isomeric with **9**, **10**, and **12** was prepared. Condensation of **1** with sodium diethyl oxalacetate (**13**), using conditions similar to those described by



Woods,[1] gave a reasonable yield of 5,6,7,8-tetrahydro-7,7-dimethyl-2,5-dioxo-2*H*-1-benzopyran-4-carboxylic acid ethyl ester (**14**). Ester **14** is isomeric with **10**, and formation of a 2-pyrone (**14**) from **1** and **13** also illustrates a general trend to form 2-pyrones when 1,3 diketones and β-keto esters are condensed in an acid medium. Ester **14** was acid hydrolyzed, and the product was characterized as the free acid **15** and sodium salt **15a**. Acid **15** was easily decarboxylated with copper powder in refluxing quinoline to 7,8-dihydro-7,7-dimethyl-2*H*-1-benzopyran-2,5(6*H*)-dione (**16**), which is isomeric with **9**.

It is clearly evident from the uv data in Table I that **4** belongs to the 2-pyrone series. The spectral data in Table I also illustrate another point: that addition of a carboxyl or ethoxycarbonyl group to a 2- or 4-pyrone does not appreciably alter the electronic chromophore. By comparing the nmr spectra of **1**,[6] **4**, and **5** with that given by Woods[1] [solvent not reported, δ 1.10 (6), 1.66 (2), 2.20–2.80 (4), 3.35 (0.4), 5.50 (0.6)] for what he presumed to be **3**, it is evident that his condensation of **1** and **2** yielded only a mixture of **1** and **5**. The vinyl proton at δ 5.94 of **4** is not present in Woods mixture but the δ 5.50 vinyl of **1** and δ 1.66 methyls of **5** are.

Experimental Section

Melting points were taken in capillary tubes in an oil bath and are uncorrected. Solvents were removed *in vacuo* on a Büchi Rotavapor R. Anhydrous magnesium sulfate was used for all solution drying. Spectra were obtained under the supervision of Mr. Bruce Hofmann. The ir spectra were determined in KBr pellets using a Perkin-Elmer Model 21 spectrophotometer. The uv spectra were taken with a Perkin-Elmer Model 450 uv–visible NIR spectrophotometer. The nmr spectra were determined with a Varian Model A-60 or a Jeolco Model C-60HL nmr spectrometer using TMS in $CDCl_3$ and DMSO-d_6 and DSS in D_2O. Analyses were carried out on a Perkin-Elmer Model 240 elemental analyzer.

7,8-Dihydro-4,7,7-trimethyl-2*H*-1-benzopyran-2,5(6*H*)-dione (4) and 3,4,6,7-Tetrahydro-3,3,6,6,9,9-hexamethylxanthene-1,8-(2*H*,5*H*)-dione (5).—A solution of 70 g (0.5 mol) of **1** and 63.5 ml (0.5 mol) of **2** in 200 ml of CF_3CO_2H was refluxed for 22 hr. The solution was concentrated and the residue was poured into an Et_2O–H_2O mixture. An interphase was filtered off and crystallized (EtOH), giving 2.7 g of **5**: mp 249–252° (lit.[2] mp 245°); ir 6.04 (C=O), 6.20 μ (C=C); nmr ($CDCl_3$) δ 1.09 [s, 12, $CH_2C(CH_3)_2CH_2$], 1.66 [s, 6, $C{=}CC(CH_3)_2C{=}C$], 2.27 (s, 4, CH_2CO), 2.35 [s, 4, $C{=}C(O)CH_2$].

Anal. Calcd for $C_{19}H_{26}O_3$: C, 75.46; H, 8.67. Found: C, 75.48; H, 8.67.

