		TABLE			
	CH_3	CCH_2	$CO_2C_2H_5$		
		11 -			
		NNHS	5O2Ar		
		II			
		Yield,			
Λr	Mp, $^{\circ}C^{a}$	$\%^{b}$	Method	$\mathbf{Formula}^{c}$	Analyses
p-CH3OC6H4	110-111	65.8	С	$\mathrm{C}_{13}\mathrm{H}_{18}\mathrm{N}_{2}\mathrm{O}_{\delta}\mathrm{S}$	C, H, N
p-C ₂ H ₅ OC ₆ H ₄	106 - 107	55.8	С	$\mathrm{C}_{14}\mathrm{H}_{20}\mathrm{N}_{2}\mathrm{O}_{5}\mathrm{S}$	C, H, N
C6H5CH2	79-80	52.7	D	$C_{13}H_{18}N_2O_4S$	N
^{a−c} See footr	notes a-c in ?	fable]	Ľ.		
		TABLE	III		



a-c See footnotes a-c in Table I.

 $50\,\mathrm{ml}$ 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 Et₂O-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-H₂O.

3-Methyl-N¹-arylsulfonyl-5-pyrazolones (III) (Table III).—The 1-arylsulfonylhydrazone of ethyl acetoacetate (0.002 mole) was dissolved in 10 ml of 5% Na₂CO₃ 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 H₂O.

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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

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synthesized (carboxymethyl)cyclohexyldimethylammonium chloride hydrazide by the method of Girard and Sandulesco³ for Girard T reagent. The new compound might be of value in isolating ketones from steroid mixtures³ and aldehydes from autoxidized fats and oils.⁴

Experimental Section

(Carboxymethyl)cyclohexyldimethylammonium Chloride Hydrazide.—N,N-Dimethylcyclohexylamine⁵ (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 $5-10^{\circ}$ for 30 min, then heated at $60-70^{\circ}$ 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 P₄O₅. Recrystallization from EtOAc-EtOH (5:1) gave 57.6 g (61%) of the hydrazide, mp 160-164°. Anal. (C₁₀H₂₂ClN₃O) 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 Carbazates¹

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The antitumor activity of such hydrazine derivatives as MIH $[CH_3NHNHCH_2C_6H_4CONHCH(CH_3)_2]$, 1acetyl-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 Section²

Ethyl 3,3-Bis(chloroallyl)carbazates.—Compounds 1-4 were prepared from the appropriate dichloroalkene (0.5 mole), ethyl carbazate³ (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 $\pm 0.4\%$ of the theoretical values.

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