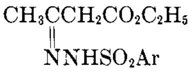
TABLE II

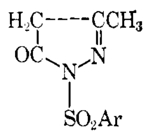

$$\underset{\displaystyle NNHSO_2Ar}{CH_3\overset{}{C}CH_2CO_2C_2H_5}$$

II

Ar	Mp, °C[a]	Yield, %[b]	Method	Formula[c]	Analyses
p-$CH_3OC_6H_4$	110–111	65.8	C	$C_{13}H_{18}N_2O_5S$	C, H, N
p-$C_2H_5OC_6H_4$	106–107	55.8	C	$C_{14}H_{20}N_2O_5S$	C, H, N
$C_6H_5CH_2$	79–80	52.7	D	$C_{13}H_{18}N_2O_4S$	N

[a–c] See footnotes *a–c* in Table I.

TABLE III



III

Ar	Mp, °C dec[a]	Yield, %[b]	Formula[c]	Analyses
p-$CH_3OC_6H_4$	137–138	34.5	$C_{11}H_{12}N_2O_4S$	C, H, N
p-$C_2H_5OC_6H_4$	168	44.6	$C_{12}H_{14}N_2O_4S$	C, H
$C_6H_6CH_2$	120–122	40.1	$C_{11}H_{12}N_2O_3S$	C, H, N

[a–c] See footnotes *a–c* in Table I.

50 ml of 95% EtOH, 0.004 mole of acetylacetone was added. The solution was refluxed 1–2 hr, then left overnight at 3°. Recrystallization from MeOH gave white crystals.

Method B.—Equimolar quantities of acetylacetone and the 1-arylsulfonylhydrazide (0.002 mole), were dissolved in 30 ml of DMF at 0°, and 3 drops of 2 *N* HCl were added. The solution was stirred at room temperature for 2 hr, then left at 3° overnight. The transparent white crystals thus obtained were recrystallized from 1:1 Et_2O–petroleum ether (40–60°).

1-Arylsulfonylhydrazones of Ethyl Acetoacetate (II) (Table II). Method C.—To a solution of 0.002 mole of the 1-arylsulfonylhydrazide in 50 ml of 95% EtOH, was added 0.004 mole of ethyl acetoacetate. The solution was refluxed 1–2 hr, then left overnight at 3°. The white crystals were filtered and recrystallized from EtOH.

Method D.—Equimolar quantities (0.002 mole) of ethyl acetoacetate and the 1-arylsulfonylhydrazide were dissolved in 50 ml of 95% EtOH, and 2 ml of 5% AcOH was added. The solution was stirred at room temperature for 2 hr, then left overnight at 3°. The white crystals were filtered and recrystallized from 1:1 MeOH–H_2O.

3-Methyl-N^1-arylsulfonyl-5-pyrazolones (III) (Table III).—The 1-arylsulfonylhydrazone of ethyl acetoacetate (0.002 mole) was dissolved in 10 ml of 5% Na_2CO_3 and held at 80–90° for 2–3 hr. It was then cooled and brought to pH 3 with 0.6 *N* HCl, then left overnight at 3°. The white powder obtained was recrystallized from H_2O.

Acknowledgment.—We thank Dr. Juan Estaven of the University of Barcelona for the elemental analyses and also the Diamond Shamrock Corp. for generous supplies of several reagents.

Preparation of (Carboxymethyl)cyclohexyldimethylammonium Chloride Hydrazide

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In studies of the reaction of cationic hydrazides with carbonyl groups in periodate-oxidized starches[1,2] we synthesized (carboxymethyl)cyclohexyldimethylammonium chloride hydrazide by the method of Girard and Sandulesco[3] for Girard T reagent. The new compound might be of value in isolating ketones from steroid mixtures[3] and aldehydes from autoxidized fats and oils.[4]

Experimental Section

(Carboxymethyl)cyclohexyldimethylammonium Chloride Hydrazide.—N,N-Dimethylcyclohexylamine[5] (53.4 g, 0.42 mole) was added dropwise to a stirred solution of ethyl chloroacetate (49.0 g, 0.40 mole) in 100 ml of absolute EtOH at 5°. The mixture was stirred at 5–10° for 30 min, then heated at 60–70° for 1 hr, and allowed to stand at room temperature overnight to form the intermediate ethyl ester of (carboxymethyl)cyclohexyldimethylammonium chloride in solution.

Hydrazine of 95+% purity (13.5 g, 0.40 mole) was added dropwise to this solution during 15 min of continuous stirring with the temperature rising to 50–60°. The reaction mixture was maintained at this temperature range for 1 hr and then concentrated *in vacuo* to about 100 ml. When an equal volume of EtOAc was added to the concentrate and it was kept at 2° for 36 hr, crystallization occurred. The extremely hygroscopic product was filtered off in an atmosphere of 11% relative humidity and dried *in vacuo* over P_2O_5. Recrystallization from EtOAc–EtOH (5:1) gave 57.6 g (61%) of the hydrazide, mp 160–164°. *Anal.* ($C_{10}H_{22}ClN_3O$) C, H, N, Cl.

Acknowledgments.—We thank Mrs. Clara McGrew and Mrs. Bonita Heaton for the microanalyses.

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3,3-Disubstituted Ethyl Carbazates[1]

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The antitumor activity of such hydrazine derivatives as MIH [$CH_3NHNHCH_2C_6H_4CONHCH(CH_3)_2$], 1-acetyl-2-picolinoylhydrazide, and 5-(3,3-dimethyl-1-triazeno)-4-imidazolecarboxamide, has encouraged us to prepare some 3,3-disubstituted ethyl carbazates for screening.

The lack of significant activity (Table I) in those compounds (**1–4**) which are not alkylating agents would seem to indicate that the activity of **5** is related to its alkylating properties rather than to any properties it may have as a substituted hydrazine.

Experimental Section[2]

Ethyl 3,3-Bis(chloroallyl)carbazates.—Compounds 1–4 were prepared from the appropriate dichloroalkene (0.5 mole), ethyl carbazate[3] (0.25 mole), and NaOH (0.5 mole) in absolute EtOH (50 ml). The mixture was shaken with cooling for 1 hr, followed by shaking for an additional 8 hr, then filtered. The filtrate was

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[2] Melting points were taken on a Fisher-Johns melting point block and are corrected. Where analyses are indicated only by symbols of the elements, analytical results obtained for those elements were within ±0.4% of the theoretical values.

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