The Et_2O–H_2O filtrate of **5** was separated and the Et_2O was washed successively with H_2O (twice), saturated $NaHCO_3$ (until basic), cold 1 *N* NaOH (twice with 300 ml), H_2O, and cold dilute HCl. After the washings, additional **5** (4.5 g, mp 244–247°) was filtered off. The Et_2O in the filtrate was washed with brine, dried, and concentrated, giving 18 g of a yellow solid, mp 105–135°, consisting of a mixture of **4** and **5**. The mixture was crystallized (EtOH), giving 7.7 g of a white solid, mp 110–210°, consisting of a 6:1 mixture of **4** and **5**. An attempt to separate the mixture on Woelm grade III neutral alumina failed, but, when 2.0 g of the mixture was sublimed at 110 ± 5° (0.05 mm) in a Nester–

(6) Varian Spectra Catalog, Vol. 2, Spectra No. 512: nmr ($CDCl_3$) δ 1.06 [s, $C(CH_3)_2$, keto form], 1.09 [s, $C(CH_3)_2$, enol form], 2.29 [s, $C(CH_3)_2$-CH_2CO, enol and keto form], 2.56 [s, $CH_2C(OH){=}CH$], 3.36 (s, $COCH_2CO$), 5.51 [s, $C(OH){=}CHCO$], 10.90 (s, OH).

Faust Model NFS-60 sublimer, 1.65 g of **4**, mp 108–112°, collected in the cooled cone and was crystallized (EtOH), giving white crystals: mp 108–111°; ir 5.77 and 6.00 (C=O), 6.17 and 6.45 μ (C=C); nmr ($CDCl_3$) δ 1.14 [s, 6, $C(CH_3)_2$], 2.45 (s, 3, $CH=CCH_3$), 2.48 (s, 2, CH_2CO),[7] 2.78 [s, 2, $C=C(O)CH_2$], 5.94 (s, 1, vinyl).

Anal. Calcd for $C_{12}H_{14}O_3$: C, 69.88; H, 6.84. Found: C, 69.68; H, 6.96.

An additional 0.4 g of **5**, mp 248–250°, collected on the outer shell of the sublimer above the oil level. An attempt to repeat this separation on a larger scale failed.

Condensation of 2 with 6 in Refluxing CF_3CO_2H.—A solution of 12.6 ml (0.10 mol) of **2** and 14.6 g (0.10 mol) of **6** in 40 ml of CF_3CO_2H was refluxed for 2 hr and the resulting mixture was poured into 400 ml of H_2O. Filtration gave 12 g of a brown solid, which was triturated three times with 400 ml of boiling hexane. Concentration of the hexane gave 6.3 g of a yellow solid, which was sublimed at 100° (0.05 mm), giving 5.8 g of **6**, mp 128–130°, mmp 128–130° with authentic **6**. The hexane-insoluble solid was triturated three times with 200 ml of boiling EtOAc. Concentration of the EtOAc gave 2.3 g of **6a** as a tan solid, mp 173–183°. The solid was recrystallized from C_6H_5Me, giving yellow crystals of **6a**: mp 205–208° (lit.[3] mp 206–208°); ir[8] 5.82, 5.93, and 6.20 (C=O), 6.35 μ (C=C); uv max (95% EtOH) 245 mμ (ε 24,100), 340 (20,300); nmr ($CDCl_3$) δ 4.15 (s, 2, CH_2), 7.60–8.40 (m, 7, aromatic), 9.50–9.78 (m, 1, aromatic).

Anal. Calcd for $C_{18}H_{10}O_3$: C, 78.82; H, 3.68. Found: C, 79.10; H, 3.87.

The remaining 3 g of solid melted above 300° and was very insoluble in DMSO, making it difficult to get a good nmr: ir 5.83, 5.95, 6.20, and 6.37 μ.

5,6,7,8-Tetrahydro-7,7-dimethyl-4,5-dioxo-4*H*-1-benzopyran-2-carboxylic acid Ethyl Ester (10).—Absolute EtOH (10.25 ml, 0.175 mol) was added to a mixture of 6.24 g (0.13 mol) of 50% NaH in 250 ml of C_6H_5Me. A solution of 9.11 g (0.050 mol) of **8** in 34 ml (0.25 mol) of $(EtO_2C)_2$ was added to the C_6H_5Me mixture at 10–20° over 20 min. The resulting mixture was stirred at 50° for 3 hr and poured into 500 ml of ice–water. The water solution was washed twice with Et_2O and acidified to pH 1 at 0–10° with concentrated HCl in the presence of Et_2O. The water layer was extracted twice with Et_2O. The ether was washed with brine, dried, and concentrated, giving 16.1 g of an amber oil. The oil was chromatographed on 160 g of Florex AA-RVM 60–90 mesh in C_6H_6. Two 500-ml fractions of C_6H_6, followed by two of $CHCl_3$, were collected. The first $CHCl_3$ fraction was concentrated, giving 1.5 g (11%) of **10**, mp 128–132°. After crystallization from ethyl acetate–hexane, the product had mp 134–137°; ir 5.74, 5.86, and 6.06 (C=O), 6.34 μ (C=C); nmr ($CDCl_3$) δ 1.16 [s, 6, $C(CH_3)_2$], 1.41 (t, 3, J = 7.2 Hz, CH_3), 2.46 (s, 2, 6-CH_2),[7] 2.90 (s, 2, 8-CH_2), 4.47 (q, 2, J = 7.2 Hz, CH_2CH_3), 7.10 (s, 1, vinyl).

Anal. Calcd for $C_{14}H_{16}O_5$: C, 63.63; H, 6.10. Found: C, 63.56; H, 6.05.

Concentration of the first C_6H_6 fraction gave 8.0 g of a light yellow solid, mp 48–90°. The solid was dissolved in 50 ml of absolute EtOH, 3 ml of EtOH saturated with HCl gas was added, and the solution was refluxed for 20 min and cooled in ice, giving 3.5 g of light pink crystals of **10**, mp 130–136°.

5,6,7,8-Tetrahydro-7,7-dimethyl-4,5-dioxo-4*H*-1-benzopyran-2-carboxylic Acid (12) and Its Sodium Salt (12a).—A solution of 20.0 g (0.076 mol) of **10** in 240 ml of 1:1 dioxane–concentrated hydrochloric acid was refluxed for 3 hr and kept overnight at room temperature. Water (250 ml) was added and the mixture was cooled to 0–5°, giving 11.7 g of **12**. The crude product was crystallized (MeCN), giving 8.7 g (49%) of **12** as white crystals: mp 210–212° dec; ir 5.73, 5.92, and 6.09 (C=O), 6.30 and 6.45 μ (C=C); nmr (DMSO-d_6) δ 1.08 [s, 6, $C(CH_3)_2$], 2.36 (s, 2, 6-CH_2), 2.89 (s, 2, 8-CH_2), 6.80 (s, 1, vinyl), 10.20 (s, 1, CO_2H).

Anal. Calcd for $C_{12}H_{12}O_5$: C, 61.01; H, 5.12. Found: C, 60.97; H, 5.12.

To a boiling, analytically filtered solution of 2.64 g (0.010 mol) of **10** in 50 ml of absolute EtOH was added, with stirring over 1 min, 1.9 ml of 5.25 *N* NaOH. Crystals formed rapidly and the mixture was kept on a steam bath for 10 min, cooled in ice, and filtered, giving 1.7 g (66%) of **12a** as yellow crystals: mp >300°; ir 5.90 and 6.13 (C=O), 6.42 μ (C=C); nmr (D_2O) δ 1.15 [s, 6, $C(CH_3)_2$], 2.56 (s, 2, 6-CH_2), 3.04 (s, 2, 8-CH_2), 6.96 (s, 1, vinyl).

Anal. Calcd for $C_{12}H_{11}NaO_5$: C, 55.82; H, 4.30. Found: C, 55.65; H, 4.45.

2-(Formylacetyl)-5,5-dimethyl-1,3-cyclohexanedione (11).—**11** was prepared in the same manner as **10**, but 20.2 ml (0.25 mol) of EtO_2CH was used instead of $(EtO_2C)_2$ and the Na salt of **11** was filtered off after the 3-hr heating period. An aqueous (300 ml) solution of the salt was washed with Et_2O and acidified to pH 1 with concentrated HCl in the presence of Et_2O. After 10 min of stirring, 5.7 g (54%) of **11**, mp 131° dec, was filtered off and crystallized (ethyl acetate–hexane), affording 4.4 g (42%) of **11** as yellow crystals: mp 135–136.5° dec; ir 6.2 (C=O), 6.62 μ (C=C); uv max (95% EtOH) 249 mμ (center of broad plateau) (ε 8380), 335 (9300); nmr (DMSO-d_6) δ 1.00 [s, $C(CH_3)_2$], 2.40 (s, CH_2), 7.04 (d, J = 12 Hz, vinyl), 8.04 (d, J = 12 Hz, vinyl), the ratios being unobtainable because of the DMSO-d_5 interference with the CH_2 peaks.

Anal. Calcd for $C_{11}H_{14}O_4$: C, 62.84; H, 6.71. Found: C, 62.74; H, 6.81.

7,8-Dihydro-7,7-dimethyl-4*H*-1-benzopyran-4,5(6*H*)-dione (9).—DCC (1.073 g, 0.0052 mol) was added to a warm solution of 1.074 g (0.00511 mol) of **11** in 20 ml of THF. After 20 hr at room temperature, the red mixture was filtered and the cake (1.0 g) was washed with THF. The filtrate was concentrated and the red residue was triturated twice with boiling Et_2O, leaving 0.36 g of a red solid. The ether was treated with charcoal and concentrated, giving 0.610 g of a gummy solid, which was chromatographed on activity I silica gel in EtOAc. Elution with 150 ml EtOAc removed the DCC. Collection of fractions with increasing amounts of MeCOMe to 100% and subsequent concentration afforded 0.30 g (31%) of **9**. Crystallization from chloroform–hexane yielded a product with mp 115–117.5°; ir 5.89 and 6.07 (C=O), 6.42 μ (C=C); nmr ($CDCl_3$) δ 1.15 [s, 6, $C(CH_3)_2$], 2.43 (s, 2, 6-CH_2), 2.77 (s, 2, 8-CH_2), 6.38 (d, 1, J = 6 Hz, vinyl), 7.72 (d, 1, J = 6 Hz, vinyl).

Anal. Calcd for $C_{11}H_{12}O_3$: C, 68.73; H, 6.29. Found: 68.44; H, 6.54.

5,6,7,8-Tetrahydro-7,7-dimethyl-2,5-dioxo-2*H*-1-benzopyran-4-carboxylic Acid Ethyl Ester (14).—A mixture of 14.0 g (0.1 mol) of **1** and 21.0 g (0.1 mol) of **13** was refluxed in 50 ml of CF_3CO_2H for 4 hr and then stirred overnight at room temperature. After concentration, the residue was poured into an Et_2O–H_2O mixture. The Et_2O was washed successively with saturated $NaHCO_3$ (until basic), cold 0.5 *N* NaOH, dilute HCl, H_2O, and brine. It was then dried and concentrated, giving 7.4 g (28%) of **14** as a white solid. Crystallization (ethyl acetate–hexane) gave 5.6 g of white crystals: mp 136–138°; ir 5.74 and 5.96 (C=O), 6.16 and 6.43 (C=C); nmr ($CDCl_3$) δ 1.18 [s, 6, C-$(CH_3)_2$], 1.38 (t, 3, J = 7.5 Hz, CH_3), 2.48 (s, 2, 6-CH_2), 2.80 (s, 2, 8-CH_2), 4.46 (q, 2, J = 7.5 Hz, CH_2CH_3), 6.25 (s, 1, vinyl).

Anal. Calcd for $C_{14}H_{16}O_5$: C, 63.63; H, 6.10. Found: C, 63.59; H, 6.01.

5,6,7,8-Tetrahydro-7,7-dimethyl-2,5-dioxo-2*H*-1-benzopyran-4-carboxylic Acid (15) and Its Sodium Salt (15a).—A solution of 10 g (0.038 mol) of **14** in 100 ml of 1:1 dioxane–20% hydrochloric acid was refluxed for 6 hr and kept at room temperature overnight. Filtration gave 8.0 g (89%) of **15**, mp 218–223° dec. The crude product was crystallized (EtOH), giving 6.4 g of **15** as white crystals: mp 222–224° dec; ir 5.65, 5.77, and 6.15 (C=O), 6.45 μ (C=C); nmr (DMSO-d_6) δ 1.11 [s, 6, $C(CH_3)_2$], 2.48 (s, 2, 6-CH_2), 2.87 (s, 2, 8-CH_2), 6.39 (s, 1, vinyl).

Anal. Calcd for $C_{12}H_{12}O_5$: C, 61.01; H, 5.12. Found: C, 60.78; H, 5.35.

To a boiling, analytically filtered solution of 2.1 g (0.0089 mol) of **15** in 75 ml of absolute EtOH was added 3.3 ml of 2.74 *N* sodium 2-ethylhexanoate in 1-butanol. The mixture was cooled, giving 1.3 g (58%) of **15a** as white crystals: mp >300°; ir 5.66, 5.72, 5.95, and 6.20 (C=O), 6.48 μ (C=C); nmr (D_2O) δ 1.10 [s, 6, $C(CH_3)_2$], 2.53 (s, 2, 6-CH_2), 2.89 (s, 2, 8-CH_2), 6.13 (s, 1, vinyl).

Anal. Calcd for $C_{12}H_{11}NaO_5$: C, 55.82; H, 4.30. Found: C, 55.88; H, 4.40.

7,8-Dihydro-7,7-dimethyl-2*H*-1-benzopyran-2,5(6*H*)-dione (16).—A stirred mixture of 5.0 g (0.021 mol) of **15**, 0.98 g of Cu powder, and 10 ml of quinoline was placed in an oil bath at 250°. Decarboxylation was essentially complete after 10 min, and the

(7) Routine assignment of the higher field methylene to the 6 position on the 1-benzopyran nucleus is based on data in Varian Spectra Catalog, Spectra No. 512.

(8) Spectrum identical with that found in the Sadtler Index (Spectra No. 18437).

mixture was cooled and filtered. An Et_2O solution of the filtrate was washed successively with 1 N HCl (five times), saturated $NaHCO_3$, H_2O, and brine. It was then dried and concentrated, giving 2.33 g of a yellow solid, mp 79–87°. The solid was recrystallized from hexane and cyclohexane, giving 1.66 g (41%) of **16** as light yellow crystals: mp 89–92°; ir 5.76 and 5.96 (C=O), 6.14 and 6.40 μ (C=C); nmr ($CDCl_3$) δ 1.16 [s, 6, $C(CH_3)_2$], 2.46 (s, 2, 6-CH_2), 2.79 (s, 2, 8-CH_2), 6.30 (d, 1, J = 9.75 Hz, vinyl), 7.91 (d, 1, J = 9.75 Hz, vinyl).

Anal. Calcd for $C_{11}H_{12}O_3$: C, 68.73; H, 6.29. Found: C, 68.31; H, 6.39.

Registry No.—**3**, 20452-84-0; **4**, 3265-69-8; **5**, 33777-60-5; **6**, 606-23-5; **6a**, 1707-95-5; **7**, 20452-88-4; **9**, 33777-64-9; **10**, 33777-65-0; **11**, 33777-66-1; **12**, 33777-67-2; **12a**, 33777-68-3; **14**, 33886-29-2; **15**, 33777-69-4; **15a**, 33777-70-7; **16**, 33777-71-8; trifluoroacetic acid, 76-05-1.

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α- and β-(Trifluoromethylthio)acrylic Acid Derivatives

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The product of the free-radical addition of CF_3SCl to methyl acrylate has been converted to a series of α-CF_3S-acrylic acid derivatives. The preparation of the corresponding β-CF_3S-substituted compounds began with the addition of CF_3SH to methyl propiolate. (Trifluoromethylthio)acetonitrile readily undergoes Knoevenagel reactions to yield α-CF_3S-substituted acrylonitriles.

Following the development of convenient laboratory syntheses for bis(trifluoromethylthio)mercury, trifluoromethanethiol, and trifluoromethanesulfenyl chloride, a modest number of CF_3S-substituted organic compounds have been synthesized.[1] To date no CF_3S-substituted, unsaturated acids or derivatives have been reported. This paper summarizes the results of a study of methods of preparation and the properties of CF_3S-substituted acrylic acid derivatives.

Results and Discussion

α-CF_3S-Substituted Acrylic Acid Derivatives.—For preparation of several α-CF_3S-substituted acrylic acid derivatives, the free-radical addition of trifluoromethanesulfenyl chloride (CF_3SCl) to methyl acrylate served as the starting point. When carried out with a large excess of CF_3SCl, the reaction yielded as the major product a 1:1 adduct fraction which contained about 90% methyl α-(trifluoromethylthio)-β-chloropropionate (**1**) and 10% of an isomeric material, presumably the other possible 1:1 adduct (**2**) (eq 1).

$$CF_3SCl + CH_2{=}CHCO_2CH_3 \xrightarrow{h\nu} \underset{\mathbf{1}}{ClCH_2\overset{CF_3S}{\overset{|}{C}}HCO_2CH_3} + \underset{\mathbf{2}}{CF_3SCH_2CHClCO_2CH_3} + \underset{\mathbf{3}}{ClCH_2\overset{CO_2CH_3}{\overset{|}{C}}HCH_2{-}\overset{SCF_3}{\overset{|}{C}}HCO_2CH_3} \quad (1)$$

A considerable quantity of a 2:1 adduct (**3**) was formed, which, according to gas chromatography and ^{19}F nmr spectroscopy, contained two isomers in roughly equal amounts.

The orientation of the major 1:1 adduct (**1**) was established by analysis of the ^{13}C nmr pattern.[2,3] The ^{13}C resonances of the hydrogen-bearing carbons along with the ^{13}C–H coupling constants are shown in Table I.

TABLE I

^{13}C NMR SPECTRUM OF METHYL α-(TRIFLUOROMETHYLTHIO)-β-CHLOROPROPIONATE (NEAT)

$$ClCH_2\overset{SCF_3}{\overset{|}{C}}HCO_2CH_3$$

Carbon atom	Chemical shift, ppm	Splitting pattern	J (^{13}C–H), Hz
CH_3	73.4	Quartet	149
CH	68.2	Doublet	148
CH_2	63.5	Triplet	158

Neither of the resonances for the carbons possibly containing the CF_3S group showed any spin–spin coupling clearly attributable to the presence of this group, and thus no structure assignment could be made on that basis. However, since values of J (^{13}C–H) for CH groups with chlorine substituents have been observed to be 150 Hz and higher,[4] it is concluded that the CH group, with J (^{13}C–H) of 148 Hz, cannot have the Cl, but must instead have the CF_3S group as substituent. This structure is consistent with the structures of the dehydrochlorination products from the 1:1 adduct discussed below.

Structure **3** was assigned to the 2:1 adduct on the basis of a dehydrochlorination experiment (eq 2), which produced a single, unsaturated ester in 78.5% yield (distilled). On the basis of the ^1H nmr and infrared spectra, **4** is the most likely structure for this product. The ^1H nmr pattern contains two unsplit CH_3 resonances, a CH_2 resonance split to a doublet, each com-

(1) J. F. Harris, Jr., *J. Org. Chem.*, **32**, 2063 (1967).

(2) Neither the ^1H nor the ^{19}F nmr pattern of the mixture of 1:1 adducts gave evidence sufficient for structure assignment.

(3) The author is indebted to Dr. G. S. Reddy of this laboratory for determination and interpretation of the ^{13}C nmr pattern of the 1:1 adduct fraction.

(4) For example, see J. W. Emsley, J. Feeney, and L. H. Sutcliffe, "High Resolution Nuclear Magnetic Resonance Spectroscopy," Vol. 1, Pergamon Press, New York, N. Y., 1965, p 195, Table 5.21.